Modification of Wettability Property of Titanium by Laser Texturing

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Abstract

Three different microstructures with line pattern, grid pattern and spot pattern were fabricated on titanium surfaces by nanosecond laser. Scanning electron microscopy (SEM), contact angle measurement, surface roughness gauge and X-ray photoelectron spectroscopy (XPS) analysis were used to characterize and measure the surface morphology, contact angle, surface roughness and chemical composition of titanium after laser processing. The results indicate that the contact angle of titanium surface is 77.8 °immediately after laser processing, which shows hydrophilicity, and the contact angle presents a rising tendency with time in general. At steady state, the maximum contact angles for line pattern, grid pattern and spot pattern increased to 157.2 °, 153 ° and 132.5 °, respectively. It can be found that the surface wettability has changed from hydrophilicity to hydrophobicity and even to superhydrophobicity. The influence of surface morphology on the surface wettability effects immediately after laser treatment and does not change with time, while the effect of surface chemical composition on the surface wettability will continue from the beginning of laser processing to the stabilization of surface chemical composition. Finally, it can be deduced that the accumulation of carbon on the surface is probably the critical factor to improve the surface hydrophobicity. Therefore, it is concluded that laser-induced modification of surface wettability correlates with surface morphology and surface chemical composition.

Keywords: wettability, titanium, nanosecond laser, surface morphology, chemical composition

1. Introduction

Wettability is one of significant characteristics of solid surface, it means the ability of a solid surface to reduce the surface tension of a liquid in contact with it such that it spreads over the surface and wets it. The wettability is generally evaluated by the contact angle (θ) on the surface. It is defined as the angle between the solid surface plane and the tangent of the liquid–vapor interface of a sessile drop, which is usually measured on the liquid side [1]. The solid surface presents hydrophilicity when the contact angle is less than 90 º and hydrophobicity with the contact angle is larger than 90 º, when the contact angle is higher than 150 º, the solid surface presents superhydrophobicity. Superhydrophobicity is an extreme example of wettability, the earliest recognition of it starts from nature, such as lotus effect. Superhydrophobic surface has wide applications in self-cleaning, anti-fog snow, anti-corrosion resistance, microftuidic chip, nondestructive liquid output [2-8], etc. Therefore, recent researches mainly focus on improving the wettability of solid surface, especially manufacturing hydrophobic surface.

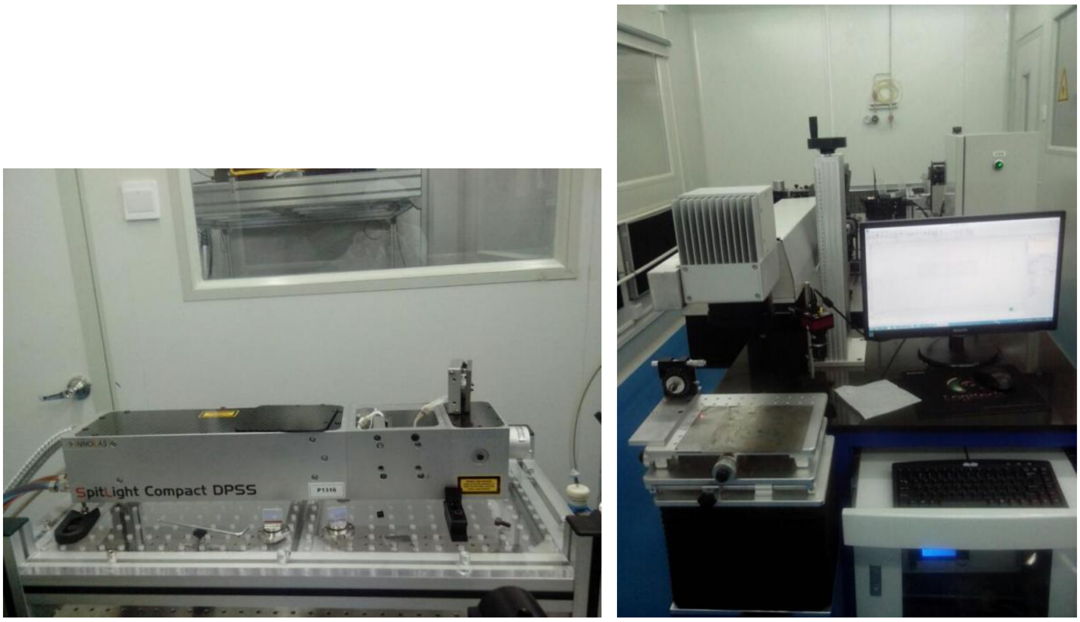
The wettability of solid surface is determined by both the chemical composition and the surface morphology, which maily concern surface energy and surface roughness of the solid surface. Therefore, there are two ways to achieve a hydrophobic surface, one is to decorate materials with low surface energy, and the other is to fabricate microscopic surface structure. Since the company of Kao in Japan firstly prepared superhydrophobic surface with contact angle of 174 º[9], many techniques have been reported to produce superhydrophobic surfaces, including self-assembly, electrospinning, polymer imprinting, plasma-treated surfaces, lithography, and so on [10-16]. In recent years, more and more researches focus on manufacturing hydrophobic surface based on the technology of laser-induced microstructure. Mirhosseini et al. [17] processed microholes on Ti6Al4V by laser and the contact angle increased from 55 ºto 90.2 º. Luo et al. [18] machined micro-patterns on 316 stainless steel by a short pulse excimer laser, and the contact angle increased from 68.5 ºto 130 º. Chunhong et al. [19] investigated surface microstructuring of SiC material using fiber optic laser, and found that contact angle varied from 89.8 º to 119 º. Jagdheesh [20] studied the wetting behavior of laser-induced micropatterns on alumina. It was found that the surface of alumina exhibited a superhydrophobic surface with a static contact angle of 150 ° ± 3 °. Hydrophobic or even superhydrophobic surface has been realized by the technology of laser-induced microstructures successfully. But these patterns are unstable, additionally, many of the superhydrophobic surfaces prepared by self-assembled technology mainly need the coating materials with low surface energy, which not only makes the research work complex but also improves the cost. Titanium is an important structural metal developed in the 1950s. Because of the excellent physicochemical properties such as low density, high intensity, good resistance to causticity, nonmagnetic, etc, it is known as "space and ocean metal" and widely used in aerospace and ocean fields [21]. So developing titanium with superhydrophobic surface can raise the value of material in aircraft and ship.

