Formation and Properties of Superhydrophobic Al Coatings on Steel

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Cite This: ACS Omega, 2021, 6, 18383−18394

ABSTRACT: Thermal sprayed aluminum coatings are widely scalable to corrosion protection of the offshore steel structure. However, the corrosion rate of the Al coating increases considerably due to the severe marine environment. It has remained a challenge to improve the corrosion resistance and protective ability of Al coatings. The superhydrophobic surface provides a potential way to improve the corrosion resistance of metal materials. Hence, the development of superhydrophobic Al coatings with superior corrosion resistance is of great interest. In this work, the feasibility of the preparation of superhydrophobic Al coatings on a steel substrate was explored. First, Al coatings were prepared onto the steel substrate by the arc-spraying process, followed by ultrasonic etching with 0.1 M NaOH solution, and afterward passivated using 1% fluorosilanes. The effects of the etching time on morphology, contact angle, and corrosion resistance of the Al coatings were evaluated. The schematic model of the fluorosilane passivation process on the Al coating surface was provided. The micro/nanoscale surface structure of the low-surface-energy fluorosilanes promotes the wetting angle of 153.4° and a rolling angle to 6.6°, denoting the superhydrophobic properties. The superhydrophobic Al coating surface displays excellent self-cleaning performance due to its weak adhesion to water droplets. The corrosion current density of the superhydrophobic Al coating (1.36 × 10^{-8} A cm^{-2}) is 2 orders of magnitude lower than that of the as-sprayed Al coating (1.18 × 10^{-6} A cm^{-2}). Similarly, the charge-transfer resistance is found to be 12 times larger for the superhydrophobic Al coating and the corresponding corrosion inhibition efficiency reaches 98.9%. The superhydrophobic Al coating displays superior corrosion resistance and promising applications in a marine corrosion environment.

1. INTRODUCTION

The corrosion protection of the offshore steel structure is a significantly important issue. Protective coatings provide a positive method to extend the life span of offshore steel structures.1−3 Among them, Al coatings are widely scalable to corrosion protection of steel due to low cost, nontoxicity, and cathodic electrochemical protection.4−6 However, under violent temperature fluctuations and high humidity conditions in a marine environment, the corrosion rate of the Al coating increases considerably and it can be only applied in a limited range. In this regard, it is still a very challenging and vital topic to improve the corrosion resistance and protective ability of Al coatings in the severe marine environment.

Superhydrophobic surfaces have come to be a hot issue and gained remarkably increasing interest from engineers and scientists during the past decades.5−11 These surfaces, with unique structure and function such as large water contact angles (CA > 150°) and little sticking to water drops, have been used to solve many thorny problems, such as corrosion prevention,12,13 anti-icing,14 antisplashing,15 self-cleaning,16,17 drag reduction,18 and so on. Generally speaking, the micro/nanostructure and low-surface-free energy are the key players in the generation of superhydrophobic surfaces.19,20 The chemical etching process is a facile method to fabricate high rough micro/nanoscale structures by the chemical reaction on the metal surface.21,22 Saleema et al. designed a one-step technique to fabricate a superhydrophobic surface with CA as high as ~166° by immersing the AA6061 alloy in NaOH and

Received: May 6, 2021
Accepted: June 24, 2021
Published: July 9, 2021
fluoroalkyl-silane (FAS-17) mixture solution. The results indicate that there is no significant difference in corrosion performance between the superhydrophobic surface and the hydrophilic surface. However, Escobar et al. produced a superhydrophobic surface on a pure Al plate via ethanol hydrochloric acid etching and lauric acid modification. The modulus of impedance of the superhydrophobic Al alloy surfaces prepared using NaOH solution etching and ethanolic stearic acid (SA) passivation was 70 times higher than that of the AA6061-Al alloy. After being etched in CuCl₂ solution and modified by SA, the superhydrophobic Al surfaces with excellent corrosion resistance and reparability were obtained by Zhan et al. Abbasi et al. reported a highly stable superhydrophobic 6020-Al alloy surface with excellent anticorrosion by a combination of shot peening-etching treatment and silane modification processes. Zhang et al. declared a method combination of droplet etching and modification to prepare a superhydrophobic Al surface with a CA of 156°. More recently, Guo et al. prepared a superhydrophobic 7055-Al alloy surface with a CA of 167.3° using MgCl₂ solution etching and then modified by perfluoroctyltriethoxysilane. The corrosion current density of the superhydrophobic sample dropped by surpass 2 orders than that of immensity of the bare Al sample, and meanwhile, the corrosion inhibition efficiency was 99.67% in 3.5% NaCl solution. These results show that the corrosion resistance of Al alloys can be enhanced remarkably by superhydrophobic manipulation. Despite notable progress for the superhydrophobic Al alloy substrate, the preparation and protective ability of the superhydrophobic Al coating on steel have remained elusive in marine corrosion protection.

