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LETTER

Efficient Preparation and Anticorrosion Mechanism of Superhydrophobic 7075 Aviation Aluminum Alloy

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Abstract: The multifunctional 7075 aviation aluminum alloy with excellent superhydrophobic property was prepared by a simple, low-cost, and efficient etching process. The impedance results show that charge transfer resistance of prepared superhydrophobic 7075 aluminum alloy increases, and the double-layer capacitance decreases obviously, thus significantly improving the corrosion resistance. This research is of great economic value and practical significance for developing low-cost and efficient anticorrosion technique for aviation materials.

Key words: aviation aluminum alloy; microstructure; superhydrophobic; corrosion resistance; anticorrosion mechanism

The 7075 aluminum alloy as an important engineering material has been widely used in aviation manufacturing[1,2]. However, the protective oxide film on the alloy is frequently vulnerable to corrosion in long-term moist environment[3]. For a long time, the coating technique has been widely used to slow down the corrosion rate[4]. Besides, the plasma oxidation[5], cold spray[6], sol-gel[7], laser peening[8], electroless deposition[9], micro arc oxidation[10], electrochemical incorporation[11], and aging treatment[12] have also been used to improve corrosion resistance of 7075 alloy. But their process cost is usually high, not to mention the fact that oxidation, chemical reaction, electroplating, and laser operations are complex, and may cause serious environment pollution. Hence, it is urgent to develop a low-cost and efficient anticorrosion technique for aluminum alloy.

Inspired by the lotus leaf effect that the superhydrophobic surface can repel liquid[13,14] due to the reduction of the contact between liquid and substrate, the superhydrophobic surface is expected to achieve excellent corrosion resistance. The specific microstructure of lotus is the direct reason for hydrophobicity[15,16], suggesting that a specific biological structure of alloy surface may improve the corrosion resistance of aluminum alloy.

Therefore, an efficient, simple, low-cost, and controllable etching technique was used to fabricate biomimetic structures in this research. A large-scale flocculent microstructure was prepared to achieve the excellent hydrophobicity and corrosion resistance. This research provides a novel method for solving the corrosion problem of aluminum alloys, which has great economic value and practical significance.

1 Experiment

7075 aluminum alloy was cut into blocks with a uniform size of 10 mm×10 mm×2 mm. Then the specimens were polished to obtain a smooth surface. After polishing, they were put into a solution of acetone, ethanol, and ultra-pure water for ultrasonic cleaning, and then dried with high purity nitrogen. Then the cleaned specimens were immersed in hydrochloric acid of 3 mol/L for 7 min. After immersion, the specimens were taken out and put into boiling water for 2, 4, and 6 min. After drying with high purity nitrogen, they were immersed in stearic ethanol solution of 20 mmol/L for 10 h. Then, the specimens were dried with high purity nitrogen for further characterization.

Surface morphology was characterized by scanning electron

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microscopy (SEM, FEI-QUANTA200FEG). Surface component was analyzed by energy dispersive spectrometer (EDS, OXFORD INSTRUMENTS). Contact angle measuring instrument (OCA20) was used to test the wettability of specimens. The results were obtained by the average of three measurements. Electrochemical workstation (CHI660D) was used to evaluate the corrosion resistance. In impedance tests, the test range was set as 10 mHz~100 kHz. Before electrochemical tests, the electrode was immersed in electrolyte for 30 min to reach a stable test status.

2 Results and Discussion

2.1 Microstructure, composition, and wettability of superhydrophobic 7075 aluminum alloy

Fig. 1a and 1b show the microstructures of 7075 aluminum alloy after HCl etching for 7 min. It can be seen that the large-scale micro-convex appears, and the convex surface is relatively smooth. After further etching in boiling water for 2 min, the nano-floccule emerges at convex edge (Fig. 1c and 1d). With prolonging the etching time, the amount of floccule is gradually increased, thus forming a distinct microstructure (Fig. 1e~1h). The formation mechanism of this composite structure is the existence of crystal defect in aluminum alloys[17]. After the alloy surface is etched by hydrochloric acid and boiling water, the crystal defect with high energy dissolves preferentially, while the crystal defect with low energy dissolves later. Besides, the activation effect of hydrochloric acid is stronger than that of boiling water. Hence, the micro-convex and nano-floccule are formed orderly with composite characteristics.

EDS spectrum of the specimen after immersion in hydrochloric acid for 7 min and then in boiling water for 4 min is shown in Fig. 2a. It can be seen that the main metal elements on the etched surface are aluminum, zinc, magnesium, and copper. This result is consistent with practical chemical composition of 7075 aluminum alloy (Al 87.6wt%, Zn 6.0wt%, Mg 2.8wt%, Cu 2.0wt%, Fe 0.5wt%, Si 0.4wt%, Mn 0.3wt%, Ti 0.2wt%, Cr 0.2 wt%). Other elements in alloy cannot be detected because of their low contents (<0.5wt%). Besides, the oxygen element can be observed for metal oxidation. Meanwhile, the chlorine element can be found due to the chlorides from chemical reactions between HCl and metal elements in alloy. Fig. 2b exhibits the element distributions of 7075 Al alloy, which indicates that the elements are distributed evenly. Hence, the etching process can change the microstructure of alloy, but has no effect on its chemical composition.

