One-step fabrication of an anti-corrosion superhydrophobic surface on stainless steel

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Abstract
A one-step laser-processing method is employed on a common laser making machine to develop superhydrophobic surfaces on stainless steel. Without any surface modification, the laser-textured substrates obtained superhydrophobicity after kept in sealing bags for 12 days. The average contact angle value of the as-prepared samples is above 150°. The superhydrophobic surfaces possess good self-cleaning and anti-corrosion properties. The facile, cost-effective and eco-friendly method will have great potential in the mass-production of superhydrophobic surfaces.

1. Introduction

Stainless steels are popular structural materials extensively used in several sectors of industry such as construction, food and health care for good resistance to high temperature and excellent mechanical performance. But corrosion is an inevitable concern for stainless steels which hamper their applications [1]. Surface treatment has played a necessary and important part in the development of high-corrosion-resistant stainless steels [2, 3]. Inspired by the water-repellent properties of natural surfaces, superhydrophobic materials were developed and received great attention for their diverse potential applications in different fields such as self-cleaning [4], anti-corrosion [5], drag reduction [6], anti-icing [7], water oil separation [8] and so on. For decades, great advancements have been made on the fabrication of superhydrophobic surfaces. Various methods have been used, including chemical etching [9], electrodeposition [10], sol–gel [11] and hydrothermal method [12] etc. As surface roughness and low surface free energy are two essential ingredients for the preparation of superhydrophobic surfaces [13], most of the preparation technologies available today generally are completed by two steps. The first step is to construct a rough surface of micro/nano structure on the substrate by physical or chemical methods. The second step involves surface chemical modification so as to reduce the surface energy and enhance the hydrophobic characteristics of the surface. However, the limitations of two-step methods are increasingly recognized. Most of these methods are still subject to certain limitations such as complicated preparation process, expensive instruments, toxic reagents, and strict experiment environment [14, 15]. Facile process, economical cost, environmental protection and preparation efficiency are crucial for the practical applications of superhydrophobic surfaces.

Recently, considerable efforts have been devoted to one-step fabrication of superhydrophobic coatings. Ashoka et al [16] developed a facile electrochemical route for tuning the superhydrophobic surface of stearic acid modified copper with over-oxidized polypyrrole. Yang et al [17] prepared a superhydrophobic cotton fabric with fluorinated TiO₂ sol by a one-step sol-gel process. Zhang et al [18] reported a superhydrophobic surface manufactured on magnesium alloy substrate by hydrothermal method. Ren et al [19] fabricated a robust superhydrophobic coating by one-step spraying the mixture of hydrophobic silica sol and synthesized epoxy-resin-based adhesives onto the steel substrate. Compared with the traditional two-step techniques, one-step approach has many obvious advantages such as the simplified fabrication procedures and saving of time. Meanwhile, they still involve surface modification of low surface energy and the use of expensive or toxic reagents, such as FAS and RF-sputtered Teflon, which will pose a threat to the environment [20–22].
Laser processing is often employed for the preparation of superhydrophobic surfaces. Compared with other alternatives, laser processing technique has become a competitive technique to fabricate superhydrophobic surfaces because of its great advantages such as short action time, easy processing operation, accurate control of structure pattern, and wide processing materials. The application of laser technique in fabrication of superhydrophobic materials has been studied by many researchers [23–25]. But most of these works mainly focused on the fabrication of superhydrophobicity on the surface with expensive picosecond, femtosecond and nanosecond lasers, common laser marking machines were rarely used. In this paper, we described a one-step method of producing superhydrophilic surface on stainless steel substrate. The laser ablation here was carried out through a common laser-marking machine on stainless steel substrate. Without any additional surface treatment, the laser-processed sample was sealed in a PE sealing bag and obtained superhydrophobicity 12 days later. The one-step method here is simple, cost-effective and eco-friendly and will have great potential in large-scale application of superhydrophobic surfaces.

