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Laser Micro/nano Surface Texturing of SS316L for Superhydrophobicity

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Suitable modification of material's surface wettability has been attracting much attention in both scientific research and industry development due to its importance for various applications, which include lab-on-a-chip devices in microfluidics, self/easy cleaning, adhesion mitigation and biomedical application. Surface morphology plays a key role to determine the wettability of a solid surface. Various techniques have been used for surface texturing to create the desired surface morphologies. Laser micro- and nano-processing is one of the main techniques. Ultrafast lasers are increasingly used as a tool for surface texturing. Laser ablation by ultra-short pulses in the pico- or femto-second range results in well controlled superimposed micro- and nano-scaled surface textures. The microscale of the texture is mainly determined by the dimensions of the laser spot, whereas the superimposed nano-structure is the result of the so-called laser induced "self organizing nanostructuring". By controlling this micro-nano surface texture, it is possible to create two-scale hierarchical surface structures with the desired properties.
In the paper, 1.06 μm ps laser is employed to fabricate micro/nano surface textures on SS316L substrate. The effects of different laser parameters including laser fluence, rep rate, scanning speed, pass number, focal position, etc on the topography, feature profile, feature dimensions of the induced surface textures have been studied. The optimum laser parameters have been identified that the uniform-distributed 2 scale micro-nano hierarchical surface patterns are fabricated on the SS316L substrates. The fabricated 2-scale micro/nano hierarchical textured SS316L sample shows stable superhydrophobic property with a water contact angle (WCA) of more than 150 degree. Also, it is demonstrated that the laser textured SS316L surface has liquid repellent property to the liquids including coke, milo, dark soya sauce, and honey liquid. The mechanism involved in the process is discussed in terms of surface morphology and surface chemistry.

1. Introduction

Controlled modification of material's surface wettability has been the subject of significant scientific research due to its importance for various applications, which include easy-cleaning, adhesion mitigation and microfluidic and biomedical application. The wettability property in terms of water contact angle and contact angle hysteresis are affected by both material surface chemistry and topology [1]. Based on the Wenzel [2] and Cassie-Baxter [3] models, the roughness of the sample surface is critical to increase its hydrophobicity or hydrophilicity. Surface morphology is one of the key factors determining the wettability of a solid surface. Various techniques have been used for surface texturing to create the desired surface morphologies, which can be classified into 2 major categories, namely top-down processes such as lithographic process, template-based method [4], plasma treatment [5] and laser surface treatment process [6], and bottom-up processes mainly consisting of self-assembly and self-organization processes [7]. As a top down approach, laser micro- and nano-processing has been extensively investigated and is developing rapidly. The pico- or femto-second ultrafast lasers have been the most employed tools for surface texturing. The pico- or femto-second laser pulse induced ablation is able to produce well controlled 2 scale micro- and nano-scaled surface textures [8] so as to fabricate some types of surfaces with the improved surface functional properties. So far, a significant amount of extensive research work has been carried out on surface treatment and modification on different types of materials such as metallic [8, 9], semiconductor material [10], and polymer material [11] to modify their wetting properties with different lasers. The mechanisms involved in the wettability conversion of structured metallic surfaces from super-hydrophilicity to super-hydrophobicity have also been well studied. [8, 12]. The mechanism for the wettability change is found to be dependent on the specific material to be laser-beam-treated. Regarding the laser surface treated stainless steel, Kietzig et al [8] proposed that the conversion in wetting property to superhydrophobicity from original hydrophilicity after laser treatment was due to the accumulation of certain amount of carbon layer on the laser treated surface through the dissociation of carbon dioxide into carbon with the active magnetite as catalyst.

In the paper, 1.06 μm ps laser is employed to fabricate micro/nano surface textures on SS316L substrate. The effects of different laser parameters including laser fluence, rep rate, scanning speed, pass number, focal position, etc on the topography, feature profile, feature dimensions of the induced surface textures have been studied. The optimum laser parameters have been identified that the uniform-distributed 2 scale micro-nano hierarchical surface patterns are fabricated on the SS316L substrates. The fabricated 2-scale micro/nano hierarchical textured SS316L sample shows stable superhydrophobic property with a water contact angle (WCA) of more than 150 degree. Also, it is demonstrated that the laser textured SS316L surface has liquid repellent property to the liquids including water, coke, milo, dark soya sauce, honey liquid. The mechanism involved in the process is discussed in terms of surface morphology and surface chemistry.

