Preparation of superamphiphobic aluminium alloy surface based on laser-EDM method

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In order to achieve superamphiphobic surface of aluminium alloy, a method based on laser-EDM (electrical discharge machining) was proposed. By means of laser etching, the size of the controllable micrometre square column structure could be prepared on the surface of aluminium alloy. Then combined with the electric processing method, the binary micro-nano rough structure was constructed and modified with fluorosilane methanol solution, and the superamphiphobic surface was achieved successfully. The morphology and size of the superamphiphobic surface were observed by scanning electron microscopy and laser confocal microscopy, and the superamphiphobic performance of the surface was detected by video optical contact angle. The results showed that the water contact angle of the surface prepared by laser-EDM was 157.06°. After the modification of fluorosilane methanol solution, the contact angle of the surface to ethylene glycol reached 156.46°. It can be discovered that the acquisition of binary micro-nano rough structure and the decrease of surface energy are important conditions to obtain superamphiphobicity. Compared with the existing methods, laser etching can be a good control surface morphology, and eventually get superamphiphobic surface.

1. Introduction: Superamphiphobic surface, the water and oil contact angle on the surface reached 150°, has superhydrophobicity and super-oily [1, 2]. A large number of studies have shown that the superhydrophobic surface has a wide application prospect in self-cleaning [3, 4], fluid drag reduction [5, 6], pipe transportation [7], anti-icing [8, 9], and oil–water separation [10]. Unfortunately, once the superhydrophobic surface encountered oil–water mixture, the superhydrophobic property could lose, which is difficult to meet people's needs. Therefore, many artificial superamphiphobic surfaces [11] had emerged by different techniques, such as self-assembly, polymerisation, and phase separation method. However, these methods require specific large-scale processing equipment and high production costs. In addition, the processing is difficult to control.

Zubayda *et al.* [12] prepared the aluminium superamphiphobic surface by sand blasting and water boiling after the modification with 1H, 1H, 2H, 2H-perfluorodecyltriethoxy silane agent to low surface energy. There is a drawback appeared that the size of the as-prepared superamphiphobic surface cannot achieve uniformity and it is difficult to control manually. Jinming Xi *et al.* [13] proposed an electro-deposition method and successfully constructed a superhydrophobic surface on different metal substrate surfaces. Then the electrolyte was added into low surface energy material, and the superamphiphobic surface could be achieved. However, some parameters were difficult to control. Haifeng Meng *et al.* [14] proposed an electrochemical method, but the length of the chain was more difficult to control. The laser-EDM (electrical discharge machining) method does not have the above drawbacks. Therefore, compared with the rigorous operation process and expensive equipment, the laser-EDM method to study an artificial binary micro-nano rough structure is of great significance.

2. Experimental section

2.1. Materials and instruments: The test material was the 6061 aluminium alloy plate, which was cut into the size of 5 mm × 10 mm, and then polished with different sizes of sandpaper. Then the samples were subjected to ultrasonic cleaning for 5 min with acetone and anhydrous ethanol. Finally, they were dried naturally.

The micro-structure of aluminium alloy was produced by YLP-ST20E fibre laser marking machine and DK7732 large taper high-speed WEDM machine. The morphology and size of micro-structure on the surface of the specimens were observed by scanning electron microscopy (SEM) FEI Quanta 250 FEG and ZEISS laser confocal microscopy. The surface wettability of the samples was measured by OCA20 video optical contact angle measuring instrument. The test liquid was deionised water and ethylene glycol, the droplet size was 4 μl, the parallel samples were 5, and the average values were eventually obtained.

2.2. Methods: The processing route for superamphiphobic aluminium alloy surface was prepared by the laser-EDM as shown in Fig. 1. First, the micrometre geometry was machined by the laser etching method on the surface of the aluminium alloy as shown in Fig. 1. The laser processing parameters are as follows: the processing power was 4 W, the spot movement speed was 600 m/s, the number of rounds were 24 times, and the grid unit was 150 μm. In addition, the high-speed EDM wire cutting technology had been used to discharge modification processing for the construction of micro-structure of aluminium alloy surface. The low-energy EDM was chosen to process in order to prevent the micro-cylinder from being destroyed. The pulse width was 2 μs, the pulse interval was 14 μs, and the feeding speed was 44 μm/s. The samples machined by laser were ultrasonically cleaned for 5 min with acetone, anhydrous ethanol, and deionised water, and finally dried for backup. So are the EDM.