2. Experiment

2.1. Sample preparation

The surface of 304 stainless steel sample with dimensions of 20 × 20 × 0.5 mm was ablated by a laser-marking machine provided by Guilin Sanhuan laser company with a laser spot diameter of 50 μm and an effective focal length of 100 mm. The pulse width and repetition rate of the laser are 120 ns and 50 kHz. With an output power of 3 W, the scanning speeds of the laser were set at 200 ~ 1200 mm s⁻¹, respectively. The stainless steel substrate was laser-textured with different scanning distance, 25 μm, 50 μm, 75 μm and 100 μm, respectively. After that, the as-prepared samples were put into sealing bags.

2.2. Characterization

Surface morphologies of the prepared samples were observed using a scanning electron microscope (SEM, KYKY-EM6900, Tiantest Optical Equipment Co., Ltd., Dongguan). Wettability of the samples was analyzed by a contact angle measurement instrument (SDC-200, Sindin Precision Instrument Co., Ltd., Dongguan) with 8 μl droplets of deionized water. The average value of contact angle was obtained by measuring six different spots of the sample. Being sealed in the sealing bags for one month, the corrosion behaviors of the samples in 3.5% NaCl aqueous solution were analyzed by potentiodynamic polarization at room temperature (about 25 °C) using an electrochemical workstation (IM6ex, Zahner).

3. Results and discussion

3.1. SEM

With the scanning speed of 600 mm s⁻¹, the morphologies of the laser-textured samples of different scanning distance at high magnification and low magnification are shown in figure 1. Figure 1(a) and (c) show that with a scanning distance of 25 μm, the microstructure is not regular because the beam paths overlap many times. Figure 1(b) and (f) indicate that with an distance of 50 μm, just some beam paths overlap. The sample surface possesses a regular microstructure. Figure 1(c) and (g) with a scanning distance of 75 μm have less overlapping. And figure 1(d) and (h) with scanning distance of 100 μm show that after laser ablation, the sample surface has a wave-shaped microstructure. With an output power of 3 W, the laser ablation does not create deep grooves on the surface.

3.2. Wettability

To test the relationship between contact angle and the scanning distance, samples with different scanning distance were tested. Figure 2 shows the contact angles of samples with the scanning speed of 600 mm s⁻¹ at 25 μm, 50 μm, 75 μm and 100 μm scanning distance, respectively. The resulting contact angles are 155.2°, 160.7°, 158.6° and 160.2°. Corresponding sliding angles are 24°, 6°, 8° and 7°. It shows that the superhydrophobic performance of the sample with 50 μm scanning distance is the best, and that with 25 μm is the worst.

To test the relationship between contact angle and scanning speed, samples were prepared at 50 μm scanning distance and with different scanning speed, 200, 400, 600, 800, 1000 and 1200 mm s⁻¹, respectively. The laser-textured samples are proved hydrophilic. Placed in the air for 3 months, they failed to turn superhydrophobic. The other samples were sealed in sealing bags. 12 days later, contact angle measurements confirm the superhydrophobicity of these samples. The result depicted in figure 3 shows that almost all the contact angles of most samples kept in sealing bags are above 150° except the one with the speed of 200 mm s⁻¹. Therefore, it can be indicated that 12 days after the laser treatment, most samples exhibit superhydrophobic...
property. And the depth of the laser-treated surface has a close relation with the scanning speed of the laser. The microstructure varies with the speed. So does the contact angle.

To observe the change of the wettability of the sample with time, we took the sample with the scanning speed of 600 mm s$^{-1}$ and scanning distance of 50 $\mu$m for observation. The samples were kept in different sealing bags.

**Figure 1.** SEM images of laser-textured stainless steel surfaces: (a)–(d) at high magnification with the scanning distance of 25 $\mu$m, 50 $\mu$m, 75 $\mu$m, 100 $\mu$m; (e)–(h) at low magnification with the scanning distance of 25 $\mu$m, 50 $\mu$m, 75 $\mu$m, 100 $\mu$m.
The water contact angle measurements were carried out every two days. The results are shown in figure 4. It can be seen that the angles of contact change significantly from the 6th to the 12th day. But after that, they remain stable.

