Effect of different micro-texture shape on corrosion resistance of metal surface

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Abstract. The 304 stainless steel is widely used in daily life. In this paper, the 304 stainless steel was taken as the substrate material and then the five different micro texture shapes were carved on them by nanosecond laser engraving machine under the same parameters. These shapes are the groove array, the square column array, the circular pit array, the regular hexagon column array and the trapezoid column array. Then these samples were immersed in 0.5 mol/l perfluorodecyl trimethoxysilane ethanol solution at 45 °C for 5 hours. Five type superhydrophobic surfaces were obtained. A series of corrosion experiments were conducted out and the influence of different micro texture on the corrosion resistance to the 304 stainless steel surface was analyzed. The results show that the square column array has the best corrosion resistance, and its corrosion rate is 4.20mm.a⁻¹, which is the lowest in all other micro texture shapes. It can be used as a reference for improving the corrosion resistance of metal surface.

1. Introduction

The surface of any machined part is in actuality not a perfect surface, with defects ever-present including superficial unevenness, residual stress and effects of cold hardening, each promoting metallographic structure and phase changes. [1, 2] Although these problems exist only in an extremely thin surface layer, it intricately affects the corrosion resistance of mechanical parts, and thereby affects the service performance and service life of the product. The surface texture shapes and roughness of a part have a great influence on the corrosion resistance of the part. The surface roughness is large, and corrosive substances tend to accumulate in the pits and corrode the metal surface [3].

Preparation of super-hydrophobic coating on the surface of metal material is an effective green anti-corrosion method [4]. Because the super-hydrophobic functional surface has high super-hydrophobicity and self-cleaning function [5, 6], this can effectively prevent the corrosion of metal surface[7]. The reason why super-hydrophobic surface can resist corrosion is that there is a certain degree of micro-texture on the surface. This super-hydrophobic surface also has a self-cleaning effect, and water droplets will carry contaminants away from the surface [8, 9].

The 304 stainless steel has good mechanical properties and is widely used in industrial manufacturing and marine shipbuilding industry. The 304 stainless steel is not really no corrosion in the natural environment, but the corrosion is relatively slow [3, 10]. Therefore, there must be the problem of material corrosion in the process of use, which will affect the service performance of the material. For example, in the marine industry, due to the strong corrosiveness of sea water, it is more easily to cause the corrosion of metal materials. At present, many scholars have developed various
methods for the preparation of super hydrophobic coatings on metal surfaces, such as self-assembly, etching, sol-gel, chemical vapor deposition, electrochemical deposition, electrochemical anodization, mechanical processing, etc. [11, 12]. However, there are few reports on the preparation of super-hydrophobic coating with micro structure on 304 stainless steel substrate by laser engraving [13].

In this paper, the 304 stainless steel was taken as the substrate of samples. Then, different micro texture shapes, such as groove array, square column array, circular pit array, regular hexagon column array and trapezoid column array, on the surface of the 304 stainless steel were carved by nanosecond laser engraving machine under the same parameters. After that, it is modified using perfluorosilane to drop the surface energy and to study the effect of micro-texture shape on the corrosion resistance of the surface. It is hoped to provide a reference for the preparation of super-hydrophobic and corrosion-resistant coatings on the surface of workpieces.

2. Experiment and results

2.1. Experimental materials
The 304 stainless steel samples of 1mm thickness and 10mm×10mm in size (Ruikai Mould Co., Ltd., Shenzhen, China) were tested in all experiment. The chemical reagents of 1H, 1H, 2H, 2H-Perfluorodecyl trimethoxysilane (Jiaye Chemical Co., Ltd. Qufu, China) and the ethanol with purity 97% were used in experiments.

2.2. Experimental steps
Before experiments, all samples were polished using the sandpaper with 800-mesh and to make the surface of the stainless steel uniform and smooth with the surface roughness about Ra 0.2µm. Firstly, the five micro texture shapes, such as the groove array, the square column array, the circular pit array, the regular hexagon column array and the trapezoid column array on the surface of samples, were carved by the high-speed nanosecond laser engraving machine with the type KN120. The carving power was 12W, carving speed was 300mm/s and the carving frequency was 20KHz. These shapes of the micro texture carved are shown in Figure 1 below. Secondly, these samples carved were placed into the ultrasonic cleaner for 10 minutes, and then, these samples were taken out and blown dry with a hair dryer. Finally, these samples were put in the solution with 0.5mol/l perfluorodecyl trimethoxysilane ethanol at 45°C for 5 hours, and then these samples modified were taken out and washed with alcohol, and then these samples were let dry naturally in the laboratory. These dried samples were used for analysis next.

2.3. Analysis methods
These samples were taken on the optical contact angle measuring instrument with the type TST-200H to measure the contact angle with the 4μl water droplets, and data of water contact angle (WCA) on the surface of each sample were measured respectively and the average value were taken. The electrochemical workstation with the type CS2350 was used to measure the anodic polarization curve (Tafel curve) to use to evaluate the corrosion resistance of the sample. The scan rate electrochemical workstation was 0.01 V/s, the auxiliary electrode was the platinum electrode and the reference electrode was the saturated calomel electrode. These experiments were performed in 3.5% NaCl solution.
Figure 1. Micro texture shapes of stainless steel surface measured by white light interferometer.

