Short Communication

Rapid laser fabrication of long-term stable superhydrophilic aluminum surface

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Abstract

A simple method for fabricating stable superhydrophilic aluminum surface is reported in this paper. Controllable micro-nanostructures were prepared on the surface of aluminum plate by nanosecond laser and then soaked in boiled 45% ethanol solution for 2 h as the post-treatment. It is demonstrated that the laser-ablated aluminum plate surface is hydrophilic and then switch to superhydrophilic after a 45% ethanol solution post-treatment. The treated superhydrophilic structure has good hydrophilic stability in a certain period of time. The mechanism of superhydrophilic behavior of aluminum surface treated with laser and ethanol solution was discussed. A new method for preparing stable superhydrophilic surface is proposed in this paper, which is of great significance for the preparation of superhydrophilic surface and the application of superhydrophilic surface in industrial production.

Keywords Superhydrophilic surface · Aluminum · Nanosecond laser · Ethanol solution · Contact angle

1 Introduction

In today's production and life, hydrophilic surface has a good application as a product with water collection capacity and moisture removal capacity [1]. Generally, the hydrophilicity of the material surface is judged by the data of contact angle (CA) [2]. When the CA value is < 90°, the material surface is judged as hydrophilic. The CA of superhydrophilic surface, one of the most excellent hydrophilic surfaces, can reach < 5° [3]. The particularity of its surface endows it with good self-cleaning ability and heat conduction ability. In industry, superhydrophilic structure can be used to make humidity sensors and underwater superhydrophobic corrosion-resistant surface. Theoretically, the smaller the CA, the better the hydrophilicity performance. However, the contact angle of some superhydrophilic surface has reached 0°. At this time, the performance of this kind of superhydrophilic surfaces was further judged by comparing the time from the contact of water droplets with the material surface to its completely absorbed by the surface of the material [4].

Artificial superhydrophilic surface is expected to have good stability and convenient process has a broad market and research value [5]. The superhydrophilic properties of solid surfaces are mainly affected by surface microstructure and surface energy. Some papers fabricated the certain rough microstructure surface to make material surface superhydrophilic. This shows that increasing the roughness of material surface can improve its hydrophilicity. Therefore, some preparation methods of superhydrophilic materials focus on changing the surface morphology of materials. Surface structures of several microns to several hundred microns can be prepared on solid materials by plasma treatment, physical surface roughness and mechanical processing, etching, vapor deposition, electrochemical method and nanotube (rod) array method [6–8].

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In order to research and develop better superhydrophilic surfaces, the combination of changing the surface morphology of materials and surface modification is also important research directions. Surface grafting modification, gelation modification and diversified modification all can change the surface energy of the material surface [9–11].

As a precision machining tool, laser has the advantages of high power density and controllable machining precision. It is a convenient, fast and controllable method to produce metal-based superhydrophilic surfaces [12–15]. Some researchers have proposed a method to prepare superhydrophilic surface by laser etching aluminum surface. By using laser to etch the grid-shaped regular rough surface on the surface of aluminum, the superhydrophilic surface is obtained and presents isotropy in the direction parallel to the surface [16]. Long J.'s laboratory investigated the reasons for the transition of superhydrophilic aluminum surface generated by laser etching to superhydrophobic surface after long exposure to air. Different substances in the air had been exposed to superhydrophilic aluminum for long periods of time. Finally, they found that the reason for this change was that organic compounds in the air combined with aluminum oxide on the surface of the laser-processed aluminum, showing hydrophobic properties [17]. Chi-vinh Ngo's laboratory explored ways to slow the transition and found that after 2 h in a boiling water bath. The transition from hydrophilic aluminum surface to hydrophobic surface was significantly inhibited [4].

In this study, a micron surface structure with high regularity was obtained by laser machining of aluminum surface. In order to increase hydrophilic ability and keep the superhydrophilic surface for a long time, a 45% ethanol boiling water bath treatment was introduced. Finally, it was found that the aluminum surface with this treatment had good superhydrophilic ability and stable property for a certain period of time.

