Development of Durable Superhydrophobic Aluminium Surfaces Synthesised by Chemical Etching Process

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Abstract: In this paper, the superhydrophobic coatings on aluminium surfaces were prepared by two-step (chemical etching followed by coating) and one-step (chemical etching and coating in a single step) processes using potassium hydroxide and lauric acid. Besides, surface immersion time in solutions was varied in both processes. Wettability and surface morphologies of treated aluminium surfaces were characterized using contact angle measurement technique and scanning electron microscopy, respectively. Microstructures are formed on the treated aluminium surfaces which lead to increase in contact angle of the surface (>150°). Also on increasing immersion time, contact angle further increases due to increase in size and depth of microstructures. Additionally, these superhydrophobic coatings show excellent self-cleaning and corrosion-resistant behaviour. Water jet impact, floatation on water surface, and low temperature condensation tests assert the excellent water-repellent nature of coatings. Further, coatings are to be found mechanically, thermally, and ultra-violet stable. Along with, these coatings are found to be excellent regeneration ability as verified experimentally. Although aforesaid both processes generate durable and regenerable superhydrophobic aluminium surfaces with excellent self-cleaning, corrosion-resistant, and water-repellent characteristics, but one-step process is proved more efficient and less time consuming than two-step process and promises to produce superhydrophobic coatings for industrial applications.

Keywords: superhydrophobic; self-cleaning; corrosion-resistant; etching

1. Introduction

Aluminium is an important industrial metal due to its high specific strength, low-specific weight, and excellent heat and electrical conductivities. It is widely used in mechanical apparatus, aerospace and powerlines. However, its application is limited due to problem of corrosion, accumulation of icing and scratching. Therefore it is required to modify the aluminium surface by changing its wettability behaviour. This can be done by developing the superhydrophobic coating on aluminium surface which can resist problem of corrosion, icing, and scratching.

Superhydrophobicity is defined when the contact angle of water droplet on surface is greater than 150° and contact angle hysteresis is lower than 10°. These surfaces can be created by taking inspiration from nature such as animals like water striders [1] and plants like lotus [2]. In order to achieve superhydrophobic properties, nano/micro-structure must be developed on the surface because the contact angle of a flat surface cannot be more than 120° even if surface energy is lowered by introducing groups of –CF₃, –CH₃ and –CH₂– on the surface [3-13]. Traditionally, superhydrophobic surfaces are made by following two-steps process: firstly introducing rough
Based on the two-step method, a lot of fabricating methods have been reported in recent years, such as anodic oxidation [22-25], chemical deposition [26], chemical etching [27-31], chemical vapor deposition [32-35], colloidal self-assembly [36-38], electrospinning [39-40], sol-gel [41-42] and some others [43-44] to make the surface rough and then passivating those using fatty acid, fluoroalkylsilane, or alkylthiol etc. All synthesis techniques are having some pro and cons. Some of these are simple and inexpensive; however, some of these involve harsh conditions or require specialized reagents and equipment, which leads to increase the cost of coating. Among these, chemical etching is one of the easiest and cheapest process which can also be used for synthesizing superhydrophobic coatings on aluminium. As aluminium has dislocations on its surface, selective dislocation etching can be easily done. Chemical etching not only impairs the metallic substrate but also increases its anti-corrosive property. Recently, Fu et al. [45] used chemical etching with Cu(NO₃)$_2$ and HNO₃ mixed solution to prepare rough aluminium alloy surfaces, and then immersed rough aluminium in a silane solution to get superhydrophobic surfaces. Wang et al. [46] used the chemical etching with the HNO₃ and H₂O₂ mixed solution to make rough aluminium surface and after this roughed aluminium was immersed in a mixed solution of stearic acid and N, N-dicyclohexylcarbodiimide, the contact angle achieved was 156°. Guo et al. [47] immersed aluminium alloy in NaOH solution, followed by spin coating with fluorinated silane and achieved superhydrophobic aluminium surfaces. Xie et al. [48] created roughness on aluminium alloy by immersing in NaOH solution and then immersed rough aluminium alloy in ethanol solution of lauric acid to get superhydrophobic surface. Liao et al. [49] fabricated anti-icing superhydrophobic aluminium surface using chemical etching with CuCl$_2$ and HCl followed by reaction with hexadecyltrimethoxy silane. Li et al. [50] prepared superhydrophobic aluminium alloy surface by hydrochloric acid etching, potassium permanganate passivation and fluoroalkyl-silane modification. On the other hand, it is also reported the preparation of superhydrophobic surfaces on aluminum alloy via a one-step procedure in which both the creation of a rough micro/nano-structure and the lowering of the surface energy take place simultaneously in one single step [51-54]. Saleema et al. [55-56] reported the creation of superhydrophobic properties on aluminium alloy surfaces treated with fluoroalkyl-silane (FAS-17) in sodium hydroxide (NaOH) solution. However, two-step methods are still subjected to certain limitations such as time consuming and expensive materials.

