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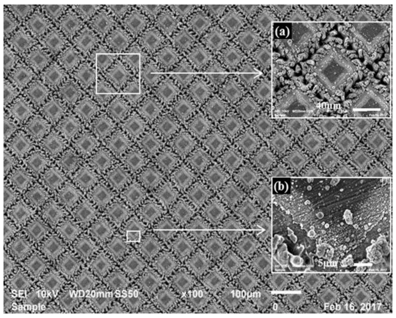
Realization of laser textured brass surface via temperature tuning for surface wettability transition



Huangping Yan[1], Mohamed Raiz B Abdul Rashid[2], Si Ying Khew[2], Fengping Li[3] and Minghui Hong[2]*

[1]School of Aerospace Engineering, Xiamen University, Xiamen 361005, China;
[2]Department of Electrical and Computer Engineering, National University of Singapore, 4 Engineering Drive 3, 117576, Singapore; [3]School of Mechanical and Electrical Engineering, Wenzhou University, Wenzhou 325035, China

Abstract: Superhydrophobic surfaces have attracted extensive interests and researches into their fundamentals and potential applications. Laser texturing provides the convenience to fabricate the hierarchical micro/nanostructures for superhydrophobicity. However, after laser texturing, long wettability transition time from superhydrophilicity to superhydrophobicity is a barrier to mass production and practical industrial applications. External stimuli have been applied to change the surface composition and/or the surface morphology to reduce wettability transition time. Herein, by temperature tuning, wettability transition of laser textured brass surfaces is investigated. Scanning electron microscopy and surface contact angle measurement are employed to characterize the surface morphology and wettability behavior of the textured brass surfaces. By low-temperature heating (100 ℃~150 ℃), partial deoxidation of the top CuO layer occurs to form hydrophobic Cu_2O. Therefore, superhydrophobicity without any chemical coating and surface modification could be achieved in a short time. Furthermore, after low-temperature heating, the low adhesive force between the water droplet and the sample surface is demonstrated for the laser textured brass surface. This study provides a simple method to fabricate the micro/nanostructure surfaces with controllable wettability for the potential applications.

Keywords: wettability transition; temperature tuning; laser texturing; superhydrophobic surface; contact angle

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1 Introduction

Superhydrophobicity is of great importance for surface functioning. Superhydrophobic surfaces have attracted extensive interests and researches into their fundamentals and potential applications, including self-cleaning [1,2], anti-icing [3,4], anti-corrosion [5], reduction of drag [6], oil/water separation [7-10], biomedical devices and microfluidic manipulation.

Many methods have been employed to fabricate hierarchical micro/nanostructures on material surfaces for superhydrophobicity [11-13], such as anodic oxidation [14], electro-deposition [15], sol-gel method [16,17], chemical etching [18,19], photolithography [20], hydrothermal processing [21], and layer-by-layer assembly [22,23]. However, these methods involve complicated multistep processes, specific reaction conditions, or chemical reagents harmful to the environment, which greatly limit the large-scale industrial applications.

Laser texturing, as a facile and promising method, has been used to make superhydrophobic metallic surfaces [24-26]. However, immediately after laser texturing, the metallic surface shows hydrophilicity or superhydrophilicity. Subsequently, chemical coating or surface modification is generally employed to achieve superhydrophobicity. Without chemical post-processing, it takes several weeks to months to achieve wettability transition from superhydrophilicity to superhydrophobicity under ambient conditions [27]. This poses a barrier to mass production and industrial applications. Therefore, external stimuli have been applied to change the surface composition and/or the surface morphology to influence wettability transition [28], such as solvent treatment [29], light illumi-

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* E-mail: elehmh@nus.edu.sg

nation [30], electrical potential and temperature tuning [31,32]. Among these methods, temperature tuning has attracted special attention due to its advantages of being a simple and controllable process.

Brass, an alloy of Cu and Zn, is widely used in industrial applications, such as heating/cooling pipes and outdoor structures because of its good mechanical and thermal properties. In this work, a nanosecond pulsed fiber laser is applied to texture the brass surface, then a post-processing is introduced to investigate the influence of temperature tuning on wettability transition of the laser textured brass surfaces. The wettability of the samples and the role of temperature tuning are discussed in details. This study presents a promising method to achieve mass production of superhydrophobic metallic surfaces with controllable wettability transition, which has extensive potential industrial applications.

2 Experimental method

The experiment is performed on commercially available brass samples with a dimension of 10 mm×10 mm×4.75 mm. The sample surfaces are initially polished by silicon carbide papers (5000 Grit, Matador, Germany). Before the laser ablation, they are cleaned with acetone, isopropanol, and deionized water ultrasonically for 5 minutes each.

