Robust Super-Hydrophobic Coating Prepared by Electrochemical Surface Engineering for Corrosion Protection

Peng Bi 1,†, Hongliang Li 1,†, Guochen Zhao 2,*, Minrui Ran 3, Lili Cao 4, Hanjie Guo 1,* and Yanpeng Xue 3,*

1 School of Metallurgical and Ecological Engineering, University of Science and Technology Beijing, Xueyuan Road 30, Beijing 100083, China
2 Shandong Provincial Key Laboratory for High Strength Lightweight Metallic Materials, Advanced Materials Institute, Qilu University of Technology (Shandong Academy of Sciences), Jinan 250000, China
3 National Center for Materials Service Safety, University of Science and Technology Beijing, Xueyuan Road 30, Beijing 100083, China
4 School of Mechanical and Energy Engineering, Zhejiang University of Science and Technology, Liuhe Road 318, Hangzhou 310023, China
* Correspondence: zhaogch@sdas.org (G.Z.); guohanjie@ustb.edu.cn (H.G.); yanpengxue@ustb.edu.cn (Y.X.)
† These authors contributed equally to this work.

Abstract: Corrosion—reactions occurring between engineering materials and their environment—can cause material failure and catastrophic accidents, which have a serious impact on economic development and social stability. Recently, super-hydrophobic coatings have received much attention due to their effectiveness in preventing engineering materials from further corrosion. In this paper, basic principles of wetting properties and corrosion protection mechanism of super-hydrophobic coatings are introduced firstly. Secondly, the fabrication methods by electrochemical surface engineering—including electrochemical anodization, micro-arc oxidation, electrochemical etching, and deposition—are presented. Finally, the stabilities and future directions of super-hydrophobic coatings are discussed in order to promote the movement of such coatings into real-world applications. The objective of this review is to bring a brief overview of the recent progress in the fabrication of super-hydrophobic coatings by electrochemical surface methods for corrosion protection of engineering materials.

Keywords: super-hydrophobic coating; corrosion protection; electrochemical surface engineering; anodization; micro-arc oxidation; etching; electrodeposition; stability

1. Introduction

Engineering materials such as steel, aluminum (Al), magnesium (Mg), titanium (Ti), and their alloys are conventional metals employed in industry due to their significant mechanical and physical performance. However, in real service, corrosion may cause partial or complete destruction due to the chemical/electrochemical reactions of engineering materials and their environment [1]. Serious corrosion will not only lead to material failure, but also cause catastrophic accidents which may have serious impacts on economic development and social stability [2]. In developed countries, the national cost of corrosion generally represents approximately 1–5% of the gross national product (GNP) [3].

Raising awareness of the importance of corrosion protection, various methods are applied on corrosion control engineering, such as development of novel corrosion resistant materials, corrosion inhibitors, coating and surface modifications, as well as electrochemical cathodic protection. Among these methods, coating is a simple and effective way for corrosion protection with low cost. In the
past several years, various coating techniques have been studied—like chemical vapor deposition (CVD) [4], plasma treatment [5–8], thermal spray [9], electrochemical methods [10–18], sol–gel [19,20], magnetron sputtering [21–23], etc. The above-mentioned methods mostly involve post-treatment or high temperatures in the fabrication process, which can damage the coating and/or substrate with relatively low melting points [24]. Therefore, among various techniques, electrochemical methods are the better choice for corrosion protection due to the merits of mild processing conditions, low cost, and applicability for large-scale production.

Super-hydrophobic surfaces, inspired by the lotus leaf [25], play a significant role in the fundamental research of functional materials [26,27]. In general, super-hydrophobic surface has water contact angle (WCA) larger than 150° and water sliding angle (WSA) below 10°, which is regarded as nearly perfect non-wetting [28]. Due to their special wetting properties, super-hydrophobic surfaces have been widely investigated in broad potential applications, such as anti-corrosion [29–34], anti-fouling [35,36], anti-icing [37,38], self-cleaning [27,39,40], oil–water separation [41,42], energy conversion [43], and catalysis [44]. Especially, the unique water repellency property of super-hydrophobic surfaces makes them practical to serve as an effective barrier to prevent the engineering materials underneath from further corrosion.

In this review, the whole layout was organized as follows: the basic principle of wetting properties on solid surface and corrosion protection mechanism of super-hydrophobic coatings are firstly described in Section 2. The fabrication of super-hydrophobic coatings by electrochemical surface engineering including electrochemical anodization, micro-arc oxidation, electrochemical etching, and deposition are presented in Section 3. The corresponding advantages and disadvantages of each method are also summarized. In Section 4, stabilities of super-hydrophobic coatings are discussed. Finally, perspectives on further development of artificial coatings are presented in Section 5.

2. Basic Principle of Wetting Properties and Corrosion Protection Mechanism of Super-Hydrophobic Coating

2.1. Basic Principle of Wetting Properties

Wetting property is one of the important parameters of the solid surface. When liquid droplets contact a solid surface, an appropriate and stable angle of contact is formed on the liquid–solid interface, which is defined as contact angle. Thomas Young described the trigonometric relations between the surface tensions and the contact angle in 1805 in his essay [45], as can be expressed as

\[ \gamma_s - \gamma_{sl} = \gamma_l \cdot \cos \theta \]  

(1)

where \( \gamma_s, \gamma_l, \gamma_{sl} \) are the tensions of the solid surface, liquid surface, solid–liquid interface, respectively, and \( \theta \) is the contact angle, shown by Figure 1a.
Figure 1. Schematic of a liquid droplet on solid surface. (a) Young’s wetting state; (b) Wenzel wetting state; (c) Cassie–Baxter wetting state.

However, wetting properties of realistic surfaces are more complex since such surfaces are generally rough and chemically heterogeneous. Wenzel explained the wetting phenomenon as a thermodynamic process from the viewpoint of specific surface energy [46]. The net energy decrease determined wetting speed; net energy decrease was greater for the rougher surface, which suggested surface wettability should be strengthened. Figure 1b shows Wenzel wetting state. A surface ratio named “roughness factor” (r) was introduced as the actual surface area divided by geometric surface area in his work. Then actual contact angle \( \theta_A \) could be calculated by

\[
\cos \theta_A = r \cos \theta
\]

From the definition of roughness factor, \( r \) is always no less than 1. Therefore, as \( 0^\circ < \theta < 90^\circ \), then \( \theta_A \leq \theta \), similarly as \( 90^\circ < \theta < 180^\circ \), then \( \theta_A \geq \theta \). Using another word, wettability—including hydrophilicity and hydrophobicity—can be enhanced by surface roughness increasement. When actual WCA is greater than 150°, the surface shows super-hydrophobicity.