In current work, superhydrophobic coatings on aluminium surfaces were prepared by two-step and one-step chemical etching technique using potassium hydroxide (KOH) and lauric acid solutions. Besides, the effect of etching time on wettability and surface morphologies was also studied and obtained results from both processes were also compared. Characterization of superhydrophobic coatings were also done to check stability for ultra-violet (UV) exposure, annealing effect, and mechanical disturbances. Additionally, regenerability of these coatings was also studied. Further, self-cleaning and corrosion-resistant properties of coatings were also analysed.

2. Experimental details

2.1 Materials required

Commercially purchased aluminium sheets (5cm X 2cm X 5mm and weight of about 1 gm) were used for the development of superhydrophobic surface. Acetone and distilled water was used for the cleaning purpose. Potassium hydroxide pellets were purchased from Fisher scientific. Ethanol (EMSURE, absolute for analysis, EMD Millipore Corporation) and lauric acid (99%, Loba
Chemie Laboratory reagent and fine chemicals Pvt. Ltd, India), and sodium chloride (RANKEM) were the chemicals used in preparation of superhydrophobic coatings.

2.2. Sample preparation

In two-step process, aluminum substrates were initially cleaned with acetone and distilled water multiple times, then aluminum substrates were immersed in a mixture of 10 gm/liter KOH in distilled water solution for 5-60 minutes. KOH solution roughed the aluminum surfaces (Figure 1). Subsequently aluminum substrates were rinsed with distilled water and ethanol. Finally they were immersed in 20 gm/liter ethanol solution of lauric acid for 30 minutes and then they were dried in air for 20 hours. Lauric acid here lowered the surface energy of aluminium surface.

In one-step process, cleaned aluminum substrates were immersed in a mixture of 10 ml of 10 gm/liter KOH in distilled water solution and 10 ml of 20 gm/liter ethanol solution of lauric acid for 5-60 minutes and then they were dried in air (Figure 1). Here, roughness and lowering the surface energy of aluminium were done in a single step by KOH and lauric acid.

2.3. Sample Characterization

By employing sessile drop method, water contact angles on the samples were measured using Drop Shape Analyzer (25, Kruss, Germany) in the normal atmospheric conditions. The volume of distilled water droplets used was 4-7 μL. The contact angles were measured on five different points on each sample and average value along with standard deviation was calculated. Surface morphologies of samples were analysed by scanning electron microscopy (SEM) (Nova Nano SEM FEI).

Surface bending tests were carried out for demonstrating mechanical durability of the superhydrophobic aluminum surfaces. Coated samples were bent in different directions and angles. Multiple times folding and de-folding bending was also done. To check the effect of bending and folding on superhydrophobicity, droplets were placed on different bending positions and contact angle was later measured.

To study the effect of post annealing, samples were kept at different elevated temperature (50 to 250 °C) in a hot air oven. After one hour annealing, samples were cooled down in normal room condition for 24 hours, and then contact angles were measured. To test the UV stability, coatings were continuously exposed to an ultraviolet light of wavelength 254 nm for 55 hours in a UV curer (UltraV-C1, Apex Instruments Co. Pvt. Ltd, India). In between, contact angle of these samples was measured at regular time interval.

