Corrosion Resistant Superhydrophobic Aluminum Alloy: A Review

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Abstract. Aluminum alloys are widely used in aerospace and space applications due to their high strength to weight ratio. The most prevalent method to prevent corrosion of aluminum alloys is anodic oxidation or anodization treatment. The anodized layer is porous and hence there are chances of penetration of moisture and corrosion of underlying substrate underneath the anodized layer. Surface modification of the aluminum alloy by superhydrophobic coating is a very attractive method to improve the corrosion resistance of aluminum alloys. The inspiration for the fabrication of superhydrophobic coatings is obtained from various examples in nature such as strider’s legs and lotus leaf. The fabrication of superhydrophobic coatings involves two important steps; generation of a rough surface and deposition of low surface energy material. The present paper reviews the various researches undertaken for the production of superhydrophobic surfaces on aluminum and aluminum alloys. Finally, the scope of future research activities in the fabrication of superhydrophobic coatings has been discussed in the paper.

1. Introduction

Aluminum alloys are abundantly used in the aviation industry. Aluminum is known to have good resistance to corrosion due to the formation of an adherent oxide coating on its surface. However, aluminum alloys are prone to corrosion in presence of aggressive environment [1]. Especially, in marine environments, aerosols are generated which contain small salt particles. These aerosols can be transported by wind and deposited on the metal surface that transform into salt solution droplet which can accelerate the corrosion process [2,3]. Earlier, chromate coatings were used which is now subjected to severe governmental regulations due to the carcinogenic nature of hexavalent chromium [4]. Aluminum alloys used in aerospace and space application are presently given anodization treatment to provide corrosion resistance. However, the porous oxide layer produced by anodization can easily allow for penetration of Cl⁻ ions in saline environment [5]. Hence, the anodic oxidation of aluminum alloys is not fully effective in aggressive environments.

There are two types of superhydrophobic surfaces. Highly adhesive surface allows the water droplets to stick to the surface even when the surface is turned upside down while low adhesive superhydrophobic surface have rolling angle less than 10° [6]. The second type of superhydrophobic surface is of great interest to researchers; recently, much attention is given to super-hydrophobic surfaces having water contact angle greater than 150° and water sliding angle less than 10° [7-10]. It is known that metals have a high surface energy such that a water droplet will be adsorbed on its surface and show a hydrophilic state (water contact angle < 90°). Superhydrophobic coatings change the wettability of the metal surface from hydrophilic to superhydrophobic, minimizing the contact area between the corrosive solution and the substrate [11]. In the presence of superhydrophobic surface, the corrosion currents are shown to reduce drastically in corrosive environments [12]. Since superhydrophobic surfaces possess excellent repulsion to water, they can be effective in preventing corrosion [2, 13,14].
2. Superhydrophobic Coatings: Inspiration and History

Nature has several non-wetting low adhesive surfaces like lotus leaves, water strider’s legs, wheat leaves, duck feathers etc. [6, 15-17]. Especially, the ‘lotus effect’ [18] has generated great interest from researchers because of the application of super-hydrophobic surfaces in generating self-cleaning [19], anti-wetting [20], anti-icing [21], anti-corrosion [22], friction reducing [23] and antimicrobial [24] surfaces. The lotus leaves have self-cleaning tendency by rolling off adhering dust particles along with water droplets [25, 26]. The research on superhydrophobic coatings is inspired by this non-wetting phenomenon present in nature [2, 27-28].

The development of superhydrophobic coatings started around 200 years [15]. Thomas Young [29], first proposed the concept of surface wettability in 1805. The first superhydrophobic surface was produced by Ollivier in 1907; he could obtain a water contact angle of around 180° using soot, lycopodium powder and arsenic trioxide [30]. Langmuir [31] reported in 1920 that an organic compound absorbed as a monolayer, could change the wetting and frictional properties of solid surfaces. This finding motivated several researchers to work on chemical modification to control surface wettability. An optimum combination of roughness along with low surface energy is important for fabricating coatings possessing superhydrophobic property (Fig. 1) [25, 26, 32].

Wenzel developed a relationship between the macroscopic surface roughness of a solid and the contact angle. He showed that surface roughness can enhance hydrophobicity [25, 33]. The model developed by Wenzel suggested that the surface area of a hydrophobic solid increases with the increase in roughness. According to Wenzel, the contact angle of water (θ) on a rough surface of any material is given by

\[ \cos \theta = r \cos \theta^* \]

where \( r \) is the roughness parameter (ratio of the real surface area to the projected surface area), \( \theta^* \) is the contact angle of water on the smooth surface made of the same material. Since \( r \) is greater than 1, a hydrophobic surface will become more superhydrophobic when it is made rough, according to the above equation.

