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The Role of Hydrophobicity in the Development of Aluminum and Copper Alloys for Industrial Applications

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Abstract

Improvement of corrosion resistance is a main challenge in surface and corrosion engineering. Water is a main part of corrosion mechanism, and the omission of this part will be helpful. By mimicking from nature, superhydrophobicity is a helpful method to decrease corrosion and water presence on the surface. Superhydrophobic surface and coating is a new type of coating that extension in recent decade and increase application of this area every day. These type of coatings are using on widespread of applications such as solar panels, displays, windows, paints and fabrics to obtain water-proof, anticorrosive, self-cleaning and stain-resistant surfaces. Many different studies have been reported to produce superhydrophobic surfaces from many diverse materials (polymers, metals and other inorganic materials, composites, textiles, paper). In this chapter, recent developments in the application of superhy-drophobic coatings for corrosion protection of aluminum and copper alloys will be discussed. This chapter includes new production methods, theoretical works, and the limitations of superhydrophobic coatings.

Keywords: Superhydrophobic, coating, Aluminum, Copper, Corrosion

1. Introduction

Investigation and research about superhydrophobic (SH) surfaces have been done as early as the 1940s, but it is just recently that this field became a great point of interest [1]. At this time,

the state of the technology is at a level to produce many possible applications. Also, there is a race to discover the best procedures, methods, and theories. During the past decade, researchers have published a lot of results in application and production methods. Polystyrene nanotube forests to nano-casting lotus leaves are examples of production methods, and the application ranges from lab-on-chip fluidics to self-cleaning paints [2]. There are widespread production methods to obtain different properties. There are two main challenging problems for researchers to solve: low effective lifetimes and high fabrication costs.

Water aggregation on the surface of metals in nature is a main problem that is responsible for many types of destruction of metals such as corrosion and erosion [3-5]. Corrosion of metals depends on the amount and state of water on the surface. The destruction of the passive layer of oxide through the impact of water, sand, and abrasive particles occurs with loss of mechanical strength and corrosion resistance [6, 7]. Concrete structures that are very prone to water penetration, as well as metallic structures, become sensitive to corrosion on coming in contact with water [8]. Aeroplanes, helicopters, all ground transports, and concrete structures are subjected to serious erosion problems [9, 10].

Over the past decade, a lot of progresses have been made on the development of artificial superhydrophobic surfaces based on lotus leaf [1, 11-13]. Lotus leaf is held as a symbol of purity in many countries, especially in some regions of Asia, due to its ability to remain clean when emerging from murky ponds [14]. The natural cleaning mechanism that originated from their microscopic structure and surface chemistry and that was first time reported by Botanists is called Lotus Effect. This is explained in terms of water contact angle [15, 16]wherein it is larger than 150º and the sliding angle is less than 10º. It is also hydrophobic as a result of a binary structure (micro- and nanoscale), as well as the wax layer present on the leaf surface [14, 17-20]. Recently, various researchers have successfully fabricated superhydrophobicity with some specific metallic substrates, such as Copper (Cu), and Aluminum (Al) [21-28].

The fabrication of engineered dust and water repellent surfaces is a novel method to eliminate destructive species and control corrosion [11, 29]. Nature has shown the way to keep the surfaces clean and the lotus flower is a good example with a hierarchical surface comprising of micro valleys and nano hills. The valleys are comprised of nanohairs and epicuticular wax particles while the hierarchical structure is responsible for dust and water repulsion. This type of surface with a high contact angle is called a superhydrophobic surface [30-34].

The wet contact angle on a flat solid surface is shown in figure 1. Surface chemical composition is the main factor which affects surface wettability. The contact angle is correlated by three interfacial free energies: free energies at the solid-air (γ_{SV}), solid-liquid (γ_{SL}), and liquid-air (γ_{LV}) interfaces, by the Young's equation [35]:

$$\cos\theta_{flat} = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}}$$
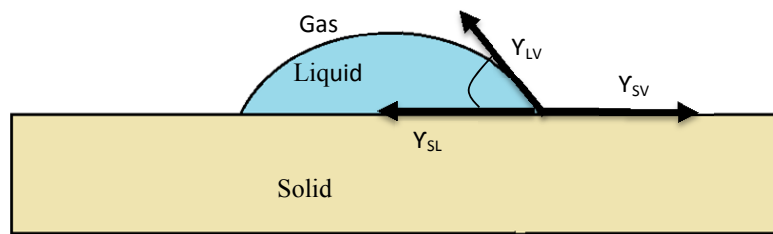
(1)

Figure 1. Young's equation equilibrium condition on a flat surface.

As shown in Equation (1), by decreasing the surface free energy of solid-air interface (γ_{SV}), hydrophobicity is increased. By the range of θ^{flat}, the surface is divided into two categories. First, when θ^{flat} is smaller than 90°, the solid surface is considered intrinsically hydrophilic. Second, when θ^{flat} is greater than 90°, the solid surface is considered intrinsically hydrophobic. According to the reports, with the lowest surface energy, the maximum water contact angle can be obtained such as in lotus flower to 120°. Further increase of the hydrophobicity can be achieved by increasing by surface roughness [36].

In 1936, Robert N. Wenzel reported the effect of surface roughness on wettability [37]. As shown in figure 2, Wenzel argued that if the droplet contours in the roughness, it should enhance the hydrophobicity with a linear relationship between the contact angle and roughness given by:

$$\cos\theta^{\omega} = r\cos\theta \tag{2}$$

In the equation 2, Static θ referred to equation (1) is the contact angle of a smooth flat, θ^{w} is the apparent contact angle enhanced by roughness and r is the roughness factor can be defined by

$$r = \frac{True\ Surface\ Area}{Horizontally\ Projected\ Surface\ Area} \tag{3}$$

The Wenzel equation shows that by increasing r (roughness factor), the hysteresis will increase but this equation is only applicable until r reaches 1.7, after which, the hysteresis begins to decrease. The Wenzel contact angle theory cannot be explained on a rough surface which signifies the transition to the Cassie-Baxter model. A. B. Cassie and S. Baxter further developed the theory to consider trapped air helping to suspend the droplet over the roughness contours. Figure (2) shows that the drop can lie on a surface and air composite state defined by the solid fraction (f), which is the fraction of solid in contact with the liquid droplet. With the Cassie-Baxter model, the apparent contact angle (θ^{c}) related by Young's contact angle (θ) and solid fraction (f) is given as [38]:

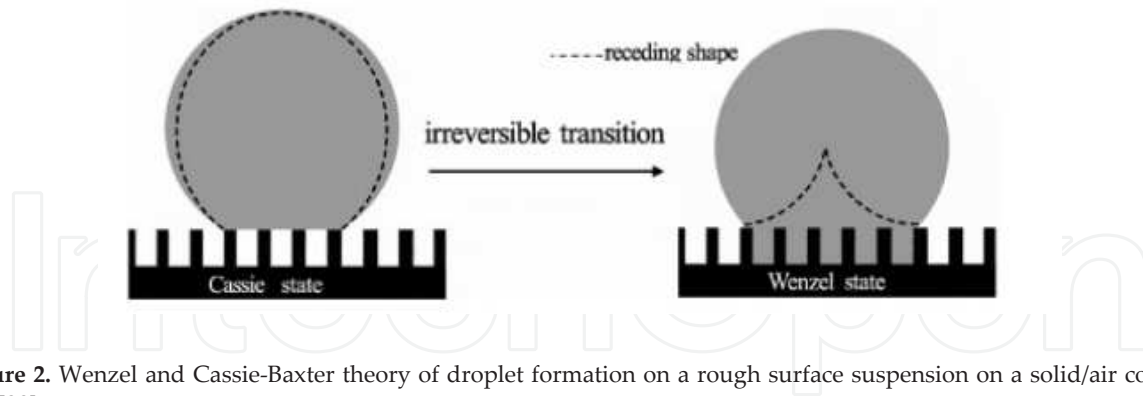$$\cos\theta^{c} = f\cos\theta + f - 1 \tag{4}$$

Figure 2. Wenzel and Cassie-Baxter theory of droplet formation on a rough surface suspension on a solid/air composite [38]

As seen in this equation, apparent contact angle (CA) is increased by decreasing the solid fraction (f) in high porous surface and increasing the CA of the smooth flat surface (θ) in low surface energy and it is going to be a superhydrophobic surface.

The Wenzel's and Cassie-Baxter's models represent the exact contact state between the liquid and the rough solid surface. These equations are applied for numerical demonstration on the superhydrophobic surface materials. The Cassie-Baxter model explains how extremely rough surfaces are energetically favourable to suspend the droplet on a composite surface of solid and air [39].

For more explanation, the dependence of surface roughness and contact angle will be further discussed. By placing a droplet on the solid surface, the three interfaces exist [40]: solid-liquid, solid-air, and liquid-air. The relationship between these three interface energies is shown in equation 1. Surfaces can be divided into two groups according to their affinity to water: hydrophilic (water attracting) and hydrophobic (water repellent). Water molecules that interact with the surface, which bear electric charges or polar groups typically are hydrophilic, while non-polar surfaces are generally hydrophobic. On hydrophilic surfaces, the water molecules suffer a loss of hydrogen bonding partners at the interface [36, 41].

For superhydrophobic surfaces, roughness by special properties plays a main role. For explaining the surface roughness, there are surface parameters such as Roughness Average (R_a), Root Mean Roughness (R_q), and Roughness Depths (R_z or R_{max}). The effects of these parameters on superhydrophobicity are not clear yet. The surface roughness in a superhydrophobic surface should be a combination of nano and micro structures. For a rough solid surface, which consists of asperities and valleys, with a typical size of roughness detail smaller than the size of the droplet, CA was calculated by the Wenzel model. Natural superhydrophobic surfaces also exhibit hierarchical roughness structure, therefore; a successful water-repellent surface should also have a multiscale roughness.