At last, the samples processed by laser-EDM were placed in a fluorosilane methanol solution with the mass ratio of 1:100, the modification time was 45 min. Then the samples are(were) taken out and placed in a drying oven at 135°C for 40 min.

3. Results and discussion

3.1. Morphology: The surface morphology of the sample was observed by SEM and laser scanning confocal microscope (LSCM). As can be seen from Fig. 2, the surfaces prepared by the laser-EDM were evenly distributed with uniform size micrometre columns, which reveal that the laser etching can be a good control for the surface micro-structure of the arrangement

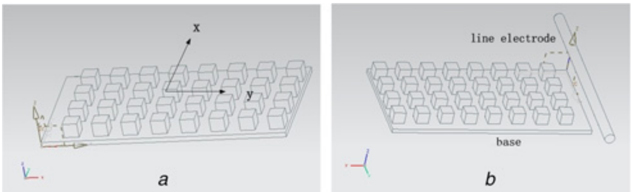

Fig. 1 *Preparation flowchart of superamphiphobic Al surface*
a Manufacturing process routes by laser textured technique
b Manufacturing process routes by HS-WEDM

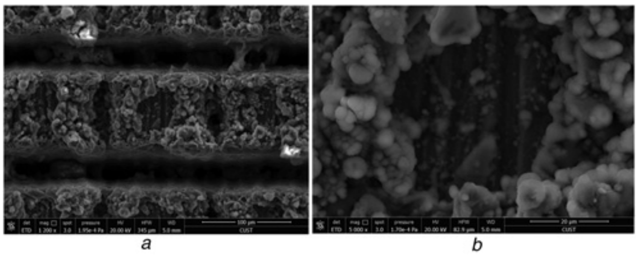

Fig. 2 *Specimens fabricated by laser textured technique and HS-WEDM processes*
a Morphology studied using scanning electronic microscope
b Morphology studied using scanning electronic microscope

and size. It is also easy to observe the dense bulge for sub-micro or even nanoscale. These protrusions are arranged along the edge of the square pillar so that the intermediate position above the square pillar is surrounded by an annular groove. It was because that EDM was discharged on the surface of the specimen so that the part of metal was melted, and adhered to the micro-column on the surface of the specimen. This kind of method has taken EDM advantages into account without destroying the micro-structure, so that the aluminium alloy free energy was more uniform, and the micro-cylinder surface has a certain degree of roughness. As a consequence, the conclusion can be drawn that the laser-EDM can produce a sub-micron or even nanoscale structure called binary micro-nano rough structure, which make the surface of aluminium alloy superhydrophobic and superoleophobic.

3.2. Analysis of surface wettability: It was found that the uniform array of micron-sized columnar arrays on the aluminium alloy surface built by applying laser etching technology can change the wettability of the aluminium alloy surface. Therefore, the hydrophobic of the smooth surface increased from 76.4° to 91.03°, but cannot achieve superhydrophobicity aluminium alloy surface. The surface processed by the laser-EDM was superhydrophobic, and the maximum contact angle was 155.82°, while the static contact angle of ethylene glycol on its surface increased from 73.59° to 140.16°. It can be seen that simply using the kind of composite processing technology on the aluminium alloy surface cannot achieve superoleophobicity. We all know that low surface free energy is a key factor in obtaining superhydrophobic surfaces. In this Letter, chemical modification method will be used to reduce the surface free energy. It was detected from the test that the static contact angles for droplets and ethylene glycol were 157.06° (Fig. 3*a*) and 156.46° (Fig. 3*b*), which shows clearly that the surface free energy of the aluminium alloy surface modified by fluorosilane after laser-EDM was decreased, and the surface of the superamphiphobic aluminium alloy was successfully prepared.

