Fabrication of a super-amphiphobic aluminium alloy surface via wire electrical discharge machining and chemical etching technology

Yanling Wan, Lining Xu ✉, *Zhigang Liu, Huadong Yu*

College of Mechanical and Electric Engineering, Changchun University of Science and Technology, Changchun 130022, People's Republic of China

✉ *E-mail: 18605453512@163.com*

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A simple method, involving twice electric machining by HS-WEDM and chemical etching, is used to fabricate super-amphiphobic (both super-hydrophobic and super-oleophobic) surfaces on aluminium alloy. The surface morphology of the samples was investigated using scanning electron microscopy and laser scanning confocal microscope. The evaluations of surface oleophobicity were carried out using the contact angles of ethylene glycol, diiodomethane and dodecane. Finally, the experimental result indicated that after the twice electric machining and chemical etching, the micro/nanometre-scale binary rough structure was presented on the sample surfaces, and the resulting sample surfaces produced in this method had super-hydrophobic and lipophilic properties (water contact angle of 155.74°). More importantly, after surface fluorination, the sample surfaces turned to super-amphiphobic surfaces and the biggest contact angles of water and oil were 156.24° and 157.34°, respectively. Therefore, it can be considered that the acquirement of the micro/nanometre-scale rough structures and the reduction of the surface energy are essential requirements to fabricate super-amphiphobic surfaces. The advantages of the present method over the other methods are that the used wire electrical discharge machining can machine most metals, and the processes of surface forming and microstructure fabrication were combined, which saves processing time greatly.

1. Introduction: If the surface had contact angles of water and oil are all larger than 150°, we called it super-amphiphobic. Namely, the surface with both super-hydrophobicity and super-oleophobicity [1]. The effect of super-hydrophobic surface has been investigated for some time, initially on the self-cleaning capability of lotus leaves. Research shows that the super-hydrophobic surface has great application prospect in fields of anti-fog, water proofing, anti-snow, anti-oxidation, anti-pollution, anti-corrosion and self-cleaning [2–5]. However, the ordinary super-hydrophobic surface does not have super-oleophobicity, once which is immersed in the water containing oil, it is easy to be contaminated by the oil and lose super-hydrophobicity [6]. The super-amphiphobic surface not only has the characteristics of super-hydrophobic surface, but also has the function of oleophobicity [7], and has great potential application in life. Therefore, compared with the ordinary super-hydrophobic surface, a large number of researchers at home and abroad think that the fabrication of super-amphiphobic surface has greater application value, in rust prevention and corrosion protection aspect of automotive industry, construction industry and metal industry [8].

The fabrication method of the super-amphiphobic surface of the metal matrix is similar to the super-hydrophobic surface. That is, fabricating rough structure on the metal substrate, and then reducing the surface energy by using the low surface energy chemical material. However, the surface tension of oily liquids is much less than that of water, so it is more difficult to obtain the surface of super-oleophobicity. Research on preparing super-amphiphobic surfaces have made considerable progress in recent years. Although there are a lot of methods been used to fabricate super-amphiphobic surface of metal matrix, yet reports about the simple and low-cost methods are few. Tuteja *et al.* obtained the rough crack-shape structure by electrochemical corrosion on the aluminium (Al) surface taking sulphuric acid as electrolyte, after modification of the sample surface by treating with fluorinated monoalkyl phosphate, the surface showed the super-amphiphobic property [9]. Wu *et al.* [10] fabricated nanohole and nanocluster structure on the Al matrix with two-step electrochemical anodic oxidation only by taking sodium sulphate and oxalic acid as electrolyte successively, and then obtained super-amphiphobic property after modification of perfluorooctyl-trichlorosilane. Xiaotao Zhua *et al.* [11] obtained microflower-shape and nanorod-shape structures that uniform distribution and dense arrangement by soaking the copper in the mixed solution of sodium hydroxide and ammonium peroxydisulphate, and obtained the super-amphiphobic surface after the modification of perfluorooctanoic acid. Yoshida [12] used a simple method that employed the conventional dispersion polymerisation of perfluoroalkyl methacrylates in methanol to prepare micro and nanospheres with super-amphiphobic surfaces. To the best of our knowledge, most of these methods require sophisticated technology, strict process control, expensive equipment and another step to machine the metal surface, which limits their widespread application. Therefore, it is of great practical significance to exploit a method to realise the fabrication of super-amphiphobic surfaces, which is simple, efficient, cost low and suits for metal materials. In contrast with the above methods, this Letter has the advantages that the used wire electrical discharge machining can machine most metals and the processes of surface forming and microstructure fabrication were combined, which saves processing time greatly.