A nanosecond pulsed fiber laser with a wavelength of 1064 nm, a repetition rate of 300 kHz and a pulse duration of 1 ns is employed to fabricate the micro/nanostructures on the prepared brass sample surfaces. The schematic diagram of the laser texturing system is illustrated in Fig. 1. The laser beam passes through an attenuator and a beam expander. Subsequently, it is coupled with a galvanometer scanner and focused by an F-theta lens to the brass surface. The designed grid patterns are directly written on the brass substrate for uniform wettability property in all directions. The laser scanning is performed line-by-line in the horizontal and vertical directions with an equivalent distance between adjacent scanning lines. All processing is performed in an atmospheric environment.

The specific laser processing parameters are summarized in Table 1. The fiber laser processing is able to fabricate the hierarchical micro/nanostructures at well controlled sizes and pitches.

After the laser ablation, a post-processing by temperature tuning is carried out to investigate the influence of temperature on wettability behavior of the laser textured brass surfaces. The samples are subjected to different temperature tuning for 3 hours at -16 ℃, 25 ℃, 100 ℃, 150 ℃, 200 ℃, 250 ℃ and 300 ℃.

The surface morphology of the laser textured samples is then characterized by a field-emission scanning electron microscope. The evolution from superhydrophilic to hydrophobic or superhydrophobic state of the laser textured surfaces is evaluated by measuring static contact angle (CA) with a CA analyzer using the sessile drop technique. All measurements are performed when the droplets reach the stability on the surface.

3 Results and discussion

3.1 Surface morphology

Surface morphology of the brass sample reveals the structuring effect due to the laser irradiation. After the laser irradiation, the brass surface becomes considerably rough. The irregular multi-scale structures consist of microstructures covered with nanostructures that are tens or hundreds of nanometers. A uniform distribution of periodic micro-scale grid patterns on the brass substrate can be clearly observed in Fig. 2, which is beneficial to uniform superhydrophobic properties in all directions with trapped air. Furthermore, the insets are the corresponding high-magnification SEM images, which indicate multi-scale structures as a consequence of melting, ablation, and resolidification of the brass during the laser texturing. There are obviously ablated traces and massive splashes that are the results of dominant heat effect due to the nanosecond laser irradiation. In Fig. 2(a), a further magnified image shows a periodic square pattern surrounded by the laser-ablated microstructures. The surface is characterized by regular ripples and trenches with a period of 75 μm, decorated with globule-like aggregates composed of nanoparticles. As shown in Fig. 2(b), there are many micro/nano-splashes deposited on the edges of the laser affected zones and laser unstructured domains, which result in an increase of surface roughness. Therefore, the microgrooves combined with irregular protrusions and randomized nanoscale particles form the hierarchical micro/nanostructures, which can support the water droplet and minimize the contact area between the

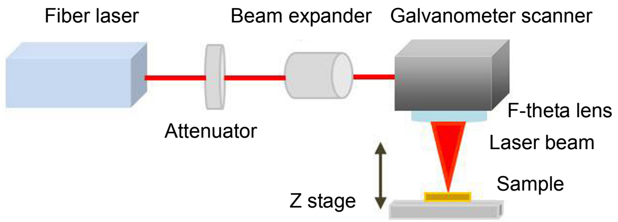

Fig. 1 Schematic diagram of laser texturing system.

Table 1 Processing parameters of laser texturing.

Parameters	Values
Pass	1
Laser fluence/(J/cm^2)	4.5
Speed/(mm/s)	5
Scan spacing/μm	75

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water droplet and the actual surface.

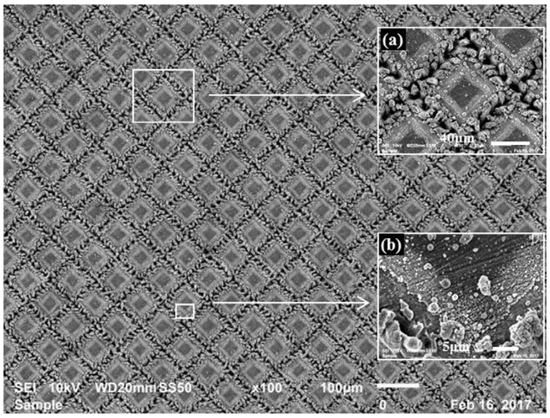

Fig. 2 SEM images of the laser textured brass surface.

