Electrochemically Etched Superhydrophobic Surface on Aeronautic Steel with Anti-Icing, Self-Cleaning and Durability Property

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Abstract. The superhydrophobic surface on 30Cr2NiWVA aeronautic steel is fabricated via electrochemical etching and FAS modification. The results of scanning electron microscopy (SEM) show that, after electrochemically etching, the aeronautic surface is covered with rough coralloid-structure film. This surface demonstrates excellent corrosion protection, anti-icing and self-cleaning property. Additionally, this surface shows outstanding superhydrophobicity after anti-icing, self-cleaning test, and even after exposure to the air in the normal ambient environment for two years, proving the durability property of superhydrophobic aeronautic surface. The proposed method is simple and has great potential applications for large-scale applications in aircraft.

1. Introduction
Superhydrophobic surface is a kind of extreme wettability solid surfaces which contact angle of water (WCA) over 150°[1]. Moreover, superhydrophobic surfaces can be divided into two kinds: high adhesive surfaces which rolling angle of water even over 90°, and low adhesive surfaces which rolling angle of water below 10°[2]. Because of unique wettability property, superhydrophobic surfaces have attracted the attention of researchers, for the potential applications in anti-icing, self-cleaning, corrosion protection, drag reduction, liquid transportation and so on.

Steel, as a king of basic alloy, has been one of widely used metals in modern societies for low-cost, outstanding processing characteristics and mechanical properties. While, in the humidity environment, steel may be rusted, resulting in a series of consequences. Thus, fabricating superhydrophobic surface on the steel can improve durability property, stability property and security property of steel in the extreme conditions. In the past decades, various preparation methods have been developed to obtain superhydrophobicity on the steels. Huang et al.[3] prepared superhydrophobic surface on the mold steel by electrochemically etching. Du et al.[4] fabricated superhydrophobic surface on Q235 carbon steel by simple and efficient chemically etching with Piranha solution. Hu et al.[5] developed superhydrophobic surface with nano/microstructure Fe$_2$O$_3$/Fe$_3$O$_4$ composite film on the N80 steel by hydrothermal. Particularly, electrochemical etching has been a hotspot of developing superhydrophobic surface on steel, due to low-cost, simple and facile[6]. Moreover, during electrochemically etching, a passive film with nano/microstructures is formed on the steel. Generally, passive film has positive influences on obtaining stable structures. 30Cr2NiWVA aeronautic steel is a kind of high-strength steel which usually used in aircraft. Whereas, water often adheres to the surface due to hydrophilic and resulting in ice when exposed to harsh environment. Thus, for practical application, aeronautic steel with
stability superhydrophobicity is significant. However, the preparation of superhydrophobic surfaces on the aeronautic steel was rarely reported.

In this work, we applied electrochemical etching and FAS modification to fabricate passive film with nano/microstructures on the 30Cr2NiWVA aeronautic steel. The morphologies of surface were investigated using scanning electron microscopy (SEM). Additionally, the corrosion protection, anti-icing and self-cleaning property of superhydrophobic aeronautic steel with passive film were investigated. The surface preserved excellent superhydrophobicity after anti-icing, self-cleaning test and exposure to air for two years, indicating outstanding durability property.

2. Experiment Section

2.1. Materials
Fluroalkylsilane [FAS, C_{8}F_{13}H_{4}Si(OCH_{2}CH_{3})_{3}] was purchased from Degussa Co., Ltd (Germany). Ethyl alcohol was purchased from Fuyu Fine Chemical Co., Ltd (China). Sodium nitrate (NaNO3) was purchased from Tianjin Kernel Chemical Co., Ltd (China). 30Cr2NiWVA aeronautic steel was purchased from Zhanghai Material Manufacturer Co., Ltd (China). Deionized water was used throughout experiments.

2.2. Fabrication of superhydrophobic surface
As shown in figure 1, the superhydrophobic aeronautic steel was fabricated by combining electrochemically etching and FAS modification. 30Cr2NiWVA aeronautic steel was firstly polished by 400 grade, 800 grade, 1500 grade and 2000 grade sandpapers. Then the polished aeronautic steel was ultrasonically cleaned with ethyl alcohol and deionized water to remove impurities. Subsequently, the aeronautic steel was electrochemically etched to obtain nano/microstructures. (The main processing parameters of electrochemically etched is shown in table 1) After washing by deionized water and drying, superhydrophilic aeronautic steel with passive film was obtained. Then the reduction of surface energy was realized by immersing superhydrophilic aeronautic steel in 1 wt% ethanol solution of FAS for 20 min. Hence, the superhydrophobic aeronautic steel with passive film was obtained.

![Figure 1. The schematics of the preparation of superhydrophobic surface](image-url)
Table 1. Processing parameters of ECM

| Processing parameters of ECM | Value |
|-----------------------------|-------|
| Electrolyte                 | NaNO₃ |
| Electrolyte concentration(\(C\)) | 25 wt% |
| Etching time(\(t\))        | 60 s  |
| Electric current density(\(I\)) | 5 A/cm² |
| Electrolyte flow(\(q\))    | 120 q/(L·h) |
| Interelectrode gap(\(h\))  | 1 mm  |

2.3. Characteristic

Micro-morphologies of the aeronautic steel were characterized by a scanning electron microscope (SEM, JSM-6360LV, Japan). The water contact angles were measured by sessile-drop method with using optical contact angle analyzer (Krüss, DAS100, Germany). The volumes of water droplets used in contact angle measurements were 5 μL.

