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Fabrication of superhydrophilic surfaces for long time preservation on 316 l stainless steel by ultraviolet laser etching

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Abstract

Due to the good biocompatibility, 316 l stainless steel is widely used in the manufacture of medical instruments and human implants. The super hydrophilic 316 l steel surface is used for reducing friction and adhesion. By choosing appropriate laser process parameters 316 l steel surfaces with super-hydrophilic were obtained. The effects of laser process parameters including repeat frequency, pulse width, scanning speed, and the number of scanning were investigated to find the relationship between surface microstructure and wetting ability. To investigate the super-hydrophilic maintenance time on the textured surface, the textured surfaces were preserved in ambident air, distilled water, and absolute ethanol. The results showed that by choosing appropriate laser process parameters surface with super-hydrophilicity can be maintained for 30 d.

1. Introduction

316 l SS is the widely used material for orthopedic implants and medical instruments because of its low cost, excellent biocompatibility, superior strength, and good resistance to corrosion in biological environments [1–4]. The wetting properties of a solid surface are of big difference in its usage. The super hydrophilicity of a solid surface is used for reducing friction and adhesion [5, 6]. While the surface with superhydrophobic properties was used for water repellence [7], antibacterial surfaces [8], and so on. There are plenty of ways to obtain super hydrophilic and super hydrophobic surfaces such as coating, corrosion, electrospinning anodizing, and so on. Compared with these techniques which all need special equipment or complex process control, laser texturing has significant advantages, such as no pollution source, high efficiency [8–11].

Both hydrophilic and hydrophobic metallic surface based on laser texturing has been investigated before [12, 13]. Fatema et al fabricated stable super hydrophilic surfaces on 316 l steel by simultaneous laser texturing and SiO2 deposition [14]. Trdan et al manufactured a super hydrophilic surface and investigated the transition from super hydrophilic to superhydrophobic state 316 l surface and its effect on corrosion resistance [15]. Wang et al obtained a superhydrophobic surface with self-cleaning property and excellent stability by coating ZnS on 316 l [16]. Sun et al manufactured superhydrophobic 316 L surface by selective laser melting after aging treatment, heat treatment, and chemical modification. However, research has been focused mainly on the change in wetting behavior from hydrophilic to hydrophobic by low temperature annealing and coating on the textured surface [10, 12, 15, 17, 18]. The vitro researches also revealed that the tribological properties were strongly affected by the surface wettability of the material in an aqueous environment [19]. However, standard laser metal texturing method often result in unstable wetting characteristics, i.e. changing from super hydrophilic to hydrophobic in a few days [14, 20–23].

In previous research, infrared nanosecond laser was usually used to obtain specific surface morphology. Compared to infrared laser the ultraviolet (UV) laser has the advantages of high machining accuracy, low cost and the most important thing is the negligible thermal effects in the process of laser deformation [24–26]. The relationship between the surface morphology and the wetting behavior has not been investigated thoroughly in
In most cases, immediately after laser texturing the surface was hydrophilic, and usually, the surface changed to superhydrophobic after several days. This phenomenon is mainly attributed to the instability of chemical composition or organic contamination when exposed to air. Surface coating is an effective way to obtain a stable superhydrophilic metal surface. These steps, however, involve multiple steps and may be inappropriate for biomedical usage. Compared to these techniques, laser surface texturing can be simple and would not change the chemical composition of the metal. Therefore, it is a challenge to maintain long-term superhydrophilic surfaces only by laser texturing.

This study will provide a comprehensive guideline for the design of laser texturing methods and the fabrication of extreme wetting surfaces for metal alloys. Such as repeat frequency, pulse width, number of scanning, and scanning speed. In this paper, the wetting behavior of superhydrophilic surfaces that can preserve in ambient air for 30 d was obtained by choosing proper laser processing parameters. The change in wettability of processed hydrophilic surfaces under different storage conditions has also been studied.