In order to demonstrate coatings’ water-repellent characteristic, the water jet impact, floatation on water surface and low temperature condensation tests were carried out. For water jet impact test, interaction between the high speed water stream jet released from syringe and the sample was observed. Coated samples were kept on the water surface and floatation time was recorded till sample started sinking. In low temperature condensation test, coated along with uncoated samples were kept in the deep freezer for overnight, then these samples were placed in humid atmosphere of about 80% relative humidity and accumulation of dew drops on the surfaces were observed.

Self-cleaning test were performed by dropping water droplets dropped on the chalk powder sprinkled surfaces and flow of chalk powder along with water droplet was recorded. In corrosion-resistant test, superhydrophobic samples were immersed in 3% by weight sodium
chloride (NaCl) solution for 10 days and contact angles were measured at regular time interval to check the wettability.

For regenerability, superhydrophobic surface was continuous annealed at 300 °C for 6 hours in hot air oven to damage the surface. To rejuvenate the superhydrophobicity, substrate was re-immersed in ethanol solution of lauric acid for 30 min followed by air dried for 24 hours and water contact angle of repaired coating was measured.

3. Results and discussions

Figure 2 shows the SEM images of as-received unmodified and modified aluminium surfaces by two-step process. Inserted images right upper corner on shown images show magnified SEM image of corresponding aluminium surfaces as well as a water drop image on corresponding aluminium surface. Contact angle of unmodified aluminium was measured as 70.6°. The contact angle of 5 min etched aluminium is found to be 120.8°. When aluminium was etched for 10 min and 20 min, the treated aluminium shows the contact angle of 137.3° and 146.2°, respectively. The contact angle of 30 min etched aluminium is observed to be 153°. Further increasing etching time to 60 min, the contact angle is found to be 150°. The major changes in surface morphologies have been noticed with increasing etching time or immersion time in acid solution [57]. A chemical reaction of KOH with aluminium results in an etching process leading to a rough microporous structure on the surface as shown in the SEM image of figure 2. When aluminium was immersed into KOH solution for 5 and 10 mins, followed by immersion in lauric acid solution, the surface morphologies are not changed much (Figure 2 (b) and (c)). But change in the morphology is noticed for 20 min immersion time samples, cracking of surface is clearly seen as shown in high magnified SEM image of figure 2 (d). Craterlike micro-features on aluminium surface are seen when etching time was 30 min as shown in figure 2 (e). Further on increasing etching time, SEM images (Figure 2 (f) and (g)) reveal that the morphological features remain similar. The formation of a rough micro-cratered surface, in combination with a modified surface chemistry arising from lauric acid, contributes to the creation of superhydrophobic surface.

In two-step process, micro-structured pits are formed using chemical etching technique. It was carried out on aluminium substrate using aqueous solution of KOH where the following dissolution reactions take place on aluminium surface:

\[ \text{Al}_2\text{O}_3(s) + 2\text{KOH(aq)} + 3\text{H}_2\text{O} \rightarrow 2\text{K}[\text{Al(OH)}_4](\text{aq}) \]  \hspace{1cm} (1)
\[ 2\text{Al(s)} + 2\text{KOH(aq)} + 6\text{H}_2\text{O} \rightarrow 2\text{K}[\text{Al(OH)}_4](\text{aq}) + 3\text{H}_2 \]  \hspace{1cm} (2)

Here potassium aluminate ([K(Al(OH)]_4)) is the product of both the reactions (1) and (2) and is soluble in the KOH solution. It enables aluminium to be etched uniformly even though it has a stable native oxide layer which can hinder the etching taking place on the aluminium surface. Therefore a high density of nucleation sites for pits is introduced on the aluminium surface. In this work, the etching time has been varied form 5 min to 60 min. On increasing etching time major change of the surface is observed (Figure 2).