2. Development of alloys by superhydrophobic surfaces

The surface treatment of metals is most important in metal production. There are various surface treatment methods such as surface hardening, painting, and coating [4, 5, 38, 42].

Superhydrophobic coating is a favourable research area in various applications because of its natural water-resistant properties. Superhydrophobic surfaces have been achieved by the controlling of surface roughness and topography in hydrophobic materials [39, 43]. For superhydrophobic surface production, a variety of methods have been reported by mimicking the surface of lotus leaves such as electrodepositing [44-46], anodic oxidation [27, 47, 48], plasma and laser treatment [49-53], physical and chemical vapour deposition [54-59], electro-spining [60-62], sol gel techniques [63-65], and other methods. Various methods that have been used to prepare superhydrophobic surfaces according to the properties of metals and the method of superhydrophobic treatment for copper and aluminium will be discussed in this review.

2.1. Superhydrophobic coatings in copper and alloys

Copper and its alloy are important materials that are used in the industry because of their high electrical and thermal conductivities, good strength formability, and some others remarkable properties. They are widely used in many applications such as electronic industry and communications as a conductor in electrical power lines, pipelines for domestic and industrial water utilities including seawater, and heat conductors and heat exchangers [13, 66]. In environments that contain chloride ion such as marine environment, the copper alloys are susceptible to various corrosion types such as pitting, stress corrosion cracking and crevice corrosion. The protection of these alloys from this attack is a main concern for researchers [67-70]. One of best method for protection is the use of superhydrophobic coatings.

The physical and chemical properties of copper play an important role in superhydrophobic coating preparation. The information on the properties can help in choosing the right chemical agent and predicting the available mechanisms during the superhydrophobic surface creation.

2.1.1. Mechanism of hydrophobic coating on copper and copper based alloys

Copper has an atomic number of 29, with valance of 1 or 2, lattice structure FCC, and oxidation state of 1 and 2. The typical blue hexaaquacopper (II) ion ($[Cu(H_2O)_6]^{2+}$) is the simplest ion that copper forms in a solution. Hydroxide ions of NaOH remove hydrogen ions from the water ligands attached to the copper ion [71].

When the hydrogen ion has been removed from two of the water molecules, a complex with no charge complex has been obtained. This neutral complex is insoluble in water and a precipitate is formed.

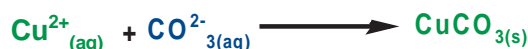$$\left[Cu(H_2O)_6\right]^{2+} + 2(OH)^- \longrightarrow \left[Cu(H_2O)_4(OH)_2\right] + 2H_2O$$

Ammonia acts as both a base and a ligand. To obtain the same neutral complex, a small amount of ammonia can be added to pull hydrogen ions off the hexaaqua ion exactly as in the hydroxide.

$$\left[Cu(H_2O)_6\right]^{2+} + 2NH_3 \longrightarrow \left[Cu(H_2O)_4(OH)_2\right] + 2NH_4^+$$

That precipitate can be dissolved if an excess of ammonia is added. The ammonia replaces water as a ligand to give tetraamminediaquacopper (II) ions. It must be noted that only 4 of the 6 water molecules are replaced.

$$\left[Cu(H_2O)_6\right]^{2+} + 4NH_3 \longrightarrow \left[Cu(NH_3)_4(H_2O)_2\right]^{2+} + 4H_2O$$

A precipitate of CuCO3 is formed as below.

$$Cu^{2+}{}_{(aq)} + CO^{2-}{}_{3(aq)} \longrightarrow CuCO_{3(s)}$$
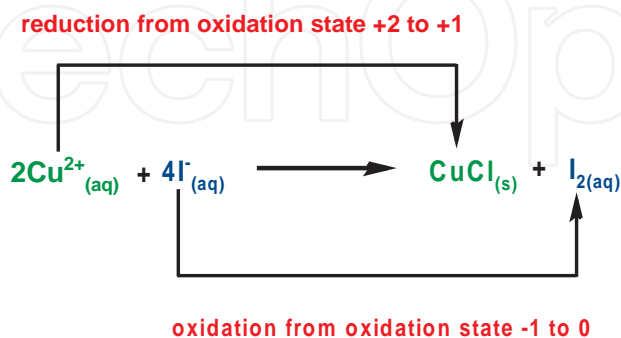
If concentrated hydrochloric acid is added to a solution containing hexaaquacopper (II) ions, the six water molecules can be replaced by four chloride ions. The reaction taking place is reversible.

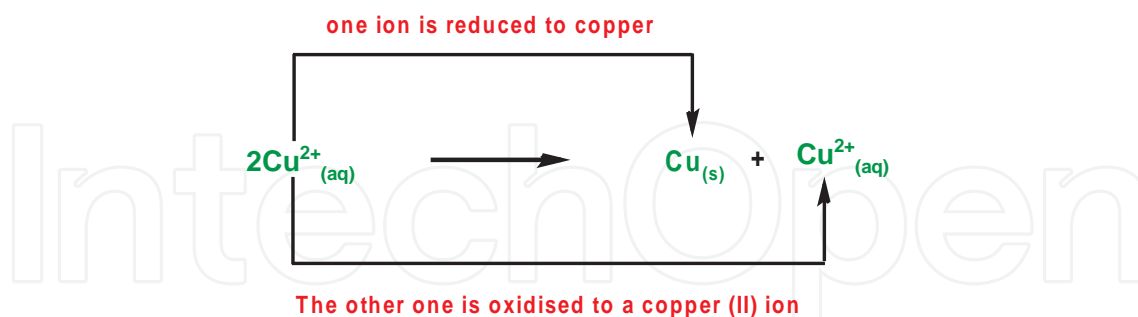$$\left[Cu(H_2O)_6\right]^{2+} + 4Cl^- \longrightarrow \left[Cu(Cl)_4\right]^{2-} + 6H_2O$$

Due to the reversible reaction, mixtures of colours of both complex ions are obtained. The colour of the tetrachlorocuprate (II) ion is variously described as olive-green. If more water is added to the green solution, it returns to its blue colour.

Copper (II) ions can oxidise iodide ions to iodine. In this process, they are reduced to copper (I) iodide.

reduction from oxidation state +2 to +1

$$2Cu^{2+}{}_{(aq)} + 4I^-{}_{(aq)} \longrightarrow CuCl_{(s)} + I_{2(aq)}$$

oxidation from oxidation state -1 to 0

Copper (I) chemistry is limited by a reaction that occurs involving simple copper (I) ions in solution. Copper (I) ions in solution disproportionate to give copper (II) ions and a precipitate of copper.

The reaction is:

one ion is reduced to copper

$$2Cu^{2+}_{(aq)} \longrightarrow Cu_{(s)} + Cu^{2+}_{(aq)}$$

The other one is oxidised to a copper (II) ion

Any attempt to produce a simple copper (I) compound in solution results to as follows: for example, if copper (I) oxide reacts with hot dilute sulphuric acid, a solution of copper (I) sulphate and water may be produced. Because of the disproportionation reaction, a brown precipitate of copper and a blue solution of copper (II) sulphate are obtained.

$$Cu_2O + H_2SO_4 \longrightarrow Cu + CuSO_4 + H_2O$$

The copper (I) oxidation state is stabilized by the formation of copper (I) complexes. For example, both [Cu (NH3)2] + and [CuCl2] are copper (I) complexes that don't disproportionate. The chlorine-containing complex is formed if copper (I) oxide is dissolved in concentrated hydrochloric acid. It is possible to think that the reaction occurs in two steps. Initially, copper (I) chloride forms:

$$Cu_2O_{(s)} + 2HCl_{(aq)} \longrightarrow 2CuCl_{(s)} + H_2O_{(l)}$$

However, in the presence of excess chloride ions from the HCl, a stable and soluble copper (I) complex is formed.

$$CuCl_{(s)} + Cl^-_{(aq)} \longrightarrow \left[CuCl_{2(aq)}\right]^-$$

Subsequently, to obtain white precipitate of copper (I) chloride (mentioned above), some water is added to this solution to strip off the extra chloride ion [72, 73].

Preparations of superhydrophobic coating on copper surface initiates by surface modification and etching in acidic environment based on copper oxidation. Liu et al. [13] have fabricated

the superhydrophobic coating on copper substrate by a simple immersion method. In their research, Cu substrates have been immersed in 13 wt. % HNO_3 for 15 s to remove surface oxides, then immersed in solution (0.06 mL 37 wt. % HCl; 0.02 mL CH3COOH; 54 mL H_2O) for 12 hours to roughen the surfaces, and then dried in the N_2 flows. They were subsequently immersed in an ethanol solution of n-tetradecanoic acid (0.1 M) at 37 ∘C for 10 days after which, they could obtain a superhydrophobic film with a contact angle larger than 150∘. In this attempt they improved corrosion resistance of copper and claim that the copper corrosion is effectively inhibited by the formation of the superhydrophobic film.

The creation of superhydrophobic surfaces by n-alkanoic acid can be explained below:

1. oxidation of copper:

$$2Cu + O_2 + 4H^+ \longrightarrow 2Cu^{2+} + 2H_2O$$

2. forming copper carboxylate:

$$Cu^{2+} + 2CH_3(CH_2)_{12}COOH \longrightarrow Cu\left[CH_3(CH_2)_{12}COO\right]_2 + 2H^+$$

N-alkanoic acid molecules capture Copper ions after being released instantly. By the reaction of copper with the above acid, the reaction is transformed to copper carboxylate and appears as a self-assembled flower-like structure. The immersion time is an important factor for this process. The superhydrophobicity of the prepared surface can be explained by Cassie-Baxter model [13, 21].