3.3. Wetting mechanism: At first, the effect of the processing to the surface micro-structure was analysed. The laser etching on the surface of aluminium alloy was a thermal processing. The high-energy spot ablation was an instantaneous heating and cooling

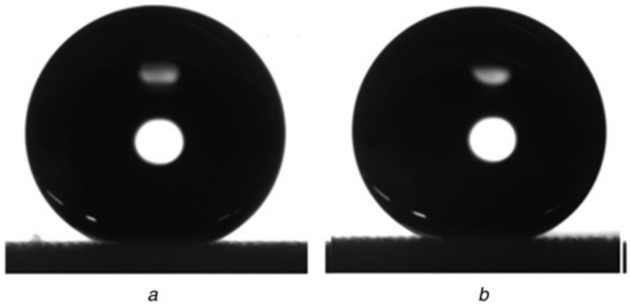

Fig. 3 *Contact angles of modified Al alloy surfaces*
a Water droplet on the processing surface
b Ethylene glycol droplet on the processing surface

process, the thermal stress for the surface layer of grooved structure between micrometre columns on aluminium alloy surface was produced through thermal effect. Consequently, the free energy distribution on the surface of the sample was not uniform, which resulted in a different surface tension compared with other location. So when the droplets dripped onto the aluminium alloy surface processed by the laser, the water droplets will be immersed in the groove micro-structure as a result of the action of the surface tension, the contact angle of the water droplets was reduced. As for EDM, the small processing parameters were selected to prevent the surface micro-structure from being destroyed, which is equivalent to the quenching process in the hot process. The surface phase change was uniform, and the roughness of the upper surface of the square column micro-structure was increased, and a binary micro-nano rough structure was constructed. Hence, the two-scale composite structures were fabricated.

The surface micro-structure has a great effect on the wetting. Since the surface tension of the oil is smaller than the water, the makeup of surface micro-structure is more important to the realisation of superoleophobic properties. Binary micro-nano rough structure can capture more air, so that oil droplets cannot contact with binary micro-nano rough structure directly. The newly constructed nanostructures enhanced the ability of binary micro-nano structures to capture air and reduced the contact area between oil droplets and solids, resulting in an increase in the contact angle of oil droplets. Thus, the presence of nano-structures will affect the surface oleophobic effect. The aluminium alloy sample after the laser-EDM were observed under scanning electron microscope, showing that there was a sub-micron or even nanometre structure called binary micro-nano rough structure. It was also easy to observe the dense bulge for sub-micron or even nanoscale. So an annular groove on the centre position above the square pillar was formed through protrusions arrangement along the edge of the square pillar. Owing to the presence of grooves between micro-columns or above the micro-pillars, the height difference of the micro-structure was increased and more air was stored. Therefore, it can be concluded that with the nanostructure increasing, more air can be deposited, and the nanostructure on the surface played a certain role in the realisation of the superoleophobic property.

From the test results, it declared that only laser-EDM cannot prepare superamphiphobic aluminium alloy surface, which must be chemically modified to obtain the superamphiphobicity. This is because the surface tension of the oil is less than the water. Therefore, to obtain a superoleophobic surface, it also needs the low surface energy to modify aluminium alloy surface. It was speculated that the combination of the preparation of binary micro-nano rough structures and the reduction of the surface energy is an indispensable condition for the preparation of superamphiphobic surfaces. Under the joint action for the binary micro-nano rough structure and low surface energy, the rough structure can capture more air, so that the droplets cannot contact with the rough structure directly, and cannot penetrate into the gap between the rough

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structure. Thereby a composite contact between the droplet and the binary micro-nano rough structure in Cassie–Baxter wetting state can be formed.

4. Conclusion: The binary micro-nano rough structure on the aluminium alloy surface was created by the laser-EDM processing technology, and the shape and size of micron-scale structure can be controlled. The static contact angles of water and ethylene glycol droplets on the surface after modification with fluoride are 157.06° and 156.46°, respectively. Ultimately, superamphiphobic aluminium alloy surface were fabricated successfully. Moreover, the final result showed that the preparation of binary micro-nano rough structure and the reduction of surface energy are essential conditions for the preparation of superamphiphobic surface.

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