As we all know, high-speed electrical discharge machining technology is a kind of widely used processing technology. The microstructure on the metal surface can be obtained by using this processing technology, but its hydrophobic and oleophobic effects are not ideal. On the basis of high-speed electrical discharge machining technology, we extended this fabricate method. For achieving super-amphiphobic property, our main objectives are three-folds: using high-speed electric spark line cutting technology to process the surface of the Al alloy two times (twice electric spark discharge), using chemical etching technology to obtain binary micro/nanostructures, reducing the surface energy by fluorine.

2. Materials and methods

2.1. Materials: Experimental material was polished 6061 Al alloy plate, and it was sliced into 20 × 20 × 2 mm samples.

Experimental reagents: acetone, ethanol, glycol, hydrofluoric acid [$w(HF)\% \geq 40.0$], ammonia ($25 \leq w(NH_3)\% \leq 28$), fluoroalkylsilane (1H, 1H, 2H, 2H- perfluorodecyl triethoxysilane) and deionised water. All experimental chemicals were analytically pure reagents.

2.2. Methods: This Letter completed the preparation of super-amphiphobic Al alloy surface mainly with three steps. The first step, using DK7732 large taper high-speed electric spark wire cutting machine tool machine the surface of Al alloy by twice electric machining. The values of twice electric machining parameters were as follows: the machining pulse width was 6 µs and the feed rate was 62 µm/s (the first time to carry out electric spark discharge) and the feed rate changed into 44 µm/s (the second time to carry out electric spark discharge). It should be noted that, after the first electric machining, the second electric machining was carried out with reverse cutting operation that was wire electrode that ran back from the stopping point to the starting point, and carried on the second electric machining under the same track. The experiment found that the surface of Al alloy was ablated under the action of strong electric field after the first electric machining, and the distance between the surfaces of Al alloy and wire electrode was about 30 µm, which can form discharge channel during the process of reverse cutting; therefore, the second electric machining could be realised. The second step, washing the fabricated specimens in the dilute solution of HF (w(HF)% ≥ 40.0) to remove the oxidising substance of surface, and then the processed Al alloy was immersed in 12% NH_3 solution for 10 min. The last step, the etched samples were modified by fluoroalkylsilane (mass ratio is 1:100) for 45 min and dried for 40 min under the environment of the temperature of 135°.

2.3. Performance test and result representation: The surface morphologies of samples were observed using laser scanning confocal microscope (Zeiss) and scanning electron microscope (FEI Quanta 250 FEG).

The wettability of the sample surfaces were tested by optical contact angle measuring device (OCA20), which was produced by German Dataphysics company. To ensure the accuracy of the surface data of processed specimens, the processed Al alloy samples were cleaned ultrasonically with acetone, ethanol and deionised water for 5 min in turn, and subsequently dried at room temperature. The process mentioned above should be finished before the measurement of contact angle. Hydrophobic property was tested by water contact angles at three different positions of each sample, and the volume of water drop was 4 µl. Ethylene glycol, diiodomethane and dodecane were used for oleophobicity evaluation, for their different surface tension value.

3. Results and discussion

3.1. Surface wettability: Using the static contact angle measuring instrument to measure the surface of Al alloy before and after electric machining. The results showed that the static contact angle of water droplets on the surface of smooth Al alloy was about 76.4° (Fig. 1*a*). After the first electric machining, the hydrophobicity of fabricated Al alloy surfaces was significantly improved, and the static contact angle was about 134.59° (Fig. 1*b*). Furthermore, after the second electric machining, the static contact angle of the specimen reached 155.74° (±0.5°) (Fig. 1*c*), which means we had got the surfaces with super-hydrophobicity.

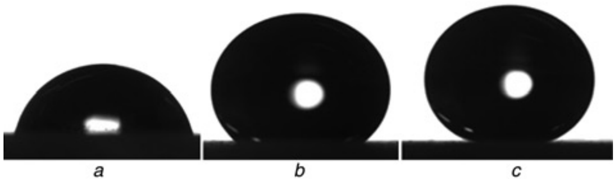

Fig. 1 *Water contact angles of fabricated Al alloy specimens*
a Smooth Al alloy
b Al alloy treated with once discharge machining
c Al alloy treated with twice discharge machining