The superhydrophobic surface on copper can be prepared by 4, 5-diphenyl-imidazole (DPI). Sheng Zhao et al. [74] have used this procedure to prepare copper superhydrophobic surface. They firstly cleaned the copper ultrasonically in ethanol, acetone, and dilute hydrochloric acid in turns for 15 min to remove the contamination, grease, and oxide etc. on the surface. The DPI solvent was with various solutions such as methanol, ethanol, acetone, acetonitrile with 0.02 M concentrations. The treated copper plate was subsequently suspended in DPI solutions, which were then put into a culture cabinet and deposited for 10–15 days at an ambient temperature of 25 ∘C. After these processes, the hierarchical DPI mesostructures assembled spontaneously at the solid–liquid interface.

Figure 3 shows the suggested mechanism in the previous process. The interface forces and $\pi - \pi$ interaction and van der Waals contacts between the building blocks is a main building mechanism for assembling mesostructures in the copper surface in DPI solutions.

It was also observed that copper easily reacts with fatty acids. Copper ions created the various bonds with ion solutions and grow flowerlike self-assembled film on the surface with low energy and rough morphology. There are various suggested mechanisms for superhydrophobic growth films on copper surface but it seems that more research is needed to provide an

acceptable mechanism. Additionally, the more important properties in copper superhydrophobic coatings such as its durability and its condensing behaviour on copper tubes, are the promising future areas of research.
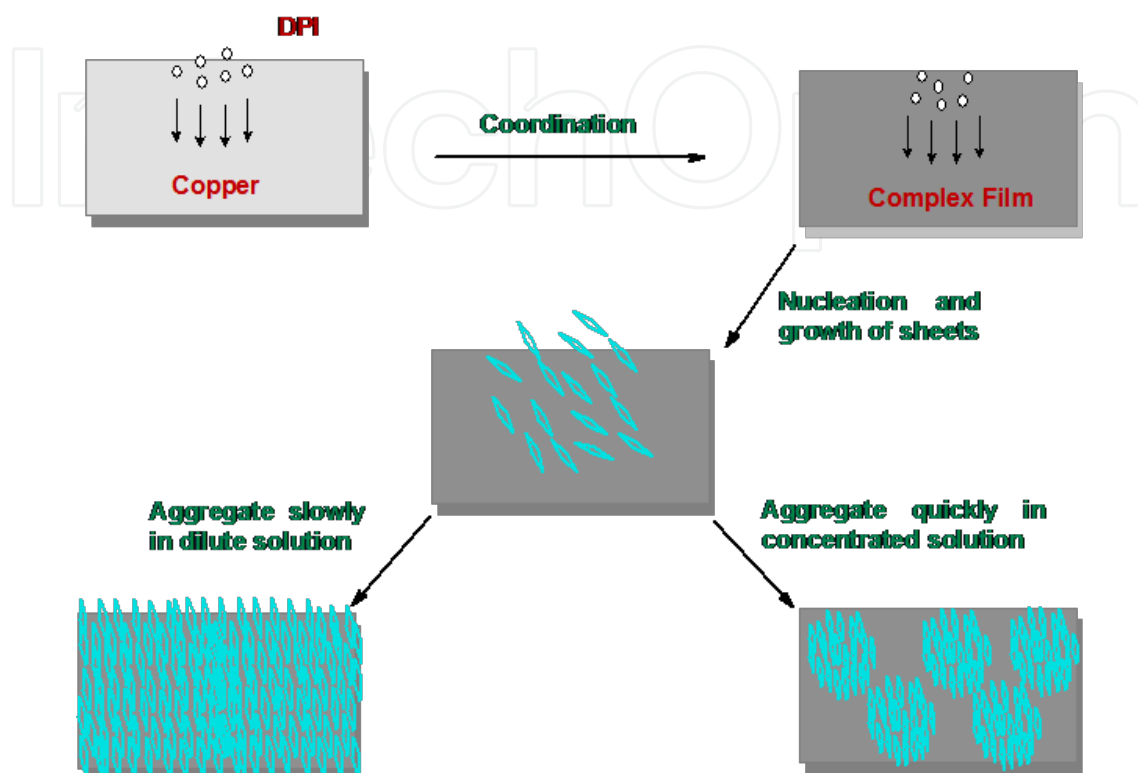

Figure 3. Suggested mechanism for hierarchical DPI mesostructures assembled at the solid–liquid interface.

For improvement of superhydrophobity and the durability of copper surface, the next method is to use additional polymeric compound with low surface energy properties. For the first time, the copper has been treated by fatty acids, and then modified and coated by a low surface energy agent. For example, by immersion, copper in oxalic acid aqueous solution at a concentration of 0.5 wt. % for about 5–7 days at ambient temperature, a superhydrophobic surface is obtained. Poly (dimethysiloxane) vinyl terminated (PDMSVT) is used as a surface modification agent, which is applied by spin coating methods and curing at in 120 °C for 2 h. water contact angle of 154°. The bis- [triethoxysilylpropyl]tetrasulfide (BTESPT) by ethanol solvent can be used as upper coating in treated copper [40].
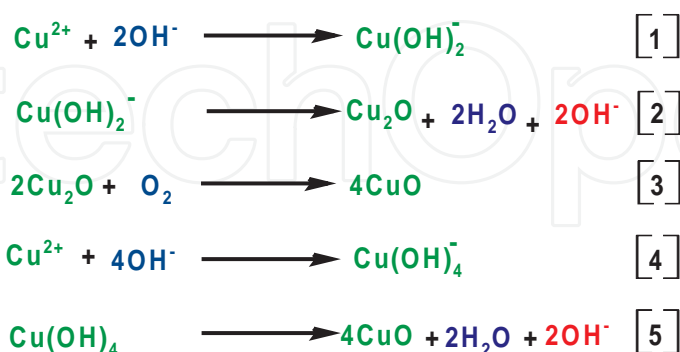
The acceptable mechanism that can be used to create a superhydrophobic surface on copper can be explained by two strategies. First strategy is through the creation of a rough surface by etching copper in suitable acid and then coating of this rough template with low surface energy agent such as silane base materials. For choosing acid as an etchant, it is important that the copper can be reacted by the acid's ions to grow the self-assemble compound on the surface. As shown, the copper ion reacts with carboxyl radical, hence, the fatty type acids can be a good choice to play this role. However, other types of acids can also be used. Another strategy is by

degreasing the copper after putting it into dilute nitric acid to get rid of the copper oxides on the surface. This should be followed by immersing in the aqueous solution of 2 M sodium hydroxide at room temperature for 24 hours, fully washing with deionized water, and drying in nitrogen stream. After that, the pre-treated copper is immersed in a formed aqueous solution of 0.8 M cupric nitrate trihydrate for 24 hours, allowing the generation of a blue slice-like Cu_2 (OH) $3NO_3$ crystals. A good rough surface can be created by the process described, followed by coating a blue slice-like Cu2 (OH)3NO3 film by immersing in an ethanol solution of 1H,1H,2H,2H-perfluorodecyltriethoxysilane for 24 hours. The specimens are washed with ethanol and dried in an oven at 120^0C for 1 hour [75].

After the formation of a superhydrophobic surface by simple immersion methods, a flowerlike morphology is observed. Copper oxide or sulphides or other suitable composition grow on the copper surface to produce a good micro-nano rough template. There are no special optimum conditions for the surface treatment of copper and in each report, different times and temperatures have been reported but the basic principle is that coating by the fatty acids is a good option for copper surface superhydrophobic treatment.

2.1.2. Techniques of deposition of superhydrophobic coating

There are various methods to create a superhydrophobic coating that still exists until now. Among these methods, the electrochemical method is favorable because there are many factors to control the film growth rate, morphology, and properties. The most common method, however, is the anodizing method where the copper plate acts as an anode in electrolyte. Caustic Soda solution can be used as an electrolyte at 3.0 mol/l concentration. The current density and temperature range is about $600\ mA/dm^2$ and 25 respectively. If the current density is decreased to $200\text{-}600\ mA/dm^2$ and the temperature enhanced to 60 centigrade, the CuO film will be converted to Cu $(OH)_2$ films. Under these conditions, oxide film formation is controlled by applied current. Below is the general mechanism [76]:

$$Cu^{2+} + 2OH^- \longrightarrow Cu(OH)_2^- \quad \boxed{1}$$

$$Cu(OH)_2^- \longrightarrow Cu_2O + 2H_2O + 2OH^- \quad \boxed{2}$$

$$2Cu_2O + O_2 \longrightarrow 4CuO \quad \boxed{3}$$

$$Cu^{2+} + 4OH^- \longrightarrow Cu(OH)_4^- \quad \boxed{4}$$

$$Cu(OH)_4 \longrightarrow 4CuO + 2H_2O + 2OH^- \quad \boxed{5}$$

The first reaction captures the released Cu^+ ions and then the captured radical are decomposed to copper oxide. After passage of time, the film grows on the surface and the nano-micro surface is obtained. After this process, various low surface energy agents can be used for surface modification.

Ethanolic stearic acid is a second choice as an electrolyte. In the anodizing system, the copper also can be made as a cathode. The voltage could be about 30 V DC. By using this type of electrolytes, the copper can be reacted by the acid's ions to be able create the low surface energy compounds with micro-nano rough surfaces. In this process, where copper acts as an anode in electrolyte, the copper ion reacts with the electrolyte's free radicals and form slow surface energy films. By using the proper voltage and time, the morphology can be controlled. The voltage used in most of the electrolytes is near 30 V DC but by altering the concentration and temperature, it can be changed [77]. This procedure can be varied because there are lots of fatty acid that copper ions can react with their free ions in electrolyte, make the stable compound and deposit on the surface [78-80]. It seems that the mechanism, optimum conditions and electrolyte comparison is a question that should be answered in the future.

