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A hybrid laser ablation and chemical etching process for manufacturing nature-inspired anisotropic superhydrophobic structures

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Abstract
The surface with anisotropic superhydrophobicity has great potential applications for drag reduction, drug delivery and microfluidic devices. Observation from natural biological surfaces proved that directional microstructures are indispensable to realize anisotropic superhydrophobicity. However, current lithography-based manufacturing approaches have limited capabilities to scale-up for real world industrial applications. This paper proposes a hybrid laser ablation and chemical etching process for manufacturing ratchet-like microstructures on 316L stainless steel for the first time. It harvests the advantages of both processes. The laser ablation will form specified recast layer and covered by oxide layer on the specimen, and these two layers can be easily removed in the chemical etching process hence to obtain the periodic ratchet-like microstructures. According to the experimental results, the direction of microstructures is same as with the laser beam feed direction. The width and depth of microstructures also can be well-controlled by laser power and pitch. The specimens with pith of 25 μm have contact angle larger than 150°. And the droplet easily rolls off along the laser beam feed direction but is pinned tightly in the opposite direction.

Laser ablation; Chemical etching; Superhydrophobic surface.

1. Introduction

Natural biological surfaces, such as lotus leaf, rice leaf, fish scale and butterfly wings have attracted so much attention over the last few decades. It is mainly due to their special wettability that formed during long-time evolution and natural selection. Surface with anisotropic hydrophobicity can realize unidirectional droplet transportation, which has tremendous applications for drag reduction, drug delivery, and microfluidic devices [1–5]. The natural surface that possesses capabilities of transporting liquid directionally exists in spider silk, shorebird's beak, butterfly wing, desert beetle, Nepenthes peristome and cactus spine [6]. For example, on a butterfly wing a water droplet will roll off along one direction with a small rolling angle while shows a pinned state along the opposite direction. This was found that the asymmetric microstructures of butterfly wings led to the unstable state of the water droplet and made it easily roll off along the radial direction away from the body [7]. Bixler reported that butterfly wings possess unique surface properties that combine the anisotropic flow, superhydrophobicity and low adhesion force with water [1,8]. The author also found that aligned shingle-like scales in butterfly wings provided anisotropic flow leading to low drag, while microgrooves on its top offered superhydrophobicity and low adhesion properties [8]. Liu et al's research concluded that unbalanced surface tension on static conditions and fog drops contract asymmetrically from the surface on dynamic conditions were the underlying mechanism for directional flow of fog drops [4]. Therefore, directional microstructures are indispensable to realize anisotropic superhydrophobicity.

In addition to the research efforts devoted to exploring the mechanisms of anisotropic flow, there is also a growing effort to develop varied manufacturing process to synthesize surface with directional transport property. The main present approaches include lithographically, replica moulding, aqueous sol-gel and chemical reduction [6–12]. For instance, Guo et al. employed soft lithography technique to replicate taper-ratchet structure of natural ryegrass leaf on polymer surface. The prepared samples displayed a robust property of directional water shedding-off [7]. Song et al. reproduced porous hierarchical architecture of butterfly wings use SnO_2 through an aqueous sol-gel soakage process with the assistance of anhydrous ethanol [9]. However, the high cost and complicated processes limit the promotion of nature-inspired structured functional surfaces for industrial-scale production and application.

In this study, a novel, highly-efficient technique for the manufacture of asymmetric microstructures is developed using nanosecond pulsed laser ablation followed by chemical etching. The new approach offers advantages for the fabrication of asymmetric microstructures. First of all, the undesired oxide layer and recast layer which result in short service life, poor surface quality and appearance, will be removed through chemical etching process. Secondly, the asymmetric microstructures will form on the surface, which realised anisotropic superhydrophobicity. Furthermore, the direction, depth and width of microstructures can be well-controlled through setting up corresponding laser machining parameters.