Many researches about laser-induced hydrophobic surface have been reported in various literatures [18-20], but the specific reason for the change of surface wettability after laser processing has no comprehensive research. In this paper, nanosecond laser is used to fabricate patterned microstructures on the surface of titanium, including line pattern, grid pattern and spot pattern. After laser processing, the surface morphology of these patterned titanium surfaces was captured by scanning electron microscopy (SEM) firstly and their surface wettability was characterized by the contact angle. Then, the variation of contact angle with time was investigated and the relationship between surface roughness and contact angle was discussed. In addition, the chemical composition of processed titanium surfaces was tested by X-ray photoelectron spectroscopy (XPS). Finally, the underlying physics of surface wettability variation was revealed successfully, which lays a foundation for preparing superhydrophobic surface.

2. Experimental details

2.1 Materials and experimental setup

The pure titanium TA2 was chosen as experimental material with a size of Φ20mm×1mm. Samples were mechanically polished and cleaned in acetone by ultrasonic bath for 10 minutes before and after laser treating. Nanosecond laser system (InnoLas Laser GmbH from Germany) was used to fabricate surface microstructures on titanium surfaces as shown in fig.1. The laser system outputs laser pulses with 1064 nm wavelength, 6ns pulse width, 1.2W output power and 100Hz output rate. The diameter of the focused laser beam is 100 μm. Therefore, laser fluence is 1.5279×10^2 J/cm^2. And the workbench moves along x and y directions with the scanning speed of about 0.5mm/s. By laser treatment, three microstructures including line pattern, grid pattern and spot pattern were produced on the surfaces. And for each kind of microstructures, the spaces between lines or spots were set as 50μm, 60μm, 70μm, 80μm, 90μm and 100μm, respectively. The whole processing region was confined in a square with a size of 10mm×10mm.



(a) Nanosecond optical system (b) Motion control system

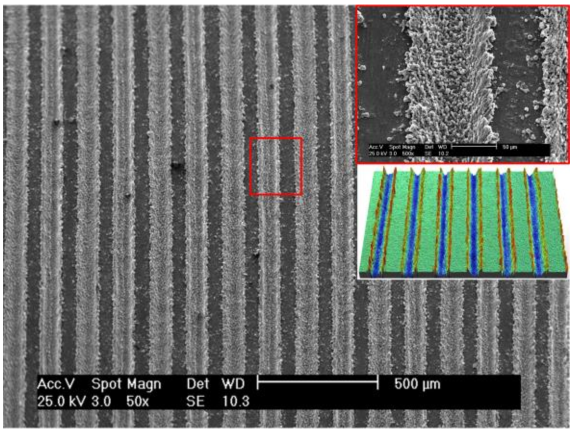
Fig.1 Nanosecond laser processing system