Although Wenzel provided a strategy in fabricating superwetting surface, i.e., increasing roughness, the solid–liquid contact area was also increased resulting in a “sticky” surface in the Wenzel state [47]. Moreover, Equation (2) breaks down at relatively large \( r \) (\(|\cos \theta| > 1\)), since in such case air is trapped within the surface rough structures. Therefore, Cassie and Baxter developed another model to describe wetting on porous surface [48], extended Wenzel’s statement, namely Cassie–Baxter wetting state as shown by Figure 1c. The liquid droplet was suspended on such surface due to the contact with the solid surface and gas phase [49]. Then apparent contact angle should be described as

\[
\cos \theta_A = f_{sl} \cos \theta_y + f_l \cos \theta_g
\]

where, \( f_{sl} \) and \( f_l \) are contacting area fractions of solid–liquid interface and liquid–gas interface in wetting part. The absolute values of both \( f_{sl} \) and \( f_l \) are less than 1, and the sum of \( f_{sl} \) and \( f_l \) is equal to 1. \( \theta_y \) is Young’s contact angle and \( \theta_g \) is liquid–gas contact angle (always 180°). Thus, Equation (3) can be substituted as

\[
\cos \theta_A = f_{sl}(\cos \theta_y + 1) - 1
\]

Cassie–Baxter equation tells us that introducing air pockets or reducing the solid–liquid contact fraction by increasing the surface roughness can forcibly enlarge the apparent contact angle, even if the solid material is naturally hydrophilic.
Super-hydrophobicity, introduced in 1976 by Reick [50], is a special wetting phenomenon which has extreme water-repellency. Normally, the super-hydrophobic surface has a WCA of at least 150°. However, contact angle can hardly exceed 120° on a smooth surface [51], even on extremely low surface energy materials, e.g., silicone resin of 22 mN/m, fluorine resin of 10 mN/m [52]. Barthlott and Neinhuis investigated the micro morphologies, surface chemicals of more than 200 water-repellent plant species and their self-cleaning abilities [25,53]. Demonstrated by the leaf of the *Nelumbo nucifera*, the waxy surface texture was indispensable in giving rise to water-repellency and self-cleaning of the plant. Water was suspended on the top of leaf rough structure and rolled off easily (evaluated by sliding angle) as well as remove any contaminants from the surface [28]. They named this mechanism the “lotus-effect”, but the fundamental mechanism was not mentioned [25]. The super-hydrophobic mechanism was clearly explained in 2002, the ‘lotus-effect’ with high contact angle and low sliding angle, resulted from micro- and nanoscale hierarchical structures: nanostructures contributed to high contact angle and nano- and microstructures effectively reduced WSA [54].

2.2. Corrosion Protection Mechanism of Super-Hydrophobic Surface

Given their water repellency for corrosion protection, super-hydrophobic surfaces have been widely applied on many metals and alloys—e.g., aluminum, magnesium, steel, titanium, zinc, copper, and so on [49,55–60]. The corrosion resistance mechanism of super-hydrophobic surfaces can be summarized as follows: when super-hydrophobic surface immerses into a corrosive medium, an air layer is formed within the valleys among the rough structures between the super-hydrophobic surface and liquid phase, which minimized the contact area as a barrier remarkably hinders the corrosion of metal and alloy surface [61]. As illustrated by Figure 2, the air layer retained on super-hydrophobic surface prevents the chloride ions in seawater from attacking metal surface, therefore providing effective corrosion protection [62]. This mechanism has been widely demonstrated by electrochemical impedance spectroscopy (EIS). Super-hydrophobic surfaces always have high impedance modulus value in the Nyquist plots, representing high polarization resistance. The trapped air hindered the electron transfer between the metal and solution resulted in an effective corrosion protection for engineering materials.

![Figure 2](image_url). Schematic image of anti-corrosion using a super-hydrophobic surface. The super-hydrophobic micro/nanostructures keep surface wettability in ‘Cassie State’ to prevent corrosive medium penetrating the air layer and contacting with the substrate.

3. Electrochemical Surface Engineering

As it known to all that special micro-nanostructures and modification with low surface energy materials are pointed out to be the critical factors to fabricate the biomimetic super-hydrophobic coating. Among the applicable techniques, electrochemical methods offer outstanding advantages such as mild processing conditions, low-cost, time-efficiency, as well as large-scale production. Herein, several electrochemical methods—including electrochemical anodization, micro-arc oxidation, electrochemical etching, and electrochemical deposition—are introduced.
3.1. Electrochemical Anodization

Electrochemical anodization is a simple and effective approach that can be used to develop hierarchical micro/nanoscale oxide layer at the top surface of valve metals and these alloys [63]. The metal oxide layer is generated from the reaction between metal ions and the electrolytes under a high voltage provided by an external power source [64]. Their characteristics of micro/nanoscale oxide layer are strongly dependent on electrochemical parameters such as the electrolyte compositions (phosphoric acid, sulfuric acid, or oxalic acid) and temperature, applied voltage, anodization time, and distance between the working electrode and the counter electrode [65]. After producing hierarchical micro/nanoscale structures, modification with low surface energy materials is necessary to endow its super-hydrophobicity. Electrochemical anodization possesses many advantages for developing super-hydrophobic surfaces on valve metals because the production processes are easy to perform, highly efficient, relatively economical, and suitable for large-scale manufacturing.

Recently, numerous chemically-stable and mechanically-robust super-hydrophobic surfaces have been produced via the electrochemical anodization technique and subsequent modification process. Aluminum and titanium are the typical substrates for fabricating super-hydrophobic surfaces by this method. For example, Kondo et al. constructed super-hydrophobic surfaces on different kinds of aluminum alloys by electrochemical anodization in concentrated pyrophosphoric acid solution and subsequent chemical modification [66]. Electrochemical anodization of aluminum alloy could cause the growth of massive anodic aluminum nanofibers which were developed with the reaction time (Figure 3a). Figure 3b illustrates the surface morphology of pure aluminum anodized for different times. A labyrinthine structure with oxide walls was observed at the initial stage of anodization. When the anodizing time reached to 4 min and 10 min, honeycomb oxide structures and rod-shaped oxides were observed on the surface, respectively. Larger bundle structures were appealed on the surface after anodizing for 30 min. As the reaction time increased, the structures of the other two kinds of Al alloys gradually changed, similar to the transform of structures of pure aluminum. All Al alloys obtained the super-hydrophobicity after modified by low surface energy chemical reagents.

