Rapid fabrication of near superhydrophobic aluminium surface through nanosecond laser texture and heat treatment

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Abstract. Controlling surface wettability inspired by nano structure of lotus leaf has attracted much attention. The superhydrophobicity on the metals is significant for the applications including water repellence, self-cleaning, anti-corrosion, and reduction of drag. Herein a near superhydrophobic surface of 5051 aluminium has been fabricated by employing a combination of nanosecond laser texture and heat treatment, without using any toxic chemicals. The aluminium surface was textured by fibre nanosecond laser and then heat treated at 150\,°C to create the near superhydrophobic surface. The evolution of heat treatment time with respect to contact angle measurements has been investigated. The contact angle became 0\,° when processed by two different kinds of laser textures (sinusoid pattern and grid pattern). The influence of heat treatment on the wettability of the laser textured aluminium surface was studied. The contact angle exhibits 134.88\,° and 136.97\,° for sinusoidal pattern and grid pattern with 72 hours heat treatment, respectively. The mechanism for fast wettability conversion time is discussed. This method is a rapid and environment-friendly process, which is feasible for fabrication.

1. Introduction

Aluminium and its alloys are widely used in aviation, transportation and other fields because of their excellent properties such as high strength and stable performance. Aluminium has a dense oxide film on the surface, which has good corrosion resistance. However, the oxide film is easy to be damaged under the condition of seawater and other environments, which seriously affects its application. Changing the wettability of aluminium alloy surface and preparing hydrophobic surface can effectively solve this problem\cite{1}. Natural functional surface has attracted much interest due to its excellent properties in the potential applications of industry\cite{2}. Self-cleaning, microfluidic control, water-oil separation and drag reduction can be employed by controlling surface wettability. Some attempts have been made to control the surface wettability by different ways, such as modifying the surface through chemical coatings and fabricating micro textures to change surface roughness.

A lot of techniques including vertically aligned carbon nanotubes, nanocasting and electron-beam lithography have been applied to fabricate the microstructures. The aim is to control the wettability by change the surface roughness on metals. However, these methods suffer from their disadvantages such as
as the high cost and time consuming due to the multiple steps. The size of micro nanostructures formed by chemical methods is affected by external conditions such as temperature and chemical solution concentration, and most of the reagents are highly corrosive reagents with poor safety and easy to pollute the environment.

With the development of laser techniques, many researchers have focus on the laser processing to fabricate the micro structures, which is less coat and complex compared with CVD and other chemical based methods[3-5]. Laser processing technology can directly prepare micro nanostructures on the surface of materials and accurately control the size of micro nanostructures. It has the characteristics of simple process, high preparation accuracy, wide range of processing materials and complex micro nanostructures. It is a preparation technology with broad application prospects and great potential. It is one of the research hotspots in the field of surface engineering in recent years. After laser processing, the surface structure is stable and it is easy to obtain stable superhydrophobic properties. Liu et al. investigated the aluminium based superhydrophobic surfaces prepared by picosecond laser. The effects of laser pulse number on the surface morphology and wettability of the samples were studied. With the increase of pulse number, the surface microstructure of the sample gradually changes from regular nano stripe structure to micro nano composite structure, and the surface roughness increases first and then decreases[6]. Li et al. studied surface of aluminium alloy textured by laser processing. The hydrophobic / superhydrophobic surface was prepared by modifying organosilane molecular film on the micro textured surface by self-assembly process. The micro morphology and wettability of micro textured surface were characterized by scanning electron microscope, three-dimensional topography instrument and contact angle measuring instrument. The results show that the interaction between laser micro texture and self-assembled molecular membrane plays an important role in the construction of superhydrophobic surface. The contact angle increases with the decrease of laser micro texture processing spacing, and is related to the morphology type of micro texture[7]. Furthermore, recent research shows that the surface of metal oxide micro nano structure formed by laser treatment is initially hydrophilic or super hydrophilic. With the passage of time, its surface becomes hydrophobic, even super hydrophobic in air[8].