Thus, the purpose of this work was to investigate the possibility of the formation of superhydrophobic Al coatings on the steel substrate and evaluate their corrosion resistance and self-cleaning performance. The superhydrophobic Al coatings were prepared by ultrasonic etching with NaOH solution and modification by FAS-17 ethanol solution. The impressions of the etching time and passivation on surface morphology and wettability of the coatings were analyzed. To better compare the properties of the as-sprayed coating and superhydrophobic coating, self-cleaning and electrochemical measurements were carried out.

Figure 1. SEM images of the coatings: (a) as-sprayed Al coating, (b) coating after etching of 1, (c) 5, (d) 7, and (e) 10 min, and (a1)–(e1) and (a2)–(e2) corresponding magnification images. The insert in (a2)–(e2) referring to the water CA after being modified.

https://doi.org/10.1021/acsomega.1c02299
ACS Omega 2021, 6, 18383–18394
2. RESULTS AND DISCUSSION

2.1. Morphology of the Coatings. Figure 1 shows the surface morphology and wettability of the Al coatings as a function of the etching time in NaOH solution. Figure 1a shows the top-view SEM image of the as-sprayed Al coating. The single flattened particle presents a smooth surface. There are some microscale irregular protrusions on the coating surface. The average water CA of the as-sprayed Al coating is 139.5°, indicating the hydrophobic surface by the arc-spraying process. To obtain a superhydrophobic surface, a rough micro/nanostructure was built by pretreatment of chemical etching the as-received Al coating. Figure 1b−d reveals the surface morphology of the coatings with an etching time of 1, 5, and 7 min, respectively. Undoubtedly, an increasing number of corrosion pits with micro/nanoscale hierarchical structures is present on the surface of Al coating as a function of etching time. It promotes the progressively rough etching surfaces of the coating. After being modified by FAS-17, the CA of three coatings increases to 141.4, 148.5, and 153.4°, respectively, demonstrating a transition from hydrophobic to superhydrophobic surface. When the etching time reaches 7 min, the coating shows superhydrophobicity. With further increase in etching time to 10 min, as shown in Figure 1e, the number density of the micro/nanoscale corrosion pits decreases dramatically and connects on the whole coating surface, indicating the falling of the roughness. The CA of the coating is 150.4°. Comparing with the coating etched for 7 min, the CA decreases slightly but it still shows superhydrophobicity. However, excessive etching will bring about a decrease significant in the coating thickness, which is detrimental to the coating.

Figure 2 exhibits the 3D morphologies and roughness of the coatings with the etching time. The coatings have a number of micro/nano irregular protrusions, which makes the coatings hydrophobic. The surface roughness of the as-sprayed Al coating shows the lowest value of 0.78 ± 0.26 μm among the tested samples, as shown in Figure 2a. In order to obtain a superhydrophobic surface, chemical etching was used to promote the surface roughness of the coating. Figure 2b,c exhibits the variation of 3D morphology and roughness of the coating with an etching time of 3 and 7 min, respectively. The roughness of the Al coating is increasing as a function of etching time, which improves the hydrophobicity of the coating. When the etching time is 7 min, the roughness of the coating reaches the maximum value of 1.10 ± 0.28 μm, and the irregular protrusion on the coating surface is the most prominent. With further increase in the etching time to 10 min, as shown in Figure 2d, the surface roughness of the coating decreases slightly to 1.06 ± 0.45 μm. Therefore, excessive etching will bring about the decrease in coating roughness, which is unfavorable to the coating.