Electrodeposition is a well-known process that was invented by Alessandro Volta in the 1800s [81]. In this method, a current is passed through an electrochemical cell from an external source to reduce the dissolved metal cations, so that they form a coherent metal coating on an electrode [82]. This method has a lot of advantages, such as being low cast, facile, highly effective, and easily controllable by simply adjusting the electrodeposition parameters, such as DC voltage, current and electrolysis time [83]. In this method, various metals and compounds can be coated on a copper surface. For this reason, copper is used as a cathode in electrolyte to deposit the coating on the surface. Various types of electrolytes can be used. For example, nickel or cerium based electrolytes, copper based electrolytes, and the proper metals salts solution with acidic media can be used as electrolytes [84]. An important point to be noted is to use a low surface energy compound in electrolytes. For example, myristic types of acid can be a good choice. Chen et al. [85] in 2012 have prepared suitable superhydrophobic coatings on copper surface by the electrodeposition method. Nickel chloride ($NiCl_2$ $6H_2O$) and myristic acid with ethanol were used as an electrolytic solution. Anode and cathode both were copper plates. The DC current of 30 V has been used. Using this method, the superhydrophobic nickel coating deposited on the copper surface. To optimize electrodeposition conditions, the concentration of nickel chloride was kept to 0.08M and that of the myristic acid to 0.071M. The superhydrophobic surface showed a high water contact angle of 160^0. The mechanism in this process can be explained by the following equation:

$$Ni^{2+} + 2e^- \longrightarrow Ni$$

$$Ni^{2+} + 2CH_3(CH_2)_{12}COOH \longrightarrow Ni\left[CH_3(CH_2)_{12}COO\right]_2 + 2H^+$$

$$2H^+ + 2e^- \longrightarrow H_2$$

Nickel ions absorbs electron with two reactions and deposited on the surface. It can be seen that the nickel deposited had two types: nickel and Ni [CH3 (CH2)12COO] 2. By passing the current for 15 minutes, the water contact angle rises to about 160^0, but in further increasing the time, the superhydrophobicity decreased because of losing micro-nano rough properties. More

time causes an increase in the film thickness. The film thickness can be chosen according to the application. For corrosion protection in aggressive environment, the thickness must be high. But, it is important that the coating thickness is not higher than a specific thickness and that it can be optimized by testing the deposition time and water contact angle. By growing the coating on the surface, the micro nano porosity by the new deposited compound and the rough surface will be destroyed.

Myristic acid with 0.038 M cerium chloride and 0.1 M myristic acid can also be a good electrolyte for the electrodeposition of superhydrophobic coatings on copper surface. The superhydrophobic properties of this deposition are because of the cerium compound (Ce [CH3 (CH2)12COO] 3 composition, which increase the water contact angle to 165^0 [85].

It is possible to use other methods to produce the superhydrophobic coating on the copper surface. If one process can make a rough surface with low surface energy properties, the superhydrophobic coating will be obtained. Hitherto, so many attempts have been done about superhydrophobic surfaces. Sol gel methods, electroless, electrodeposition and sputtering, etc. are available methods to surface modification in copper. But the main concern is the durability of the coating and the wear and erosion performance. Future research must focus on durability and application of the superhydrophobic coatings in aggressive media.

2.2. Superhydrophobic coatings in aluminium and alloys

Aluminium is widely used in various industrial fields as a basic material because of its excellent properties such as low density, excellent thermal and electrical conductivity, high specific strength, and good castability [86, 87]. However, the application and development of aluminium alloy are limited due to high metal reactivity and poor corrosion resistance in aqueous solution, especially in corrosive environment such as in aqueous solution containing Cl^- ions [88]. So, it is necessary to enhance the corrosion resistance property of aluminium in corrosive environment, which will greatly extend their applications as engineering materials [89]. For this reason, making an aluminium surface superhydrophobic has many application possibilities. By anticorrosive coating, the corrosion performance of aluminium alloys can be improved. Feng et al. [90] introduced facile and environment-friendly methods to fabricate hydrophobic surfaces to mitigate corrosion.

Aluminium has special properties due to its oxide layer on the surface that protects aluminium. Anodizing of aluminium can achieve a very durable surface that may be unaffected by weather for many years and many chemicals, if done properly. In this process, a thick film of aluminium oxide is built up on the surface of the aluminium, through the use of a direct current electrical supply. During the process, the aluminium located in the electrochemical cell is used as anode in an acidic media. The electrolyte can be a solution of sulphuric acid, phosphoric acid, oxalic acid, etc. and a direct current is applied to start the anodizing process [91].

The important point is it to optimize parameters which control the oxide layer thickness. This oxide layer contains hexagonal pores. The aluminium porous oxide layer consists of two layers that are a thick porous outer layer and a thin inner layer of oxide called barrier layer. The outer oxide layer of barrier-type alumina strongly depends on the type of electrolyte, the concen-

tration of adsorbed anions, and the faradaic efficiency of film growth. The oxide layer can be achieved with pores of various sizes and shapes which are important for roughness as roughening depends on pores [92, 93]. Several attempts have been made to create superhydrophobic coatings on aluminium surface by anodizing method.

Shibuichi et al. [94] have reported a new research about super water- and oil-repellent surfaces in 1998. The rough aluminum surface was fabricated in o.5 M of acid sulfuric solution, 10 mA/cm^2 the current density and 3 hours anodizing time. Anodizing is a good method for surface roughening of Al. The chemical additives in the anodizing electrolyte affect the surface morphology and pore size. Holes and pores can be ordered by configuration of anodic porous alumina with two types of processes: naturally occurring long-range ordering, and ordering with ideally arranged hole configuration formed using anodization of pretextured [95].

In the pretexturing methods, the ordered convexes are generated as a mold by nanoindentation. The ordered sites are an initial nucleation location for holes during the anodizing process.

During anodizing for each application, the pore size and distance can be controlled. For superhydrophobic applications, obtaining suitable rough surface with micro-nano specifications is an important part. By increasing the voltage in each media, the distance of interpores is maintained between 0-500nm. The pH and conductivity of electrolyte lead to smaller pore size. There is no clear result on the effects of temperature to the pore size but it is obvious that temperature is very important. In addition, obtaining room or lower temperature depends on the electrolyte and choosing suitable temperature types provide uniformity on oxide film with low defects. The aluminum alloy types have various impurity caused to be defects in the film. It seems that the research in this area is so rare and needs to concentrate on the effect of alloy elements on pore formation and surface roughening. So many parameters can affect the final surface morphology during anodizing, such as grain size, residual stress, stirring the electrolyte, and so many additives to electrolyte [47, 48]. Here, we will focus on the effect of additives on the sulphuric acid electrolyte to obtain optimum conditions.

In anodizing with sulphuric acid, the concentration of sulphuric acid can be around 165-225 g/l but a concentration of 185g/l has shown better results. The current density can be varied between 0.8-1.8 A/dm2. There are many additives which can be used for changing pore size and morphology. Sodium chloride, by delivering of Cl$^-$ ions in electrolyte, changes the pore size. The possible mechanism is that the Cl$^-$ ions create a corrosive media attack on to the surface and generate pits on the oxide film. There are many reports on the effect of chloride ions on the pore geometry [47, 48, 96].

Wu et al. [47] have reported the effects of various additives in sulphuric acid electrolyte on superhydrophobicity of aluminum. The aluminum was placed in a sulphuric acid bath at 30 ^{0}C temperature. The additives were oxalic acid, potassium dichromate, chloride sodium, and glycerol.

The pore growth may be due to a field-assisted hydrogen ion attack on the oxide layer. By decreasing the hydrogen ion concentration, this attack will be slowed down or stopped and a barrier-type film layer will be formed. But it should be noted that the hydrogen ion attack must be fundamental to pore nucleation and development. So, the oxalic acid addition can increase

the film thickness by retarding the dissolution rate of aluminum oxidation film and widen the oxidation temperature range without prominent effect on the morphology variation of the oxidation film and structural properties, which is in favor of controlling the anodic oxidation process. The optimal concentration of oxalic acid is at a range of 5–10 g/L.

Chloride ion is a highly active ion that reacts with Al ion to create the pits. The mechanism of pitting can be explained as below:

$$Al^{3+} + H_2O \longrightarrow Al(OH)^{2+}$$

$$Al(OH)^{2+} + Cl^- \longrightarrow Al(OH)Cl^+$$
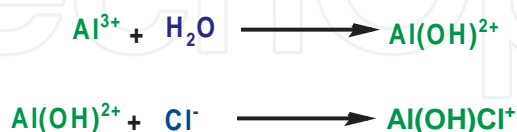
After production of chloride complex, the final reaction is acid production and this process is a main reason of pitting production. This reaction is:

$$Al(OH)Cl^+ + H_2O \longrightarrow Al(OH)_2Cl^+H^+$$

Acidic condition is corrosive than the other sides. This reaction creates a corrosive location by which holes and pits are generated in the oxide film, resulting in bigger porous structures occurring on the surface of the aluminum alloy. Therefore, the roughness further increases and leads to a good superhydrophobic surface. Presence of glycerol in electrolyte can minimize the corrosive effect of electrolyte and also may increase the ductility of the oxidation film. The chromate components such as potassium dichromate can improve uniformity of oxide films. The chromate plays the role of an inhibitor in aluminum corrosion and pitting, and by control, the film pitting may improve uniformity [27, 47, 48, 55, 91-93]. The mechanism and real effect of glycerol and chromate is not clear and needs more research.

In the first 5 minutes during anodizing, the pores are heterogeneous. With the passage of time, the film formation becomes homogenous and the pore size and shape becomes suitable for superhydrophobic surfaces with adequate roughness. The optimum time can be changed from 10 to 60 minutes according to the electrolyte composition.