After this the etched aluminium surfaces were immersed in ethanol solution of lauric acid which results in the formation of sponge like layer on the surface. This happens because the carboxyl in the positive end of the lauric acid reacts with the hydroxyl or the aluminium atom through dehydrating process (reaction 3).

\[ \text{Al}^{3+} + 3\text{CH}_3\text{(CH}_2)_3\text{COO} \rightarrow \text{Al}\text{(CH}_3\text{(CH}_2)_3\text{COO)}_3 \]  \hspace{1cm} (3)
Bonding the long non-positive end of the alkyl to the etched aluminium surface creates a low surface energy aluminium surface. This helps in the better achievement of high contact angle. Contact angle increased from 70.6° of virgin aluminium to 153° of etched aluminium (Figure 2), when it etched in KOH for 30 min or more time and followed by coating of lauric acid for 30 min. The tilt angle about 5° is measured. In 30 min of etching with KOH, aluminium surface becomes very rough due to the formation of increased depth of pits. Air can entrap within these pits and provide better geometrical conditions for the superhydrophobic characteristic. This is confirmed by Cassie-Baxter theory [58].

Figure 3 shows the SEM images of as-received (virgin aluminium) and modified aluminium surfaces by one-step process. Inserted image shows a magnified SEM image of corresponding aluminium surfaces as well as a water drop image on corresponding aluminium surface. Contact angle of as-received (virgin) aluminium was measured as 70.6°. When aluminium was dipped into mixture solution of KOH and lauric acid for 30 min, the contact angle of aluminium is found 136.4°. When aluminium was dipped into mixture solution of KOH and lauric acid for 60 min, the treated aluminium shows the contact angle of 150°. The tilt angle about 5° is measured. The major changes in surface morphologies have been noticed with increasing immersing time. A chemical reaction of KOH and lauric acid with aluminium results in an etching process leading to a rough microporous structure on the surface as shown in the SEM image of figure 3. When aluminium was immersed into mixture solution of KOH and lauric acid for 30 min, minor changes in the morphology are noticed but cracking on surface are clearly seen as shown in high magnified SEM image of figure 3 (b). Craterlike micro-features on aluminium surface are seen when immersing time was increased to 60 min as shown in figure 3 (c). The formation of a rough micro-cratered surface, in combination with a modified surface chemistry arising from lauric acid, contributes to the creation of superhydrophobic surface.

In one-step process, chemical etching with KOH and coating with lauric acid are together done at a time. For this aluminium substrates were immersed in a mixture of 10 gm/liter KOH solution and 20 gm/liter ethanol solution of lauric acid for 5-60 minutes. In this process, OH- ions attack the higher energy sites on aluminium surface such as grain boundaries and dislocations and release Al3+ (reaction 4).

\[
\text{Al} + 3\text{KOH} \rightarrow \text{Al(OH)}_3 + 3\text{K}^+ + 3\text{e}^- \tag{4}
\]

The released Al3+ immediately combines with CH3(CH2)10COO- ions to form compound according to the reaction 3. The etching of KOH creates roughness on the surface. Aluminium laureate makes a hydrophobic tails on the rough structure. These hydrophobic tails promotes the water repellency on original hydrophilic aluminium surfaces. On increasing etching time from 30 min to 60 min, major changes on the surface are observed (Figure 3). At 60 min etching aluminium surface becomes very rough due to the formation of pits of increased depth. Air can entrap within these pits and provide better geometrical conditions for the superhydrophobic characteristic. This is confirmed by Cassie-Baxter theory [58].

In order to compare both processes, the contact angle versus immersing or etching time is plotted in figure 4. Superhydrophobic surfaces are achieved by both processes. In two-step process, superhydrophobicity (contact angle greater than 150°) appears when aluminium substrate was chemically etched with KOH solution for 30 min and followed by treatment with ethanol solution of lauric acid for 30 min. Similar results are observed when aluminium substrate was chemically etched with KOH solution for 45 and 60 min and followed by treated with ethanol solution of lauric acid for 30 min. In one-step process, superhydrophobicity appears when aluminium substrate was treated with a mixture of KOH solution and ethanol solution of lauric acid for 60 min. One-step process takes more etching time than two-step process because etching with KOH and treatment
with lauric acid are done together in single step. \( \text{Al}^3+ \) and \( \text{CH}_3(\text{CH}_2)_{10}\text{COO}^- \) ions form simultaneously in one-step-process. Reaction 3 and 4 also occur simultaneously and they interfere each other. So the overall etching slows down and it takes 60 min in etching. It is to be noted that total experiment time in both processes is same. One-step process is however more easier and convenient method. This easy and effective one-step process of making aluminium surfaces superhydrophobic may find its potential applications in areas where problems such as corrosion, cleaning, friction and wear materials exist.