Figure 3 depicts more details of the coating with an etching time of 7 min. It can be seen from Figure 3a,b that numerous irregular protrudes and micron-scale corrosion pits are distributed on the coating surface, which improves the roughness of the coating. Meanwhile, a large number of nanoscale corrosion pits are also detected on protrusions, as shown in Figure 3c,d. Inspired by the lotus leaf, its superhydrophobicity mostly comes from the microscale papillae structure and a large number of nanoscale cylindrical protrudes. The hierarchical micro/nanoscale porous structure...
plays a positive role in surface wettability of the coating. According to the Cassie Baxter equation\(^8\)

\[
\cos \theta = f_1 \cos \theta_1 + f_2 \cos \theta_2
\]

where \(\theta_1\) and \(\theta_2\) represent the apparent CA and intrinsic CA, respectively. \(f_1\) and \(f_2\) are the surface fraction of droplets in contact with the solid surface and air \((f_1 + f_2 = 1)\), respectively. When the etching time increases to 7 min, the maximum CA of 153.4° reveals a water droplet 14% contact with the coating surface while leaving the remaining 86% with air. Therefore, the droplet looks like a sphere standing on the Al coating.

2.2. XPS Analysis of the Superhydrophobic Surface. X-ray photoelectron spectroscopy (XPS) was used to analyze the difference between the as-sprayed Al coating and the superhydrophobic Al coatings. Figure 4a illustrates the survey spectra of the coatings. The C 1s, O 1s, and Al 2p peaks are detected for both coatings. The intensity of these peaks of the as-sprayed Al coating is slightly stronger than that of the superhydrophobic Al coating. That is to say, numbers of FAS-17 molecules were adsorbed on the NaOH-etched Al coating throughout the modification process.

Figure 4b–f shows the XPS high-resolution spectra of the superhydrophobic coating. Figure 4b,c shows the spectra of F 1s and Si 2p that are composed of a strong peak at 688.8 and 104.1 eV, respectively. The Al 2p spectrum shows only a peak at 75.7 eV because of the bonding of Al–O, as seen in Figure 4d. Figure 4e depicts the O 1s peak that is composed of three strong peaks having a binding energy of 532.4, 533.3, and 534.1 eV, corresponding to Al–O–Si, O–C, and Si–O–Si bond, respectively.\(^29\) The presence of the \(-Si–O–Al– component indicates that the removal of \(C_2H_5\) from the FAS-17 molecules may give rise to the formation of \(-Si–O–Al– bond at the substrate via the process of hydrolysis.\(^23\) \(-Si–O–Al– bonds induce the strong adhesion between the Al surface and FAS-17 molecules and it is the main contribution of the mechanical stability of the superhydrophobic. Figure 4f shows the spectrum of the C 1s peak. The limited peaks at 288.6, 291.7, and 294.1 eV are attributing to the \(-CF_2–CF_3, –CF_2, and –CF_3\) groups of FAS-17, respectively. The successful derivatization of the ultralow surface energy terminal group of \(-CF_2 and \(-CF_3\) on the rough Al coating surface is the key to improve the repellent capability and superhydrophobicity. In addition, the two strong peaks at 285.3 and 286.3 eV correspond to the bonding of C–C and C–O, respectively. The high-resolution XPS peak analysis on the C 1s, O 1s, F 1s, Si 2p, and Al 2p validates the presence of Al–O–Si–CF_2–CF_3 and –Si–O–Si–. These results are regarded as evidence that the low-surface-energy fluoroalkylsilane film was successfully assembled on the Al coating surface, which is consistent with the results in reference reported by Sarkar.\(^30\)
From the XPS analysis, the mechanism for the management with NaOH and FAS-17 molecules can be inferred. Figure 5 proposes a schematic presentation of the reaction mechanisms leading to the superhydrophobic coating. After etching in NaOH solution followed by FAS-17 modification, aluminum hydroxide and the integration of CF$_2$ functional group are formed on the surface of the coating. During the hydrolysis process, the C$_2$H$_5$ component is erased from FAS-17 molecules. The Si bonds with O in the surface and the C–F functional groups are oriented outward from the surface. The growing amount of FAS-17 molecules adhered to the surface with the low-surface-energy C–F functional groups provides favorable ways for the formation of superhydrophobic properties.31,32