In another report, Liu et al. [48] also prepared superhydrophobic coatings by anodizing and depositing polymeric coating on the surface of the aluminum alloy. They fabricated a superhydrophobic surface by polypropylene (PP) coating after anodizing, and obtained a superhydrophobic surface on aluminum with a contact angle (CA) of 162º and a sliding angle of 2º. They chose sulfuric acid concentration at a constant value of about 170 g/L and the oxalic acid and sodium chloride concentration as variable. Results showed that the optimum concentration of oxalic acid was 10 g/l and thess results were confirmed in Ruomei Wu's report. The optimum concentration for sodium chloride reached about 1.2 g/l. This electrolyte consist of a solution with acid sulphuric, oxalic acid, and sodium chloride

[49].The concentration of chloride ion could not be increased like the electrolyte which contained potassium dichromate because this additive inhibits the corrosive effect of chloride ions. It could increase only up to 50 g/L.

As a conclusion, the current, time, temperature can be varied by additive agents and it should be noted that the additive amount is also affected by each other's presence at the same time. Anodizing process is a good method to create suitable rough surface by controlling the pore size and morphology. After anodizing the surface modification by low surface energy agents such as propylene, superhydrophobic coating can be obtained.

Surface modification is a final process to fabricate superhydrophobic surfaces after anodizing. In this process, various low energy agents can be used but it should be noted that these agents should have good bonding characteristics with aluminum oxide and also do not destroy the rough templates [14, 19, 22-27, 63, 65, 95, 97-99].

In a study, anticorrosive superhydrophobic surfaces have been fabricated by melting myristic acid ($CH3 (CH2)12COOH$) adsorbed onto the anodized aluminum [97]. The static contact angle for seawater on the surface was about 154º. The predictive reaction can be shown as:

$$Al^{3+} + 3(CH_2)_{12}COOH \longrightarrow \left[3(CH_2)_{12}COO\right]_3 Al + 3H^+$$

The myristic acid is a fatty acid and its component by metal ions on the surface generated low energy agents. As it is shown in the previous formula, the released Al ions, during the process of chemical modification, can be immediately captured by coordination with n-tetradecanoic acid molecules, forming aluminum carboxylate. This is the final coating that makes the anodized aluminum surface superhydrophobic.

Polypropylene is another inexpensive polymer with low surface energy properties to prepare superhydrophobic surfaces on anodized aluminum. The sample can be coated by dipping it in a polymer solution. Acetone or dimethyl-benzene can be used as a solvent and the concentration can be around 6-7 g/l [48, 100].

All low surface energy polymers and agents, by ability of absorbing on anodized aluminum surface, can be used to surface modification like methacrylate polymer, silane coupling agent, etc.

Surface pretreatment or clearly roughening of aluminum can be done by other chemical etching. It is important to choose one chemical agent to have the ability to have aluminum corroded in this environment to obtain a rough surface by presenting pores. Strong mineral acid solutions like hydrochloric acid in the presence of some additives are a good etchant for surface roughening. Aluminum, in normal conditions, is an active metal so it can be oxidized by acids and aggressive conditions. For this reason, various methods can be used to surface roughening by corrosion of surface. Cl⁻ ions form complex with Al ion, hydrogen, and hydroxide ions. The concentration, temperature, etching time, and additives are important parameters for aluminum roughening by chemical etching. Hydrofluoric acid is one of

additives to the acid solution. Acid nitric and sodium hydroxide solutions are other options to use as an etchant to roughen the aluminum surface [101, 102]. Putting aluminum in boiling water can also change the surface morphology [89, 90]. Results show that the lotus like structure has been obtained after surface treatment in boiling water. By increasing the boiling time, denser and more interconnected network structures form.

The following reactions are possible in this condition:

$$2Al + 6H_2O \longrightarrow 2Al(OH)_3 + 3H_2$$

$$2Al + 4H_2O \longrightarrow 2AlO(OH) + 3H_2$$

$$2Al + 3H_2O \longrightarrow Al_2O_3 + 3H_2$$

When aluminum is placed in boiling water, the intrinsic oxid layer starts to dissolve and react with water. After aluminum starts to react with water, hydrogen gas is released after the oxidation reaction of aluminum. It can change the film growth mechanism like nanograss.

Here, we will review recent attempts to fabricate superhydrophobic coatings on aluminium. Feng et al. [90] introduced facile and environment-friendly methods to produce excellent corrosion resistance. They treated the aluminum alloy surface in boiling water and immersed it in a stearic acid (STA)–ethanol–H_2O solution. They fabricated a porous and rough structure surface by superhydrophobic performance with a water contact angle of 155º and a rolling angle of 5º. The superhydrophobic aluminum alloy also gained excellent corrosion resistance. [89] in another research, Feng et al., fabricated the anticorrosion superhydrophobic coating on aluminum alloy with boiling water treatment and stearic acid modification. They showed that a superhydrophobic surface with a contact angle of 154.1º can be obtained when the aluminum alloy was treated in boiling water for 30 seconds and modified with 5 mmol/L of stearic acid for 24 hours at room temperature. Also, the corrosion resistance of the aluminum alloy improved with the increase of the water contact angle, and the superhydrophobic aluminum alloy has the best corrosion resistance as compared to the other aluminum alloys. Also, Han et al. [103] made aluminum surface as superhydrophobic by the same process (boiling in water and modification by low surface energy agent) and they evaluated an icephobic behaviour of this coating. It was found that the superhydrophobic durability is remarkably affected by the preparation conditions, even if the surfaces initially showed almost identical superhydrophobicity. The best result was observed for the Al substrate etched for 2 hours and octadecyltrichlorosilane (OTS) coating with 0.09 wt. % concentration in toluene. Zubayda et al. [104] improved this method by the two simple and environmentally friendly techniques of mechanical sand blasting and boiling water treatment, and lowering of surface energy by 2H-perfluorodecyltriethoxysilane agent. The highest contact angles of 158º for water, 156º for ethylene glycol, and 154º for peanut oil were obtained after forming hierarchical structures involving shapes of microgrooves obtained by one directional sanding and nano grass by

immersing in boiling water for 1 minute. Guo et al. [14] made aluminum and its alloy surfaces superhydrophobic by immersing them in sodium hydroxide for several hours followed by the spin coating with a layer of perfluorononane or poly (dimethysiloxane) vinyl terminated(PDMSVT). This treatment increases the water contact angle from about 67º to above 160º. In similar reports, they obtained a stable biomimetic superhydrophobic surface on aluminum alloy by wet chemical etching following modification with cross-linked silicone elastomer, perfluorononane (C9F20), and perfluoropolyether (PFPE), respectively. They claimed that "The trapped air with the binary structure plays a key role in fabricating superhydrophobic surface on aluminum alloy." In other words, the unusual structure on the surface, which has a binary structure consisted of micro protrusions and nanoparticles, plays a very vital role in the constructing of a stable biomimetic superhydrophobic surface on the aluminum alloy [14, 19, 20]. Zhang et al. [105], with a simple method, rendered a stable superhydrophobic surface on the aluminum alloy by a low-cost, one-step method, which is simply immersing the substrates in a solution containing hydrochloric acid and fatty acid molecules. High water contact angle was about 163º and low adhesion was achieved on the treated surfaces. Cho et al. [106] provided a superhydrophobic surface with uniformly superhydrophobic surface where nano-scale structures were fabricated through an alkali surface modification method and self-assembled monolayer coating. The fabrication process for dual-scale hierarchical structures combining both microstructure via sandblasting techniques and the nano-structured aluminum hydroxide layer was done to enhance the mechanical durability of the superhydrophobicity. They remarked that the resulting hierarchical structures are suitable for diverse applications of aluminum in various industrial areas, including self-cleaning, anti-frosting, and microfluidic devices for rigorous environments. In another attempt, a superhydrophobic surface with a water contact angle of 166º was fabricated on an aluminum substrate by electrochemical machining using neutral NaNO3 electrolytes, followed by fluorination [26]. In another similar work, a superhydrophobic surface on an aluminum substrate by one-step electrochemical machining using sodium chloride (NaCl) aqueous solution containing fluoroalkylsilane as the electrolyte have been fabricated [86]. Static water contact angle obtained was about 166º and a tilting angle of about 10º. Saleema et al. [23]with a simple one-step process made aluminum alloy surfaces superhydrophobic by immersing the aluminum alloy substrates in a solution containing NaOH and fluoroalkyl-silane (FAS-17) molecules. In this report, the surfaces provided a water contact angle as high as ∼162º and a contact angle hysteresis as low as ∼4º. The study indicates that it is possible to fabricate superhydrophobic aluminum surfaces easily and effectively without involving the traditional two-step processes.

Liu et al. [99]coated aluminum surface by the following procedure. First, the aluminum foil was immersed in a sealed autoclave containing an aqueous solution (dissolved AlCl3 and triethanolamine (TEA, 0.75 M) in deionized water). And then it is heated in the oven at 100 ºC for 5 hours washing the as-obtained aluminum foil several times with deionized water and drying at ambient temperature. Finally, the film was modified by dipping the substrate in an ethanol solution of 5 mM stearic acid (STA) for 10 hours followed by rinsing the sample in absolute ethanol. The obtained surface demonstrates superhydrophobicity with a water CA of 169º and a sliding angle of about 4º after STA modification. The non-sticking behaviour, long-term storage stability, and relatively good mechanical strength were also obtained.

