Influence of laser surface texturing on a low-adhesion and superhydrophobic aluminium alloy surface

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An aluminium alloy surface with a microgroove array was fabricated via laser processing, and exhibited superhydrophobicity. The as-prepared surface showed excellent anti-adhesion properties and potential self-cleaning behaviour. The wettability of the fabricated surface was investigated by measurement of the water contact angle. The surface morphology and chemical composition were characterised by scanning electron microscopy and X-ray photoelectron spectroscopy, respectively. The wettability of the surface was successfully modified from hydrophilicity to superhydrophobicity by the laser processing. The water contact angle was increased to 155°, and the sliding angle reduced to <5°, without any chemical modification. Water droplets on the surface existed in an almost perfectly suspended state, resembling a model Cassie state. The superhydrophobic surface showed excellent stability under conditions of external extrusion. This easy and inexpensive modification method is expected to play an important role in extending the applications of aluminium alloys.

1. Introduction: Wettability, an inherent property of solid materials, is usually defined with respect to the contact angle and sliding angle. A surface is considered superhydrophobic if it has a contact angle of >150° and a sliding angle of <10°. Superhydrophobic surfaces are an increasing target of research because of their practical importance in many industries. Their potential uses include self-cleaning [1], anti-adhesion [2, 3], anti-icing [4, 5], water repellence [6], drag reduction in micro-fluidics [7] and prevention of corrosion [8, 9]. Naturally occurring surfaces vary widely in wettability, depending on their geometrical structure and chemical composition. In recent years, a number of techniques for preparing superhydrophobic surfaces have been developed, such as chemical etching [10, 11], electrodeposition [12, 13], flow plating [14], solution immersion [15], interference lithography [16] and High Speed-Wire Cut Electrical Discharge Machining (HS-WEDM) processing [17]. However, most of these methods are limited by their technical complexity and the need for expensive equipment, which greatly increase the final production costs. The development of an easy and economical method is therefore an essential but difficult challenge.

In this study, a superhydrophobic surface was successfully fabricated on an aluminium alloy. The initially hydrophobic structure was successfully modified to a superhydrophobic structure without any chemical modification by an easy and efficient laser technique. The superhydrophobic surface showed excellent low-adhesion properties and remarkable stability against stress.

2. Experimental

2.1. Materials: 20 mm × 20 mm × 2 mm 7075 aluminium alloy was purchased from Shanghai Aofeng Metal Product Co. Ltd., China. Sandpaper (nos. 600–2000) was provided by Hubei Yuli Abrasive Belts Group.

2.2. Fabrication: First, the aluminium alloy was polished using sandpaper (nos. 600–2000), cleaned ultrasonically with acetone followed by deionised water, and then blow-dried under atmospheric conditions. Next, groove structures were etched onto the polished aluminium alloy surface, with a distance of 50 µm between the centres of adjacent grooves, by a laser-marking machine (HBS-GQ-20, Beijing, China). The laser scanning was performed twice, with a speed of 500 mm/s, the power of 8 W, the focal spot size of 0.05 mm, the frequency of 20 kHz and the laser type of fibre laser marking machine. Finally, the as-prepared surfaces were cleaned ultrasonically in deionised water and placed in air for 30 days. Fig. 1 shows a schematic representation of the process. The labels P and D represent the spacing and width of the grooves, respectively.

2.3. Characterisation: The morphologies of the aluminium alloy surfaces were observed by scanning electron microscopy (SEM, COXEM-30) and confocal laser scanning microscopy (CLSM; LEXT-OLS3000). The surface chemical composition was examined by X-ray photoelectron spectroscopy (XPS, SPECS XR50). The wettability of the surfaces was determined from the static contact angle and sliding angle, which were measured using a contact angle meter (Data Physics OCA15 Pro) with a water droplet volume of 4 µL at room temperature.