2.3. Superhydrophobic Property. To further analyze the water adhesion of the coatings with different processing, the CA measurements and rolling angle (RA) measurements of the coatings were conducted, just as shown in Figure 6. For the as-sprayed Al coating, the CA is 139.4° and RA is 82.9°. After being modified by FAS-17, the CA and RA of the as-sprayed Al coating are 141.4 and 33.4, respectively. Compared with the as-sprayed Al coating, the CA of the modified coating increases slightly, indicating a decrease in surface energy. As the etching time prolongs to 4 min, the droplet is right impacting the coating surface and comes into being the maximum deformation (Figure 8b). Thereafter, the retractable droplet begins to rebound fully upward (Figure 8c–f). Moreover, the droplet can bounce elastically several times before falling down the surface (Figure 8g) and there is no water vestigial on the coating. The dynamic droplet-bouncing experiment shows that the irregular micro/nanoscale porous structure prepared by the proper process has an extraordinarily weak water adhesion and drag resistance. So far, a straightforward and low-cost process for preparing a superhydrophobic Al coating has been successfully developed.

2.4. Self-Cleaning Behaviors of the Coatings. Figure 9 demonstrates the jet flow experiment on the superhydrophobic coating. The dripped droplets are suspended on the protuberances and contact indirectly with the coating. It further demonstrates an extremely high repelling water property (Figure 7).

Figure 6. CA and RA of the coatings with different processes.

Sprayed Al coating, the CA is 139.4° and RA is 82.9°. After being modified by FAS-17, the CA and RA of the as-sprayed Al coating are 141.4 and 33.4, respectively. Compared with the as-sprayed Al coating, the CA of the modified coating increases slightly, indicating a decrease in surface energy. As the etching time increases from 1 to 10 min, the CA increases at first, reaches a local maximum, and then decreases. The RA displays an inverse trend. When the etching time is 7 min, the CA of the coating reaches the maximum value of 153.4° and RA is 5.8°. After etching, the coating surface shows a micro/nanoscale structure. The surface free energy of the coating is merely 0.82 mN/m, which is much lower than the surface tension of water (72.1 mN/m$^{-1}$). Therefore, the droplets cannot spread on the coating surface, but it can contact with the irregular multivoid and the gap filled with air, which prevents droplets to wet the surface.33 Figure 6 shows the deionized water, blue ink, and red ink (10 μL) spread slightly on the hydrophobic Al coating. The dripped droplets are suspended on the protuberances and contact indirectly with the coating. It further demonstrates an extremely high repelling water property (Figure 7).

Figure 8. Sequence of snapshots of droplets (2 μL) impacting the superhydrophobic Al coating surface: (a) 0, (b) 4, (c) 8, (d) 12, (e) 16, (f) 20, and (g) 24 ms.

Figure 9. Diagram of water droplet jet experimental (figure reference scale: the samples in a size of 50 mm × 25 mm × 8 mm).
Al coating. It can be seen that the coating surface presents good water repellency and high stability under high-speed water flow.

Figure 10 shows the antifouling performance tests of the coating. First, the coating was placed in the glass dish with a slight inclination of 10° (Figure 10a,b), and then, the blue or red ink was slowly dropped onto the coating surface. The droplets rolled on the slightly inclined coating surface without leaving any trace on the coating (Figure 10(a1−3),(b1−3)). Therefore, the coating has excellent antifouling properties. This is mainly due to the interaction of low-energy materials and surface micro/nanoscale structure on the coating surface. When the droplet is on the surface, the actual contacting area is very small. Therefore, the droplet is approximately spherical and rolls easily on the coating surface.