![Figure 3](image-url)

**Figure 3.** (a) Growth process of anodic aluminum nanofibers and nanofiber-tangled intermetallic particles; (b) SEM of samples anodized for \( t_a = 2 \text{ min}, 4 \text{ min}, 10 \text{ min}, \) and 30 min, respectively. Reprinted from [66], Copyright (2017), with permission from Elsevier.
Zhang et al. fabricated a new anti-corrosion hierarchical alumina structure based on self-congregated nanowires through high-speed hard anodization technique on the high purity aluminum foils [29]. Figure 4a showed the fabricating process, the pure aluminum plates were pretreated first to obtain electropolished aluminum surface (EP surface) and then the anodization process was carried out in phosphoric acid solution under a constant voltage (120 V) to get super-hydrophilic (SHPL) surface. After that, the as-anodized sample was modified under the immersion of a 1% ethanol solution for 10 min and then dried at 120 °C. The as-prepared super-hydrophobic (SHPB) sample showed Dianthus caryophyllus-like structure (Figure 4b) and displayed WCA of 168°, showing excellent water repellency. The EIS results showed that the impedance modulus of SHPB surface was greater than 10^8 Ω·cm², which was much higher than that of EP and SHPL surface (Figure 4c). The corrosion inhibition efficiency was reached up to 99.99%, exhibiting the outstanding corrosion resistance of the SHPB surface. Besides, the as-received SHPB surface presented outstanding thermal stability to hot water droplets, which could retain contact angle higher than 150° under water droplets of 90 °C (Figure 4d).

Figure 4. (a) Scheme of the preparation and evaluation of SHPL and SHPB surface by high-speed hard anodization; (b) SEM images of the Dianthus caryophyllus-like structure; (c) Nyquist plots and fittings of EP surface, SHPL surface, and SHPB surface; (d) The variations of WCAs and sliding angels of the
SHPB surface under hot water droplets with different temperatures. Reprinted from [29]. Copyright (2017), with permission from Elsevier.

Besides favorable corrosion resistance, abrasion performance is another important aspect needed to be considered in coating production. Peng and co-workers fabricated a robust super-hydrophobic aluminum surface possessing outstanding chemical stability and mechanical durability as well as resistance to many kinds of hot liquids. The coating was produced at 0.3 M oxalic acid electrolyte with a current density of 0.16 A/cm² within 10 min under room temperature, then modified with PDES (1H, 1H, 2H, 2H-perfluorodecyltriethoxysilane) [67]. After abrasion for 50 cycles, the nano-scaled structures of the PDES-modified surface were still retained and the WCA still remained above 150° both after ultra-sonication and abrasion test (Figure 5a–c). Moreover, the as-fabricated surface exhibited the improved corrosion resistance due to the promising water repellency. As shown by potentiodynamic polarization curves in Figure 5d, the corrosion current density (Icorr) of the PDES-modified surfaces, 1.31×10⁻¹¹ A/cm², is two times of magnitude lower than that of the bare surfaces (9.70×10⁻⁸ A/cm²).

![Figure 5](image)

**Figure 5.** Mechanical stability and corrosion resistance evaluation of the PDES-MS surface: (a) Surface morphologies of the PDES-MS surface before and after abrasion test for 10, 30, and 50 cycles with sandpaper; (b) The variations of WCAs and WSAs under different ultrasonication time; (c) Variations of WCAs and WSAs of the PDES-MS surface after abrasion tests; (d) Potentiodynamic polarization curves of the unmodified and modified surfaces in 3.5 wt % NaCl solution. Reprinted with permission from [67]. Copyright (2014) American Chemical Society.

As is known, anodizing voltage has a great impact on the surface morphology of the coating. The effects of different anodizing voltages on the final contact angle have been investigated on a super-hydrophobic aluminum surface with prominent anticorrosive property via one-step anodization and chemically modification with stearic acid [68]. The WCA increased with the increase of the anodizing voltage until reached a peak at 25 V, and then declined. Excessive increase in voltage also leads to side effect on the size and order of the pores on the surface, which can decrease the uniform surface roughness. Combined with the suitable surface roughness of anodized aluminum and the following chemical modification, super-hydrophobic surface with contact angle of 152° ± 0.3° was received. At the optimized conditions, the result of electrochemical tests performed by 3.5 wt % NaCl solution showed that the Icorr of bare Al substrate and super-hydrophobic Al surface were 1.9 μA/cm² and 0.0562 μA/cm², respectively. The inhibition efficiency of super-hydrophobic Al surface was 97%, indicating the excellent corrosion resistance of super-hydrophobic surface.

Similar studies were conducted on anodized TiO₂ coatings [69]. Differ from the super-hydrophobic aluminum surface, the super-hydrophilicity of the Ti surfaces can be continuously enhanced with the increment of the anodization voltage from 20 V to 80 V without decline. Besides the anodizing voltage, parameters like electrolyte temperature also influence the final super-hydrophobicity. The increase in electrolyte temperature could improve the surface super-
hydrophilicity in the low range of anodization voltages (< 40 V). However, when the voltages rose up to 60 V, it showed the opposite trend. Suitable anodization voltage and electrolyte temperature can balance the growth and dissolution of the roughness surface structure, thereby producing the favorite superhydrophobic Ti surface. The WCA and WSA on the best super-hydrophobic TiO₂ surface were recorded as 160° and 2°, respectively. Moreover, the as-prepared super-hydrophobic Ti surfaces exhibited outstanding corrosion resistance in acidic, neutral, and alkaline aqueous solutions. The electrochemical reaction mechanism in super-hydrophobic Ti surface fabrication has been reported by Gao et al. [12]. They fabricated a super-hydrophobic Ti surface with a WCA of 158.5° ± 1.9° using anodization technique and subsequent modification with the fluoroalkylsilane (FAS). Anodization process was performed in a 1.5 mol/L NaOH and 0.15 mol/L H₂O₂ mixed solution at a DC voltage of 10 V within 30 min. During this process, the main electrochemical reaction was the anodic oxidation of Ti into TiO₂ and transformation of TiO₂ into Na₂TiO₃, as the equations

\[ \text{Ti} + 4\text{OH}^- \rightarrow \text{TiO}_2 + 2\text{H}_2\text{O} + 4e^- \]  
\[ \text{TiO}_2 + 2\text{NaOH} \rightarrow \text{Na}_2\text{TiO}_3 + \text{H}_2\text{O} \]

The anodic oxidation reactions occurred immediately after the immersion of Ti alloy, and the chemical dissolution occurred due to the instability of TiO₂ in alkaline or acidic environment. The measurements by immersion and abrasion suggested that the as-received super-hydrophobic surfaces possessed good stability under various harsh conditions.