3.1 Mechanical durability

Figure 5 shows the optical images of bent and folded samples. It is observed that surface bending of coating do not have much effect on the superhydrophobicity. Figure 5 shows the water droplets in kink region formed due to 90 and 180° bending and water droplets here are still able to maintain spherical shape and roll off easily. When checked after 4 times folding and de-folding, surface starts to worn out and becomes sticky superhydrophobic. This implies that static contact angle decreases and tilt angle increases drastically. In this condition, water drop cannot roll down and remains sticky on the surface [59].

3.2 Thermal and UV stability

Figure 6 shows the water contact angle of annealed samples at different elevated temperatures. When annealed temperature is reaches 125 °C, not much changes occur but on increasing temperature to 150 °C, the contact angle slightly decreasing from 152 to 145°, indicating the stable coatings within this temperature range. On increasing temperature further, the surface not only loses its superhydrophobicity but starts becoming hydrophilic.

The superhydrophobic surfaces were also exposed to an open environment and UV light in UV curer to check stability. It is found that superhydrophobic nature of the surface remains unchanged even after leaving it in open environment for one year. Figure 7 shows the water contact angle of samples versus UV exposer time. The wettability is found to be unaffected upto 24 hours of UV exposure and after this, contact angle slightly reduces, showing UV durability of coating.

3.3 Corrosion-resistance and self-cleaning properties

In order to check corrosion-resistant property, superhydrophobic samples are immersed in 3% NaCl for 10 days. Contact angle continuously decreases with increasing immersion time. Along with, negligible deviation in decreasing trend is noticed after one and two day’s immersion and this is due to error in measurements (figure 8). After 10 days of test, the contact angle is found to be 146° from its initial contact angle of 152°. This confirms the excellent corrosion-resistance properties of coatings.

Figure 9 shows the self-cleaning ability of the superhydrophobic aluminium surface along with as-received aluminium surface. It is clearly shown in figure that original aluminium sample does not possess self-cleaning properties as water and dust particles remain stick on the surface. On the other hand, dust particles on superhydrophobic aluminium surface are easily removed by water droplets’ rolling action, confirming the strong self-cleaning ability of the coatings.

3.4 Water repelling nature

Impact of high speed water jet on superhydrophobic aluminium surface was observed and compared with impact on as-received aluminium surface (Figure 10). On spraying water, it spreads immediately on as-received aluminium surface but it bounces in opposite direction on
superhydrophobic aluminium surface as shown in figure 10. On keeping superhydrophobic aluminium surface on water, it starts floating and maintains its floating status for many weeks (Figure 11). On the other hand, the original aluminium surface is not able to float and sink immediately in water. Superhydrophobic aluminium repels the water and weight of displaced water becomes more than the body of sample. Therefore it remains floated for several weeks. In another experiment, when superhydrophobic aluminium surface was kept overnight in deep freezer and then was taken out to be exposed in air. It is observed that only few water air moisture drops are able to condense and settle on this surface as shown in figure 12. Whereas on original aluminium surface, air moisture condense very quickly and completely cover the entire surface as seen in figure 12. Above water jet impact, flotation on water surface, and low temperature condensation tests indicate excellent water repelling and buoyancy nature of coatings.

3.5 Regeneration of superhydrophobic surface

Regeneration of superhydrophobic coating is very important for its practical application because often surface undergoes in extremely harsh conditions and surface can get easily damage. For instance, when coated sample was continuously annealed at 300 °C for 6 hours, water contact angle is also found to be less than 10°, i.e. surface is completely damaged due to high and continuous heating and superhydrophobicity of surface is switched to superhydrophilicity. Under this high heat treatment, surface structures changes due to melting of aluminium laurate present on the surface and surface chemical modification which dramatically affect the wettability of the surface [60].