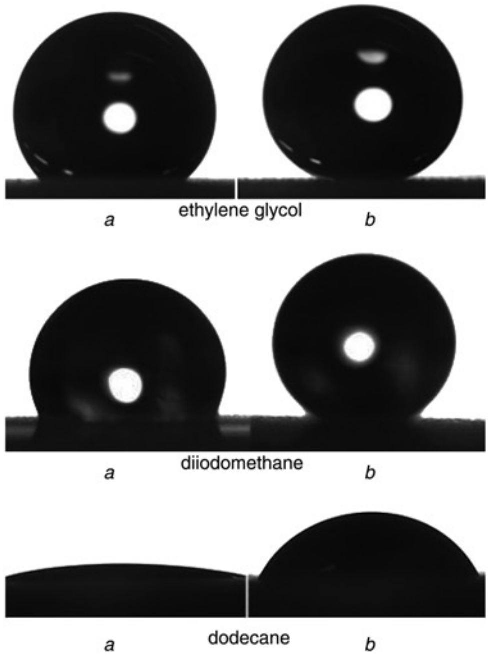

Fig. 2 *Contact angles of fabricated Al alloy specimens (ethylene glycol, diiodomethane and dodecane)*
a Samples treated with twice discharge machining and chemical etching
b Samples treated with twice discharge machining, chemical etching and chemical modification

Using the contact angles of ethylene glycol, diiodomethane and dodecane droplets to describe the wetting property of the Al alloy surface. After the second electric machining, the contact angles were 127.81°, 118.37° and 12.30°, respectively (Fig. 2*a*). However, after chemical modification, the contact angles of as-obtained samples reached 157.34°, 153.96° and 61.76°, respectively (Fig. 2*b*). The contact angles of ethylene glycol and diiodomethane showed super-oleophobic property of samples, whereas the dodecane contact angle showed lipophilic property of samples, which was caused by the low surface tension value and low surface energy of dodecane. The surface tension value of dodecane is about 27.12 mN/m and that of ethylene glycol and diiodomethane are about 50 mN/m. Consequently, the preparation of super-hydrophobic Al alloy surface can be realised only using electric machining. However, in order to get the super-oleophobicity, the chemical etching and chemical modification are also needed.

3.2. Surface morphology: Scanning electron microscopy was used to observe the morphology of the samples, the results indicated

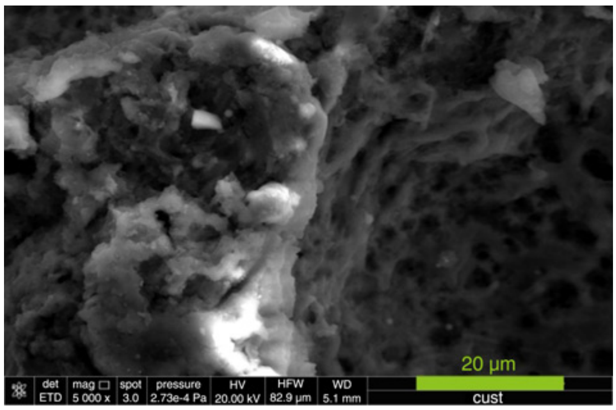

Fig. 3 *Samples treated with once electric machining*

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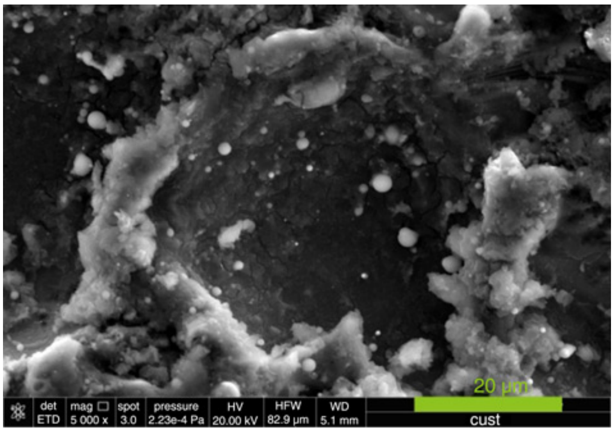

Fig. 4 *Samples treated with twice electric machining*

that the surfaces of both once electric machining and twice electric machining appeared the uniformly distributed convex and concave structures with irregular shape. Compared with once discharge machining (Fig. 3), the microscopic appearance of the specimen surface with twice electric machining (Fig. 4) was more rough and the number of pits was obviously increased, the diameter of the pits was distinctly decreased, from original 90–120 µm reduced to 30–60 µm. Compared with twice discharge machining, the microscopic appearance of the specimen surface after chemical etching (Fig. 5) was rougher and a large number of pits and bumps with a diameter range of 0–5 µm presented on the as-obtained rough surface. Further using confocal microscopy to observe the surface of the processed specimen, it can be found that the depth of pit was about 13–50 µm, and the specimen surface was covered with a large number of irregular bumps and pits in sub-micron scale. The surface morphology of samples was observed under the smaller magnification, and it can be seen in Fig. 6. Therefore, a conclusion can be drawn from above, the micron level surface with sub-micro or even nanostructure can be prepared with the twice electric machining and chemical etching, and finally get the micro/nanosised composite structure. It is precisely because of the existence of that structure made the surface of Al alloy has super-hydrophobicity, which was also a preparation work for super-oleophobic surface.