In this study, nanosecond laser of 20 W was employed on the substrate of 5051 aluminium to fabricate the textures. The evolution of contact angles was investigated for the laser textures on aluminium surface with the sinusoidal pattern and grid pattern before and after heat treatment at 150°C. The resulted textures were analysed by 3D profile measurement microscope, scanning electron microscope (SEM), and optical contact angle measuring device to demonstrate the microstructure. The mechanism for the influence of laser textures and heat treatment on wettability was analysed in terms of surface roughness and surface energy.

2. Experiment

2.1. Material

5051 aluminium plate with 2 mm thickness was employed as the substrate. Before the laser texture process, the plate was cut into small pieces of 20 mm×20 mm. The samples were ultrasonically cleaned with ethanol for 10 minutes, and then cleaned with deionized water to remove the initial contaminants on the aluminium surface.

2.2. Fabrication method

Figure 1 presents the schematic diagram of the nanosecond laser fabrication process. Samples were fixed on the system. The laser of 20 W was employed to fabricate the different textures on aluminium with laser scanning speed 500 mm/s and pulse frequency 40 kHz. Before heating the samples with laser textured, a mechanical pump was applied to remove the existent gas in the oven and then fill the fresh air in it. Furthermore, the samples were put inside the oven at 150 °C with various times (30 min, 5h, 10h, 24h, 72h) for heat treatment.
2.3. Surface characterization method
Scanning electron microscopy (SEM: Hitachi S-3400N) were used to investigate the morphology of the aluminium surface. The 3D profile measurement microscope (VHX-5000, KEYENCE) was employed to evaluate the geometry of the texture. The water repellence of the samples was studied by measuring the contact angle using the sessile drop technique, with a video-based optical contact angle measuring device (JC2000D3M, Zhongchen, China). An 8 μL droplet of distilled deionized water was dispensed on the laser textured surface under atmospheric conditions, and the contact angle was calculated by analysing droplet images recorded just after the deposition.

3. Results and discussion
Figure 2 illustrates the 3D profile micrograph of the aluminium surface with different textures fabricated by nanosecond laser. The height of the micro-valleys was appropriately 17 μm. During the fabrication process of laser texture on the aluminium surface, some nano-particles and micro-particles were generated. These particles can attribute to the re-deposition along two sides of the texture lines.

Many nano and/or micro particles appeared on the aluminium surface along the texture as shown in Figure 3. The sinusoid and grid patterns are produced with the laser power of 20 W. Figure 3 demonstrates the micro-wall like structure or nano/micro particles stemming from recast material during the formation of laser texture. The aluminium have been removed by the nanosecond laser as illustrated in Figure 1, which is similar to the process of the Al₂O₃ treated by picosecond laser[9]. The re-deposited layer formed and accumulated along the valleys. Therefore, the height of the micro-wall structure increases the depth of the textures on aluminium surface. It affects the surface roughness, which can further have influence on the wettability. Once laser textured, the nano/microstructures generated. Nevertheless, it will change the shapes and/or structures via heat treatment at 150 °C. That means the microstructures did not change over time since nanosecond laser fabrication.
Figure 3. SEM images of: laser texture with (a) sinusoidal pattern and (b) grid pattern on aluminium surface after heat treatment at 150°C for 72 hours.

The contact angle of the flat aluminium surface was 51°. After nanosecond laser textured, the contact angle became 0° for both patterns. The contact angle increases gradually with the development of heat treatment. The evolution of contact angle is presented in Figure 4. When heating the laser textured samples at 150°C for 30 minutes, the contact angles reach 96.59° and 100.9° for the case of sinusoid and grid patterns, respectively. The value rises and climbs to 134.88° and 136.97° after 72 hours, respectively. Herein it can be summarized that the laser textured aluminium surface with different patterns converted from superhydrophilicity to near superhydrophobicity under the control of heat treatment.