Combining electrochemical anodization with nano-silver deposition and post modification, Zhu et al. produced an anticorrosion super-hydrophobic film on Ti substrate [70]. With an appropriate immersion time of 7 h, micro-nano roughness structures was obtained. The WCA was reported to be 154°. Also, the corrosion resistance of super-hydrophobic surface was studied. As shown in Figure 6a, the specimen covered by the super-hydrophobic surface present much larger impedance semicircles whose diameter is around a few thousand of kΩ·cm². However, the pure Ti sample showed a small semicircle. At the frequency of 0.01 Hz, the super-hydrophobic sample displayed a high impedance modulus \(|Z|\) value of 1.319 × 10⁹ kΩ·cm², which was nearly six times as large as that of the untreated Ti substrate (Figure 6b). Additionally, the super-hydrophobic sample presented more positive corrosion potential (Ecorr) and lower Icorr compared with that of the untreated Ti (Figure 6c). The Nyquist plots and Bode plots, as well as polarization curves, demonstrated that the presence of the super-hydrophobic surface can effectively reduce the anodic dissolution of the Ti substrate and inhibit the development of corrosion.
Figure 6. (a,b) Nyquist and Bode plots for the super-hydrophobic Ti surface and bare Ti substrate, respectively; (c) Polarization curves of super-hydrophobic Ti surface and bare Ti substrate. Reprinted from [70]. Copyright (2017), with permission from MDPI AG.

3.2. Micro-Arc Oxidation Coating

Micro-arc oxidation (MAO), also named as plasma electrolytic oxidation (PEO), is an electrochemical process to develop oxide coatings on metals. MAO employs high voltage plasma to modify the multi-layered ceramic structure which shows high hardness, high anti-corrosion behavior and strong adhesion to the metal surface [71–73]. The present of micro-pores on the coatings can provide the structure to fabricate super-hydrophobic surface. However, it can also increase the tendency to absorb the corrosive medium and penetrate into the substrate, which restrict its anti-corrosion applications [74]. Thus, in order to reduce or seal the micro-pores, many researchers combined MAO with other techniques.

Cui et al. fabricated a MAO/zinc stearate (ZnSA) composite coating with micro plate-like structure by MAO processing and electrochemical deposition method [75]. The hydrophilic coating was produced first by MAO in phosphate-containing electrolyte, then followed by the roughness control process and low surface energy material deposition to obtain the super-hydrophobic coating. After a short heating process, the MAO/ZnSA composite coating was received. As shown by Figure 7a,b, MAO coating with micro-pores provide mechanical connection for the super-hydrophobic coating and the MAO coating was sealed by the super-hydrophobic coating. The as-received white MAO coating shows a typical porous morphology with micro-pores and micro-cracks, while the surface of MAO/ZnSA coating exhibits whiter and rougher than the MAO sample (Figure 7b). The obtained super-hydrophobic coating showed a significant increase in contact angle of above 153° compare to the MAO of 37.5°. Based on the immersion tests, the MAO/ZnSA coated sample appealed no obvious corrosion pits after immersed in 3.5 wt % NaCl solution for 85 h, demonstrating excellent performance of corrosion resistance. Moreover, the relationship between the immersion time in NaCl and corresponding contact angles of the coating revealed that the contact angles change from 153.5° to 128.0° after immersion for 85 h, thus the long-term stability of the MAO coating need to be enhanced further.
In another study, a super-hydrophobic surface on MAO coating on Mg-1Li-1Ca magnesium alloy with good performance of long-term stability was obtained by surface modification with stearic acid (SA) [76]. The porous structure of MAO coating was hydrophilic and the contact angle was below 35°. After SA modification, it was covered with thick petal-like clusters and exhibited super-hydrophobicity with contact angle over 155°, which was attributed to the high surface roughness of MAO coating as well as low surface energy of SA coating. As can be seen in Figure 8a, the sectional view of the MAO/SA coating showed a relatively dense and uniform structure with no obvious interface between the super-hydrophobic layer and the MAO coating, indicating that SA penetrating into the MAO layers and seals the micro-pores/cracks completely. Figure 8b presented the polarization curves of samples under different treatments, the $I_{corr}$ of the substrate, MAO coating and MAO/SA coatings were in descending order and the $I_{corr}$ of the MAO/SA coatings decreased with the extension of heating time. The $I_{corr}$ of MAO/SA-7h coating was about 3 orders of magnitude lower compared with the bare substrate, suggesting a lower corrosion rate after surface modification. Also, the EIS results showed a significant increase in impedance modulus for MAO/SA coatings, revealing a higher corrosion resistance. Moreover, after 7 days’ immersion in 3.5 wt % NaCl solution, the
surface structures of the MAO/SA 7 h coating were still similar to the non-immersion specimen and the contact angle remained higher than 145°. As such, the fabricated MAO/SA coating demonstrated satisfactory stability and can perform well in long-term protection.

Figure 8. (a) Cross-view image of the MAO/SA 7h coating; (b) Polarization curves of the AZ31 substrate and the MAO coatings before and after modification with SA in 3.5 wt % NaCl solution. Reprinted from [76], Copyright (2017), with permission from Elsevier.

Similarly, Cui et al. [74] reported a simple process for synthesizing hydrophobic surface on AZ31 Mg alloy by MAO and surface modification of stearic acid. Combining with the rough micro-pore structures of MAO coating and the low surface energy of stearic acid monolayer, the super-hydrophobic surface with a maximum WCA over 151° was obtained after 10 h of modification (Figure 9a). The MAO-coated Mg alloy showed more positive $E_{\text{corr}}$ and much lower $I_{\text{corr}}$ than the uncoated substrate (Figure 9b), revealing a decreased corrosion susceptibility and a reduced corrosion rate.

The corrosion resistances of uncoated and coated alloys were investigated by EIS. As shown in Figure 9c, the MAO coating modified for 5 h (H-MAO) exhibited the largest diameter of the capacitive loop and no low-frequency inductive loop compared with the uncoated and unmodified coatings, which means a better corrosion resistance.