3. Results and discussion

3.1. Surface morphology: The contact angle and microstructure of the surface of a rice leaf are presented in Figs. 2*a* and *b*. The contact angle on the rice leaf surface is roughly 150°. It can be seen in Fig. 2*b* that the rice leaf surface is composed of many uniformly distributed, micro-scale trough-type structures and mastoids. The distance between nearest-neighbour troughs is generally in the range of 20–30 µm, and the diameter of the micro-mastoids is about 4–20 µm. The micro-mastoids and troughs endow the rice leaf with superhydrophobic properties. This is consistent with the knowledge that hydrophobic surfaces are usually associated with geometrical micro-structures and surface roughness. An SEM image of the as-prepared aluminium surface is shown in Fig. 2*c*. The surface is covered with multiple groove structures, where the distance between the centres of adjacent grooves is about 48 µm, and the width of each groove is 35–40 µm. Numerous folded structures are also distributed on the surface, as a result of which the surface roughness is increased significantly. A single groove structure is shown in magnification in Fig. 2*d*. From this picture, it is clear that the grooved surface is covered with micro- and submicro-sized grains, with grain diameters of 0.8–5.2 µm. The intense energy transmitted by the scanning laser beam produced an immediate jump in temperature on the alloy surface. This led to the formation of shoulders on the

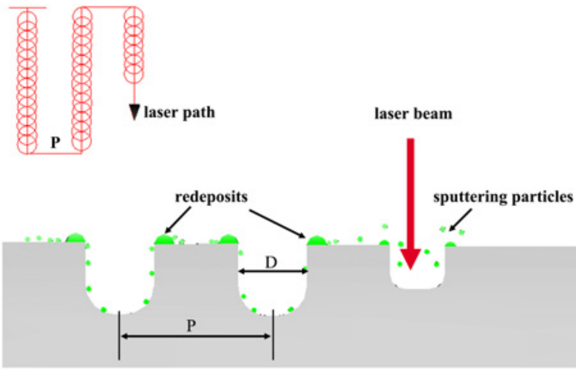

Fig. 1 *Schematic of laser processing*

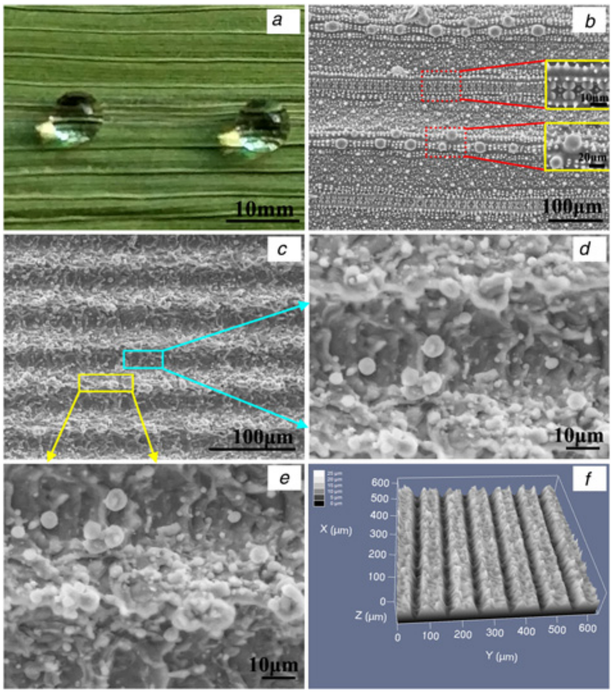

Fig. 2 *Morphologies of the surface of a rice leaf and the superhydrophobic surface of aluminium alloy*
a Photographs of water droplets on a rice leaf
b SEM image of a rice leaf
c–e SEM images of the groove structure of the as-prepared sample
f 3D image from CLSM of the sample

surface, surrounded by areas of redeposited material. The resulting surface presented a microstructure of myriad wave-like laminated structures, arranged regularly on the inner walls of the grooves. The height of the groove gaps was determined by the stacking of the sputtering grains, as shown in Fig. 2*e*. The grains were densely distributed on the surface. This rough structure was capable of trapping a large amount of air, which prevented the wetting of the solid surface by water droplets by significantly reducing the actual contact area between droplet and surface. A more intuitive image of the morphology of the superhydrophobic surface was obtained by CLSM (Fig. 2*f*). The 3D morphology of the as-prepared surface presented uniform grooves, clearly visible in the figure. The upper edges of the grooves were covered by numerous conical protrusions. The depth of each groove was about 20 µm.