2. Materials and methods

The wettability measurement experiment was carried out on the surface of the square block sample. The chemical composition of 316L SS used in the experiment is shown in table 1.

| Element | C | Si | Mn | P | S | Ni | Cr | Mo | N | Co | Fe |
|---------|---|----|----|---|---|----|----|----|---|----|----|
| wt%     | 0.02 | 0.57 | 1.56 | 0.03 | 0.03 | 10.10 | 16.76 | 2.01 | 0.06 | 0.08 | 68.78 |

Table 1. Chemical composition of the commercial 316 L stainless steel.

| Number | Repeat frequency (KHz) | Pulse width (ns) | Scanning speed (mm/s) | Number of Scanning |
|--------|------------------------|------------------|-----------------------|-------------------|
| 1      | 25, 30, 35, 40, 45, 50, 55, 60, 65 | 10 | 300 | 1 |
| 2      | 40 | 2, 4, 6, 8, 10, 12, 16, 20 | 300 | 1 |
| 3      | 40 | 10 | 50, 100, 150, 200, 250, 300, 400, 500 | 1 |
| 4      | 40 | 10 | 300 | 1, 2, 4, 6, 8, 10, 15 |

Table 2. Single-factor experiments of laser processing.

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Table 2. Single-factor experiments of laser processing.
3. Results

3.1. Surface morphology

3.1.1. Effect of repeat frequency on surface morphology

Figure 2 shows the SEM images of groove texture at different repetition frequencies. Under low frequency such as 25 kHz, the overlap between the spots is small, the shape of the groove is irregular. Once the repeat frequency increased to 40 kHz the distance between the spot decreased and the apparent groove was fabricated. The fused particles were splashed significantly. While at 60 kHz repeat frequency the light spots are closely connected to form regular grooves.

The width and depth of the groove were measured by a laser scanning confocal microscope (LSM 800, Germany) as shown in figure 3. With the increase of repeat frequency, the width and depth of the groove first increase and then decrease. When the repeat frequency is 35 kHz, The depth and width of the groove reach the maximum value, which is 24.44 μm and 1.68 μm respectively.

3.1.2. Effect of pulse width on surface morphology

Figure 4 shows the SEM images of groove texture with different pulse widths. When the pulse width increase from 2 μs to 12 μs, the groove morphology has little change. While the pulse width increase to 20 μs, the ablation degree of the sample surface is greatly weakened. There is only the trace of the light spot on the surfaces, without the formation of obvious splashing fused particles. Figure 5(b) shows that with the increase of the pulse width the groove width and depth decrease.

3.1.3. Effect of scanning speed on surface morphology

Figure 6 shows the SEM images of groove texture at different scanning speeds. When scanning speed is 50 mm s⁻¹, the ablation effect is obvious and a thick recast layer is formed. The overlap of light spots cannot be observed and the size of splashed fused particles on both sides of the groove is so large even form a thick wall. As scanning speed increase to 150 mm s⁻¹ the outline of the light spot overlaps and still forms a dense groove bottom. As scanning speed continues to increase to 500 mm s⁻¹ the profile of light spot appears at the bottom of
Figure 3. (a) Laser confocal microscopic image of surface texture ($f = 35$ kHz) (b) groove depth and width at different repeat frequency (c) measurement of the width and depth of the groove.

Figure 4. 1000 fold SEM images of groove texture with a different pulse width (scale bar is 10 $\mu$m) (a) $T = 2$ $\mu$s (b) $T = 12$ $\mu$s (c) $T = 20$ $\mu$s.

Figure 5. (a) Laser confocal microscopic image of surface texture (pulse width = 12 ns) (b) groove depth and width with different pulse width.
the groove, and the melting recast phenomenon of the material is greatly weakened. Compared with repeat frequency and pulse width the scanning speed has little effect on groove width. The depth decrease significantly with the increase of scanning speed as shown in figure 7(b).