2 Experiment

In this experiment, high-purity aluminum sheet (99.999% purity, Beijing institute of nonferrous metals) was used as the experimental material. The aluminum sheet was cut into a square of 15 mm*15 mm, and its surface oil stains and impurities were removed by ultrasonic cleaning with acetone for 20 min. After acetone cleaning, the aluminum sheet was cleaned with deionized water. Sodium hydroxide solution (1 mol/l) is used to clean the aluminum sheet, remove the alumina on the surface, soak for 10 min and clean the aluminum sheet with deionized water after cleaning.

Aluminum sheets were processed with a nanosecond laser (HANS laser EP-20-SHG). The laser processing parameters are shown in Table 1. One-way filling was performed by laser with a processing area of 10 mm*10 mm. The morphology of the sample was observed by field emission electron microscope (FEI Apreo) after laser burning. The surface chemical composition was analyzed by XRD.

The laser-processed aluminum sheets were placed in deionized water and 45% ethanol solution, respectively, and heated to a boil in a water bath pot for 120 min (both heat to 100°). Another group was prepared without water bath for comparison. Contact angle measurement instrument (Nakatomi JC2000DM) was used to test the contact angle of three groups of samples. If the contact angle is 0°, the time from the first contact of water droplets with the material surface to its completely absorbed by the surface of the material (using deionized water, droplet volume 3 μl, ambient temperature 25 °C) was measured. The surface functional groups of three groups of samples were detected by infrared spectrometer (Nicolet IS10).

Three groups of samples were placed in the same natural air environment and let stand for 1 h, 4 days, 10 days, 20 days and 40 days. Contact angle measurement instrument (Nakatomi JC2000DM) was used to test the contact angle of three groups of samples in different time periods (using deionized water, droplet volume 8 μl and ambient temperature 25 °C).

3 Results and discussion

3.1 Morphology

The morphology and structure of the aluminum plate after ablation under the condition of laser power of 8 W, scanning speed of 1300 mm/s and scanning interval of 0.005 mm are plotted in Fig. 1. Ablative traces can be clearly observed from the figure, which is because of the high laser intensity, the energy density of which is much higher than the ablative threshold of pure aluminum plate,

Table 1 Laser-ablated aluminum parameters

Laser parameter	Value
Power (W)	8
Wavelength (nm)	532
Pulse frequency (kHz)	20
Spot size (μm)	20
pulse duration (ns)	10–200
Focal length (mm)	224
Scanning line separation (mm)	0.005
Scanning speed (mm/s)	1300

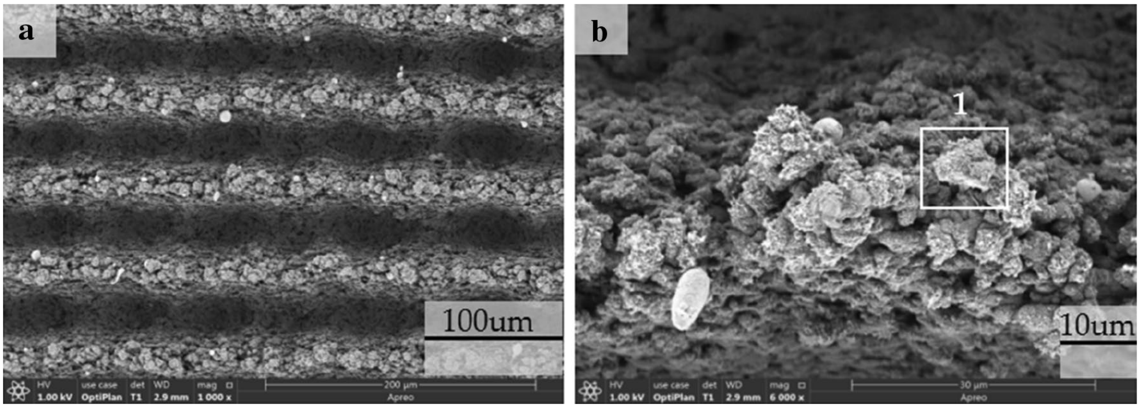

Fig. 1 SEM image of aluminum plate surface after laser-ablated aluminum: scanning speed 1300 mm/s and scanning interval 0.005 mm (1. micro-nanoparticles)