Figure 9. (a) Surface morphologies and inserted corresponding contact angles of the MAO coatings modified for 0, 1, 3, 5, and 10 h; (b) Potentiodynamic polarization curves of bare AZ31 Mg alloy and
MAO coatings modified for different times; (c) EIS results and fitting curves for uncoated AZ31 Mg alloy, MAO coating, and H-MAO coating in 3.5 wt % NaCl solution. Reprinted from [74], Copyright (2015), with permission from Elsevier.

MAO method is also widely applied on Ti alloys. Jiang et al. [77] produced super-hydrophobic TiO$_2$ coatings on biomedical Ti-6Al-4V alloys by utilizing the MAO technique and super-hydrophobic treatment in 1H, 1H, 2H, 2H-perfluorooctyl-trichlorosilane (PFOTS) solution. The surface roughness Ra of the polished Ti-6Al-4V alloys was only 0.253 μm, while it increased remarkably to 0.535 μm after MAO treatment and further modification. Benefit from the increased surface roughness, the WCA of Ti-6Al-4V sample dropped slightly after MAO treatment and increased drastically after modification (Figure 10a), showing a high WCA over 153°. The potentiodynamic polarization curves shown by Figure 10b reveals that the $E_{corr}$ of super-hydrophobic sample was about 0.2 V nobler than the uncoated Ti-6Al-4V sample, while the $I_{corr}$ was reduced by one order of magnitude compared with that of uncoated sample, exhibiting an enhanced corrosion resistance. The super-hydrophobic TiO$_2$ coatings also exhibited better hemocompatibility and biocompatibility due to the reduced hemolysis ratio and platelets adhesion. As shown in Figure 10c, it is obvious that the surface of the uncoated alloy was adhered by a plenty of platelets while the platelets adhered on the surface of MAO sample reduced significantly and almost no platelet can be observed on the MAO + TFOS sample, indicating an enhanced hemocompatibility after MAO treatment and further super-hydrophobic treatment.

![Figure 10](image_url)

**Figure 10.** (a,b) Variations on contact angles and potentiodynamic polarization curves of the Ti-6Al-4V, MAO and MAO + PFOTS samples; (c) The morphologies of platelets adhered on the surface of the obtained samples. Reprinted from [77], Copyright (2015), with permission from Elsevier.

### 3.3. Electrochemical Etching

Etching is also a common technique to realize super-hydrophobic surfaces on various metals, such as titanium, stainless steel, aluminum and their alloys, etc. By electrochemical/chemical etching,
hierarchical micro-nano structures can be obtained. However, direct chemical etching is time consuming. Here, we mainly focus on electrochemical etching method.

For the preparation of super-hydrophobic titanium surfaces, Lu et al. reported the formation of surface microstructures via electrochemical etching in neutral sodium chloride electrolyte and subsequent modification by FAS to gain low surface energy [10]. The as-prepared Ti surfaces showed the super-hydrophobic properties with contact angles over 163°, and exhibited high stability and abrasion resistance. The same group also reported that the Ti surfaces can acquire both super-oleophobicity and super-hydrophobicity at the same time by adjusting the electrochemical etching parameters in NaBr solution [78]. Figure 11a–d showed that the droplets of the super-oleophobic and the super-hydrophobic Ti surface are both in spherical shape with contact angles greater than 150° in water and glycerol, while the liquids were spread out on unprocessed surface. This economical and environmentally-friendly electrochemical etching method is identified as a promising method suitable for industrial production of super-oleophobic and super-hydrophobic Ti surfaces for future applications in many fields.

![Figure 11.](image)

Stainless steel (SS) is a basic alloy widely applied in industrial, living and medical fields due to its low price and reliable mechanical properties. With the growing need for high-performance SS, fabrication of super-hydrophobic coatings on SS with corrosion resistance properties arouse many researchers’ concern. Recently, Song et al. developed a simple and low cost approach to prepare super-hydrophobic surfaces on mold steel GCr15 substrate by electrochemical etching and FAS modification with WCAs over 167° [79]. The bare substrates after electrochemical etching were covered with passive films composed of two-dimensional micro/nano rough structures, which is beneficial to fabricate super-hydrophobic surfaces. Jang et al. prepared a nanostructured stainless steel 316L (NT SS316L) surface by electrochemical etching for biomedical applications [80]. The NT SS316L surface showed nanopores with pore diameters between 20–25 nm which inhibited bacterial adhesion (Figure 12a,b). This electrochemical surface modification method can form outstanding passive layer on the surface of SS316L, which can improve corrosion resistance. The potentiodynamic polarization tests showed the as-received SS316L samples (AR-SS316L) exhibited localized corrosion.
with breakdown potential of 0.53 V (Figure 12c), while the local breakdowns of NT-SS316L samples were not observed. Additionally, the $E_{\text{corr}}$ of NT SS316L is about 0.3 V nobler than the as-received SS316L sample, suggesting a less corrosive structure after surface modification.

![Figure 12.](image)

**Figure 12.** (a) Scheme of electrochemical etching method. (b) Surface morphologies of AR-SS316L and NT-SS316L surfaces. The scale bar of the inset image is 200 nm. (c) Potentiodynamic polarization curves of AR-SS316L and NT-SS316L specimens in Hank’s balanced salt solution. Reprinted from [80]. Copyright (2017), with permission from American Chemical Society.

Other researchers also applied electrochemical etching method on aluminum surface. Yang et al. reported a two-step electrochemical-etching method combining electrochemical-etching and masking technology to fabricate super-hydrophilic dimple patterns on etched super-hydrophobic Al substrates [81]. The super-hydrophobic layer exhibited high $E_{\text{corr}}$ due to the adhesion of the bubbles on the surface and the flat super-hydrophilic dimples can be controlled by switching different etching voltages. The findings will contribute to the design of new fog harvest devices. Chen et al. fabricated super-hydrophobic surfaces on aluminum film by electrochemical etching and myristic acid modification with WCA greater than 165° [82]. The results of potential polarization tests revealed that the anti-corrosion property of the super-hydrophobic surfaces were improved remarkably. Based on the data extracted from the polarization curves, after the super-hydrophobic treatment, the $E_{\text{corr}}$ positively shifted from $-0.87$ V to $-0.28$ V and the $I_{\text{corr}}$ dropped significantly for three times of magnitude, demonstrating that the Al coating had lower corrosion susceptibility and less corrosion rate in the natural environment.