3.2. Chemical composition: The chemical composition of superhydrophilic surface and superhydrophobic surface was examined by XPS. The XPS survey spectrum of superhydrophilic surface and superhydrophobic surface is shown in Fig. 3, revealing the presence of C, O, Si and Al. Strong peaks of C1s at 284.57 eV and Si2p at 101.7 eV in the XPS spectra of superhydrophilic surface (Fig. 3*a*) and C1s at 283.86 eV and Si2p at 101.16 eV in the XPS spectra of superhydrophobic surface (Fig. 3*c*) can be seen respectively. Compared with the initial aluminium alloy substrate, the contents of C and Si were decreased on the superhydrophilic surface by laser processing, but the contents of C were markedly decreased and the contents of Si increased on the superhydrophobic surface. This implies the formation of a silica thin film on the superhydrophobic surface.

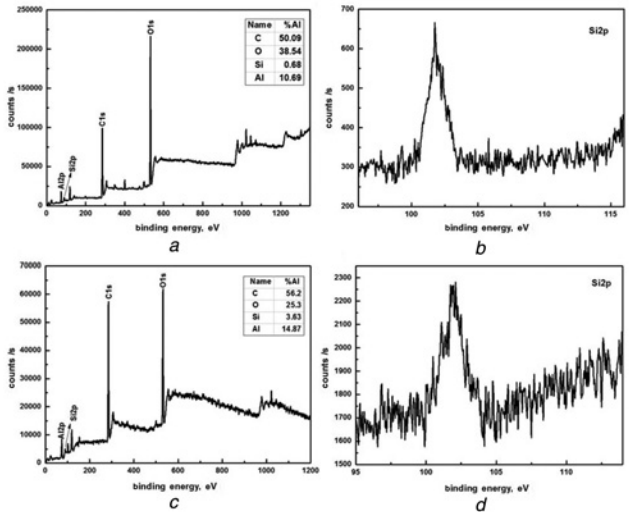

Fig. 3 *XPS spectra of the sample surface*
a Survey spectrum of superhydrophilic surface
b Si2p spectrum of superhydrophilic surface
c Survey spectrum of superhydrophobic surface
d Si2p spectrum of superhydrophobic surface

After the fabricated sample via laser processing was placed in air for a period of time, a silica thin film can be formed on the sample surface because of the contact between the sample and the air, and the surface energy was decreased. With the increasing of the bareness time in air, the surface energy was decreased continuously, which made the contact state between the droplet and the sample surface transform into Cassie theoretical model. Considering that microstructures with thin films are known to stabilise Cassie states [18], this would be expected to amplify the hydrophobicity of the rough substrate.

3.3. Modification of wettability: The wettability of the as-prepared surfaces was determined by measurement of the water contact angle. The obtained results are shown in Fig. 4. The contact angle of the surface newly prepared by laser processing was ~0°, indicating completely hydrophilic properties (Fig. 4*a*). Microscopically rough structures enable a large actual contact area between water droplets and the solid surface. The roughness of superhydrophilic surfaces therefore increases their wettability [19]. We also evaluated the contact angle on the surface of the sample that had been placed in air for 30 days. The contact angle increased to 154.5 ± 1.5°, with a sliding angle of 4.5 ± 1.1°. This indicated that the aerated surface not only had greater superhydrophobicity but also lower adhesiveness for water (Figs. 4*b* and *c*). The photograph in Fig. 4*d* clearly illustrates the morphology of water droplets on the surface, which present a perfect spherical state.