Fig. 3 shows the wettability of 7075 aluminum alloys after different etching processes. It can be seen that the water contact angle (CA) of the untreated specimen is 59.3°, and there is no droplet rolling, which shows the obvious hydrophilicity. After HCl etching for 7 min, CA of specimen is increased to 145.4° with a sliding angle (SA) of 21.3°, thus displaying a distinct hydrophobicity. Under this condition, the etched micro-convex improves the hydrophobicity of specimen. As the specimen is further etched by boiling water for 2 min, only a small amount of nano-floccule forms on convex edge, so the hydrophobic effect is increased slightly. When the boiling water-etching time is extended to 4 min, the specimen shows superior superhydrophobic effect with CA of 159.3° and SA of 6.7° due to the distinct bionic composite microstructure. As the etching time is extended to 6 min, SA and CA are stable. This is due to the already formed microstructure of specimen after etching by boiling water for 4 min. Excessive etching time in boiling water has little effect on the resultant microstructure, so the wettability remains steady. Besides, the small standard deviation (SD) can be achieved, indicating that as-prepared surfaces are relatively stable.

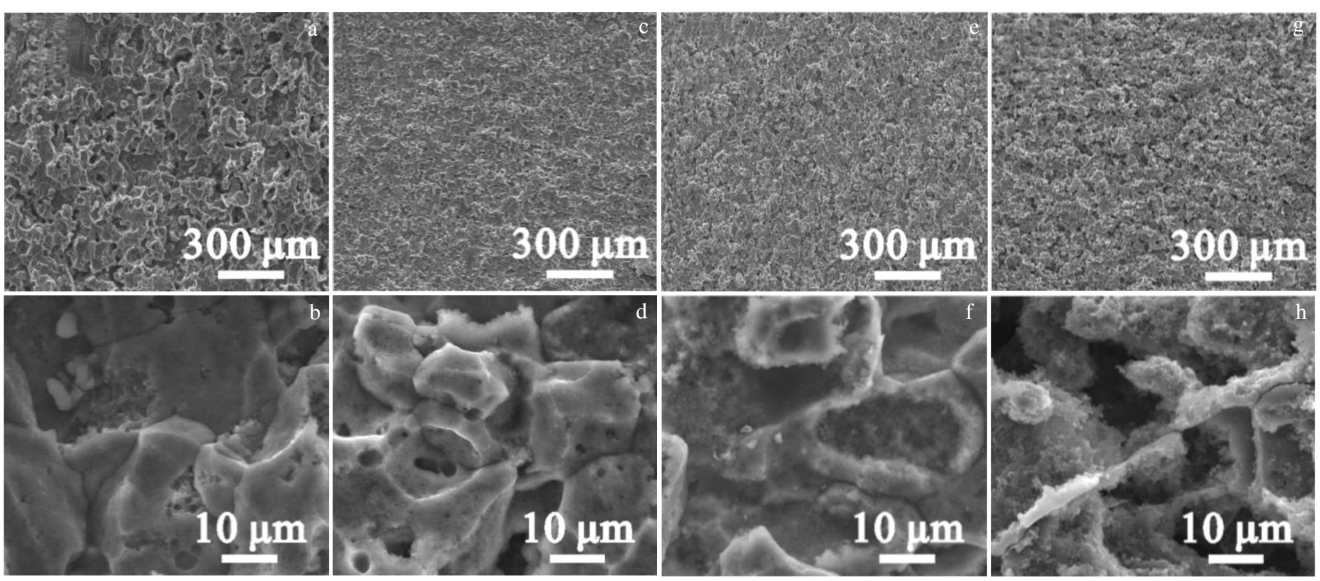

Fig.1 SEM images of 7075 Al alloys after different treatments: (a, b) HCl-7 min, (c, d) HCl-7 min/boiling water-2 min, (e, f) HCl-7 min/boiling water-4 min, and (g, h) HCl-7 min/boiling water-6 min