3.4. Electrochemical Deposition

Currently, electrodeposition technique has aroused many concerns in fabricating super-hydrophobic surfaces due to its advantages compared with conventional coatings, such as simplicity, controllability, affordability, and ease of large-area modification. Moreover, the inherent connection of coating and base material is promising to enhance the mechanical robustness and corrosion properties, which is essential in practical applications.

For magnesium alloy, She et al. reported a robust and stable super-hydrophobic surface on AZ91D magnesium alloy by electrodeposition of nickel and chemical modification process [83]. The obtained surface showed pinecone-like hierarchical structure with WCA over 163° and can maintain the WCA above 150° after mechanical abrasion for 0.7 m under applied pressure of 1.2 kPa with 800 grit SiC sandpapers. It can still show super-hydrophobicity after long term expose in atmosphere for 240 days. The super-hydrophobic surfaces possess superior corrosion resistance in neutral 3.5 wt %
NaCl solution, with only 0.003% of the corrosion rate of bare alloy in the potentiodynamic polarization test.

However, the above-mentioned two-step method requires the fabrication of a transition-metal layer and modification with the low-surface-energy material, which is complicated and time consuming. To solve this problem, Liu et al. developed a rapid one-step electrodeposition method to fabricate anticorrosion super-hydrophobic surface on Mg–Mn–Ce alloy by electrodepositing [11]. They studied the effect of deposition voltage and deposition time on the morphology and wettability of the coatings, finding that hierarchical structures were constructed at 30 V. The electrodeposition time can be as short as 1 min to obtain a super-hydrophobic surface and the papillae continued to agglomerate to form homogeneous hierarchical papillae structures until the electrodeposition time reached 20 min, all the contact angles were larger than 155° (Figure 13a). The super-hydrophobic surface exhibited strong corrosion resistance after immersion in corrosive aqueous solutions. The potentiodynamic polarization test results of the Mg alloy surfaces with and without treatment showed that all the $E_{corr}$ shift nobly and $I_{corr}$ decreased drastically after electrodeposition process (Figure 13b). Moreover, the Nyquist plots in Figure 13c confirmed that the super-hydrophobic surface showed much higher impedance values comparing with the bare alloy. To evaluate the mechanical stability, an abrasion test shown in Figure 13d was analyzed. The results revealed that the as-received surface can hold a contact angle over 150° after abrasion length of 0.4 m, suggesting a good mechanical durability.
Figure 13. (a) SEM images and corresponding WCAs of the super-hydrophobic surfaces with various electrodeposition times: 1, 5, 10, 20, 30, and 60 min; (b,c) Potentiodynamic polarization curves and Nyquist plots of the untreated and super-hydrophobic Mg alloy surfaces in 3.5 wt % NaCl solution; (d) Schematic of the abrasion test and contact angles of the super-hydrophobic surface as a function of abrasion length. Reprinted with permission from [11]. Copyright (2015), American Chemical Society.

For controllable fabrication of super-hydrophobic surface on copper substrate, Su et al. [60] reported a novel and low-cost method by electrodeposition in traditional Watts bath and modification process (Figure 14a). The surface roughness increased from 0.08 μm for the Cu substrate to 1.86 μm for the deposited Ni surface, followed by a slightly decrease to 1.18 μm after surface modification process. The increased roughness of deposited layer contributed to the formation of superhydrophobic surface, which showed pine-cone-like hierarchical micro-nanostructure with a WCA of 162° ± 1°, possessed high microhardness and outstanding wear resistance after mechanical
abrasion against 800 grit SiC sandpaper for 1.0 m at 2.4 kPa. When the applied pressure increased to 6.0 kPa, the pine-cone-like structure was partially damaged and the contact angle of the surface decreased (Figure 14b–e). Moreover, the super-hydrophobic surface exhibited good chemical stability both in acidic and alkaline environments. It is shown in Figure 14c that the Cu substrate showed higher E\text{corr} and lower current density after Ni electrodeposition. The EIS test revealed that the impedance value of the super-hydrophobic surface is 75 times higher than that of the bare Cu substrate (Figure 14d), confirming the excellent corrosion protection properties of the super-hydrophobic surface.

![Figure 14](image)

Figure 14. (a) Schematic of the electrochemical deposition process; (b) SEM images and contact angle of super-hydrophobic Ni (Ni-III) surface; (c–e) SEM images and contact angle of the super-hydrophobic surface (c) before and after abrasion for 1.0 m at applied pressure of (d) 2.4 kPa and (e) 6.0 kPa; (f,g) Potentiodynamic polarization curves and Nyquist plots of Cu substrate, electrodeposited Ni and the super-hydrophobic surface in 3.5 wt % NaCl solution. Reprinted with permission from [60]. Copyright (2014) American Chemical Society.

Similarly, a robust copper-based super-hydrophobic surface with cauliflower shaped fractal morphology was prepared by Jain et al. via an electrodeposition route [84]. The inherently generated super-hydrophobic surface showed extreme water repellency with CA above 160° (Figure 15a). The as-received coating exhibited slight reduction in E\text{corr} and one order of magnitude lower I\text{corr} in comparison to a bare copper substrate, indicating a significant increase of anticorrosion properties (Figure 15b). Moreover, the super-hydrophobic surface maintained integrity after the mechanical abrasion tests, showing favorable wear resistance (Figure 15c,d).
4. Stability of Super-Hydrophobic Coating

So far, the fabricating strategies of super-hydrophobic surfaces have been developed a lot as discussed above. However, the instability of super-hydrophobicity seriously hinders its practical applications. Generally, super-hydrophobicity highly depends on both surface energy and micro-nano hierarchical structures. Such structures of surfaces are mechanically weak and stop functioning when facial chemicals are changed in various engineering conditions [85]. The surface energy could be easily increased with chemical attacks in aqueous acid, alkaline, salt solutions, or organic solvent. Meanwhile, the porous structures always get defects when mechanical damage applied on the surface. Additionally, normal ultraviolet (UV) irradiation and temperature variation may cause degradation of hydrophobic chemicals on surface. In this view, one of the future trends in developing super-hydrophobic surfaces with long-lasting corrosion resistance is to improve their stabilities [51]. Most recently published works have focused on improving the mechanical stability, chemical stability, and long-term durability of super-hydrophobicity. In this section, we discuss several types of stability as reference for the future fabrication of robust super-hydrophobic coatings.