causing the surface material to melt and evaporate, thus obtaining micro-nanosurface structures. As shown in Fig. 1a, a distinct periodic ripple (transverse texture) with periods of about 90–100 µm was observed. Since the laser focusing spot is 20 µm, more than the scanning interval of 5 µm and the adjacent spot overlaps (the spot overlap rate is 75%), the texture direction is parallel to the scanning direction. Figure 1b shows an enlarged view of the local crest. From the figure, it can be observed that a large number of micro-nanoparticles are distributed on the surface of wave peak (shown in Fig. 1b, numbered 1), which is due to the evaporation and solidification of molten metal and metallic oxide, some of which are attached to the original surface, forming nanostructures. Therefore, the surface roughness of aluminum plate increases obviously after laser ablation. According to the Wenzel model, the construction of the micro-nanostructure can magnify the inherent wettability energy of the material surface. Therefore, it can be inferred that the striated micron structure formed by laser ablation improves the hydrophilic energy of the surface and even converts to superhydrophilic [18]. This is consistent with the morphological characteristics of aluminum sheet processed by nanosecond laser by Zhao team [15].

3.2 Wettability test

In order to evaluate the influence of water bath treatment and ethanol solution water bath treatment on the wettability of aluminum plate after laser ablation, CA measurement and other methods were used for comprehensive evaluation. Since the samples after boiling water bath treatment are superhydrophilic and the difference of measuring CA is small, the time of 3 µl water droplets completely spread on the sample surface is measured here. Figure 2 shows the process of water droplets diffusing

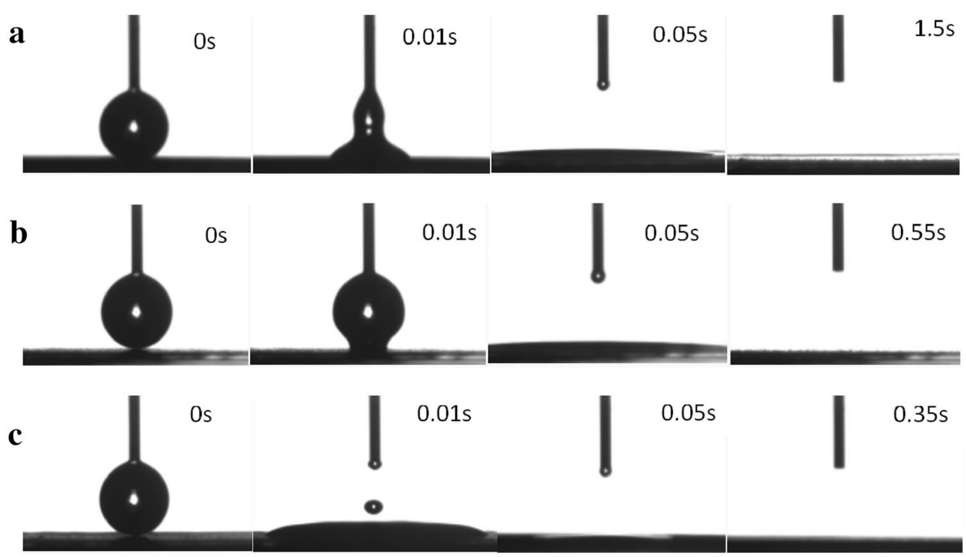

Fig. 2 Test the CA of aluminum plate after laser-ablated aluminum and post-treated: **a** experimental group with only laser treatment. **b** Laser and the boiling water bath heating treatment. **c** Laser and the ethanol solution boiling water bath heating treatment

on the surface of aluminum plate after three groups of tests. It can be seen that the water droplets have not completely spread on the surface of the sample without any post-treatment (laser-ablated aluminum plate) after 1.5 s. Boiling water bath treatment: water droplets are completely flattened within 0–0.05 s and completely spread on the surface at 0.55 s. Ethanol solution boiling water bath treatment: water droplets are completely spread in 0–0.05 s. From the diffusion time of water droplets, it can be observed that the wettability of the sample after boiling water bath and boiling water bath with ethanol solution is significantly better than that of the sample without any post-treatment, while the hydrophilicity of the sample after boiling water bath with ethanol solution is better than that of the sample after boiling water bath.