3.3. Analysis of the mechanism of super-amphiphobic surface: The micro/nanometre rough structure can capture more air, so that air cushion will appear and reduce the actual area between the metal surface and the oil droplets. With the increasing number of nanostructures, the ability to capture the air is enhanced through the presence of micro/nanometre rough structure, and the contact

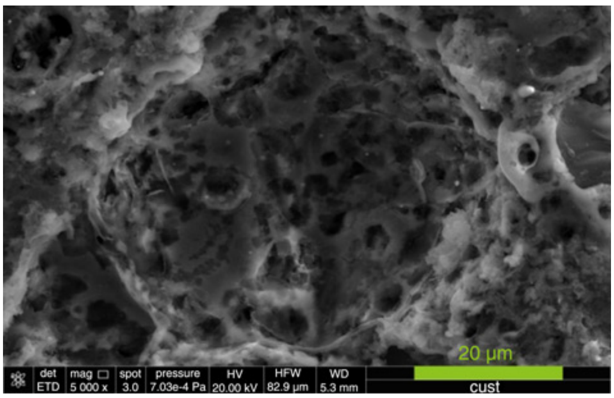

Fig. 5 *Samples treated with twice electric machining and chemical etching*

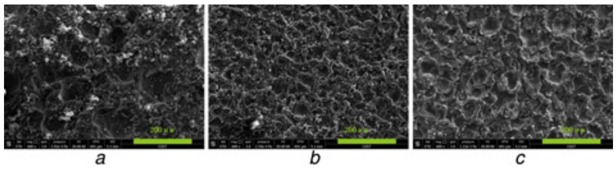

Fig. 6 *Samples observed under the smaller magnification*
a Samples treated with once electric machining
b Samples treated with twice electric machining
c Samples treated with twice electric machining and chemical etching

area between oil droplets and solid is reduced. Which will increase the contact angle of the oil droplets, hence the existence of the nanostructure will improve the surface oleophobic ability. The morphology of the Al alloy specimen was observed by scanning electron microscope after twice electric machining and chemical etching. It can be found that, the number of micropits and microbumps on the surface of the resulting samples was significantly increased as compared with the surface of the specimens without chemical etching. Moreover, a large number of nanometre convex and concave structures existed on the sub-micrometre scaled structures. Investigating its reason, the Al element inside the specimens reacted with NH_3 water (bubbles can be observed during the experiment) when the Al alloy specimens were immersed into NH_3 solution. When the specimens were immersed into NH_3 solution, and generated Al hydroxide, it dissolved in NH_3 water, and promoted the further reaction of Al with NH_3 [13]. Moreover, the number of the surface nanostructure becomes larger and larger with the extension of chemical processing time [14], thus more tiny structures appeared on the specimen surface by chemical etching. Overall, it can be concluded that the chemical etching can make the number of nanoscale structures significantly increased, which is one of the necessary conditions to obtain the super-oleophobic surface.

It is found that the super-amphiphobic surface cannot be obtained by only twice electric machining and chemical etching, but can be obtained by adding the process of chemical modification. That is because the surface tension of the oil is less than that of water, it is needed to modify the surface of the Al alloy with a low surface energy material, and finally get the super-oleophobic surface. It can be inferred that the preparation of micronanometre rough structure and the reduction of the surface energy are the necessary conditions for the fabrication of super-amphiphobic surface. The droplet volume is much larger than the surface structure, under the combined action of micronanometre rough structure and low surface energy that leads to the air cushion can exist between the metal surface and the droplet. The droplet can only partly contact with the structure, and cannot penetrate into the gap between the rough structure, thereby forming a complex contact that among droplet, micronanometre rough structure and the air cushion, and finally obtaining the super-amphiphobic surface of CASSIE-BAXTER state [15].

4. Conclusion: High-speed electric spark wire cutting technology was used to make twice electric machining on the surface of Al alloy, which leads to a large number of micro and even sub-micron pits and folds appear on the surface of the Al alloy, so as to realise the super-hydrophobic performance of Al alloy surface, and the static water contact angle can reach 155.74°. Then, the electric machined specimens were dealt with chemical etching and fluoride modification that made the micronanometre rough structure formed and low surface energy substance appeared on its surface, thereby the super-amphiphobic property of the Al alloy surface can be realised. The samples were treated with chemically etching and the nanoscale structures on the surfaces were significantly increased. Finally, the super-amphiphobic surface can be obtained by chemical modification. It can be safely inferred that the preparation of micronanometre structure and the reduction of the surface energy are essential conditions for the fabrication of super-amphiphobic surface.

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