4.1. Mechanical Stability

Improving mechanical stability is a key issue in fabricating robust super-hydrophobic surface. In other words, enhancing structural stability contributes to resist the external force to maintain original facial structures. The recently reported manners have been used to character such stability includes: linear abrasion [86], tape-peeling [55], knife scratching [87], finger pressing [88], bending [89], etc. Although so many approaches have been published for testing, there is still lack of standardization to make comparison of different surfaces. A general strategy to evaluate mechanical stability was suggested by Tian et al. (Figure 16). They reported that the linear abrasion test appears to best fulfill this requirement [90], which also is the most common applied manner to test robustness of super-hydrophobic surface in recent years [49,55,85–87,91–93].
For instance, Lu et al. created an ethanol-based suspension containing perfluorooctyltriethoxysilane coated dual-scale TiO₂ nanoparticles, which could be coated onto steel surface to create super-hydrophobicity by facile spray, dipping, or painting [85]. The paint directly coated on substrate could be easily removed by finger-wipe, whereas the double-sided tape-bonded paint (double-sided tape treated substrate and paint) could still retain its super-hydrophobicity after finger-wipe, knife-scratch, etc. Above all, the super-hydrophobicity of robust paint was not lost in the 0.4 m linear abrasion length (similar as Figure 16), which had potential in large-scale industrial applications. The linear abrasion test also applied on the surface of Ni-WC-WS₂ composite coating [94]. Such super-hydrophobic coating was fabricated by electrodeposition on mild steel with a WCA of approx. 170°. WS₂ nanoparticles (NPs) as solid self-lubricant could significantly reduce the coefficients of friction between solid–solid contacts, while WC NPs were hard materials to increase the abrasive resistance. Thus, the abrasive resistance of coating was further enhanced: with a bearing capacity ≥10,000 mm abrasion length on the 360# grit aluminum oxide paper under 3 kPa during the test.

Wang et al. carried out a facile oxidation to fabricated FAS-17 modified steel hierarchical surface [86]. The surface could withstand abrasion by 400 grids SiC sandpaper for 1.1 m under 16 kPa without losing super-hydrophobicity. Tam et al. applied co-electrodeposition process on nickel to synthesized a super-hydrophobic nanocrystalline nickel-polytetrafluoroethylene (Ni-PTFE) composite coating [95]. Due to the dual-scale surface roughness with lotus leaf-like morphology formed by the embedded PTFE particles in Ni matrix, the composite coatings possessed excellent wear resistance in abrasion test. The results in Figure 17a,b showed that, on 400 grit SiC sandpaper, the Ni-PTFE composites can only remain a high WCA above 150° for about 3 m of abrasion length and gradually decreased to about 130° after 18 m of abrasion. However, on the 800-grit sandpaper, stronger stability of super-hydrophobic properties was observed, the WCA of the Ni-PTFE composite coating can retain 150° after 48 m of abrasion under the applied pressure of 2.0 kPa. Xue et al. presented an electrodeposition route for super-hydrophobic Co–Ni coatings on carbon steel substrate which exhibited outstanding wear resistance [96]. The Co–Ni coating with micro-nano structures deposited at -1.7 V showed the highest surface roughness with Ra of 7.77 μm, which was much higher than that of −1.0 V (0.63 μm) and −1.4 V (1.71 μm). It shows that higher surface roughness structures can be favored to be generated by adjusting the applied potential to a more negative direction. The results of abrasion testing showed that the super-hydrophobic properties kept well after 12 m of abrasion under 5 kPa pressure (Figure 17c–f), which showed that the abrasion resistance was remarkably improved by the increase of Co content.
Before being applied on a large-scale, super-hydrophobic surfaces should pass the examinations of other mechanical tests, such as hand twisting, tape-peeling, knife scratching. Test selection varies by the application of surface. Generally, particles or debris peeled off from the substrate indicates the structures are damaged and super-hydrophobicity may be failed [97]. Porous, loose, and uncompact surfaces can hardly bear such tear force (~300 N/m), whereas there is little influence on the surfaces like fluorination treated aluminum oxide [55], methyltrichlorosilane-Fe [89], FAS-17 modified rough steel [86], HVOF TiO2/h-BN coating [97], and micro-nanostructure PDMS/SiO2 composite coatings on Mg substrate [88], which demonstrates their robustness.

4.2. Chemical Stability

Most super-hydrophobic surfaces need to be modified by organic chemicals to minimize the surface energy. These surface modification agents might be degraded in harsh condition, which may cause increase of surface energy and decrease of super-hydrophobicity [87]. Thus, chemical stability
of coating should be investigated in acid and base (or aqueous with various pH value), even aqua regia [87,98–101], salt aqueous [100–103], and organic solvent [85,87]. Besides, UV irradiation [86,104] and temperature variation [87,105] also should be taken into consideration which might cause degradation of surface chemicals.

To improve corrosion resistance of aluminum, Lv et al. used NaClO to the surface of aluminum and acquired super-hydrophobic surface after passivated by hexadecyltrimethoxysilane [103]. The sample maintained high contact angle (about 160.8°) after 7 days immersing in 3.5 wt % NaCl aqueous solution. The work reported by Qian et al. showed solution pH and salt aqueous including NaCl, MgCl2, NaI, and CH3COONa, have limited influence on the wetting properties of silica-based super-hydrophobic coating on AZ31B Mg Alloy [102]. Particularly, the organics like C2H5OH, C17H33COONa, and sodium dodecylbenzene sulfonate had obvious detrimental effects on the wetting properties. Khorsand et al. prepared super-hydrophobic nickel–cobalt alloy coating by a two-step-electrodeposition [100]. In the stability test, the coating was immersed into H2SO4 with pH of 2, NaOH with pH of 13 and neutral 3.5 wt % NaCl solution for 24 h. The results showed only in basic solution, the WCA decreased drastically with the increase of immersion time, which suggested the coating possessed favorable chemical stability in acidic and saline solution. Other products with super-hydrophobicity such as Zr-based MOFs [101] and silica gel [87] showed an excellent chemical stability in aqueous solution with various pH values ranging from 1 to 13, NaCl (0.5 M), Na2SO4 (0.5 M), n-hexane, xylene, butyl acetate, and acetone.

As for UV stability, UV exposure test was carried out for the super-hydrophobic steel surface [86]. The super-hydrophobic steel surface was prepared by FAS-17 modification of hierarchical steel. The C–F bonds of FAS-17 had a high bond energy (485 kJ/mol) which could not be broken by UV light. Thus, such surface still exhibited super-hydrophobicity with a contact angle of 151° and a sliding angle of 9° after 50 h of exposure under UV light, which suggested an excellent UV stability (Figure 18a). Xu et al. exploited a kind of transparent porous silica coating with the help of electrodeposited PEDOT template [106]. The coating showed super-hydrophobicity with excellent thermal stability. Its super-hydrophobicity remained constant in various temperatures ranging from 22 to 400 °C, see Figure 18b, and was lost when fluorosilane started decomposing at more than 400 °C.