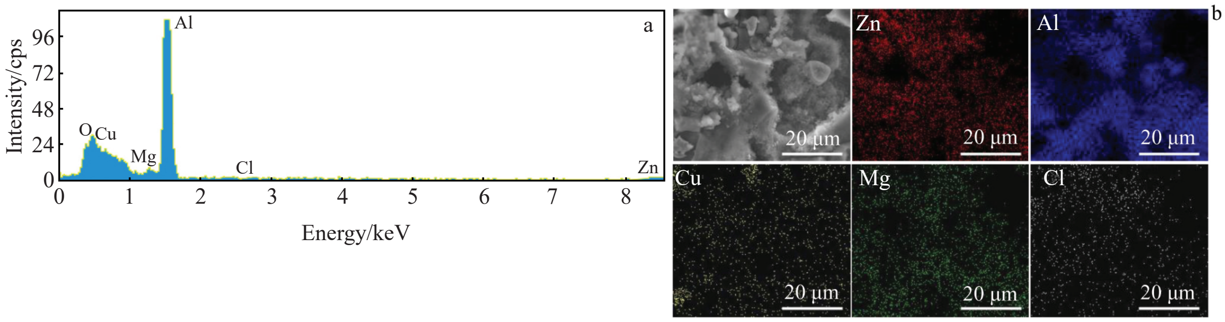

Fig.2 EDS spectrum (a) and element distributions (b) of 7075 Al alloy after immersion treatment of HCl-7 min/boiling water-4 min

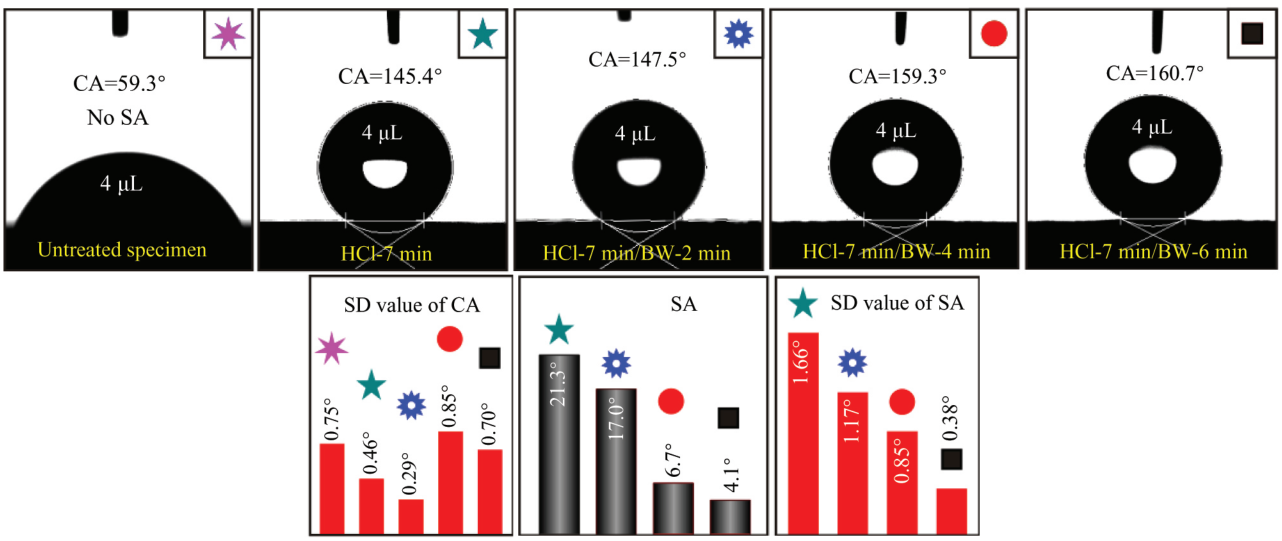

Fig.3 Wettability of 7075 Al alloys after different etching processes and comparison results of SA, SD value of CA, and SD value of SA (BW: boiling water)

2.2 Anticorrosion mechanism of 7075 aluminum alloy

Impedance spectroscopies were measured to characterize the corrosion behavior of as-prepared Al alloys, as shown in Fig.4a. In an impedance spectroscopy, the larger the capacitive arc, the stronger the corrosion resistance[18,19]. It can be seen that the untreated specimen has the smallest capacitive arc, thus possessing the worst corrosion resistance. The untreated specimen exhibits obvious hydrophilic characteristics, so it directly contacts with corrosive medium, thereby forming the solid-liquid contacting interface (Fig. 4b). In this state, the corrosion medium directly corrodes the alloy surface, so it shows the most serious corrosion. After HCl etching for 7 min, the impedance arc size increases, suggesting an enhanced anticorrosion ability. This is because the etched micro-convex displays the enhanced hydrophobicity, which helps to trap air, thus forming a solid-gas-liquid contact interface (Fig.4c). The introduction of air phase can effectively hinder the erosion by corrosive ions. As the specimen is further etched in boiling water for 2 min, the impedance arc size also increases. Furthermore, with the extension of etching time in boiling water, the impedance arc size still increases, indicating a gradually improved corrosion resistance. This is due to the gradual formation of the composite microstructure after boiling water etching. It can be concluded that such structure shows an obvious superhydrophobic character, which can trap more air (Fig.4d), thus forming a stronger impedance against the corrosion ion. As a result, the corresponding corrosion resistance is significantly enhanced.