The behaviour of a water droplet was tested in response to compressive deformation on the surface, as shown in Fig. 5. The water droplet maintained its shape in the initial (uncompressed) state, as

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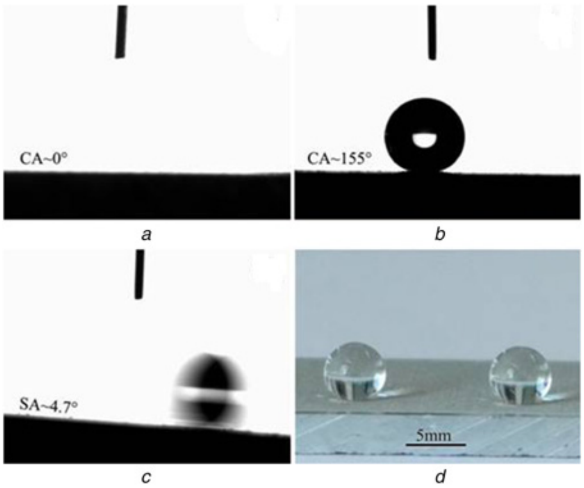

Fig. 4 *Water CA and SA of the as-prepared sample and photographs of water droplets on the surface*
a CA ≃ 0° (newly prepared)
b CA = 155° (stored in air for 30 days)
c SA ≃ 4.7°
d Water droplets placed on the surface

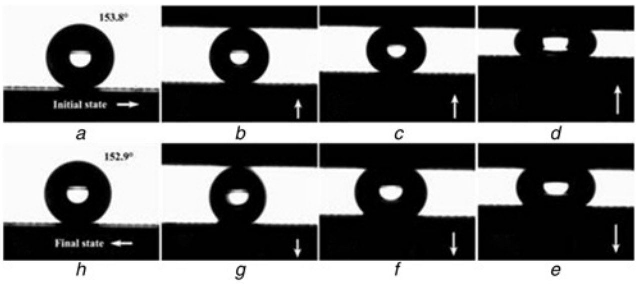

Fig. 5 *Sequence of photographs in the compression test of a water droplet on the sample surface*
a Initial state
b–d Compressed state
e–g Decompression (removal from the upper surface)
h Final state

shown in Fig. 5*a*. When the water droplet was raised, bringing it into contact with the solid surface above it, no deformation was evident at first (Fig. 5*b*). However, as the water droplet was raised further into a progressively narrower space, the deformation of its morphology became increasingly evident (Figs. 5*c* and *d*). At the moment of maximum deformation, the water droplet was held in place for 2 s (Fig. 5*d*). When the water droplet was removed from the upper solid surface, it almost perfectly regained its initial shape (Figs. 5*e–h*). The wettability of the surface had not been affected by the external stress. Meanwhile, the contact angle was also found to be nearly unchanged before and after loading of the droplet, with a reduction of only about 1.1°. Under the applied pressure, the water infiltrated downwards into the grooves. However, the air captured by the internal microstructure prevented the complete infiltration of water. Contact between liquid and solid occurred at the top of the surface protrusions, as predicted by the Cassie model. The pockets of captured air limited the infiltration of liquid. Therefore, the wetting state of the as-prepared rough surface can be considered as a model Cassie state. The superhydrophobic surface showed excellent stability under the applied pressure.

4. Conclusions: In summary, we have fabricated a superhydrophobic surface on an aluminium alloy substrate via laser processing. The wettability of the surface changed from hydrophilicity to superhydrophobicity without any chemical modification. The superhydrophobic surface repels water droplets, which do not stick and can easily slide off the surface with a slight tilt. The as-prepared surface shows excellent anti-adhesion properties and potential self-cleaning behaviour. In addition, the superhydrophobicity of the surface enhances its stability under applied pressure, and water droplets on the surface remain suspended in a model Cassie state. The modification method is efficient and technically straightforward, and has the potential for extensive practical application.