3.2 Surface wettability

Surface wettability is evaluated by measuring the static CA, which depends on surface chemical composition and morphology [33]. After the laser ablation of all 7 samples, one sample is exposed to air and used as the reference. The 5 laser textured samples are subjected to post-processing temperature tuning using a hotplate for 3 hours at 100 ℃, 150 ℃, 200 ℃, 250 ℃ and 300 ℃. The last sample is stored in the refrigerator at -16 ℃ for 3 hours. After the post-processing, all samples are kept in ambient air. Difference in wettability behavior among the laser textured brass surfaces subjected to various temperature tuning treatments is investigated by the measurement of CAs using a 2 μl droplet of distilled water. The data is shown in Figs. 3(a)~3(g) with each data point averaged over 3 measurement.

The surfaces of the brass samples immediately after the laser texturing are superhydrophilic with the CA of ~2.0 ° compared to the original polished sample with the CA of ~75.0 °. The small CA enables the water droplet to spread quickly over the laser textured surfaces. The sample stored in the refrigerator at -16 ℃ for 3 hours exhibits hydrophilic surface property on the first day (CA: 48.0 °). Thereafter, there is a rapid increase in CA in the first 8 days before gradually stabilizing to a CA of 136.7 ° (Fig. 3(a)). When the laser textured sample is exposed to air, the CA increases from 33.9 ° to 136.4 ° within 18 days (Fig. 3(b)).

For the other 5 samples heated for 3 hours at 100 ℃, 150 ℃, 200 ℃, 250 ℃ and 300 ℃, the sample surfaces all show hydrophilic and the CAs of the laser textured surfaces are found to be 47.6 °, 48.7 °, 73.0 °, 53.7 ° and 29.4 °, respectively. Compared to the CAs immediately after the laser texturing, the CAs have greatly increased from 2.0 ° after post-processing temperature tuning, which indicates a decrease in wettability behavior.

After 100 ℃ temperature heating for 3 hours, there is a sharp increase in CA in the first 8 days from 47.6 ° to 132.2 °. The overall transition from a hydrophilic surface to a superhydrophobic surface (CA: 150.2 °) takes 18 days (Fig. 3(c)). After 150 ℃ temperature heating for 3 hours, the CA increases from 48.7 ° to 147.6 ° within 15 days. Subsequently, the CA decreases to 130.7 ° in the next 3 days (Fig. 3(d)). After 200 ℃ temperature heating for 3 hours, the CA reveals the relatively little change from the second day to the ninth day, before it increases gradually to 128.5 ° on the 18th day (Fig. 3(e)). After 3-hour temperature heating at 250 ℃ and 300 ℃, both sample surfaces become hydrophobic with the CA of ~90 ° on the eighth day and then the CAs increase. Finally, both samples achieve the similar wettability transition trend and reach steady states over the period of 18 days with the CA of 135.1 ° and 134.3 °, respectively (Figs. 3(f) and 3(g)).

Fig. 3(h) shows a comparison of the time taken to reach the CA of 135.0 ° for all 7 textured brass samples. Time taken to reach the CA of 135 ° is 14, 18, 9, 9, 24, 17 and 17 days for temperature tuning at -16 ℃, 25 ℃, 100 ℃, 150 ℃, 200 ℃, 250 ℃ and 300 ℃, respectively. It can be concluded that low-temperature heating (100 ℃~150 ℃) greatly speeds up the rate of wettability transition.

3.3 Mechanism of wettability transition

As mentioned in the previous section, the wettability behavior of a solid surface depends on the surface chemical composition and morphology. Based on the SEM images before and after the temperature tuning, there are no obvious changes of the surface morphology. Therefore, the variation in CA is attributed to changes in the chemical composition of the top sample surface with time.

In this study, the mechanism of wettability transition can be explained by the formation of hydrophobic material, as well as the absorption, accumulation and attachment of organic compounds at the laser textured surface in ambient air. During the laser irradiation, molten copper can easily react with oxygen in ambient air to form copper oxide (CuO). CuO is hydrophilic, thus the initial CA of the laser textured surface shows hydrophilicity or superhydrophilicity. However, since CuO is unstable at the air-surface interface, partial deoxidation causes the surface composition to evolve with time. The top layer of CuO gradually transforms to Cu_2O when the sample is exposed to air at room temperature due to its thermodynamic instability at the surface. It is well known that Cu_2O is hydrophobic by nature [34]. The development of hydrophobicity on the top layer of the sample surface is spontaneous in ambient air, but wettability transition from superhydrophilicity to hydrophobicity or superhydrophobicity takes a period of time.