2. Work principle of hybrid laser ablation and chemical etching process and experimental setup

2.1 Work principle of hybrid laser ablation and chemical etching process

The schematic of the hybrid laser ablation and chemical etching process is illustrated in Figure 1. First, the laser pulses are focused on the specimen by an objective lens, inducing microchannels on the surface of specimen. The laser pulses will be obliquely irradiated to the surface due to the resultant motion of feed and pulsed direction and result in asymmetric ratchet-like recast layer. Then, the laser ablated specimen is treated by an aqueous solution of ferric chloride hexahydrate (32g FeCl3 · 6H2O, 3ml of 37% HCl, 3ml of 85% H_3PO_4, 120ml H_2O) to remove the oxide layer, laser induced recast layer and obtain periodic ratchet-like laminar structures. Lastly, the specimens were cleaned ultrasonically with deionized water, acetone and ethanol successively and silanized in a vacuum oven using silane reagent (1H, 1H, 2H, 2H-Perfluorooctyltriethoxysilane, 97%, Alfa Aesar Ltd), at 100℃ for 12 hours to reduce their surface free energies.

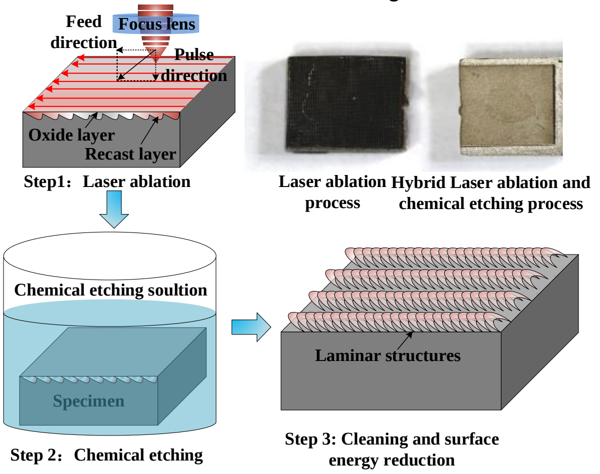


Figure 1. Schematic illustration of the manufacturing process of superhydrophobic ratchet structures.

2.2 Materials and experimental setup

The AISI 316L stainless steel was used as the experimental material in this research. Before laser machining, the stainless steel plates were machining by a flat end mill (with a diameter of 6 mm). The surface roughness (Sa) was 0.2 µm after the milling operation. A nanosecond pulsed fibre laser which has a central emission wavelength of 1064 nm. The laser source has a nominal average output power of 20 W and its maximum pulse repetition rate is 200 kHz. Details of the operational conditions for the experiments are shown in Table 1.

Table 1 Operational conditions for experiments

Number	Pitch (µm)	Laser power (W)	Feed rate (mm/min)	Feed direction
1	25	10	30	Unidirectional
2	25	15	30	Unidirectional
3	25	20	30	Unidirectional
4	25	20	30	Bidirectional
5	50	10	30	Unidirectional
6	50	15	30	Unidirectional
7	50	20	30	Unidirectional

The surface morphologies of specimens were measured by a scanning electron microscope (SEM). The contact angle on surfaces was measured by a drop shape analyzer (Kruss Ltd.). The selected water droplet volume was 5 µL. For each specimen, the contact angle of the water droplet was measured three times and the average value was adopted.

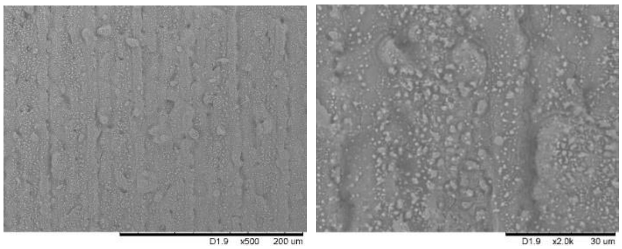
3. Results and discussion

3.1 Surface morphologies and composition

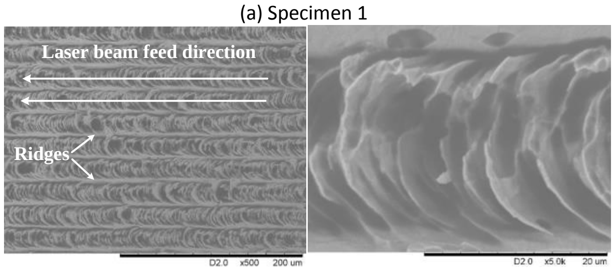
The morphologies of specimens after laser ablation and chemical etching process are presented in Figure 2. the absorbed energy from the nanosecond laser pulses melts the stainless steel and heats it to a temperature at which the atoms gain sufficient energy to enter into a gaseous state. Due to the vapour and plasma pressure, the molten materials are partially ejected from the cavity and form surface debris. At the end of a pulse, the heat quickly dissipates into the bulk of the work material and recast layer are formed as shown in Figure 2 (a).