Some other attempts were conducted by anodizing process and showed very interesting result [27, 47, 48, 100, 107]. Zhang et al. [105] simply coated superhydrophobic alumina films with a 2D close-packed array of nano-spheres on industrial aluminum foils by an anodization method and following modification. The water contact angle of the resultant surfaces was about 154.6° ± 1.4° and the adhesion of water droplets was very weak. Wu et al. [48]obtained a superhydrophobic surface of the aluminum alloy micro/nano film with porous structures anodized and polypropylene coating under the difference test parameters. They obtained the best superhydrophobic film on aluminum alloy with the contact angle (CA) of 162° and the sliding angle of 2°. Liu et al. [47]also prepared a superhydrophobic coating by anodizing and polymeric coating on the surface of aluminum alloy. They fabricated a superhydrophobic surface by polypropylene (PP) coating after anodizing and the best superhydrophobic surface on aluminum alloy achieved was with the contact angle (CA) of 162° and the sliding angle of 2°. He et al. [97] fabricated underwater anticorrosive superhydrophobic surface by melting myristic acid (CH_3 ($CH_2)_{12}COOH$) adsorbed onto the anodized aluminum. The static contact angle for seawater on the surface was about 154°. They showed that the superhydrophobic surface significantly improved the corrosion resistance of aluminum in sterile seawater. Liu et al. [24] prepared a superhydrophobic surface by anodizing and surface modification to evaluate reducing microbiologically influenced corrosion of aluminum. They showed that the superhydrophobic surface significantly reduced the corrosion rate of aluminum. Some others also reported the same by fabricating superhydrophobic coatings with chemical modification on the anodized aluminum and this has been shown that the aluminum alloy corrosion resistance is effectively improved by the formation of a stable superhydrophobic coating and this can be widely applied in the corrosion protection of various engineering materials [48]. In some others researches, the superhydrophobic coating was prepared by using additional deposition methods like CVD and dip coating with a combination of anodic oxidation [20, 108-111]. As a conclusion, it can be said that superhydrophobic coatings with excellent properties and long term durability can be a good selection for various industrial applications.

3. Corrosion prevention through superhydrophobic surfaces for various alloys

All metals have a tendency to corrode in most of atmospheric conditions. The metal corrosion accrues because of the interaction between water and a metal substrate. Deposition of soluble salt particles at a certain relative humidity can accelerate the corrosion rate most of the time [111].

Salt particles tend to adsorb moisture and form saline droplets, which can in turn accelerate atmospheric corrosion due to the presence of corrosive ions [112]. In principle, the presence of a water droplet (or a film) over a metal surface, electrochemically changes its surface condition from homogeneity to heterogeneity. Improvement of corrosion resistance is a main challenge of surface and corrosion engineering [113-115]. Water is a main part of the corrosion mechanism and the absence of water will be helpful. By mimicking from nature, superhydrophobicity is a helpful method to decreasing corrosion and water presence on the surface. Superhydro-

phobic surfaces and coatings are the focus of attention in the recent decade and their applications are increasing every day [116, 117].

The advantage of superhydrophobic coatings in corrosion protection can be explained by two observations. Firstly, the hydrophobicity prevents water absorbing on the surface while the air gets trapped in the grooves of a superhydrophobic film, by which water droplets comes into contact with the film through composite interface of both air and solid. Secondly the superhydrophobic coating acts as a protective coating against corrosion. The self-cleaning properties of superhydrophobic coating prevent deposition of corrosive salts water droplet, which easily rolls off and takes away salt particles adhered to the surface [118]. In this section, the principle of corrosion prevention by superhydrophobic coatings would be discussed.

The relative humidity (RH) of the atmosphere is an important factor for generating water droplets on the surface and absorbing by solid salt particles. The salt deposition on the surface followed by water absorption creates a suitable condition for corrosion. Deliquescence happens when water molecules absorbed on a salt particle surface form a film of saline solution until the salt particles are dissolved completely. This process is an important factor that induces atmospheric corrosion. It is important that the salt particle present on superhydrophobic surfaces will be removed after it transforms into saline droplets as a preventive measure.

In one study, the corrosion behavior of superhydrophobic surfaces on copper has been investigated under humid condition. The RH of the atmosphere was 90% and the NaCl particles were located on the surface. The samples were inclined at an angle about 200 $^\circ$ and the behavior of salt particles during water absorption was monitored. The observed results were interesting because the superhydrophobic surface acted as a lubricant by reducing friction between two solid particles and caused water absorption by salt and condensing the water. The water did not spread over the surface compared to hydrophilic surface. The water droplets located in the spherical shape by low surface came into contact with the superhydrophobic surface. It showed a significant improvement in the corrosion resistance of copper alloys by superhydrophobic coatings in humid environment which is more aggressive than dry environment.

The trapped air played an important role to create superhydrophobic surfaces because the trapped air decreased the solid surface connection by water droplets. In the same work, the effects of the trapped air on corrosion performance of copper superhydrophobic coatings have been evaluated. The corrosion performance was electrochemically measured. Three samples, hydrophilic copper plates, degassed superhydrophobic, and superhydrophobic coatings in the same condition were tested. Results showed that the absence of air decreased the corrosion resistance. It can also be found that the air trapped in the film is the main contributor for the barrier performance and stability of the superhydrophobic film. The trapped air inhibited electrochemical reactions between the substrate and corrosive medium. Also, air can play as an isolation film between the corrosive medium and Cu substrate.

Aluminum alloys are tendentious to corrosion and a superhydrophobic coating is the best choice for the improvement of corrosion resistance. From the literature, it can be seen that the superhydrophobic coating can improve the corrosion performance of aluminum in simulated

marine environment. He et al. [97]studied the corrosion protection for aluminum in seawater, where the results showed that the superhydrophobic coating has highly protective properties against aluminum corrosion in sea water. They claim that "this method should be easily applied to large-scale production of superhydrophobic engineering materials with ocean industrial applications." Also in another work, Liu et al. [97] showed that the superhydrophobic coating can reduce biofilm formation on the surface because of the low binding strength between bacteria and the surface, and probably due to a cohesive failure within the conditioning layer.

4. Conclusion

In conclusion, it is established that the superhydrophobic surface is the best choice as a coating and protection layer against environmental effects such as surface corrosion, biofouling, dust and water interaction by mitigating the effect of humidity and other gasses, and accumulation of particulate matters on the surface. The superhydrophobic coatings offer the unique advantage of ease of fabrication, and their capability to withstand harsh environment which deteriorates the properties of metals and non-metals.

These surfaces are also limited in withstanding erosion, high flow rates, and elevated temperatures under aggressive conditions. However, the ongoing research is likely to resolve the above mentioned problems. These coatings also possess multiple qualities and properties such as anti-corrosion performance, self-cleaning and other properties which depend on the fabrication method.

The major limitation of these coatings is their durability because these coatings lose their properties with the passage of time. From an economical view, this coating is expensive and this concern may possibly be solved in the future by adopting cheaper fabrication methods and using cheaper superhydrophobic materials for coating.

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References

[1] Li, X.-M., D. Reinhoudt, and M. Crego-Calama, *What do we need for a superhydrophobic surface? A review on the recent progress in the preparation of superhydrophobic surfaces.* Chemical Society Reviews, 2007. 36(8): p. 1350-1368.

[2] Roach, P., N.J. Shirtcliffe, and M.I. Newton, *Progess in superhydrophobic surface development.* Soft Matter, 2008. 4(2): p. 224-240.

[3] Malik, M.A., et al., *Anti-corrosion ability of surfactants: a review.* Int. J. Electrochem. Sci, 2011. 6(6): p. 1927-1948.

[4] Farzaneh, A., et al., *Electrochemical and structural properties of electroless Ni-P-SiC nano-composite coatings.* Applied Surface Science, 2013. 276: p. 697-704.

[5] Farzaneh, A., M. Ehteshamzadeh, and M. Mohammadi, *Corrosion performance of the electroless Ni–P coatings prepared in different conditions and optimized by the Taguchi method.* Journal of Applied Electrochemistry, 2011. 41(1): p. 19-27.

[6] Wood, R.J., *Erosion-corrosion interactions of copper and aluminium alloys.* European Federation Of Corrosion Publications, 2007. 50: p. 19.

[7] Ahmad, Z. and B. Abdul Aleem, *Erosion-Corrosion Behavior of Plasma-Sprayed Nanostructured Titanium Dioxide Coating in Sodium Chloride-Polystyrene Slurry.* Corrosion, 2009. 65(9): p. 611-623.

[8] Bertolini, L., et al., *Corrosion of steel in concrete: prevention, diagnosis, repair.* 2013: John Wiley & Sons.

[9] McKinney, M., R. Kirby, and W. Newsom, *Aerodynamic Factors To Be Considered In The Design Of Tilt-Wing V/Stol Airplanes.* Annals of the New York Academy of Sciences, 1963. 107(1): p. 221-248.

[10] Hammitt, F.G., et al., *Cavitation and droplet impingement damage of aircraft rain erosion materials.* 1970.

[11] Mohamed, A.M.A., A.M. Abdullah, and N.A. Younan, *Corrosion behavior of superhydrophobic surfaces: A review.* Arabian Journal of Chemistry, (0).

[12] Ma, M. and R.M. Hill, *Superhydrophobic surfaces.* Current Opinion in Colloid & Interface Science, 2006. 11(4): p. 193-202.

[13] Liu, T., et al., *Corrosion behavior of super-hydrophobic surface on copper in seawater.* Electrochimica Acta, 2007. 52(28): p. 8003-8007.

[14] Guo, Z., et al., *Effects of system parameters on making aluminum alloy lotus.* Journal of Colloid and Interface Science, 2006. 303(1): p. 298-305.

[15] Barthlott, W. and C. Neinhuis, *Purity of the sacred lotus, or escape from contamination in biological surfaces.* Planta, 1997. 202(1): p. 1-8.

[16] Yu, Y., Z.-H. Zhao, and Q.-S. Zheng, *Mechanical and superhydrophobic stabilities of two-scale surfacial structure of lotus leaves.* Langmuir, 2007. 23(15): p. 8212-8216.

[17] Neinhuis, C. and W. Barthlott, *Characterization and distribution of water-repellent, self-cleaning plant surfaces.* Annals of Botany, 1997. 79(6): p. 667-677.