Cassie and Baxter [25, 34] proposed that porous and rough surfaces have the capability to trap air between water and solid. This theory proposed by Cassie and Baxter is known as the composite wetting model. According to this model, a composite interface of solid and gas is formed between a water droplet and a superhydrophobic surface. The apparent contact angle (θ) of a water droplet on a solid superhydrophobic surface is given by
\[
cos \theta = r_f \cos \theta_o f_{SL} - 1 + f_{SL} \tag{2}
\]

where \( \theta_o \) is Young’s contact angle on an ideally flat surface, \( f_{SL} \) is the fraction of the wetted surface and \( r_f \) is the roughness of the wetted surface. From Eq. 2, it can be understood that a small value of \( f_{SL} \) would result in a high value \( \theta \) on a rough hydrophobic surface. The two models discussed above are schematically shown in Fig. 2.

![Schematic representation of (a) Wenzel model and (b) Cassie-Baxter model](image)

**Fig. 2** Schematic representation of (a) Wenzel model and (b) Cassie-Baxter model

### 3. Fabrication of Superhydrophobic Coating on Aluminum/Aluminum Alloys

In case of lotus leaves, water droplet readily remains on the peak of the micrometer/nanometer scale rough structure on the leaf because air is trapped in the grooves present in between the rough structures [6, 35-37]. Similarly, the superhydrophobic coating is composed of hills and valleys; the air gets trapped in the valleys. Hence, it becomes difficult for the corroding anion (like Cl\(^-\)) to reach the bare metal surface [12]. Artificially, superhydrophobic surfaces can be fabricated in two steps: generation of a rough surface and the reduction of surface energy of the surface [6, 9, 38]. Methods such as anodic oxidation [39,40], electrochemical etching [41,42], chemical etching [43,44], laser etching [45], boiling water immersion [46], and coating [47,48] were developed to fabricate suitable rough structures required by superhydrophobic surfaces on aluminum substrates. The surface energy can be reduced by grafting a low surface energy material like triethoxyoctylsilane, flouroalkylsilane and fatty acids onto the roughened surface [6, 9]. Some reported research work carried out by various researchers is discussed in the following paragraphs.

Song et al. [6] produced a superhydrophobic coating on aluminum substrate (≥99.9 wt% purity) in two steps; the first step involved dipping the substrate in a solution of CuCl\(_2\) for roughening the surface while the second step was to produce the desired low surface energy by dipping the roughened substrate in an ethanolic solution of flouroalkylsilane.

In one research, superhydrophobic coating (contact angle of around 160°) was fabricated on silicon substrate by repeatedly dipping in a saturated fatty acid solution (stearic acid) and consequent drying in air [26]. The repeated dipping and drying produced a natural double scaled rough coating of low surface energy. Hence, the low surface energy material used also increased the surface roughness of coating with each dip-dry cycle.

A solution containing NaCl, intended for electrochemical machining of the aluminium metal substrate, along with flouroalkylsilane for creating a rough surface, was reported to produce a superhydrophobic surface having static water contact angle of 166° and a tilting angle of around 1° [42]. Guo et al. [49] produced superhydrophobic surfaces by etching aluminum alloy AA 2024 in an alkali solution followed by coating with low surface energy materials; perfluorononane(C\(_9\)F\(_{20}\)) and perfluoropolyether (PFPE).
They studied the effect of etching time and the concentration of NaOH on the surface roughness and its effect on the superhydrophobicity. At an optimum surface roughness of 2.7-5.8 μm, they could obtain superhydrophobicity on the aluminum alloy surface. This was possible due to the entrapment of air between microprotrusions and nanoparticles formed on the surface of the aluminum alloy.

Boiling water has been used for obtaining a rough surface on aluminium 6061 alloy followed by sputtering of polytetrafluoroethylene (PTFE) on the aluminum substrate surface to reduce the surface energy [46]. The treatment of aluminum surface with boiling water leads to the formation of boehmite (Al₂O₃(H₂O)) which is used in industries for corrosion protection. The consequent superhydrophobic coating obtained had a static water contact angle of around 164°. Zhang et al. [50] fabricated a simple superhydrophobic coating on aluminium alloy by immersing it in a solution containing hydrochloric acid and fatty acid molecules. Xie et al. [9] developed a two step method to fabricate superhydrophobic surfaces on aluminium (chemical composition: 4.5%Cu, 1.5%Mg, 0.6%Mn, 0.5%Si, 0.5%Fe, 0.3%Zn). They obtained this by treatment of the aluminum with boiling NaOH solution, followed by immersion in an ethanolic solution of lauric acid.