Liu et al. reported super-hydrophobic fluorinated ZIF-90 showed high thermal stability in the temperature range 80–300 °C, and most bio-alcohol could be recovered and removed from mixture at 20 °C, which was very promising to be used as an effective and reusable adsorbent for bio-alcohols recovery from aqueous solution [105].

![Figure 18. (a) WCAs and WSAs vary by different UV exposure time on super-hydrophobic steel. Reprinted (adapted) with permission from [86]. Copyright (2015) American Chemical Society; (b) The thermal stability of transparent porous silica coating. Reproduced with permission from [106]. Copyright (2015), with permission from Royal Society of Chemistry.](image)

### 4.3. Long-Term Durability

The long-term durability is one of the most important properties for super-hydrophobic surface in actual applications, which determines the maximum lifespan of such functional surface. Generally speaking, the durability test is to measure the effective time of the surface having stayed in an
unwetted state, which is always carried out at normal conditions, including atmospheric air [56,100,103,107], highly humid air [108], and water [107].

Ke et al. fabricated FAS-17 modified Al/Fe_{2}O_{3} nanothermite film by electrophoretic deposition [108]. They put the film into humidity chamber with 60% relative humidity for 20 days. Due to infiltration of water vapor and air, the WCAs decreased slowly and the coating lost super-hydrophobicity after 7 days, but still showed strong hydrophobicity in the end of the test (about 145°). As for long-term water immersion, the copper-based super-hydrophobic blocks fabricated by Feng et al. [107] kept strong water repellent after immersing in water for a month, the WCAs of electrodeposited Ni-Co alloy super-hydrophobic coating on AA5052 aluminum increased from 151.3° to 160.0° during 15 weeks of exposure in open air, rather than decreased [109], and the HDYMS modified AA5083 aluminum could keep its water-repellent super-hydrophobicity stable in 12 days of 3.5 wt % NaCl immersion [110].

5. Perspectives

The mechanical durability and chemical stability of the as-prepared super-hydrophobic coatings needs to be further studied. Some possible directions to fabricate robust super-hydrophobic coatings are summarized as follows:

Self-healing coatings: One of the efficient ways to improve the durability and stability of the coatings is to endow it with self-healing ability. Generally, based on the healing mechanism, the repair process is divided into two categories: autonomous and non-autonomous. The healing effect and mechanism of the self-healing coatings have been elaborately discussed elsewhere [111]. For non-autonomous coatings, the external intervention, such as UV and heat, is indispensable to self-recovery. Under suitable stimuli, non-autonomous coatings can accurately repair the destroyed region. For the autonomous healing coatings, self-healing agents or inhibitors embedded in the coating layers can continuously provide corrosion protection at the defected region when the coating is damaged. For instance, corrosion inhibitors, along with polymerizable healing agents, can be mixed and packaged together in microcapsules. Figure 19a showed smart-coating-combined microcapsules containing linseed oil by the in situ polymerization method with polyelectrolytes layers entrapped benzotriazole (BTA) corrosion inhibitor. After application to the carbon steel surface, the coating exhibited self-healing property, which can release linseed oil under the stimulation of mechanical impact or release BTA by pH change [112]. Another novel study confirmed that the graphene oxides microcapsules containing linseed oil endowed self-healing properties to the waterborne polyurethane coatings (Figure 19b) [113]. Figure 19c,d depicted the self-healing process of the coating on cold-rolled steel, the rupture of microcapsules induced the polymerization of PDMS within the crack, resulting in recovery of corrosion protection [114].
Figure 19. (a) Schematic of the structure of the microcapsules and the self-healing mechanisms of the coating. Reprinted from [112] Copyright (2018), with permission from Elsevier; (b) Formation process of oil-containing graphene oxide microcapsules (GOMCs) and the processing of GOMCs/PU coatings. Reprinted from [113], Copyright (2017), with permission from Elsevier; (c,d) SEM images of self-healing coating before and after healing. Reprinted from [114], Copyright (2009), with permission from John Wiley and Sons.

Slippery liquid-infused porous surface (SLIPs): Inspired by Nepenthes pitcher plant, Wong et al. first designed slippery liquid-infused porous surface, which was conceptually different from the lotus effect [115]. In contrast with a super-hydrophobic surface with lotus-like structures, SLIPs use the micro/nanostructure to lock in place the infused lubricant instead of air (Figure 20). Therefore, SLIPs can withstand higher external pressure showing longer service life than the traditional super-hydrophobic surface. Additionally, SLIPs appealed outstanding liquid and ice-repellency, self-healing property, and corrosion resistance. These properties endow SLIPs with advantages in practical application for the corrosive environments.

Multi-functional: Water repellency and anti-corrosion is the already achieved function of the super-hydrophobic surfaces. The future super-hydrophobic surfaces must combine the above-mentioned properties with additional functions, such as super-oleophobicity and anti-biofouling. That is, the surface is multifunctional.
Figure 20. (a) Schematics of the fabrication process of a SLIPS; (b) Schematics and time-lapse images showing the stability and displacement of SLIPS. Reprinted from [115], Copyright (2011), with permission from Springer Nature.

6. Conclusions

Super-hydrophobic surfaces have received continuous attention in corrosion protection engineering, especially for long-time service safety under sensitive medium. Basic fundamentals for fabricating super-hydrophobic surfaces lie on the formation of rough micro/nanostructures and low surface energy materials. The corrosion protection of the super-hydrophobic surface is obtained by the air layer forms between the rough structures, which acts as a barrier between the alloy surface and corrosive medium.

In this review, we summarized the most currently used methods and techniques—including electrochemical anodization, micro-arc oxidation, electrochemical etching and deposition—to achieve surface roughness. After modification, the corrosion resistance and durability of super-hydrophobicity coatings were improved compared with bare substrate. Moreover, the mechanical and chemical stability of super-hydrophobic coating were discussed while the long-term stability of them still need to be enhanced. The development of robust super-hydrophobic coatings with anticorrosion properties lies on the recent progress in self-healing coatings, slippery liquid-infused porous surface, as well as multi-functional coatings.

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References


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