[18] Baker, E. and G.M. Hunt, *Erosion of waxes from leaf surfaces by simulated rain.* New Phytologist, 1986. 102(1): p. 161-173.

[19] Guo, Z. and W. Liu, *Biomimic from the superhydrophobic plant leaves in nature: Binary structure and unitary structure.* Plant Science, 2007. 172(6): p. 1103-1112.

[20] Guo, Z., W. Liu, and B.-L. Su, *Superhydrophobic surfaces: From natural to biomimetic to functional.* Journal of Colloid and Interface Science, 2011. 353(2): p. 335-355.

[21] Liu, T., et al., *Super-hydrophobic surfaces improve corrosion resistance of copper in seawater.* Electrochimica Acta, 2007. 52(11): p. 3709-3713.

[22] Fu, X. and X. He, *Fabrication of super-hydrophobic surfaces on aluminum alloy substrates.* Applied Surface Science, 2008. 255(5, Part 1): p. 1776-1781.

[23] Saleema, N., et al., *Superhydrophobic aluminum alloy surfaces by a novel one-step process.* ACS Appl Mater Interfaces, 2010. 2(9): p. 2500-2.

[24] Liu, T., et al., *Investigations on reducing microbiologically-influenced corrosion of aluminum by using super-hydrophobic surfaces.* Electrochimica Acta, 2010. 55(18): p. 5281-5285.

[25] Park, B.G., et al., *Superhydrophobic fabrication of anodic aluminum oxide with durable and pitch-controlled nanostructure.* Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2010. 370(1–3): p. 15-19.

[26] Xu, W., et al., *Fabrication of superhydrophobic surfaces on aluminum substrates using NaNO3 electrolytes.* Journal of Materials Science, 2011. 46(18): p. 5925-5930.

[27] Menini, R., Z. Ghalmi, and M. Farzaneh, *Highly resistant icephobic coatings on aluminum alloys.* Cold Regions Science and Technology, 2011. 65(1): p. 65-69.

[28] Kulinich, S.A. and M. Farzaneh, *On ice-releasing properties of rough hydrophobic coatings*. Cold Regions Science and Technology, 2011. 65(1): p. 60-64.

[29] Yao, L. and J. He, *Recent progress in antireflection and self-cleaning technology–From surface engineering to functional surfaces.* Progress in Materials Science, 2014. 61: p. 94-143.

[30] Solga, A., et al., *The dream of staying clean: Lotus and biomimetic surfac*es. Bioinspiration & biomimetics, 2007. 2(4): p. S126.

[31] Bhushan, B., *Biomimetics: lessons from nature–an overview*. Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences, 2009. 367(1893): p. 1445-1486.

[32] Sun, M., et al., *Artificial lotus leaf by nanocasting.* Langmuir, 2005. 21(19): p. 8978-8981.

[33] Kwon, Y., et al., *Design of surface hierarchy for extreme hydrophobicity*. Langmuir, 2009. 25(11): p. 6129-6136.

[34] Saifaldeen, Z.S., et al., *Superamphiphobic aluminum alloy surfaces with micro and nanoscale hierarchical roughness produced by a simple and environmentally friendly technique.* Journal of Materials Science, 2014. 49(4): p. 1839-1853.

[35] Mortazavi, V. and M. Nosonovsky, *Wear-Induced Microtopography Evolution and Wetting Properties of Self-Cleaning, Lubricating and Healing Surfaces.* Journal of Adhesion Science and Technology, 2011. 25(12): p. 1337-1359.

[36] Kim, S.H., *Fabrication of Superhydrophobic Surfaces*. Journal of Adhesion Science and Technology, 2008. 22(3-4): p. 235-250.

[37] Wenzel, R.N., *Resistance Of Solid Surfaces To Wetting By Water*. Industrial & Engineering Chemistry, 1936. 28(8): p. 988-994.

[38] Amir Farzaneh, et al., *Aluminium Alloys in Solar Power – Benefits and Limitations*, Aluminium Alloys – New Trends in Fabrication and Applications, 2012. InTech.

[39] Mengnan Qu, J. He, and J. Zhang, *Superhydrophobicity, Learn from the Lotus Leaf, Biomimetics Learning from Nature* InTech publisher, 2010.

[40] Guo, Z., et al., *Fabrication of superhydrophobic copper by wet chemical reaction*. Thin Solid Films, 2007. 515(18): p. 7190-7194.

[41] Sendner, C., et al., *Interfacial Water at Hydrophobic and Hydrophilic Surfaces: Slip, Viscosity, and Diffusion*. Langmuir, 2009. 25(18): p. 10768-10781.

[42] Farzaneh, A., et al., *Investigation and optimization of SDS and key parameters effect on the nickel electroless coatings properties by Taguchi method.* Journal of coatings technology and research, 2010. 7(5): p. 547-555.

[43] Bisetto, A., et al. *Dropwise condensation on superhydrophobic nanostructured surfaces: literature review and experimental analysis.* in *Journal of Physics: Conference Series*. 2014. IOP Publishing.

[44] Zhao, N., et al., *Combining layer-by-layer assembly with electrodeposition of silver aggregates for fabricating superhydrophobic surfaces.* Langmuir, 2005. 21(10): p. 4713-4716.

[45] Darmanin, T. and F. Guittard, *Superhydrophobic fiber mats by electrodeposition of fluorinated poly (3, 4-ethyleneoxythiathiophene).* Journal of the American Chemical Society, 2011. 133(39): p. 15627-15634.

[46] Hang, T., et al., *Super-hydrophobic nickel films with micro-nano hierarchical structure prepared by electrodeposition.* Applied Surface Science, 2010. 256(8): p. 2400-2404.

[47] Liu, W., et al., *Fabrication of the superhydrophobic surface on aluminum alloy by anodizing and polymeric coating.* Applied Surface Science, 2013. 264(0): p. 872-878.

[48] Wu, R., et al., *Fabrication of the micro/nano-structure superhydrophobic surface on aluminum alloy by sulfuric acid anodizing and polypropylene coating.* J Nanosci Nanotechnol, 2013. 13(3): p. 2362-8.

[49] Balu, B., V. Breedveld, and D.W. Hess, *Fabrication of "roll-off" and "sticky" superhydrophobic cellulose surfaces via plasma processing.* Langmuir, 2008. 24(9): p. 4785-4790.

[50] Fadeeva, E., et al., *Bacterial retention on superhydrophobic titanium surfaces fabricated by femtosecond laser ablation.* Langmuir, 2011. 27(6): p. 3012-3019.

[51] Ramos, S., et al., *Wettability control on vertically-aligned multi-walled carbon nanotube surfaces with oxygen pulsed DC plasma and CO 2 laser treatments.* Diamond and Related Materials, 2010. 19(7): p. 752-755.

[52] Wu, B., et al., *Superhydrophobic surfaces fabricated by microstructuring of stainless steel using a femtosecond laser.* Applied Surface Science, 2009. 256(1): p. 61-66.

[53] Wagterveld, R.M., et al., *Ultralow hysteresis superhydrophobic surfaces by excimer laser modification of SU-8.* Langmuir, 2006. 22(26): p. 10904-10908.

[54] Zhang, X., et al., *Superhydrophobic surfaces: from structural control to functional application.* Journal of Materials Chemistry, 2008. 18(6): p. 621-633.

[55] Fujii, T., Y. Aoki, and H. Habazaki, *Superhydrophobic hierarchical surfaces fabricated by anodizing of oblique angle deposited Al–Nb alloy columnar films.* Applied Surface Science, 2011. 257(19): p. 8282-8288.

[56] Chung, J.W., et al., *Self-assembled perpendicular growth of organic nanoneedles via simple vapor-phase deposition: one-step fabrication of a superhydrophobic surface.* Chemical Communications, 2008(26): p. 2998-3000.

[57] Li, Y., F. Liu, and J. Sun, *A facile layer-by-layer deposition process for the fabrication of highly transparent superhydrophobic coatings.* Chemical communications, 2009(19): p. 2730-2732.

[58] Crick, C.R. and I.P. Parkin, *CVD of copper and copper oxide thin films via the in situ reduction of copper (ii) nitrate—a route to conformal superhydrophobic coatings*. Journal of Materials Chemistry, 2011. 21(38): p. 14712-14716.

[59] Li, Y., L. Li, and J. Sun, *Bioinspired Self-Healing Superhydrophobic Coatings*. Angewandte Chemie, 2010. 122(35): p. 6265-6269.

[60] Ma, M., et al., *Superhydrophobic fabrics produced by electrospinning and chemical vapor deposition*. Macromolecules, 2005. 38(23): p. 9742-9748.

[61] Han, D. and A.J. Steckl, *Superhydrophobic and oleophobic fibers by coaxial electrospinning*. Langmuir, 2009. 25(16): p. 9454-9462.

[62] Miyauchi, Y., B. Ding, and S. Shiratori, *Fabrication of a silver-ragwort-leaf-like super-hydrophobic micro/nanoporous fibrous mat surface by electrospinning*. Nanotechnology, 2006. 17(20): p. 5151.

[63] Tadanaga, K., et al., *Superhydrophobic-superhydrophilic micropatterning on flowerlike alumina coating film by the sol-gel method*. Chemistry of materials, 2000. 12(3): p. 590-592.

[64] Manca, M., et al., *Durable superhydrophobic and antireflective surfaces by trimethylsilanized silica nanoparticles-based sol– gel processing*. Langmuir, 2009. 25(11): p. 6357-6362.

[65] Tadanaga, K., J. Morinaga, and T. Minami, *Formation of superhydrophobic-superhydrophilic pattern on flowerlike alumina thin film by the sol-gel method*. Journal of Sol-Gel Science and Technology, 2000. 19(1-3): p. 211-214.