3.3. XRD

XRD measurements were used to test the change of chemical compositions of the samples before and after laser treatment. As it can be seen in figure 5, the existence of a Cr$_{0.19}$Fe$_{0.7}$Ni$_{0.11}$ peak can be found on the unfabricated stainless steel. Additionally, peaks of Fe-Cr, Fe, Ni-Cr-Fe and [Fe,Ni] appear on the superhydrophobic sample after laser fabrication. In the sealing bags, Cr$_{0.19}$Fe$_{0.7}$Ni$_{0.11}$ decomposition reaction occurred and peaks of Fe-Cr, Fe, Ni-Cr-Fe and [Fe,Ni] were newly identified for the treated sample.

XPS spectra are shown in figure 6. By comparing XPS wide scan spectra of (a) and (f), it can be seen that among all elements, peak intensity of C and O changes most significantly. After laser treatment, the surface of
stainless steel is oxidized. The spectra of (c), (h), (d), (i) show that Fe and Cr are the main oxidized metal elements. The C 1s spectra of (d), (i) and O 1s spectra of (E), (J) show that the peak intensities of C–C single bond and C–O single bond do not change obviously, but the peak intensities of C–O double bond increase, indicating that there are new carboxyl compounds. Therefore, XPS test results show that the formation of superhydrophobic surface is related to the presence of carbon and oxygen, similar result was reported by Kietzig et al [26], who reported a variation of the carbon and oxygen percentage during the slow decomposition of carbon dioxide on the sample surface. The transition of the surface wettability from superhydrophilicity to superhydrophobicity after laser treatment correlated with the amount of carbon on the surface.

3.4. Self-cleaning
To test the self-cleaning behavior of the laser-treated samples, samples with the scanning distance of 50 μm and scanning speed of 600 mm s⁻¹ were used for test. The test was shown in figure 7(a)–(f). Soil was spread on the
sample surface. Droplets were dripped 50 mm away from the sample. When the water dripped down the sample surface, it soon rolled with the soil on the surface under the action of gravity. It rolled for about 6 mm and then stopped. When the second and third droplets fell, the mud ball continued to roll forward. By the time the fifth

Figure 6. (a) XPS wide scan spectrum of untreated stainless steel; (b)–(e) XPS spectra of Fe 2p, Cr 2p, C 1s and O 1s; (f) XPS wide scan spectrum of superhydrophobic stainless steel surface; (g)–(j) XPS spectra of Fe 2p, Cr 2p, C 1s and O 1s.
one dropped, it can be seen that there was no soil where the mud passed. The test shows that the as-prepared superhydrophobic stainless steel surfaces have excellent self-cleaning property.

3.5. Bouncing test

Diluted black ink was used to test the bouncing behavior of the droplet on the stainless steel substrate as shown in figure 8(a)–(h). The sample used was prepared with the scanning distance of 50 μm and scanning speed of 600 mm s⁻¹, the droplet first bounced off due to the effect of gravity and the reaction force of the sample surface. Soon the droplet bounced again and jumped out of the sample surface until it fell into the glassware. Therefore, it can be known that the superhydrophobic stainless steel surface must have a low adhesion, which enables the droplet to bounce.

Figure 7. Self-cleaning test of superhydrophobic surface.

Figure 8. Video screenshot of the bouncing ink on sample surface.
3.6. Corrosion resistance performance

The samples were exposed to 3.5% NaCl corrosive solution for the corrosion protection. The potentiodynamic polarization curves of the bare stainless steel, laser-treated stainless steels with different scanning speed, 25 μm, 50 μm, 75 μm, 100 μm, respectively, were shown in figure 9 (a)–(e) and relevant electrochemical parameters were presented in table 1. It can be seen in figure 9(a) that the Ecorr and Icorr in 3.5 wt% NaCl solution is −0.05 V and 1.26 × 10^{-6} A·cm^{-2} for bare stainless steel. Accordingly, the Ecorrs for the superhydrophobic surface with the distance of 50 μm is increased to 1.32 V, while the Icorr is decreased to 7.18 × 10^{-10} A·cm^{-2}.

Compared with the Icorr value of the bare substrate, the superhydrophobic surface with distance of 50 μm is smaller by more than 3 or 4 orders of magnitude. Therefore, the corrosion rate of the superhydrophobic sample was much lower than that of the bare substrate in the corrosive solution. Superhydrophobicity of stainless steel greatly improved the corrosion resistance in 3.5% NaCl solution.