3.1.4. Effect of the number of scanning on surface morphology
Figure 8 shows the SEM images of groove texture with a different number of scanning. When the number of scanning increase from 1 to 4 times, the bottom of the groove is covered by the melt recast material and the unprocessed surface is also splashed with the fused particles. When the number of scanning increased to 10 times, the fused particles increased and splattered on both sides of the groove even forming a thick wall at the edge of the groove. As figure 8(b) shows with the increase of the number of scanning the width fluctuates around 22 μm and the variation range is small while the depth increase significantly.
3.2. Wettability

The contact angle of groove texture with different laser processing conditions were shown in figure 10. When the repeat frequency ranges from 25 kHz to 55 kHz, the contact angle of distilled water fluctuates around 0°. The surface is super hydrophilic and the droplet completely spread on the surface. As the repeat frequency increase to 60 kHz the contact angle increase to 3.2°. When the repeat frequency increase to 65 kHz, the contact angle increase to 12.3°. Figure 10(b) shows the contact angle of groove texture with different pulse widths. When the pulse width ranges from 2 ns to 16 ns the contact angle fluctuates around 2°. When the pulse width increase to 20 ns the contact angle of distilled water increases to 14.8°. It seems that no matter how the process parameters change the surface shows hydrophilic.

Figure 9. (a) Laser confocal microscopic image of surface texture (scanning times = 10) (b) groove depth and width with different scanning times.

Figure 10. Contact angle (a) groove texture at different repeat frequency (b) groove texture with different pulse width.

Figure 11. (a) Wenzel wettability model and (b) the intrinsic contact angle of 316 L stainless steel.
As for the texture groove with different scanning speeds and different scanning times, the contact angle shows no significant difference which both fluctuates around 2°. Under different laser processing conditions of several scanning and scanning speeds, both surfaces showed superhydrophilic properties. While the spreading state of the droplets is quite different. When the scanning speed is low ($v = 50\, \text{mm s}^{-1}$) or the number of scanning are large than 6, the droplets penetrate the groove at a very fast speed. The traces of the droplets on the surface are linear. While on the other surface with superhydrophilic property the droplet spread out into liquid films. To distinguish these two different phenomenon, we called the wettability of droplets penetrating the groove quickly and completely extreme hydrophilicity.

Figure 12. Surface roughness measured by the White light interferometer (Sa-arithmetical mean height of the surface; Sq-surface root mean square height; Sz-surface maximum height; Ssk-surface skewness; Sku-surface kurtosis).

Figure 13. (a) surface roughness with different repeat frequency (b) surface roughness with a different pulse width (c) surface roughness with different scanning speed (d) surface roughness with different scanning times (Sa-arithmetical mean height of the surface; Sdr-developed interfacial area ratio of the surface).
4. Discussion

4.1. Mechanism

According to the Wenzel model as shown in figure 11, the rough surface will increase the interface of solid and liquid [30].

\[ \cos \theta_w = r \cos \theta_i \]  

(1)

Where \( \theta_w \) is Wenzel contact angle and \( \theta_i \) is the intrinsic contact angle and \( r \) is the roughness factor. According to equation (1), the contact angle decreases while \( r \) increase if the intrinsic contact angle is less than 90°. The hydrophilic surface will change to a super-hydrophilic surface after increasing its roughness [14, 31].

In our study, the intrinsic contact angle of 316 L stainless steel is 76°. The laser etching increases the surface roughness which will decrease the contact angle. The surface roughness was measured by the White light interferometer (NT-9300, USA) as figure 12 shows.

We worked mainly on two parameters to characterize the 3D surface morphology. \( S_a \) is the arithmetical mean height of the surface. It can be used to distinguish the surfaces with the same surface roughness but different morphology. The larger the size and shape of the surface texture, the larger the \( S_d \). Figure 13 shows the 3D surface parameters with different process parameters. Based on the Wenzel model with the increase of \( S_a \) and \( S_d \), the CA will decrease. The \( S_a \) and \( S_d \) have the same trend with the change of process parameters.

\[ S_d = \frac{1}{MN} \sum \left( \sqrt{1 + \left( \frac{\partial z}{\partial x} \right)^2 + \left( \frac{\partial z}{\partial y} \right)^2} - 1 \right) \]

Table 3. Laser processing parameters for surface with the different wetting ability and groove SEM with 20000 magnification.

|                         | hydrophilic | Super hydrophilic | Extreme hydrophilic |
|-------------------------|-------------|-------------------|--------------------|
| Repeat frequency(kHz)   | 40          | 40                | 40                 |
| Pulse width(ns)         | 20          | 10                | 10                 |
| Scanning speed(mm/s)    | 300         | 300               | 50                 |
| Scanning times          | 1           | 1                 | 1                  |