During the chemical etching process, the oxide layer and recast layer were removed from the surface, and the laminar microstructures were formed. As shown in Figure 2 (b), (c), (d), (f), (g), (h), the direction of titled microstructures is towards the laser beam feed direction. To verify the above rules, the specimen 4 was employed bidirectional laser beam feed direction. As expected, bidirectional microstructures were formed as shown in Figure 2 (e). Therefore, we can conclude that the direction of microstructures can be well-controlled by the laser beam feed direction.

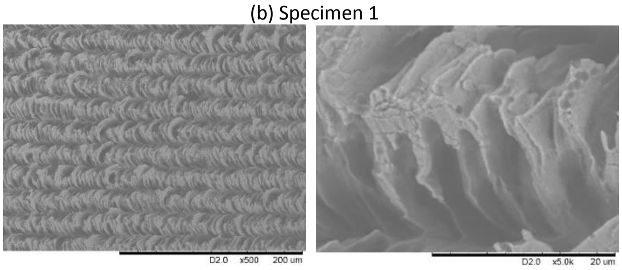
At the laser power of 10 W (Figure 2 (b)), the surface morphologies are laminar periodic microstructures with clear boundaries between the adjacent rows and well-separated by ridges. However, the adjacent rows of microstructures are connected together when the laser power further increased to 15 W and 20 W and no ridges are observed after the chemical etching process. The underlying principle is the increased laser power result in larger recast layer. Thus, the depth and width of etched microstructures also show an increasing trend with the increase of laser power. For a larger pitch of 50 µm, the space between adjacent rows shows a similar decreasing trend with laser power increase as shown in Fig .2 (f), (g), (h). In addition, it can be observed that the depth of microstructures shows an increasing trend with the increase of lase power. Thus, the width and depth of microstructures are determined by the pitch of microstructures and the laser power.