Song et al. [51] fabricated petal like structure, similar to lotus leaf on the surface of aluminum by a one step immersion process using perfluorodecyltriethoxysilane (PDES). Saleema et al. [38, 52] prepared superhydrophobic surface on aluminum alloys (AA 6061) by immersing the substrate in a solution comprising of sodium hydroxide and fluoroalkyl-silane molecules. Ou et al. [53] fabricated a single step superhydrophobic coating on aluminium alloy AA 5083 by dipping the sample in a solution containing low surface energy perfluorooctyltrichlorosilane (PFOTS) molecules, ethanol and water. The treated alloys produced a rough surface covered by PFOTS molecules, showing a contact angle of 150° and sliding angle lower than 10°. Chen et al. [10] used chemical etching method using an alkali treatment in 1 mole /l NaOH aqueous solution, followed by immersing in a solution of hydrochloric acid and acetic acid to produce a superhydrophobic surface on aluminium (99.8 % purity). They could obtain a water contact angle of around 154° and water sliding angle of around 5° due to the presence of a combination of protuberances and micro-pores, which effectively trapped air. Moreover, as the etching time increased, the protuberances and micro-pores increased in number and decreased in size, leading to more effective air entrapment. However, beyond a certain etching time, the structure formed was destroyed due to excessive etching.

Electrochemical machining in NaNO₃ is found to help in dissolving grain boundaries and dislocations and produce a micro-nano rough surface [41]. Another work involves the development of superhydrophobic coating by brush-painting process [54]. This was achieved by using poly (furfuryl alcohol)/copper composite coatings followed by immersion in stearic acid. Superhydrophobic property was obtained due to the formation of copper stearate. The low surface energy of copper stearate has been reported elsewhere [55]. Immersion of aluminum alloy (chemical composition: 5.51 wt% Cu, 1.68 wt% Mg and balance Al) in a solution of stearic acid and N,N-dicyclohexylcarbodiimide in n-hexane for 24 h can produce the desired low surface energy after surface roughening in HNO₃/H₂O₂ solution [56].

4. Enhancement of Corrosion Resistance of Aluminum Alloys

Some published research articles have specifically focused on the corrosion resistance of superhydrophobic coatings. These are discussed in this section. One research mentions the use of a solution of myristic acid in ethanol and immersion of anodized aluminum in the solution for obtaining the super-hydrophobic coating [57]. They found that aluminum corrosion was largely inhibited due to the formation of superhydrophobic film on the anodized aluminum surface.

Similarly, He et al. [5] fabricated superhydrophobic coating by melting myristic acid adsorbed onto anodized aluminium of 99.9 % purity. The anodization was carried out in 15 wt. % sulphuric acid. They
reported that the surface treatment of anodized aluminum significantly improved the corrosion resistance of the substrate in seawater environment. The static contact angle in NaCl solution was found to be 154°. The surface roughness was increased by the anodization treatment. When the chemical modification was done by melting myristic acid, the acid filled up the nano-pores of the anodized surface.

Shi et al. [47] fabricated superhydrophobic surfaces on aluminum substrates (99.9 % purity) by acid etch followed by nano-silica particle deposition and then heat treatment. The nano-silica particles were deposited by immersing the substrate in an aqueous solution of nano-silica in tetramethyldiamonium hydroxide. The surface was then reacted with fluorosilane. They found improvement in the corrosion performance of the aluminum in NaCl environment.

Lu et al. [2] fabricated a superhydrophobic surface on aluminium (99.9 % purity) by first producing an anodized layer and then subjecting the surface to a fluorination treatment. The anodization treatment was done using phosphoric acid in which aluminum was used as the working electrode and stainless steel was used as the counter electrode. The anodization treatment produced the desired surface roughness with a pillar-like or pore-like structure, depending on the time of anodization treatment given to the substrate. It was observed from Eq. 2 that the pillar like structure has lower \( f_{SL} \) than pore like structure and the pillar like structure results in a higher contact angle compared to pore like structure. The fluorination treatment was done by coating with silane-ethanol solution for 5 minutes at room temperature. The resultant coating was found to be highly adherent and scratch resistant. The deliquesced NaCl particle easily slipped off the superhydrophobic surface produced. The corrosion performance of the aluminum was largely improved in marine atmospheric condition. This was due to the presence of an air film between the saline solution and the superhydrophobic layer.