Inspired by the repelling dust behaviors of the lotus leaf, the self-cleaning behaviors of the superhydrophobic Al coating were performed, as shown in Figure 11. First, a film of dirt was well-distributed on the superhydrophobic Al coating surface, as seen in Figure 11(a1). As the droplets roll over the slightly sloped coating surface, they can remove dust along the rolling track (Figure 11(a2)). Subsequently, as the droplets were dripped down consecutively, a resembling self-cleaning behavior was detected until all the covered dust was swept away, as shown in Figure 11(a3),(a4) (Video S1). When the coating surface is shrouded by sand (Figure 11(b1)) and chalk ash (Figure 11(c1)), similar results were obtained, as seen in Figure 11(b4),(c4) (Videos S2 and S3). Consequently, the superhydrophobic Al coating displays superior self-cleaning performance.

2.5. Corrosion Resistance of the Coatings. For the sake of studying the effect of different etching times on the corrosion resistance of the coating surface, electrochemical tests in 3.5 wt % NaCl solution were conducted on the coating samples modified by FAS-17 with different etching times (1, 3, 5, 7, 9, and 11 min). Figure 12a shows the polarization curves of the coatings. The corrosion potential ($E_{\text{corr}}$) and corrosion current density ($I_{\text{corr}}$) of the coatings originated from the
potentiodynamic polarization curve are listed in Table 1. With prolonging the etching time, $I_{\text{corr}}$ of the coating decreases at first and then increases slightly. Compared with the as-sprayed Al coating, the $I_{\text{corr}}$ decreases by 2 orders of magnitude with an etching time of 7 min. When the etching time further increases from 9 to 11 min, the $I_{\text{corr}}$ of the coating increases slightly. However, it is still lower than that of the as-sprayed Al coating. The higher corrosion potential and lower corrosion current density indicate that the coating has superior corrosion resistance.

Figure 12b–d plots Nyquist and Bode curves of the coatings. With the increase in the etching time, the impedance arc radius of the coatings first increases and follows a slight decrease. It is well-known that at a lower frequency, a higher Z-modulus shows better corrosion resistance to metallic substrates.\(^{34,35}\) Under a low frequency, with prolonging the etching time, the Z modulus of the coating shows an increasing trend and Bode phase angles in the Bode diagram peak also show a similar trend.\(^{36}\)

Figure 13 describes the electrochemical corrosion behaviors of the as-sprayed Al coating, the Al coating etched with NaOH solution for 7 min, the as-sprayed Al coating modified by FAS-17, and the superhydrophobic Al coating. The polarization diagrams for the coatings are depicted in Figure 13a, while Table 2 summarizes the relevant parameters. For the as-sprayed Al coating, the $E_{\text{corr}}$ and $I_{\text{corr}}$ are $-0.78$ V and $1.18 \times 10^{-6}$ A cm\(^{-2}\), respectively. After being modified by FAS-17, $E_{\text{corr}}$ of the coating shifts positively from $-0.78$ to $-0.69$ V while $I_{\text{corr}}$ enlarges slightly to $1.27 \times 10^{-6}$ A cm\(^{-2}\). After being etched in NaOH solution, the Al coating has the lowest $E_{\text{corr}}$ and the highest $I_{\text{corr}}$, indicating the worst corrosion resistance among the tested samples. In comparison, the superhydrophobic coating holds superior anticorrosion behavior among the tested samples. It has the largest $E_{\text{corr}}$ and smallest $I_{\text{corr}}$ in the coatings. The $I_{\text{corr}}$ of the superhydrophobic Al coating is 2 orders of magnitude lower than that of other coatings, revealing excellent corrosion resistance. The corresponding corrosion inhibition efficiency ($\eta_p$) can be calculated using the equation:\(^{26}\)

$$\eta_p \% = \frac{i_{\text{corr}}^0 - i_{\text{corr}}}{i_{\text{corr}}^0} \times 100$$  \hspace{1cm} (2)

where $i_{\text{corr}}^0$ and $i_{\text{corr}}$ are corrosion current density of the as-sprayed coating and the superhydrophobic coating, respectively. According to Formula 2, the $\eta_p$ of the superhydrophobic coating is 98.9%, which further confirms its excellent corrosion resistance. The main reasons are that the etched as-sprayed coating surface has an irregular multivoid structure at the micro/nanolevel. After FAS-17 modification, the surface freedom of the etched coating surface significantly decreases from 13.07 to 0.82 mN/m. When the coating is soaked in NaCl solution, the air film is formed between the solution and the coating, which postpones the penetration of Cl\(^-\) into the Al coating.\(^{35}\)
Therefore, the corrosion resistance of the coating is significantly improved.