(a) Specimen 1



(b) Specimen 1



(c) Specimen 2

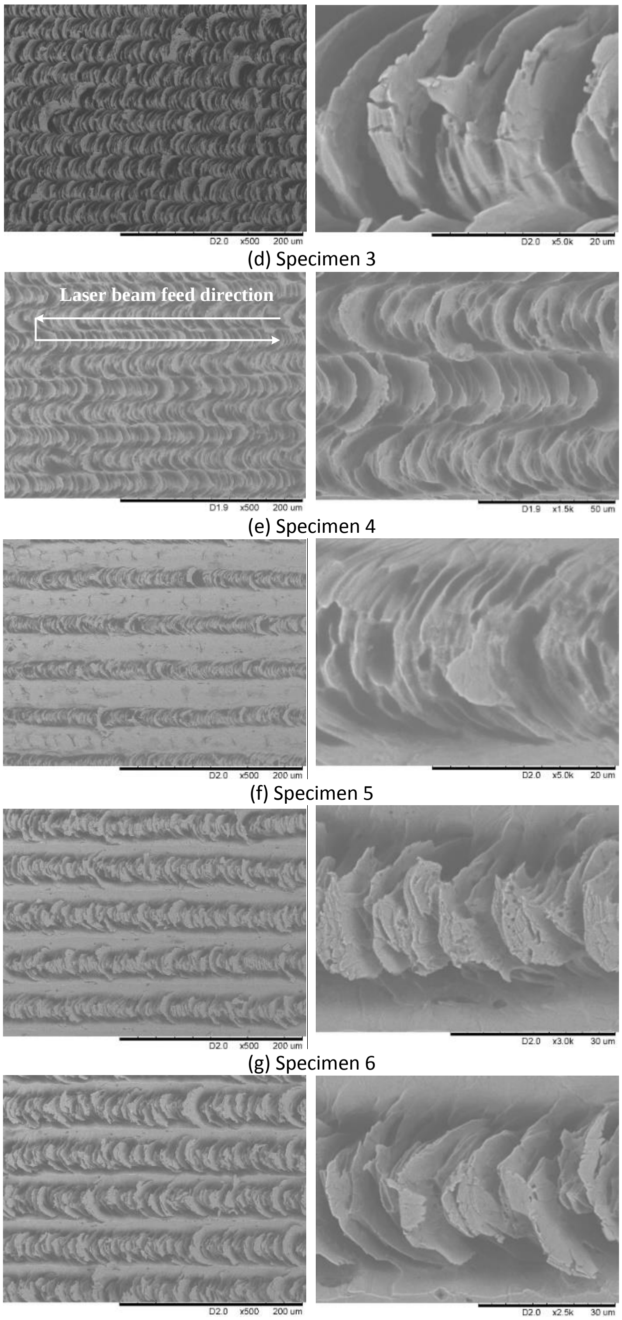


Figure 2. SEM image (left) and high-magnification image (right) of Specimens (a), Specimen 1 with pitch of 25 μm after laser ablation (b),(c),(d),(e),(f),(g),(h) surface morphologies of specimens 1 to 7 after chemical etching.

Figure 3 show X-ray diffraction patterns (XRD) of smooth surface, laser ablated surface and surface fabricated by hybrid laser ablation and chemical etching process of 316L stainless steel. In Figure 3(a), there are four sharp diffraction peaks corresponding to the XRD pattern of austenite and one peak for ferrite. For the laser-machined surface, it was found that austenite, Fe_3O_4 and Fe_2O_3 were recognized on the XRD pattern. Figure 3 (c) shows that there is no iron oxide stay on the surface machined by the hybrid laser ablation and chemical etching process.

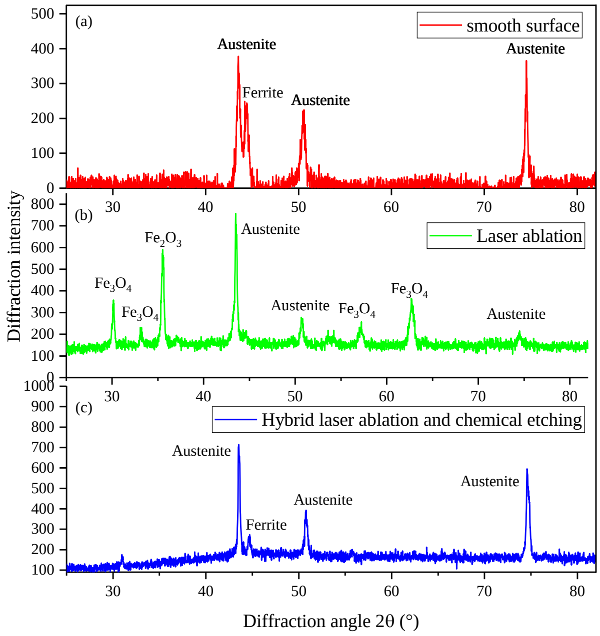


Figure 3. X-ray diffraction pattern of 316L stainless steel at different process (a) smooth surface (b) laser ablation (c) Hybrid laser ablation and chemical etching.

The above results proved that the main components of oxide layer are Fe_3O_4 and Fe_2O_3 on the specimen. Hence, the details of the chemical reaction can be expressed as:

$Fe_3O_4 + 8HCl \rightarrow FeCl_2 + 2FeCl_3 + 4H_2O$ (1)

$3Fe_3O_4 + 8\ H_3PO_4 \rightarrow 6\ FePO_4 + Fe_3(PO_4)_2 + 12\ H2O$ (2)

$Fe_2O_3 + 6HCl \rightarrow 2FeCl_3 + 3H_2O$ (3)