Figure 10 shows Nyquist plots, Bode plots and equivalent circuit of samples with different scanning distances in 3.5% NaCl corrosive solution, and the corresponding EIS fitted data are listed in table 2. From the Nyquist plots in figure 10(a), it can be seen that the high frequency capacitive impedance arc of the electrochemical impedance spectrum of the untreated sample is the smallest, indicating that the resistance value of the sample after laser treatment is significantly increased. According to figure 10(b), the initial resistance of all samples is large and 50 μm is the maximum while the untreated sample has the smallest initial resistance. With the increase of immersion time, the resistance of all samples will become smaller. In figure 10(c), it can be seen that the phase angles increase first and then decreases, and the phase angles of all the laser treated samples are larger than that of the untreated sample. Therefore, the anti-corrosion performance of the superhydrophobic sample surface is significantly improved compared with the untreated stainless steel sample, and the sample has the best anti-corrosion performance when the laser scanning distance is 50 μm.

As shown in figure 2, the as-prepared sample has a small sliding angle. Generally speaking, the superhydrophobic surface with a low sliding angle is in a Cassie–Baxter state [27]. When immersed in the corrosive medium, the stainless steel substrate has a reaction with corrosive ions. Air trapped on the

| Specimen | Ecorr (V) | Icorr (A·cm^{-2}) |
|----------|----------|-----------------|
| a        | −0.05    | 1.26 × 10^{-6}  |
| b        | 0.39     | 1.41 × 10^{-8}  |
| c        | 1.32     | 7.18 × 10^{-10} |
| d        | 0.90     | 4.31 × 10^{-9}  |
| e        | 0.57     | 2.16 × 10^{-9}  |

Figure 9. Potentiodynamic polarization curves of bare stainless steel and superhydrophobic surface in 3.5% NaCl corrosive solution with different scanning distance (a)–(e) 25 μm, 50 μm, 75 μm, 100 μm.
microstructure of the superhydrophobic surface inhibits the contact between the substrate and corrosive solution, thus protecting the substrate from being corroded. Therefore, when air is trapped in the microstructures of surface, hydrophobicity of the sample is enhanced. The superhydrophobic sample has a good anti-corrosion performance.

4. Conclusion

Here, we reported a laser-textured method to prepare superhydrophobic surfaces on stainless steel substrate. The experiment was performed on a common laser marking machine. The laser-treated substrates remained hydrophilic when exposed to the air for 3 months. But when they were sealed in sealing bag for 12 days, the samples soon obtained superhydrophobicity. The as-prepared superhydrophobic stainless steel samples were tested and confirmed to possess excellent self-cleaning, corrosion-resistant properties. Compared with the traditional laser processing method, it has great advantages such as facile operation and low cost. Without any surface modification, the method is also free of any chemical reagents. So it is environmental-friendly. The attempt to obtain superhydrophobic stainless steel by common laser marking machine will offer a wide prospect for the mass-production of superhydrophobic surfaces.

![Figure 10.](image)

**Figure 10.** (A)Nyquist plots, (B)Bode amplitude plots,(C)Bode phase angle plots and (D)Equivalent circuit.

| Sample  | Rs(Ω·cm⁻²) | CPER(Ω·cm⁻²) | Rf(Ω·cm⁻²) | CPEdl(F·cm⁻²) | Rct(Ω·cm⁻²) |
|---------|-------------|--------------|-------------|---------------|-------------|
| bare    | 3.619       | 5.5017 × 10⁻⁶ | 1786        | 8 × 10⁻¹⁵     | 0.32695     |
| 25 µm   | 87.69       | 3.6171 × 10⁻⁸ | 8.396 × 10⁷ | 0.37895       | 0.61409     |
| 50 µm   | 244.8       | 3.727 × 10⁻⁹ | 2.453 × 10⁸ | 0.37895       | 0.61409     |
| 75 µm   | 142.5       | 4.378 × 10⁻⁹ | 4.415 × 10⁸ | 0.663         | 0.68603     |
| 100 µm  | 75.3        | 8.17 × 10⁻⁹  | 5.761 × 10⁸ | 1.97          | 0.5729      |
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