Figure 13b illustrates the Nyquist plots of the coatings with different processes. All of the coatings show a trend to capacitive semiarcs up to frequencies of about 1 Hz. The diameter of the semicircle represents a higher charge-transfer resistance ($R_{ct}$) and a lower corrosion current density and correlated with the mechanism of superhydrophobic film resistance. The superhydrophobic Al coating has the largest capacitive semiarc among the tested samples, as seen in Figure 13b. The larger impedance value of the superhydrophobic Al coating denotes that the superhydrophobic surface is more resistant against corrosion.

Figure 13c plots the Bode modulus diagram of the coatings. It can be observed that the as-sprayed Al coating has a $|Z|$ value of 19.37 $\Omega$ cm$^2$ at a high frequency of $10^4$ Hz, while the superhydrophobic Al coating exhibited a $|Z|$ value of 38.88 $\Omega$ cm$^2$, which is almost two orders of the as-sprayed Al coating at the same frequency. Similarly, at a low frequency of 0.1 Hz, the $|Z|$ value of the as-sprayed Al coating is 65.3 k$\Omega$ cm$^2$. In contrast, it was as high as 584.4 k$\Omega$ cm$^2$ on the superhydrophobic Al coating. Generally speaking, the high-frequency AC impedance indicates the response of the coatings with the solution, while at a low frequency, it reflects $R_{ct}$ and the double-layer capacitance. The higher $|Z|$ value in the low-frequency region shows a better barrier in the coating. Compared with the as-sprayed Al coating, the $|Z|$ value of the superhydrophobic Al coating is close to one order of magnitude larger at low frequencies. On the basis of the

| the tested samples                  | $E_{corr}$ (V) | $I_{corr}$ ($\times 10^{-6}$ A cm$^{-2}$) |
|-----------------------------------|----------------|------------------------------------------|
| the as-sprayed Al coating         | −0.78          | 1.18                                      |
| the modified Al coating           | −0.69          | 1.27                                      |
| the etched Al coating             | −0.82          | 5.27                                      |
| the superhydrophobic Al coating   | −0.62          | 0.0136                                    |

Table 2. Corrosion Potential and Corrosion Current Density of the Coatings

Figure 14. Electrical equivalent circuits for EIS of the coatings: (a) $R(Q(R(QR)))$ and (b) $R(Q(R(Q(RW))))$. 

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of the superhydrophobic Al coating is about 12 times that of the substrate is more different due to the inhomogeneity of the electrode surface, the frequency analysis of Bode modulus curves, the superhydrophobic Al coating has a better anticorrosion in comparison with the as-sprayed Al coating. The Bode phase angle diagrams of the coatings present a shoulder followed by two time constants, as shown in Figure 13c. The first time constant provided by the shoulder is relevant to the properties of the coating. Another time constant at the low-frequency region is related to the corrosion behavior of the substrate. From Figure 13c, the superhydrophobic Al coating exhibits a time constant at a lower frequency and a higher phase angle of 78.4° than other coatings, suggesting a better barrier performance.

In order to obtain impedance parameters such as resistances and capacitances, two well-known equivalent circuits are chosen using the ZSimpwin software, as shown in Figure 14. The relative parameters are listed in Table 3. Table 3 shows the equivalent electrical circuit for the as-sprayed Al coating, the etched Al coating, and the superhydrophobic Al coating.