In order to compare the hydrophilic persistence of the three groups of samples, the aluminum samples of the three groups after treatment were exposed to constant temperature air at 26 °C for a period of time. The difference of persistence was judged by comparing the degree of CA changes in three groups of samples over a period of time [2]. If CA changes little in a certain period of time, the hydrophilic stability is good. According to the experimental results (as shown in Table 1), wettability changes in all three groups of samples after being exposed to air for a period of time. Without any treatment, the CA in the experimental group began to increase at 10 days and changed to 150.5° at 40 days. The CA in the boiling water bath heating and ethanol solution boiling water bath heating groups both began to increase at 20 days and reached 75.9° and 11.3° at 40 days, respectively. In conclusion, the samples treated with 45% alcohol solution boiling water bath showed strong hydrophilic persistence (Table 2).

3.3 Mechanism

The test results of XRD analysis of the aluminum surface after laser ablation are plotted in Fig. 3. The results show that the materials on the surface of aluminum after laser burning are mainly aluminum and alumina. In the pretreatment process of aluminum sheet, sodium hydroxide is used to remove the original alumina on the surface of aluminum sheet, so it can be considered that the alumina observed in the XRD analysis belongs to the products after laser ablation. Polar molecules on the surface of materials have an important influence on the hydrophilicity of materials. The hydrophilicity of materials increases with the increase in the number of polar molecules and the number of polar sites of polar molecules. Alumina has a large number of polar sites, so aluminum oxide produced by laser burning of aluminum increases the hydrophilicity of the surface.

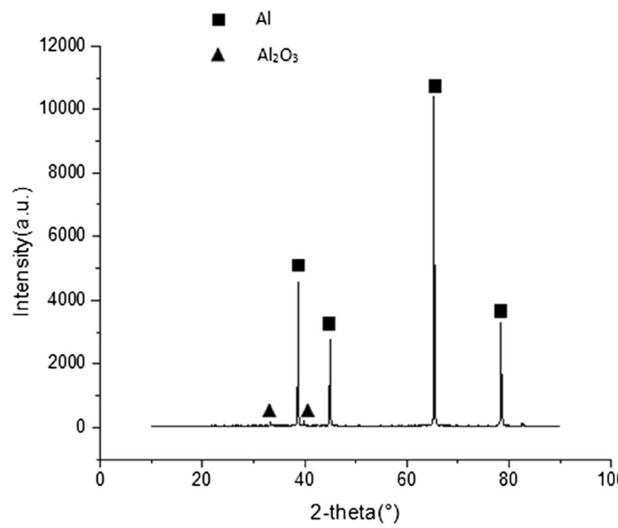

Fig. 3 XRD test results of laser-ablated aluminum samples surface

The FT-IR results obtained in 1 h after the laser-ablated only and laser-ablated plus post-treated aluminum surface are plotted in Fig. 4. Functional groups (–OH) were detected on the surfaces of the untreated group. It was found from previous experiments that alumina was the main reason for the superhydrophilic aluminum surface to become superhydrophobic in air (–OH on the surface of alumina adsorbed hydrophobic organic matter in air) [19–21]. This group causes the sample surface to adsorb organic substances in the air, so the weak hydrophobic group (–CH_3) is also detected in the untreated group. It explained that the laser ablation of aluminum surface without any treatment changed the superhydrophilic surface to superhydrophobic in 40 days.