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6 References

[1] Celia E., Darmanin T., Givenchy E.T.D., ET AL.: 'Recent advances in designing superhydrophobic surfaces', *J. Colloid Interface Sci.*, 2013, **402**, pp. 1–18
[2] Watson G.S., Green D.W., Schwarzkopf L., ET AL.: 'A gecko skin micro/nano structure – a low adhesion, superhydrophobic, anti-wetting, self-cleaning, biocompatible, antibacterial surface', *Acta Biomater.*, 2015, **21**, pp. 109–122
[3] Liu Y., Liu J.D., Li S.Y., ET AL.: 'Fabrication of biomimetic superhydrophobic surface on aluminum alloy', *J. Mater. Sci.*, 2014, **49**, (4), pp. 1624–1629
[4] Yang C., Wang F.J., Li W., ET AL.: 'Anti-icing properties of superhydrophobic ZnO/PDMS composite coating', *Appl. Phys. A.*, 2016, **122**, (1), pp. 1–10
[5] Durret J., Frolet N., Gourgon C.: 'Hydrophobicity and anti-icing performances of nanoimprinted and roughened fluoropolymers films under overcooled temperature', *Microelectron. Eng.*, 2016, **155**, pp. 1–6
[6] Lai Y., Gao X., Zhuang H., ET AL.: 'Designing superhydrophobic porous nano-structures with tunable water adhesion', *Adv. Mater.*, 2009, **21**, (37), pp. 3799–3803
[7] Brassard J.-D., Sarkar D.K., Perron J.: 'Studies of drag on the nanocomposite superhydrophobic surfaces', *Appl. Surf. Sci.*, 2015, **324**, pp. 525–531
[8] Shi Y.L., Yang W., Feng X.J., ET AL.: 'Fabrication of superhydrophobic Zn Onanorods surface with corrosion resistance via combining thermal oxidation and surface modification', *Mater. Lett.*, 2015, **151**, pp. 24–27
[9] Gu C.D., Yan W., Zhang J.L., ET AL.: 'Corrosion resistance of AZ31B magnesium alloy with a conversion coating produced from a choline chloride—Urea based deep eutectic solvent', *Corros. Sci.*, 2016, **106**, pp. 108–116
[10] Darmanin T., Givenchy E.T.D., Amiqoni S., ET AL.: 'Superhydrophobic surfaces by electroche-mical processes', *Adv. Mater.*, 2013, **25**, (10), pp. 1378–1394
[11] Zhang J.L., Gu C.D., Tu J.: 'Robust slippery coating with superior corrosion resistance and anti-icing performance for AZ31B Mg alloy protection', *ACS Appl. Mater. Inter.*, 2017, **9**, (12), pp. 11247–11257
[12] Ju L.L., Xiao H., Ye L., ET AL.: 'Wettability evolution of different nanostructured cobalt films based on electrodeposition', *Micro Nano Lett.*, 2017, **12**, (7), pp. 470–473
[13] Huang Y., Sarkar D.K., Chen X.-G.: 'Fabrication of superhydrophobic surfaces on aluminum alloy via electrodeposition of copper followed by electrochemical modification', *Micro Nano Lett.*, 2017, **3**, (3), pp. 160–165
[14] Sun J., Wang L., Hu K., ET AL.: 'Fabrication of superhydrophobic surfaces on copper substrates via flow plating technology', *Micro Nano Lett.*, 2015, **10**, (2), pp. 88–92
[15] Liu Y., Yin X.M., Zhang J.J., ET AL.: 'Biomimetic hydrophobic surface fabricated by chemical etching method from hierarchically structured magnesium alloy substrate', *Appl. Surf. Sci.*, 2013, **280**, pp. 845–849
[16] Chaudhary A., Barshilia H.C.: 'Nanometric multiscale rough CuO/$Cu(OH)_2$ superhydrophobic surfaces prepared by a facile one-step solution-immersion process: transition to superhydrophilicity with

oxygen plasma treatment', *J. Phys. Chem. C.*, 2011, **115**, (37), pp. 18213–18220
[17] Wu S.Z., Wang J.N., Niu L.G., ET AL.: 'Reversible switching between isotropic and anisotropic wetting by one-direction curvature tuning on flexible superhydrophobic surfaces', *Appl. Phys. Lett.*, 2011, **98**, (8), pp. 81902–81904
[18] Wan Y.L., Lian Z.X., Xu J.K., ET AL.: 'Fabrication of the stainless steel surface with super durable one-direction superhydrophobicity and two-direction anisotropic wettability', *Micro Nano Lett.*, 2014, **9**, (10), pp. 712–716
[19] Cassie A.B.D., Baxter S.: 'Wettability of porous surfaces', *Trans. Faraday Soc.*, 1944, **40**, pp. 546–550

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