2.4. Corrosion protection test

Corrosion protection comparison of ordinary aeronautic steel and superhydrophobic aeronautic steel used to examine corrosion protection property of superhydrophobic steel. Corrosion protection property was assessed by flat-bottom cell three-electrode device in 3.5 wt% NaCl solution. The platinum sheet was the counter electrode, and the saturated calomel electrode acted as the reference electrode.

2.5. Anti-icing test

Anti-icing comparison of ordinary aeronautic steel and superhydrophobic aeronautic steel was used to examine anti-icing property of superhydrophobic steel. During the test, ordinary aeronautic steel and superhydrophobic aeronautic steel were placed in an environment test chamber (DHTH-27-40-P-SD) which temperature was set at -16.5°C with 10° tilt angle. Then, the distance between needle tip and the centre of specimen was set at 70 mm. Meanwhile, deionized water was cooled down at -16.5°C for 1 min. The volume of single rain droplet was 15.2 μl, and the rate of flow of each specimen was 1.46 ml/min.

2.6. Self-cleaning test

Self-cleaning comparison of ordinary aeronautic steel and superhydrophobic aeronautic steel was used to examine self-cleaning property of superhydrophobic steel. During the test, ordinary aeronautic steel and superhydrophobic aeronautic steel were placed with 45° tilting angle. The volume of each water droplet was 45 μL, and chalk dust was used as contaminant.

3. Experiment Section

3.1. Surface morphologies

The SEM images of the ordinary aeronautic steel surface and the superhydrophobic aeronautic steel surface are shown in figure 2(a)-(b). As shown in figure 2(a₁), the ordinary aeronautic surface was smooth and flat. Meanwhile, owing to the usage of sandpapers during the polishing step, the directional microgrooves were distributed on the ordinary aeronautic surface as shown in figure 2(a₂)-(a₃). Whereas, the superhydrophobic aeronautic surface was rough and was covered by a heterogeneous film. This heterogeneous film was compact coralloid structures with the length of 10-20 μm and the width of 1-2 μm, as shown in figure 2(b₁)-(b₂).
3.2. Corrosion protection property of superhydrophobic aeronautic steel

The corrosion protection property was estimated by the polarization (Tafel) curve in 3.5 wt% NaCl solution. As shown in figure 3 the corrosion potential and corrosion current density of superhydrophobic aeronautic steel were -0.375 V and 3.16×10^{-8} A/cm^2, respectively. However, the corrosion potential and corrosion current density of ordinary aeronautic steel were -0.47 V and 1.78×10^{-7} A/cm^2, respectively. The increase of corrosion potential and the decrease of corrosion current density shown that superhydrophobic surface protected aeronautic steel from corrosion. The corrosion protection property was attributed to the air film which was distributed among nano/microstructures. Air film prevented ion diffusion into inner of aeronautic steel. Hence, galvanic corrosion was restricted and aeronautic steel was protected.

![Figure 3. Tafel plots of ordinary aeronautic steel surface and superhydrophobic aeronautic steel surface.](image)

3.3. Anti-icing property of superhydrophobic aeronautic steel

The aeronautic steel was widely used in aerocraft as structure materials; thus, it was necessary to test the anti-icing property of superhydrophobic aeronautic steel. An ordinary aeronautic steel and a superhydrophobic steel were titled 10° in the environment test chamber which environment...
temperature was set at 16.5℃. The icing process on the surface is shown in figure 4. Water easily wet ordinary aeronautic surface. Ice gradually formed on the ordinary aeronautic surface, and the volume of ice was increased with the increase of time. Nevertheless, water did not wet the superhydrophobic aeronautic surface. Furthermore, no ice was formed on the superhydrophobic aeronautic surface, resulting in superhydrophobic aeronautic surface exhibiting outstanding anti-icing property.

Figure 4. The digital photos of ordinary aeronautic steel(left) and superhydrophobic surface(right) after 7 min anti-icing test.

3.4. Self-cleaning property of superhydrophobic aeronautic steel

The contaminant spread over the ordinary aeronautic steel surface and superhydrophobic aeronautic steel surface which were titled 45°, followed by water droplets to test self-cleaning property. Figure 5(a) shows the cleaning process on the ordinary surface. Contaminant was dissolved by water and stored on the ordinary aeronautic surface with water droplet. Whereas, contaminant was picked up and rolled off from the superhydrophobic aeronautic surface, indicating an excellent self-cleaning property, as shown in figure 5(b).

Figure 5. The digital photos of ordinary aeronautic steel(a) and superhydrophobic surface(b) after self-cleaning test.

3.5. Durability property of superhydrophobic aeronautic steel

As shown in figure 6(a)-(b), the superhydrophobic aeronautic steel surface did not damage after anti-icing and self-cleaning test. Meanwhile, the triple-phrase contact line(lₚ) of surface was constant before and after tests. Moreover, the contact angle of superhydrophobic aeronautic steel surface before and after exposure to air for two years under normal ambient environment were 165° and 154°, respectively. These phenomena indicate that the superhydrophobic aeronautic surface which was fabricated by electrochemical etching and FAS modification has good durability property.
4. Conclusion

In this paper, the superhydrophobic aeronautic steel surface was fabricated by electrochemical etching and FAS modification. The main processing parameters of electrochemically etched were $C=25$ wt%, $I=5$ A/cm$^2$ and $t=60$ s. It can be observed from the SEM images that the passive film of superhydrophobic aeronautic steel surface has rough nano/microscale coralloid structures with the length of 10-20 μm and the width of 1-2 μm. Additionally, the superhydrophobic aeronautic steel surface demonstrated outstanding corrosion protection, anti-icing, self-cleaning and durability properties. The superhydrophobic aeronautic steel surface even showed superhydrophobicity after exposure to air for two years under normal ambient conditions. This work had potential application as structure material of airplane, rocket, space station and so on.

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