Figure 14. Schematic diagram of three different wettability surfaces and the groove bottom SEM with 20000 magnifications.
4.2. Stability and storage conditions

Based on the CA test before, we obtained three surfaces with different wetting abilities. The process parameters are listed in table 3. Corresponding to the hydrophilic surface (CA > 2°), super hydrophilic surface (CA < 2°), and extreme hydrophilic surface (CA < 2° and droplet penetrate the groove at a very fast speed). For hydrophilic surfaces the first day CA is 12.9°. On the 7th day, the CA of surface stored in the air increased fast, and the CA is 56°. For a surface with super hydrophilic, the first-day contact angle is 2°. As time went on, the hydrophilicity of the surface stored in the air decreased most obviously, CA reaching 54.1° on the 30th-day. The wettability of the sample surface stored in anhydrous ethanol is also greatly weakened, and the contact angle changes from 0° to 30.7°. For the extremely hydrophilic surface, the contact angle did not change significantly in the three storage environments. After 30 d in the air, the contact angle was only 11.9°. In absolute ethanol and distilled water, the samples always keep super hydrophilicity. We attribute this phenomenon to the capillary. Nosonovsky et al attributed the change of the contact angle to the surface roughness [32]. Drelich et al attributed the change of the wettability to the capillary forces which helped the spread of the droplet [33]. We observed the surface groove bottom with different wettability by SEM with 200000 magnifications (figure 14). The surface with hydrophilicity showed a smooth surface with little fused particles. The super hydrophilic surface showed microparticles while the extreme hydrophilic surface is covered by layers of grass-like microstructure. This grass-like multilayers microstructure and nanoparticles may cause a capillary effect. Since metal oxides are hydrophilic, the samples behave like a 3D porous medium, fully wetting the surface. Others also obtained surface structure with super capillary effect in silicon and glass [34–39]. Surface with this microstructure will suck water rapidly and water even spreads on a vertical surface. Surface processed in our study also showed this phenomenon. The schematic diagram of the surface with different wettability surfaces was shown in figure 14. The droplet in extreme hydrophilic surface penetrates groove rapidly due to capillary effect. Although they already found this effect they didn’t investigate the change of wettability with time and the relationship between laser process parameters with surface wettability. In most previous research, the wettability of the surface changes with time due to organic material contamination when exposed to air [28, 29]. This means that the
surface changes to hydrophilic in a few days. While in this research, the wettability of the extreme hydrophilic surface changes little when exposed to air. We suggested that the surface microstructure help form the capillary forces. Even the surface was contaminated by organic material the capillary force is still large enough to help droplets spread on the surface. Here in this study, we provide a comprehensive guideline for the design of laser texturing methods and the fabrication of extreme wetting surfaces for metal alloys which can preserve a long time in ambient air. The results revealed that once the $S_a > 1 \, \mu m$ with $S_{dr} > 15$, the extremely hydrophilic surface was obtained and the CA changed less with time.

5. Conclusions

Compared with other techniques such as coating and chemical electrolytic, the laser process is simple and environment clean. Maintaining long-term super hydrophilic surface only by laser processing is a challenge. This study intends to investigate the relationship between wettability and surface morphology processed by laser etching and obtain super hydrophilic surface can preserve a long time. The effects of multiparameter of the laser system and storage conditions on super hydrophilicity were analyzed. With increasing repeat frequency and pulse width, the CA increase. While with large scanning times and low scanning speed the surface roughness increase which affects the CA apparently and will form an appropriate morphology that CA change less with time as shown in figure 15. This means that choosing appropriate processing parameters can fabricate the desired extreme hydrophilic surface that its wettability changes less with time. For the storage of hydrophilic surfaces, distilled water is a good candidate. The obtained results will give a useful guide to select proper parameters to get surfaces with different wetting abilities.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

Author contributions

Chunyang Pan conceived the experiments, analyzed the results, and wrote the manuscript; Changfeng Xu conducted the experiments, prepared figures 1–6; Jun Zhou supervised the study. All authors reviewed the manuscript.

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Conflicts of interest

The authors declare no conflict of interest.

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