In another published work, anodization treatment was done followed by low temperature plasma treatment to produce the required combination of micro and nano structure [58]. Trichlorooctadecyl-silane was used to reduce the surface energy of the aluminum substrate. They could obtain a static water contact angle of around 158°.

It has been reported by Wang et al. [58] and Lu et al. [2] that anodization on aluminum alloys gives a suitable rough nano-pore structure film which was found to be beneficial in depositing the low surface energy materials for producing a superhydrophobic surface. Li et al [40] have shown that hard anodization of 2A12 aluminum alloy resulted in a composite structure made up of micro-scaled alumina columns and pores which results in an increase in water contact angle. The improved wetting property was reported to be due to decrease in surface energy caused. Moreover, the anodized layer not only provides a rough surface, but also an insulating layer with superior adherence to the substrate [2].

In general, the anodic as well as cathodic current densities decrease when an aluminum substrate is provided with a superhydrophobic coating. In addition, the corrosion potential also shifts to more noble potential [5, 44, 57]. The corrosion currents have been reported to reduce by around three orders of magnitude [57].

The superhydrophobic coatings on anodized aluminum substrate show a two time constant behavior under electrochemical impedance spectroscopy studies [5]. The two types of equivalent circuit models are shown in Fig. 3 (a) and (b). \( R_{ct} \) is the charge transfer resistance at the Al-coating interface, \( C_{dl} \) is the double layer capacitance corresponding to interaction at the substrate/coating interface and \( R_s \) is the solution. \( R_c \) correspond to resistance to the electrolyte in the pores on the coating or the resistance of ion conducting paths that develop in the coating. \( C_c \) is the capacitance of the surface coating [47]. The \( R_c \) of superhydrophobic film is found be higher when the anodized aluminum is treated with the organic coating. Higher \( R_c \) values are ascribed to the improved anticorrosive property of the aluminum substrate.

Air is entrapped in the roughness grooves of the anodized layer due to which the penetration of aggressive species like Cl⁻ ions is largely reduced while the adsorbed organic coating gives the excellent
anti corrosion properties. A Warburg impedance element can occasionally be observed, which indicates the penetration of water into the coating and the formation of a new electrolyte/Al interface under the coating [47].

Fig. 3 Schematic of the equivalent circuit model for roughened and organic compounds

5. Future Prospects
All the published literature mentions superhydrophobicity as the reason for improved corrosion resistance. However, what has largely been overlooked by most of the studies is that in a superhydrophobic surface, capillary condensation in groove of the film may induce penetration of the corrosive solution (like saline solution) into the film. This, in fact, has been reported by Wang et al. [13]. If the water or moisture is able to penetrate to reach the substrate under such condition, the corrosion of the substrate can easily take place. Hence, if additional metal ions are incorporated in the organic base, it can provide anodic/cathodic protection to the substrate.

Another important aspect which has been addressed to a lesser extent is the production of an optimum rough surface on the aluminum alloy. Very few of the published research have shown the effect of different surface roughness on the superhydrophobicity and the corrosion resistance of the alloy. The process parameters can play an important role in the roughness of the surface, which in turn will affect the superhydrophobicity of the immersion coating as well as its adherence.

6. Conclusions
Aluminum alloys are usually prevented from corrosion by anodic oxidation or anodization treatment. However, the anodized layer is porous and there are chances of penetration of moisture and corrosion of underlying substrate underneath the anodized layer can take place. Surface modification of the aluminum alloy by superhydrophobic coating is a very attractive method to improve the corrosion resistance of aluminum alloys. The paper reviews the various methods by which fabrication of superhydrophobic coatings have been done by various researchers. The important steps involve the generation of a rough surface and deposition of low surface energy material. These have been done either in one or in multiple steps. The simplest method reported is by immersion as no special equipment is required and the process is relatively simple and can be carried out on an industrial scale. Anodization treatment of aluminum
alloys seems to be a very versatile method for producing a combination of micro and nano scale rough structure. Future scope of work can be to improve the corrosion resistance of the substrate by anodic/cathodic protection by incorporating additional metal ions to the organic coating and the study of effect of surface roughness on the corrosion resistance of the substrate.

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