Figure 14b summarizes the equivalent circuit of the modified Al coating due to the two semicircles observed on the Nyquist plot. In the circuits, $R_c$ is the solution resistance, $R_s$ is the coating resistance, and $R_{ct}$ is the charge-transfer resistance. Due to the inhomogeneity of the electrode surface, the frequency response characteristics of the double-layer capacitor are inconsistent with those of the pure capacitor. To obtain a better fitting result, the constant phase angle element is used to replace the ideal capacitance in the equivalent circuit. $Q$ and $Q_{dl}$ represent the coating capacitance and the double-layer capacitance, respectively. Due to the obvious dielectric difference between the as-sprayed Al coating and the substrate, there are two time constants on the fitting circuit diagram, namely, $R_c$ and $Q_c$, which corresponds to the dielectric property of the as-sprayed Al coating and the first time constant. Another parallel subcircuit, $R_s$ and $Q_{dl}$ means the dielectric properties of the coating-substrate interface, giving a second time constant. In addition, for the modified Al coating, since the charge transfer is affected by the semi-infinite diffusion process, Warburg impedance $W$ appears in the equivalent circuit. From Table 3, the $R_{ct}$ value of the superhydrophobic Al coating is about 12 times that of the as-sprayed Al coating. The large $R_{ct}$ value denotes that the charge-transfer process at the interface between the coating and the substrate is more difficult. Therefore, the superhydrophobic Al coating dominates a superior corrosion resistance.

Table 4. Corrosion Resistance Property of the Superhydrophobic Surfaces from This Work and Literature Studies

| matrix       | Methods                      | low surface energy materials | $E_{corr}$ (V) | $I_{corr}$ (μA/cm²) | NaCl solution (wt %) | time (h) | refs |
|--------------|-------------------------------|-----------------------------|----------------|---------------------|----------------------|----------|------|
| Al foils     | chemical etching (CuCl₂)     | SA                          | -1.38          | 6.10                | 3.5                  | 1        | 26   |
| Al plates    | chemical etching (NaOH)      | ZnAl-LDH-La                 | -0.76          | 0.0674              | 3.5                  | 1        | 41   |
| 6061-Al alloy| chemical etching (NaOH)      | SA                          | -0.58          | 0.0350              | 3.5                  | 1        | 25   |
| 6061-Al alloy| chemical etching (HCl)       | FAS-17                      | -0.74          | 0.205               | 3.5                  | 1        | 42   |
| Al coating   | chemical etching (NaOH)      | FAS-17                      | -0.62          | 0.0136              | 3.5                  | 1        | this work |

In addition, Table 4 summarizes the $E_{corr}$ and $I_{corr}$ of the superhydrophobic surfaces prepared by the chemical etching method of this work and some previous works from the references. It is found that the superhydrophobic Al coating investigated in this work not only has a lower $I_{corr}$ but also manifests a higher $E_{corr}$ than the other superhydrophobic surfaces on the Al substrate and 6061-Al alloy. Therefore, the developed superhydrophobic Al coating has superior corrosion resistance. It can provide valuable guidance for the protection of the marine engineering steel structure.

3. CONCLUSIONS

In summary, a superhydrophobic surface was prepared onto the arc-sprayed Al coating by chemical etching using NaOH solution followed by passivation with FAS-17 ethanol solution. The typical micro/nanoscale structures are presented on the surface of the superhydrophobic Al coatings. The wetting angle and RA of the superhydrophobic Al coating are 153.4 and 6.6°, respectively. The superhydrophobic Al coating surface displays excellent self-cleaning performance. The electrochemical results show that the corrosion current density of the superhydrophobic Al coating ($1.36 \times 10^{-8}$ A cm⁻²) is 2 orders of magnitude lower than that of the as-sprayed Al coating ($1.18 \times 10^{-6}$ A cm⁻²), and the corresponding corrosion inhibition efficiency of the superhydrophobic surface reaches 98.9%. At the low frequency, the moduli of impedance $|Z|$ values of the as-sprayed Al coating and the superhydrophobic Al coating are 65.3 and 584.4 kΩ cm², respectively. Compared with the as-sprayed Al coating, the charge-transfer resistance is found to be 12 times larger for the superhydrophobic Al coating. The superhydrophobic Al coating demonstrates superior corrosion resistance properties and it has potential application prospect in a marine corrosion environment.

4. EXPERIMENTAL PROCEDURES

4.1. Materials. Commercial Q235 steel plates (chemical compositions wt %: Fe of 98.96%, C of 0.18%, Mn of 0.60%, Si of 0.22%, S of 0.02%, and P of 0.02%) were selected for substrate materials. Solid pure Al wires with a diameter of 2 mm were obtained from Beijing Yida Kuntai Technology Co., LTD. Trimethoxy(1H,1H,2H,2H-perfluorodecyl)silane was bought from Aladdin Chemical Reagent Co., LTD. (China). Sodium hydroxide, sodium chloride, ethanol, and
acetone were supplied by Chengdu Cologne Chemicals Co., LTD. (China).