2. Experimental

SS316L plates with dimensions of 30 mm x 30mm x 3mm and 50 mm x 50 mm x 2 mm with good finishing on one side was used for the laser surface texturing. Before laser texturing, the SS316L plates underwent sonication cleaning with DI water for 10 min and dried with compressor air. After laser texturing process, the samples were also going through the same cleaning process with ultrasonic bath in the DI water for 10 min, then dried with compressor air.

A TIME BANDWIDTH; DUETTO ps laser system was employed to do the laser surface treatment. The laser has Gaussian profiled spatial mode (TEM_{00}) with a beam quality of $M^2 < 1.3$ and the beam divergence of less than 0.3 mrad. The laser wavelength is near-infrared 1.06 μm, the output power is up to 10W, and the laser pulse width is 10.3 ps. The pulse repetition frequency can be set at a minimum value of 50 kHz and continuously tuned up to 8200 kHz. The incident laser beam was focused and manipulated by a galvo-scanner, which was equipped with a telecentric f-theta lens. The focus length of the f-theta focus lens is 100 mm. The linear polarized raw laser beam has a diameter of 7 mm (@ $1/e^2$), which was focused and directed on to the sample surface with a beam diameter of 25 μm. The laser machining control software can produce various different machining patterns. The patterns can be lines, circular and rectangular shapes, and also hatched patterns, etc. The maximum scanning speed is 2000 mm per second. For the surface treatment process, the focused laser beam was raster scanned a designed pattern as shown in Fig. 1. The effects of the following were investigated – the rate of the repetition, velocity of the scanning, the density of laser power, the pass number, the pulse number on each spot as well as the pitch of the hatched pattern on properties of the produced surface textures such as the morphology, the feature size, and the uniformity of the produced pattern.

The sample surfaces were characterized by using the Scanning Electron Microscopy (SEM). The surface wettability was characterized via measuring the water contact angle (WCA) and oil contact angle (OCA). With the sessile drop method, the WCA and OCA was obtained with VCA Optima (VCA-2500XE AST products, Inc.). During the WCA/OCA measurement, a specific volume of water droplet was created with a syringe connected to a capillary tip. The droplet was then detached gently onto the substrate. The image of the droplet was recorded with a camera and analyzed with the software to determine the tangent line for the contact angle.

3. Results and Discussion

Fig. 1 schematically shows the designed pattern to be employed to produce the desired micro-bumps based texturing. The process is conducted through scanning the focused laser beam along the regular hatched raster pattern so as to produce the desired surface textures such as micro-bumps array pattern. Combining ultrafast laser induced self-organizing effect, the dependence of the induced surface patterns was investigated on the different laser parameters including laser fluence, pulse repetition rate, beam scanning velocity, pass number, hatching density. It was found that hierarchical 2D array micro-bumps –based surface pattern could be produced.

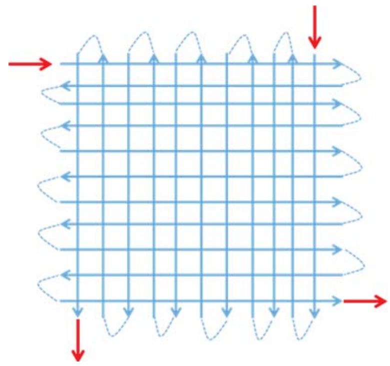
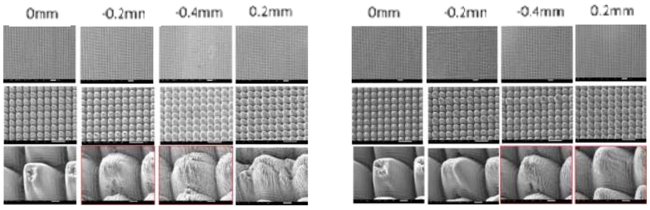