2.4. Measuring results
The WCA, the corrosion rate of each sample were measured. See Table 1 and Figure 2.
Table 1. Measuring results of each sample.

| Factor                      | a           | b           | c           | d           | e           | f           |
|-----------------------------|-------------|-------------|-------------|-------------|-------------|-------------|
| Micro texture shape         | No micro texture | Groove array | Square column array | Circular pit array | Regular hexagon column array | Trapezoid column array |
| WCA (mean ± SD)             | 123°±0.59   | 162°±0.49   | 165°±0.43   | 154°±0.46   | 158°±0.58   | 144°±0.64   |
| Sample number of WCA        | 5           | 5           | 5           | 5           | 5           | 5           |
| Corrosion Rate \(R_{CORR}(\text{mm.a}^{-1})\) | 20.67±0.57  | 4.28±0.11   | 4.20±0.10   | 5.79±0.16   | 8.61±0.15   | 12.17±0.26  |
| Sample number of Corrosion rate | 5           | 5           | 5           | 5           | 5           | 5           |
| \(F \left( \frac{\text{SDWCA}}{\text{SDCR}} \right) \) | 1.04        | 4.46        | 4.30        | 2.88        | 3.87        | 1.77        |

3. Discussion

It can be seen from Table 1 and Figure 2 that the corrosion rate (4.20 mm.a\(^{-1}\)) with micro texture shape of square column array is the lowest in all shapes. The corrosion resistance (4.28 mm.a\(^{-1}\)) with micro texture shape of groove array on the surface takes the second place. The corrosion rate (20.69 mm.a\(^{-1}\)) with surface without carving micro texture is the largest.

Figure 2. Polarization curves of different shapes on the surface of samples.

By the statistical analysis of the two factor ANOVA without repetition, at the 0.05 level (\(p<0.05\)), the two samples between the WCA and the corrosion rate in all shapes is NOT significantly different.

According to the F value of each group in the Table 1, the F Test can be conducted to analyze whether there is the significant difference of the standard deviation or variance between WCA values and corrosion rate values. Set \(\alpha=0.05\) (at the 0.05 level), the \(F_{0.025} (4, 4) =6.39\) and the \(F_{0.975} (4, 4) =0.157 \) [14]. By comparison, the F value of each group is between the \(F_{0.025} (4, 4)\) and the \(F_{0.975} (4, 4)\).
This is $F_{0.975}(4, 4) = 0.157 < F_{i} (i = a, b, c, d, e, f) < F_{0.025}(4, 4) = 6.39$. It can be considered that there is no significant difference in variance of each group.

On the other hand, in order to explain the relationship between WCA values and corrosion rate values, the statistical analysis of the correlation also was conducted. By the correlation data analysis, the correlation coefficient of the WCA values and corrosion rate values is 0.974. It fully shows that the hydrophobic angle of the surface has a great relationship with the corrosion resistance of the surface.

Based on the above, it is shown that the corrosion rate is related to the WCA value on the surface. Then, it is can be said that when the WCA value of the surface increases, the corrosion rate gradually decreases by the Table 1 and the Figure 3.

According to the super-hydrophobic micro texture on the surface of metal material, the anti-corrosion mechanism is shown in Figure 4. On the one hand, when the metal material with the super-hydrophobic surface is immersed in the corrosive medium, an air layer will be formed on the surface of the super-hydrophobic surface. With the help of the air layer, the corrosion phenomenon can be effectively prevented. See Figure 4. On the other hand, when the surface of the metal material has the performance of super-hydrophobic, the contact angle between the water droplet and the surface of the solid object will become very large and the adsorption performance of water droplets on the surface is reduced because of the self-cleaning action of super-hydrophobic surface. This will affect the exchange rate between ions [15]. Therefore, if the WCA on the surface is larger, the contact area between the water droplet and the surface is smaller, and the corrosion rate is lower. The polarization curve in Figure 2 also shows that the corrosion resistance of the surface with micro texture shape of the square column array and the groove array are the best, and the corrosion resistance of the surface without micro texture is the worst.

![Figure 3](image1.png)

**Figure 3** The relationship between corrosion rate and the water contact angle.

![Figure 4](image2.png)

**Figure 4.** The schematic of anti-corrosion mechanism on the super-hydrophobic surface.
4. Conclusion
In this paper, took the 304 stainless steel as the substrate material of samples, the five different micro texture shapes on the surface of the 304 stainless steel were carved. According to experimental results and analysis, the conclusion is as follows.

The corrosion resistance without micro texture shape on the surface of the 304 stainless steel is worse than that of with the suitable micro texture shape on the surface.

The corrosion resistance with micro texture shape of square column array on the surface of the 304 stainless steel is the best. The corrosion resistance with micro texture shape of groove array on the surface takes the second place.

The corrosion resistance has the relationship with the water contact angle. After comparison with the WCA value and the corrosion rate on the surface, the corrosion resistance increases with the increase of WCA.

These results can be used as a reference for improving the corrosion resistance of metal surface.

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