4.2. Preparation of Al Coating. Before spraying, the Q235 steel matrix was rinsed with acetone solution and then grit-blasted. The parameters of sand blasting were as follows: the compressed air pressure 0.7 MPa, the angle 70°−90°, and the distance 100 mm. After that, the matrix samples were ultrasonicated with acetone solution. The Al coatings were fabricated using an automatic arc-spraying system. The de Laval nozzle gun was manipulated by a Motoman HP20 robot equipped with an NX100 system. The optimum parameters were as follows: voltage 34 V, current 150 A, spraying distance 200 mm, and compressed air pressure 0.7 MPa. The thickness of the Al coating is approximately 700 μm, as shown in Figure 15.

Figure 15. SEM cross-sectional morphology images of the Al coating.

4.3. Preparation of Superhydrophobic Al Coating. First, the as-sprayed Al coatings were fully washed with acetone, absolute ethanol, and deionized water for 10 min under sonication to remove oil and other impurities and then subjected to drying at 110 °C for 10 min. Second, the Al coatings were chemically etched in an ultrasonic bath at an ambient temperature with 0.1 mol/L NaOH solution for 1, 2, 3, 4, 5, 6, 7, 8, 9, and 10 min, respectively. After etching, the coatings were instantly ultrasonically cleaned with deionized water for 1 min and then dried at 110 °C for 10 min. Subsequently, the etched coatings were immersed in 1% trimethoxy(1H,1H,2H,2H-heptadecafluorodecyl)silane ethanol solution at 60 °C for 2 h and dried at 120 °C for 1 h. The proposed process for the superhydrophobic Al coatings is schematically shown in Figure 16.

Figure 16. Schematic of the fabrication process for the superhydrophobic coating.

4.4. Characterizations. The top-view images and roughness of the coatings were observed using an environmental scanning electron microscope (Carl Zeiss Microscopy GmbH, 73447 Oberkochen, Germany) and UP laser confocal microscope (RTEC, America), respectively. The surface topography images were analyzed using Gwyddion software. XPS measurements were employed using an ESCALAB 250Xi (Thermo Scientific) instrument using Al Kα radiation to analyze the elements and functional groups. The CA and CA hysteresis were measured with 2 μL of deionized water droplets at room temperature using an OCA20 system equipped with a CCD camera and SCA 20 software (Dataphysics GmbH, Germany). Five tests with an average CA for every specimen were conducted.

Corrosion electrochemical properties of the as-sprayed coating and the superhydrophobic coatings were assessed by potentiodynamic polarization measurements in 3.5 wt % NaCl solution using a computer-controlled electrochemical workstation (CHI660D, Chen Hua Instruments Co., Ltd., China) at ambient temperature. The experiments were conducted in a standard three-electrode system with the saturated calomel electrode as a reference electrode, the platinum plate as a counter electrode, and the coating (exposing area 1 cm²) as a working electrode. Before testing, all specimens were submerged in 3.5 wt % NaCl solution for 60 min to obtain a stable open-circuit potential (OCP). The potentiodynamic polarization curves were performed from −1000 to −200 mV versus OCP with a scan rate of 10 mV/s. The electrochemical impedance spectroscopy (EIS) curves were executed at OCP with a frequency range of 10⁴ to 10⁻² Hz and an amplitude of 10 mV. The EIS experimental data were fitted to proper equivalent circuits using ZSimpWin Commercial Software (USA) to get the significant R−C electrocircuit parameters. In order to realize appropriate repeatability, all the tests were duplicated thrice.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c02299.
Droplets are released to the superhydrophobic Al surface and the dust on the surface is taken away with the droplets rolling down Dirt (AVI) (MP4)
Sand (MP4)
Chalk dust (MP4)

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Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS
This project is supported by the National Natural Science Foundation of China (grant nos. 51975183 and 51979083) and the Natural Science Foundation of Jiangsu Province, China (grant no. BK20201316).

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