After laser burning, the treated surface consists of the mixture of aluminum and alumina. After the treatment of

Table 2 CA of aluminum samples after laser-ablated aluminum and post-treated changes with time

Treating processes	CA (°)				
	After 1 h	After 4 days	After 10 days	After 20 days	After 40 days
Without any treatment	0	0	10.5 ± 0.5	30.4 ± 1.2	150.5 ± 1.7
Boiling water bath heating 2 h	0	0	0	15.7 ± 0.5	75.9 ± 1.5
Ethanol solution boiling water bath heating 2 h	0	0	0	4.6 ± 0.2	11.3 ± 0.2

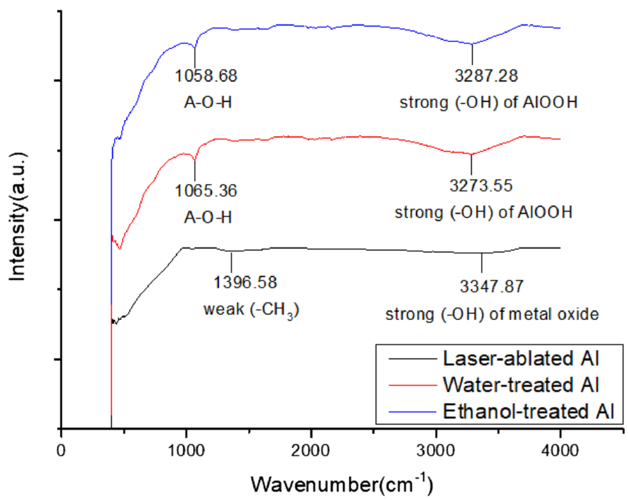

Fig. 4 FT-IR results of laser-ablated aluminum surface and post-treated aluminum surface

boiling water bath, aluminum reacts to form pseudoboehmite [22, 23]. Aluminum can form pseudoboehmite in boiling water, as shown in Eq. 1 [24]:

$$Al + 2H_2O \rightarrow AlOOH + \frac{2}{3}H_2. \tag{1}$$

As shown in Fig. 4, the formation of pseudoboehmite in the boiling water bath and boiling water bath with ethanol solution samples was observed. Strong groups (–OH) were detected at 3273.55 cm^{-1} and 3287.28 cm^{-1} and Al–O–H was detected at 1065.36 cm^{-1} and 1058.68 cm^{-1} in the bands of water bath treatment and alcohol solution treatment, respectively, which is the characteristic of AlOOH [25–28]. It is well known that both pseudoboehmite (have a lot of hydroxyl) and alumina are good hydrophilic substances, and the formation of them on the surface of aluminum increases the hydrophilic energy of the surface [29]. That explains the wettability of the sample after boiling water bath and boiling water bath with ethanol solution is significantly better than that of the sample without any post-treatment.

The polarity of ethanol is less than that of water, so the polarity of the solution decreases when ethanol and water are mixed in proportion, thus reducing the inter-molecular gravity, and prevent rapid agglomeration after the formation of pseudoboehmite. Adding ethanol as a kind of structure regulator in the preparation of pseudoboehmite can make the morphology of the resultant pseudoboehmite more regular [30, 31]. After passing through the boiling water bath, the pseudoboehmite is more evenly generated on the surface of the sample due to the action of ethanol. In this way, more hydrophilic groups are exposed to the outside world at the same boiling water bath time. That explains the hydrophilicity of the sample after boiling water bath with ethanol solution is better than that of the sample after boiling water bath.

4 Conclusion

Superhydrophilic structure was prepared by nanosecond laser on an aluminum plate. Soaking in a water bath with ethanol solution provides good superhydrophilicity, and the contact angle only increases to 11.3° after being placed in the air for 40 days, which shows good hydrophilic persistence. In this way, stable superhydrophilic surfaces can be prepared quickly, which is a simple and cost-effective way to be widely used for industrial production. In addition, the potential application of this method also shows that the treated surface is superhydrophilic and has strong hydrophilic persistence, so it can be widely used in anti-atomization, medical devices, sensors and other industries.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no competing interests.

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