Temperature tuning is effective to accelerate the oxidation or reduction processing. Chang et al. reported that low-temperature annealing could accelerate wettability transition on CuO film [34]. By low-temperature heating (100 ℃ ~150 ℃), partial deoxidation of the top CuO layer occurs faster, resulting in the formation of hydrophobic Cu_2O. It demonstrates that applying low-temperature heating could greatly reduce the time required for wettability transition from super-hydrophilicity to hydrophobicity or superhydrophobicity of brass surfaces subjected to the laser texturing. The accelerated wettability transition can be verified by the measurement of CAs. High temperature heating (250 ℃ ~300 ℃) in ambient air has an effect on both oxidation and reduction rate but tends to favor oxidation, resulting

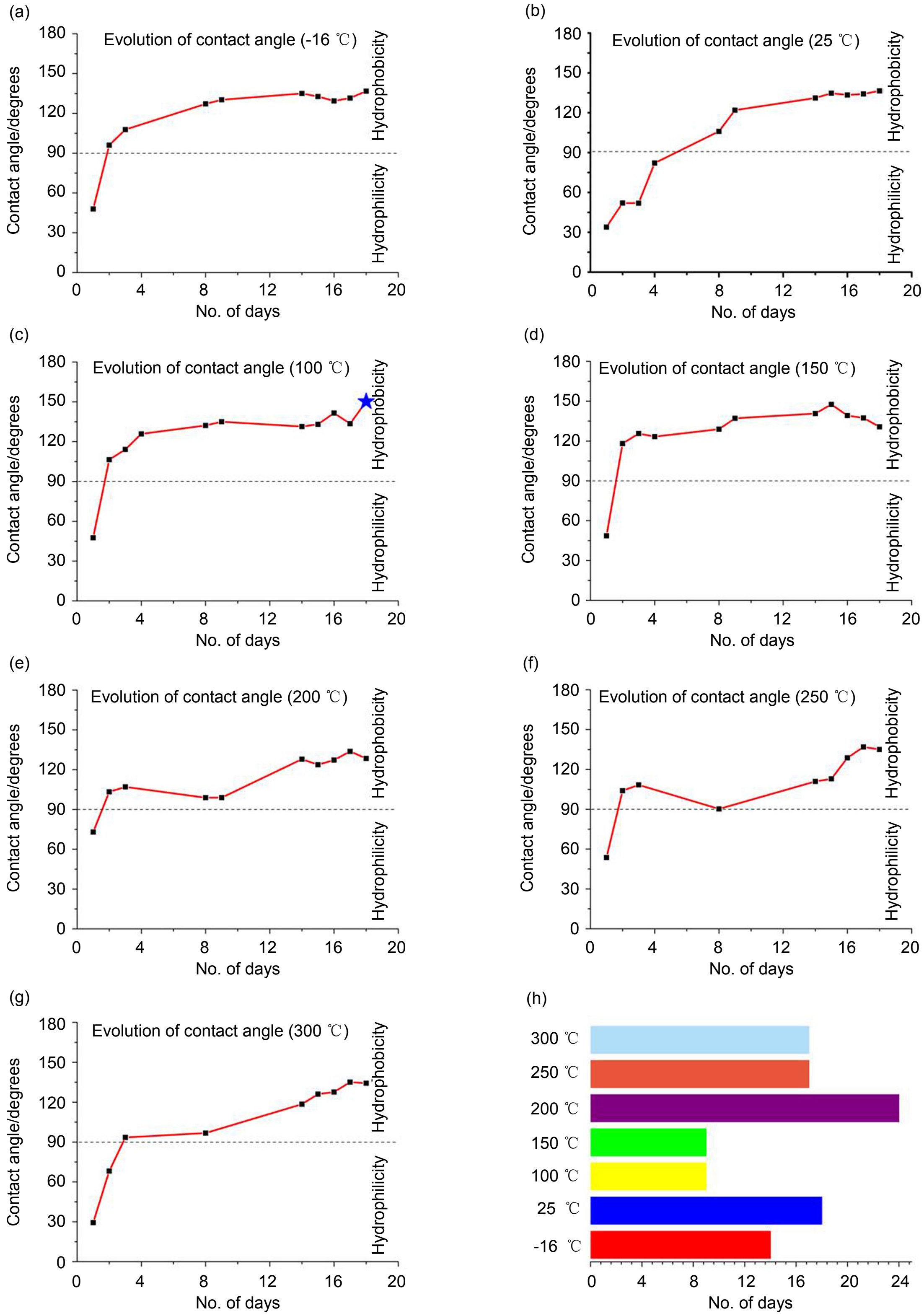

Fig. 3 Contact angle evolution of the laser textured brass surfaces after different temperature tuning. (a) -16 ℃. (b) 25 ℃. (c) 100 ℃. (d) 150 ℃. (e) 200 ℃. (f) 250 ℃. (g) 300 ℃. (h) Days taken to reach CA of 135 °.