Figure 4. The evolution of contact angles on laser textured aluminium surface with (a) sinusoidal pattern and (b) grid pattern for different heat treatment time.

Figure 5 shows the schematic diagram for the process of the surface conversion from superhydrophilic to near superhydrophobic on aluminium surface. The change of wettability can attribute to the surface roughness and the low surface energy of the metal surface. The surface roughness increases relying on the nano/micro structures with sinusoid and grid patterns fabricated by nanosecond laser. Alkyl, the main component of most organics, is nonpolar, so the adsorbed organics can effectively reduce the polarity of alumina surface, resulting in the change of surface wettability[4]. The heat treatment at 150 °C can accelerate the organic adsorption on the laser treated aluminium surface with two kinds of patterns to generate an organic layer. The surface near superhydrophobic can be obtained under the combination of laser textures and hydrophobic organic layer.
4. Conclusions
In this paper, 5051 aluminium was textured with nanosecond laser. The near hydrophobic surface was fabricated after heat treatment at 150 °C. Compared with other techniques, the method is environmentally friendly and feasible to fabricate. It can be obtained directly by nanosecond laser with sinusoidal pattern and grid pattern. In addition, it does not require toxic chemicals. The contact angle with 0° can be observed after laser textured. It can be also noticed that the heat treatment influenced the contact angle or the wettability on the laser textured aluminium surface. Contact angles reach 134.88° and 136.97° for the cases of sinusoidal pattern and grid pattern with 72 hours heat treatment due to the absorption of organic matter in the air, respectively. Generally, this study can shed light on understanding the mechanism on the combination of laser texture and heat treatment for the fabrication of near superhydrophobic aluminium surface. Further information on the fabrication parameters is essential to elucidate the mechanism. The influence of laser processing and heat treatment parameters on the properties of aluminium surface including corrosion resistance and abrasion resistance will be further discussed.

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References
[1] Li, X.W., Zhang, Q.X., Guo, Z. (2015) Low-cost and large-scale fabrication of superhydrophobic 5052 aluminum alloy surface with enhanced corrosion resistance. RSC Adv., 5: 29639-29646.
[2] Long, J.Y., Fan, P.X., Gong, D.W. (2016) Ultrafast laser fabricated bio-inspired surfaces with special wettability. Chinese J. Lasers, 43: 0800001.
[3] Vorobyev, A.Y., Guo, C.L. (2013) Direct femtosecond laser surface nano/microstructuring and its application. Laser & Photonics Rev., 7: 385-407.
[4] Long, J.Y., Zhong, M.L., Fan, P.X. (2015) Wettability conversion of ultrafast laser structured copper surface. J. Laser Appl., 27: S29107.
[5] Vorobyev, A.Y., Guo, C.L. (2015) Multifunctional surfaces produced by femtosecond laser pulses. J. Appl. Phys., 117: 033103.
[6] Liu, D., Wu, Y.G., Hu, Y.T. (2016) Fabrication of super-hydrophobic aluminum surface by picosecond laser. Laser Optoelectron. P., 53: 101408.
[7] Li, J., Wang, C.L., Liu, Y.D., Gao, D.M., Zhang, H.C. (2018) Wettability of surface on aluminum alloy based on laser micro-textured and self-assembled technique. J. Mat. Eng.,46: 53-60.
[8] Zheng, B.X., Jiang, G.D., Wang, W.J. (2016) Fabrication of superhydrophilic or superhydrophobic self-cleaning metal surfaces using picosecond laser pulses and chemical fluorination. Radiat. Eff. Defect. S., 171: 461-473.
[9] Jagdheesh, R. (2007) Fabrication of a superhydrophobic Al2O3 surface using picosecond laser pulses. Langmuir the ACS Journal of Surfaces & Colloids, 30: 12067.