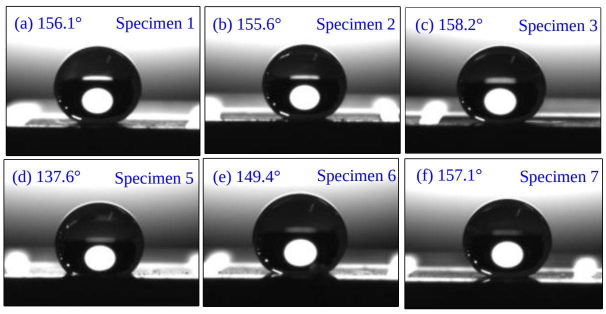
$Fe_2O_3 + 2H_3PO_4 \rightarrow 2FePO_4 + 3H_2O$ (4)

$Fe+2FeCl_3 \rightarrow 3FeCl_2$ (5)

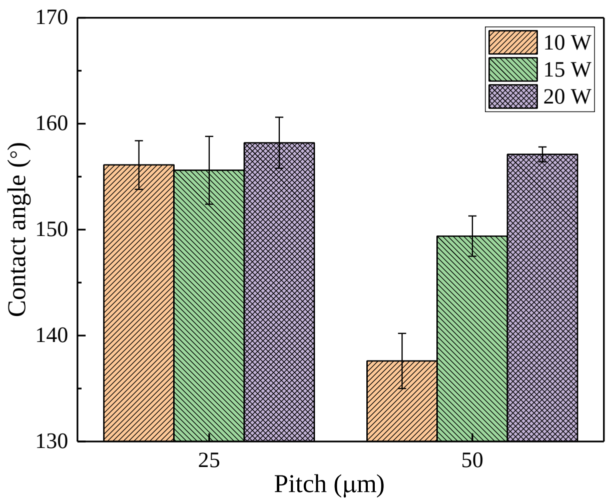
As shown in Eq (1), (2), (3) and (4), the oxide layer will react with acid to form corresponding salt and water. And the iron will react with ferric chloride to produce iron(II) chloride simultaneously.

3.2 Hydrophobicity of specimens

Figure 4 (a) shows the captured images of water droplets on different specimens. Figure 4 (b) shows the variation of the contact angle of the machined surfaces versus pitches obtained under different laser power. The contact angle for the specimens with the pitch of 25 μm are similar when the average laser power were increase from 10 W to 20 W, which are 156.1°, 155.6°, 158.2° respectively. However, increasing laser power will lead to the contact angle increase significantly from 137.6° to 157.1° for specimens with the larger pitch of 50 μm. The larger laser power results in a smaller unstructured region in a smaller solid-liquid contact area, which will be beneficial to hydrophobicity of the specimen.



(a)



(b)

Figure 4 (a) Captured images of water droplets (b)Variation of contact angle versus pitches for different laser power

Figure 5 shows the anisotropic superhydrophobicity of Specimen 3. A 5 μl drop has a rolling-off angle of 7° when the dip direction of specimen is the same as the laser beam feed direction. However, the water droplet shows a pinning state in the opposite direction, due to the taper-ratchet structure (illustrated as the right insets). The decreaseing dynamic solid-liquid contact area results in smaller adhesion force when the specimen has the same dip direction as the direction of ratchet-like microstructures. In contrast, the adhesion force shows an increasing trend when the water droplet flows along the opposite direction of microstructures.

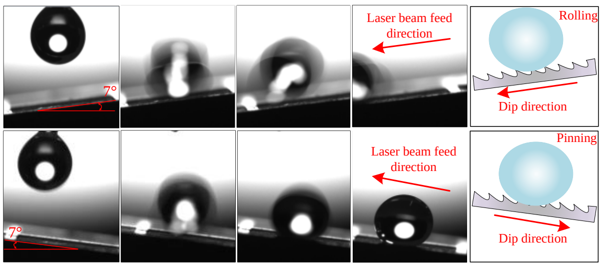


Figure 5 Anisotropic superhydrophobicity of Specimen 3

4. Conclusions

A hybrid laser ablation and chemical etching process was proposed for the first time in this paper to generate anisotropic superhydrophobic structures on 316L stainless steel. The experimental investigation concluded that the direction of microstructures is same as the laser beam feed direction. The width and depth of microstructures are determined by the pitch of microstructures and the laser power. The specimens with pitch of 25 μm will have contact angle larger than 150°. The droplet easily rolls off along the laser beam feed direction but is pinned tightly in the opposite direction.

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