Fig. 1 Schematic designed pattern for micro-bumps array based texture

When the SS316L steel substrate was treated with the following laser parameters: laser energy fluence was set at 1.23 J/cm^2, the repetition frequency was set at 1 MHz, the scanning velocity was set at 1000 mm/s, repetition pass number is set to be in a range of 50 - 200, and the hatched distance was set to be 25μm for both directions in the hatched pattern as shown in Fig. 1, a uniform micro-bump array based surface pattern was produced on the SS316L substrate with a textured area of 5 × 5 mm as shown in Fig. 2. In order to identify the optimum texturing parameters, the process was also conducted at different focal positions of 0 (on the surface), -0.2mm, -0.4 mm (below surface) and +0.2mm (above surface). It was observed that a uniform and consistent 2D micro-bump array surface pattern was produced. For the produced micro-bump array textures, the micro-bump size was measured to have a diameter of around 15 μm, and the height of the micro-bump pattern was about 12 to 30 μm depending the pass number and focal position; the periods of the patterns was 25 μm. From the magnified SEM image of the micro-bump, the periodic surface ripples were observed to be superimposed on the surface of the micro-bump at some parameters such as in Fig. 2 (a) at focal position of -0.2mm and -0.4 mm and in Fig. 2 (b) at focal position of -0.4mm and 0.2 mm which are highlighted with a red frame. So, the two-scale hierarchical 2D array micro-bumps –based surface textures have been produced.



(a) (b)

Fig. 2 laser produced surface texture with a period of 25 μm for pass number of 100 (a) and 200 (b) at different focal position

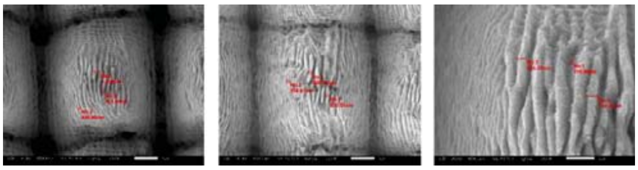


Fig. 3 Nano features generated on the surface of the micro-bumps

Fig. 3 showed the magnified SEM images of the surface of the micro-bumps. It can be seen that the nano-ripple features are produced with dimension range of 350 – 630 nm. Also, the nano-dots with a dimension of ~100 nm were found in-between the ripples.

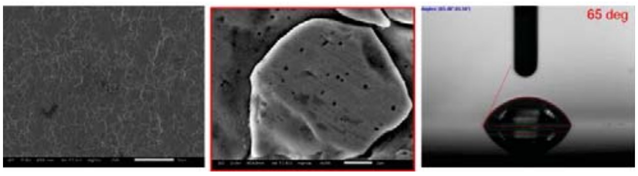


Fig. 4 SEM images and measured WCA on the original SS316L surface

Fig. 4 showed the SEM images and measured WCA on the untreated SS316L substrate. The original SS316L is hydrophilic with a WCA of 65 deg.

With identified the optimum laser surface texturing process parameters of laser fluence of 1.23 J/cm^2, the repetition frequency at 1 MHz, the scanning velocity at 1000 mm/s, and pass number of 75. A micro/nano 2 scale surface texture was fabricated on the SS316L substrate with a textured area of 30 mm x 30 mm as shown in Fig. 5. It can be seen that the induced surface textures are quite uniform and consistent. From the magnified SEM images, the 2-scale micro/nano surface structures have been achieved with nano-ripples to be formed on the surface of the bumps.

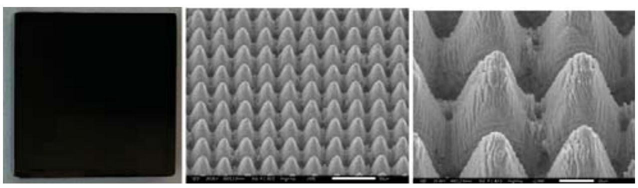


Fig. 5 Laser fabricated micro/nano 2-scale surface patterns with a textured area of 30 mm x 30 mm with a period of 25 μm

Immediately after laser texturing treatment, the surface of the treated samples is found to be superhydophilic with a measured WCA of almost zero deg as shown in Fig. 6 (a). However, it was found that after some amount of timing, the WCA on the laser textured SS316L surface increased gradually up to highly-hydrophobicity and even superhydrophobicity. As shown in Fig. 6, for 14 weeks after laser texturing process, the WCA for laser textured sample has been increased up to more than 150 degree that the superhydrophobicity has been achieved.