Through ZSimDemo software, $R_1(CR_2)$ circuit can better simulate the electrochemical process of etched alloys. In this circuit, R_1 represents the solution resistance, C refers to the capacitance between etched alloy and electrolyte, and R_2 denotes the charge transfer resistance between electrolyte and specimen. It is known that the smaller the value of C and the larger that of R_2, the stronger the resistance to charge transfer as well as the better the corrosion resistance[20]. The parameters of circuit elements obtained after fitting are achieved and shown in Table 1. It is clear that R_1 is relatively stable in the whole process, indicating that electrochemical process remains stable in experiment. Meanwhile, R_2 for untreated specimen is the smallest and C is the largest, which shows the worst corrosion resistance. The value of R_2 and C of HCl-etched alloy is similar to that of the specimen after treatment of HCl-7 min/boiling water-2 min. Thus these two

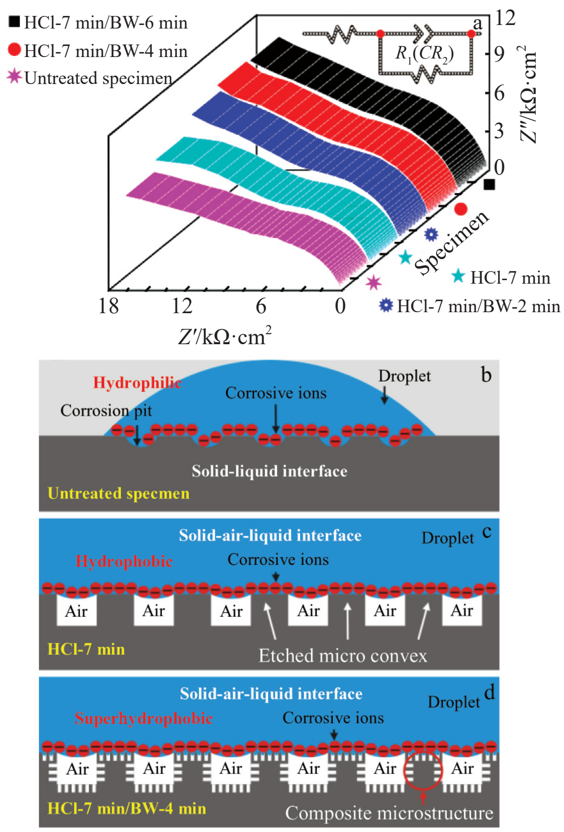

Fig.4 Impedance spectra of 7075 Al alloys after different etching processes (a); anticorrosion mechanisms of untreated specimen (b), hydrophobic alloy (c), and superhydrophobic alloy (d)

Table 1 Fitted electrochemical parameters of 7075 Al alloys after different etching processes

Specimen	R_1/Ω·cm^2	R_2/Ω·cm^2	C/μF·cm^{-2}
Untreated specimen	7.2	504.0	40.0
HCl-7 min	7.0	10 191.8	4.1
HCl-7 min/BW-2 min	7.0	11 242.6	4.0
HCl-7 min/BW-4 min	6.9	15 417.0	2.3
HCl-7 min/BW-6 min	7.2	15 520.1	2.1

alloys have similar corrosion resistance. With prolonging the etching time in boiling water, C is gradually decreased and R_2 is increased, so the corrosion resistance is improved. Hence, based on the superhydrophobic preparation, the excellent corrosion resistance of aluminum alloy for aviation industry can be obtained. Meanwhile, the quantitative characterization of anticorrosion behavior can also be achieved by establishing equivalent circuit. Besides, the corresponding anticorrosion mechanisms have also been systematically discussed.

3 Conclusions

1) The large-scale bionic micro-convex with nano-flocculent appearance shows excellent static and dynamic superhydrophobic effects, because this composite microstructure can trap air to form a solid-gas-liquid contact interface. The introduction of air phase can effectively hinder the erosion by corrosive ions, which significantly improves the corrosion resistance of 7075 Al alloy.

2) The equivalent circuit model properly simulates the corrosion behavior of etched 7075 Al alloys, and the quantitative analysis of the corrosion behavior can be achieved.

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航空用超疏水7075铝合金的高效可控制备及防腐机理

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摘　要：采用简单、高效、低成本的刻蚀技术，实现了航空用超疏水7075铝合金的规模化可控制备。阻抗测试表明，制备得到的超疏水7075铝合金的电荷转移电阻增大，双层电容明显减小，耐腐蚀性能得到显著改善。该研究对开拓绿色航空时代、创新合金材料腐蚀防护新技术具有重要经济价值和现实意义。

关键词：航空铝合金；微纳结构；超疏水；耐腐蚀；防腐机理

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