To regain the superhydrophobicity, damaged sample was again immersed in ethanol solution of lauric acid for 30 min, followed by air drying for 24 hours. After this, water contact angle was measured and it is observed that coating is regenerated and restored its superhydrophobicity with static contact angle of more than 150°. This is showing regeneration ability of superhydrophobic coating.

4. Conclusions

In this paper, superhydrophobic coatings on aluminium surfaces was synthesized using two-step and one-step processes. In two-step process, roughening of aluminium surface by immersing in KOH solution followed by lowering surface energy by immersing rough aluminium in ethanol solution of lauric acid solution were done. Whereas in one-step process, roughening and lowering surface energy were done by immersing aluminium surfaces in mixture of KOH and lauric acid. The SEM studies reveal the presence of a rough micropattern on the treated surfaces, roughness of treated surfaces increases with etching time and the contact angle measurements confirm the superhydrophobicity. Water contact angle as high as 153° was obtained on treated surface via two-step process and water contact angle of 150° was also obtained on treated surface via one-step process. Superhydrophobic aluminium coatings show the excellent self-cleaning nature. Superhydrophobicity of coatings does not change even after 10 days immersion in 3% NaCl solutions, confirming the anti-corrosion properties of coatings. No effect of water jet of high speed stream on surfaces and almost no accumulation of moisture from air on the cooled surfaces shows the excellent water-repellent nature of coatings. Besides, the sample remains floating on the water surface for several weeks without shrinking, indicating excellent buoyancy nature of coatings. Experimentally it is observed that superhydrophobicity of coatings withstand without unaffected upto 150 °C and is UV stable for 24 hours. Additionally, superhydrophobic nature withstands on 90° and 180° surface bending, and repeated folding and de-folding, revealing the mechanical strength of coatings. Further, upon 6 hours continuous heating at 300 °C, superhydrophobicity of coatings lost and turns into superhydrophilicity; however, superhydrophobicity of coatings restores by simply immersing in lauric acid for 30 min. The aforesaid durable and regenerable
superhydrophobic aluminium surfaces with excellent water-repellent, self-cleaning, and anti-corrosive properties have potential industrial applications.

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**Figure captions**

Figure 1. Schematic diagram of two-step and one-step processes.

Figure 2. SEM images of aluminium surfaces (a) as-received, and etched with KOH for (b) 5 min, (c) 10 min, (d) 20 min, (e) 30 min, (f) 45 min, (g) 60 min, followed by treated with lauric acid. Insert shows a magnified SEM image of corresponding aluminium surfaces as well as a water drop image on corresponding aluminium surface.

Figure 3. SEM images of aluminium surfaces (a) as-received, and treated with KOH and lauric acid for (b) 30 min, (c) 60 min. Insert shows a magnified SEM image of corresponding aluminium surfaces as well as a water drop image on corresponding aluminium surface.

Figure 4. Contact angle as a function of etching time for two-step and one-step processes.

Figure 5. Optical image of side view of water droplet on the bendable (about 90°) superhydrophobic aluminium surface and optical images of water droplets on the superhydrophobic aluminium surface after bending at 180° and released back to the original position.

Figure 6. Effect of one hour annealing of superhydrophobic aluminium surfaces at different temperatures on static contact angles.

Figure 7. Static contact angle of superhydrophobic aluminium surface versus UV exposure time

Figure 8. Static contact angle of superhydrophobic aluminium surfaces versus immersing time in 3% NaCl solutions

Figure 9. Optical images of self-cleaning behaviour of as-received untreated and superhydrophobic aluminium surfaces

Figure 10. Optical images of water jet impact on untreated and superhydrophobic aluminium surfaces

Figure 11. Optical images of superhydrophobic aluminium surface floating on the water surface

Figure 12. Optical images of condense droplets due to low temperature on untreated and superhydrophobic aluminium surfaces
Figure 1.

Figure 2.
Figure 3.

Figure 4.
Figure 5.

Figure 6.
Figure 7.

Figure 8.
Figure 9.

Figure 10.