[66] Syrett, B.C., *Erosion-corrosion of copper-nickel alloys in sea water and other aqueous environments-a literature review*. Corrosion, 1976. 32(6): p. 242-252.

[67] Gilbert, P., *Corrosion Resisting Properties of 90/10 Copper–Nickel–Iron Alloy with Particular Reference to Offshore Oil and Gas Applications*. British Corrosion Journal, 1979. 14(1): p. 20-25.

[68] Schweitzer, P.A., *Corrosion Engineering Handbook, -3 Volume Set*. 1996: CRC Press.

[69] Li, J., J. Mayer, and E. Colgan, *Oxidation and protection in copper and copper alloy thin films*. Journal of applied physics, 1991. 70(5): p. 2820-2827.

[70] Kear, G., B. Barker, and F. Walsh, *Electrochemical corrosion of unalloyed copper in chloride media—a critical review*. Corrosion science, 2004. 46(1): p. 109-135.

[71] Smith, W.F., *Structure and properties of engineering alloys*. 1993.

[72] Manuals, M., *Online medical library*. Copper. [URL: http://www. en. wikipedia. org/ wiki/Copper# Toxic ity] accessed, 2012.

[73] http://www.chemguide.co.uk/.

[74] Zhao, Y.S., et al., *A hierarchical self-assembly of 4, 5-diphenylimidazole on copper*. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2006. 277(1): p. 111-118.

[75] Kong, L., et al., *Preparation and characterization of slice-like Cu 2 (OH) 3 NO 3 superhydrophobic structure on copper foil.* Applied Surface Science, 2008. 254(22): p. 7255-7258.

[76] Tan, C., et al., *Fabrication of color-controllable superhydrophobic copper compound coating with decoration performance.* Applied Surface Science, 2015. 328: p. 623-631.

[77] Wang, P., et al., *Green approach to fabrication of a super-hydrophobic film on copper and the consequent corrosion resistance.* Corrosion Science, 2014. 80: p. 366-373.

[78] Xi, W., et al., *The preparation of lotus-like super-hydrophobic copper surfaces by electroplating.* Applied surface science, 2009. 255(9): p. 4836-4839.

[79] Wang, P., et al., *Fabricated super-hydrophobic film with potentiostatic electrolysis method on copper for corrosion protection.* Electrochimica Acta, 2010. 56(1): p. 517-522.

[80] Huang, Y., et al., *Corrosion resistance properties of superhydrophobic copper surfaces fabricated by one-step electrochemical modification process.* Applied Surface Science, 2013. 282: p. 689-694.

[81] Kalvoda, R. and R. Parsons, *Electrochemistry in research and development.* 1985: Springer.

[82] Brenner, A., *Electrodeposition of alloys: principles and practice.* 2013: Elsevier.

[83] Crick, C.R. and I.P. Parkin, *Preparation and Characterisation of Super‐Hydrophobic Surfaces.* Chemistry-A European Journal, 2010. 16(12): p. 3568-3588.

[84] Liu, Y., et al., *Fabrication of biomimetic superhydrophobic surface with controlled adhesion by electrodeposition.* Chemical Engineering Journal, 2014. 248: p. 440-447.

[85] Chen, Z., et al., *A rapid one-step process for fabrication of superhydrophobic surface by electrodeposition method.* Electrochimica Acta, 2012. 59: p. 168-171.

[86] Song, J., W. Xu, and Y. Lu, *One-step electrochemical machining of superhydrophobic surfaces on aluminum substrates.* Journal of Materials Science, 2012. 47(1): p. 162-168.

[87] Liu, Y., et al., *Biomimetic superhydrophobic surface of high adhesion fabricated with micronano binary structure on aluminum alloy.* ACS applied materials & interfaces, 2013. 5(18): p. 8907-8914.

[88] Yin, B., et al., *Novel strategy in increasing stability and corrosion resistance for super-hydrophobic coating on aluminum alloy surfaces.* Applied Surface Science, 2011. 258(1): p. 580-585.

[89] Feng, L., et al., *Superhydrophobic aluminum alloy surface: Fabrication, structure, and corrosion resistance.* Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2014. 441(0): p. 319-325.

[90] Feng, L., et al., *Fabrication of superhydrophobic aluminium alloy surface with excellent corrosion resistance by a facile and environment-friendly method.* Applied Surface Science, 2013. 283(0): p. 367-374.

[91] Grubbs, C.A., *Anodizing of aluminum*. Metal Finishing, 1999. 97(1): p. 476-493.

[92] Grubbs, C.A., *Anodizing of aluminum*. Metal Finishing, 2002. 100: p. 463-478.

[93] Soekrisno, S. and B. Anggoro, *Effect of Anodizing in Surface Finishing on Speed Boat Impeller Made of Aluminum*. Advanced Materials Research, 2014. 896: p. 253-256.

[94] Shibuichi, S., et al., *Super water-and oil-repellent surfaces resulting from fractal structure*. Journal of Colloid and Interface Science, 1998. 208(1): p. 287-294.

[95] Masuda, H., *Highly ordered nanohole arrays in anodic porous alumina*, in *Ordered Porous Nanostructures and Applications*. 2005, Springer. p. 37-55.

[96] Wu, R., et al., *Fabrication of nano-structured super-hydrophobic film on aluminum by controllable immersing method*. Applied Surface Science, 2012. 258(16): p. 5933-5937.

[97] He, T., et al., *Super-hydrophobic surface treatment as corrosion protection for aluminum in seawater*. Corrosion Science, 2009. 51(8): p. 1757-1761.

[98] Menini, R. and M. Farzaneh, *Elaboration of Al2O3/PTFE icephobic coatings for protecting aluminum surfaces*. Metal Finishing, 2009. 107(7–8): p. 40-46.

[99] Liu, L., et al., *Fabrication of superhydrophobic surface by hierarchical growth of lotus-leaf-like boehmite on aluminum foil*. Journal of Colloid and Interface Science, 2011. 358(1): p. 277-283.

[100] Jiang, H., et al., *Manufacturing a durable superhydrophobic polypropylene coating on aluminum alloy substrate by adding nano-titania nanoparticles*. Journal of nanoscience and nanotechnology, 2014. 14(7): p. 5421-5425.

[101] Kumar, C.S., et al., *Studies on white anodizing on aluminum alloy for space applications*. Applied Surface Science, 1999. 151(3): p. 280-286.

[102] Xie, D. and W. Li, *A novel simple approach to preparation of superhydrophobic surfaces of aluminum alloys*. Applied Surface Science, 2011. 258(3): p. 1004-1007.

[103] Han, S., J. Jeong, and D. Lee, *Ice-phobic behavior of superhydrophobic Al surface undervarious etching conditions*. Journal of Electroceramics, 2014: p. 1-7.

[104] Saifaldeen, Z., et al., *Superamphiphobic aluminum alloy surfaces with micro and nanoscale hierarchical roughness produced by a simple and environmentally friendly technique*. Journal of Materials Science, 2014. 49(4): p. 1839-1853.

[105] Zhang, Y., et al., *Facile fabrication of superhydrophobic nanostructures on aluminum foils with controlled-condensation and delayed-icing effects*. Applied Surface Science, 2012. 258(20): p. 8253-8257.

[106] Cho, H., et al., *A simple fabrication method for mechanically robust superhydrophobic surface by hierarchical aluminum hydroxide structures*. Current Applied Physics, 2013. 13(4): p. 762-767.

[107] Liang, J., et al., *Fabrication and Corrosion Resistance of Superhydrophobic Hydroxide Zinc Carbonate Film on Aluminum Substrates.* Journal of Nanomaterials, 2013. 2013: p. 6.

[108] Jafari, R., R. Menini, and M. Farzaneh, *Superhydrophobic and icephobic surfaces prepared by RF-sputtered polytetrafluoroethylene coatings.* Applied Surface Science, 2010. 257(5): p. 1540-1543.

[109] Nguyen, D.D., et al., *Superhydrophobic and superoleophilic properties of graphene-based sponges fabricated using a facile dip coating method.* Energy & Environmental Science, 2012. 5(7): p. 7908-7912.

[110] Zhang, G., et al., *Fabrication of superhydrophobic surfaces from binary colloidal assembly.* Langmuir, 2005. 21(20): p. 9143-9148.

[111] Farhadi, S., M. Farzaneh, and S. Kulinich, *Anti-icing performance of superhydrophobic surface*s. Applied Surface Science, 2011. 257(14): p. 6264-6269.

[112] Wang, P., D. Zhang, and Z. Lu, *Advantage of super-hydrophobic surface as a barrier against atmospheric corrosion induced by salt deliquescence.* Corrosion Science, 2015. 90: p. 23-32.

[113] Roberge, P., *Atmospheric corrosion.* Uhlig's Corrosion Handbook, 2011. 51: p. 299.

[114] Ahmad, Z., A. Ul-Hamid, and B. Abdul-Aleem, *The corrosion behavior of scandium alloyed Al 5052 in neutral sodium chloride solution.* Corrosion Science, 2001. 43(7): p. 1227-1243.

[115] Ahmad, Z. and B.A. Aleem, *Degradation of aluminum metal matrix composites in salt water and its control.* Materials & design, 2002. 23(2): p. 173-180.

[116] Ahmad, Z. and F. Patel, *Development of Novel Corrosion Techniques for a Green Environment.* International Journal of Corrosion, 2012. 2012.

[117] Ahmad, Z., I. Ahmad, and F. Patel. *Fog Collection by Mimicking Nature.* in *Journal of Biomimetics, Biomaterials and Biomedical Engineering.* 2010. Trans Tech Publ.

[118] Ahmad, Z., S. Rehman, and M. Ahsan, *Methods of Fabrication of Superhydrophobic Engineering Surfaces: A Review.* International Review of Mechanical Engineering, 2009. 3(3).