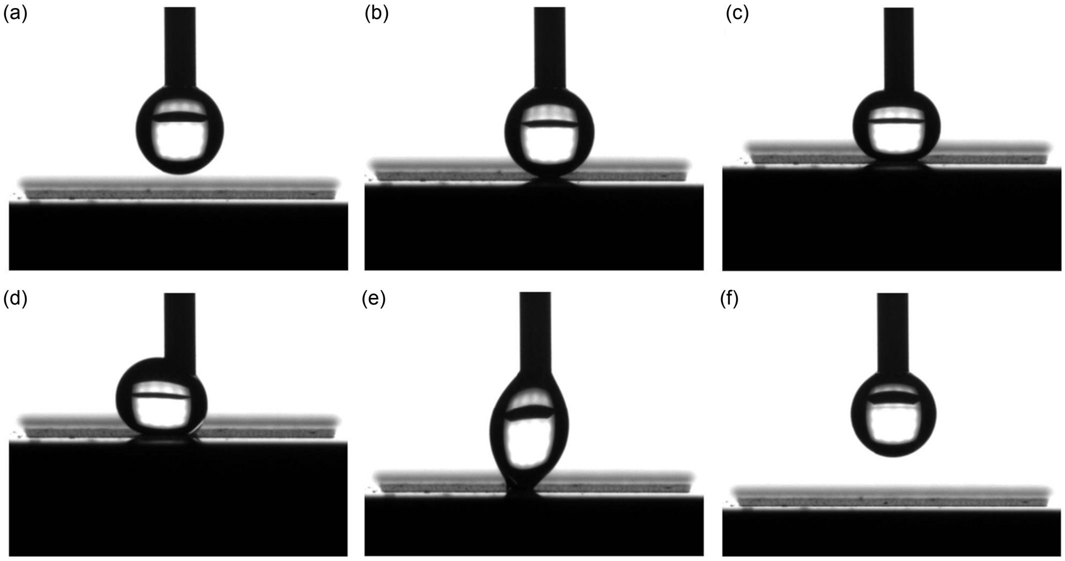

Fig. 4 Sequential images before and after the water droplet contact with the laser textured brass surface.

in restricting the development of hydrophobicity or superhydrophobicity on the top layer of the sample surface.

In addition to the formation of hydrophobic Cu_2O, the absorption, accumulation and attachment of organic compounds at the laser textured surfaces in ambient air after the temperature tuning also plays a role in the wettability transition. Accordingly, it could be noticed that the CAs of the laser textured surfaces increase over time based on the combined effects of both factors.

3.4 Low water adhesion

To further demonstrate the superhydrophobic behavior of the laser textured brass surface after 100 ℃ temperature heating, a contacting experiment is carried out. Fig. 4 shows a series photos of a 2 μl water droplet approaches onto the laser textured brass surface. In the initial state, the droplet is suspended from a syringe and shows a normal shape due to the self-gravity (Fig. 4(a)). Then, the water droplet just exactly touches the surface by lifting the sample stage. The shape of the droplet is not deformed compared to the initial state (Fig. 4(b)). As the sample stage is gradually raised to a certain height, the droplet tightly contacts with the surface (Fig. 4(c)). The droplet slides on the surface due to the increase of upward force. Therefore, when the water droplet further contacts the sample surface, it is greatly deformed (Fig. 4(d)). The distortion in the droplet is also observed when the sample stage is gradually removed from the droplet (Fig. 4(e)). Eventually, the droplet completely departs from the surface without any water residue (Fig. 4(f)). Similar phenomena are observed in the literature [35-37]. Accordingly, the above results indicate the superhydrophobic performance of the laser textured surface and the low adhesive force between the droplet and the surface.

4 Conclusions

In summary, a laser textured surface with hierarchical micro/nanostructures is fabricated on a brass substrate by nanosecond fiber laser ablation. A post-processing by temperature tuning is introduced to investigate the influence on the wettability transition without any chemical coating and surface modification. The wettability transition time to reach the CA of 135 ° is the shortest at low-temperature heating (100 ℃~150 ℃). After 100 ℃ temperature heating, the sample surface achieves superhydrophobicity with the CA of 150.2 ° after 18 days. A low adhesive force between the water droplet and the sample surface is demonstrated for the laser textured brass surface at low-temperature heating. This promising method of temperature tuning for wettability transition is effective for mass production of superhydrophobic metallic surfaces.

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