(a) (b)

Fig. 6 the measured WCA immediately (a) and 14 weeks (b) after laser surface texturing.

The WCA of the non-treated SS316L is 65 degree as shown in Fig. 4. With laser surface texturing, the surface WCA was increased up to more than 150 degree after some timing, indicating that laser surface treatment was able to convert the original hydrophilic SS316L steel surface into superhydrophobic surface under certain laser parameters.

The surface wetting property on a solid substrate is determined by its surface morphological structure and the surface chemistry property. So, the XPS analysis was conducted to characterize the elemental composition and chemical status on the SS316L substrate surfaces before and after laser treatment to study its surface chemistry effects. Before collecting the spectra, the samples were first treated with Ar+ ion sputtering for 20 s to make the surface clean with no contaminants by the ambient atmosphere.

From the measured XPS survey spectra of the untreated and laser treated SS316L surfaces (not shown here), it was observed that for untreated SS316L steel, the C1s peak's intensity was very weak, in contrast, for laser treated SS316L substrate the C1s peak's intensity was much higher in comparison with the untreated sample. The increment in the C1s peak relative intensity indicated that the carbon elemental concentration on the laser textured SS316L surface has increased. Based on the elements' relative intensities in the XPS spectra, the C, O, Fe and Cr elemental concentrations (atom %) on the untreated and laser treated steel substrate surfaces were derived and found that the C concentration on the laser treated SS316L surface increased to 29.7% from 9.6% of the C concentration on the untreated SS316L surface. As a result, it was believed that there should be a thin layer of nonpolar carbon to be accumulated on the laser treated SS316L surface. The dissociation of carbon dioxide into carbon was supposed to be the major reason for the carbon layer formation [8]. The dissociative reaction of the carbon dioxide was initiated with the active magnetite $Fe_3O_{4-\delta}$ ($0<\delta<1$) induced by the ultrafast laser surface treatment. Here, ultrafast laser irradiation might produce an active magnetite $Fe_3O_{4-\delta}$ ($0<\delta<1$), an oxygen deficient iron oxide. This nonstoichiometric magnetite $Fe_3O_{4-\delta}$ ($0<\delta<1$) was supposed to initiate the dissociative adsorption of carbon dioxide as a catalyst, where the carbon monoxide and carbon was produced as the outcome of carbon dioxide dissociation, and oxygen anions were moved into lattice vacancies of the steel alloy to form stoichiometric Fe_3O_4. So, a nonpolar amorphous carbon accumulation layer was formed on the laser treated SS316L steel surface as a result of the CO_2 decomposition reaction. This amorphous carbon layer has a low surface energy. So, together with the laser treatment induced dual scale hierarchical surface texture (Fig. 5), a superhydrophobic SS316L steel surface has been formed with a WCA of more than 150 degree.

The textured SS316L samples are tested on the liquid repellency of some types of liquids including water, cola, milo, dark soya sauce, and honey liquid. It was found as shown in Fig. 7 that these liquids droplets falling on the tilted textured sample are able to roll off the sample surface indicating the laser textured SS316L showed the liquid repellency for these liquids.

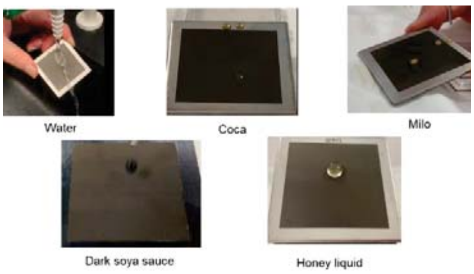


Fig. 7 Snapshots on the repellence of various liquids on the laser textured SS316L surface

4. Conclusions

In conclusion, a systematic investigation on ps laser surface texturing of SS316L substrate had been conducted. The 2 scale micro-nano hierarchical surface patterns was fabricated on the SS316L substrates. Also it was found that an amorphous carbon layer with a low surface energy was formed on the laser textured SS316L surface. As a result, a superhydrophobic SS316L steel surface has been obtained with a WCA of more than 150 degree. Also, the laser textured SS316L surface has been demonstrated to be liquid repellent to the liquids including water, coke, milo, dark soya sauce, honey liquid. indicating the laser textured surface has anti-sticking properties to these types of liquids.

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