2.2 Characterization and measurement

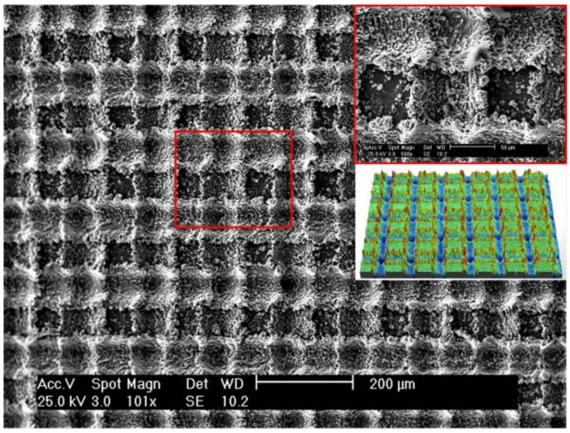
In order to evaluate the effect of surface morphology on the surface wettability, three types of microstructures including line pattern, grid pattern and spot pattern were fabricated by laser texturing on the titanium surfaces and their surface morphology was firstly investigated by SEM. Then the contact angle was measured using the sessile drop method, and the evolvements of the contact angles with time for various samples with line pattern, grid pattern and spot pattern were analyzed. In addition, the surface roughness was tested by Surface Profilometer and the relationship between surface roughness and contact angle was discussed. For the sake of revealing the effect of chemical composition on surface wettability, XPS analysis was used to quantify the chemical composition of laser processed surface. All of these experiments were carried out in air at atmospheric environment.

3. Results and discussion

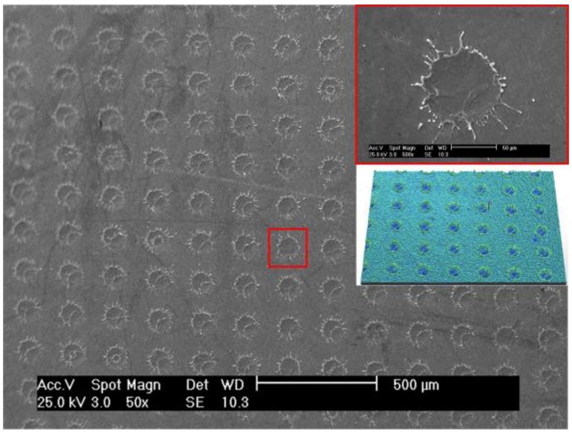
3.1 Analysis of surface morphology



(a) Line pattern



(b) Grid pattern



(c) Spot pattern

Fig.2 SEM images of line, grid and spot patterns on titanium surfaces

After laser processing, regular microstructures including line pattern, grid pattern and spot pattern were formed on the surfaces of titanium. Their surface SEM images have been captured and shown in fig.2. Under the irradiation of laser pulses, the surface material underwent the processes of melting, splashing and freezing in sequence. The splashing material can be observed clearly especially in fig. 2(c).

The modified surface morphology varies with the specific processing method. The way of grid pattern affected the surface morphology most seriously among the three, because its structure is the most complex and the proportion of laser processed region is also the largest as shown in fig. 2(b). The space between spots or lines also shows great impact on the surface morphology. In this study, the spaces of patterns were set to 50μm, 60μm, 70μm, 80μm, 90μm and 100μm, respectively. With the space increasing, the effect degree on the surface morphology decreases.

Besides, there was some debris deposited on the unprocessed area, which changed the surface morphology to some extent in comparison to the original design. However, laser processing shows no mechanical deformation in material and the smallest machining error in contrast to those traditional mechanical processing methods, so it is still a relative perfect processing method.

Additionally, these different types of microstructures have different effects on the surface contact angle, surface roughness and surface chemical composition, which are discussed in bellow sections.

3.2 Analysis of contact angle and roughness

The surface wettability is evaluated by the contact angle. Fig.3 and fig.4 show the measurement process of contact angle. A droplet of distilled water of 3ul is dispensed on the sample surface in air at atmospheric pressure. When the droplet stays still, a side view of the droplet is captured and analyzed by the software Drop Shape Analysis in order to obtain the contact angle.

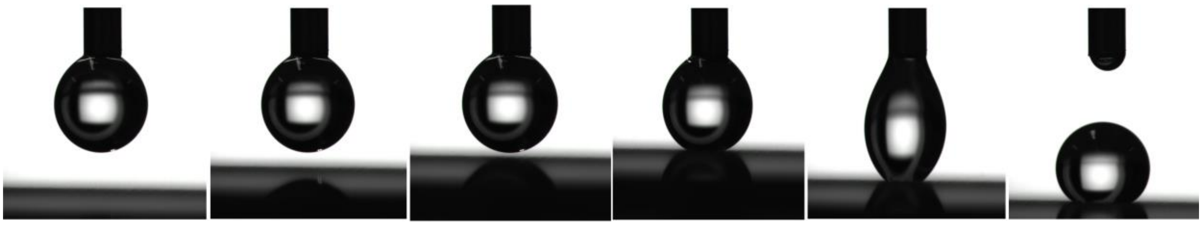


Fig.3 Process of dispensing water droplet

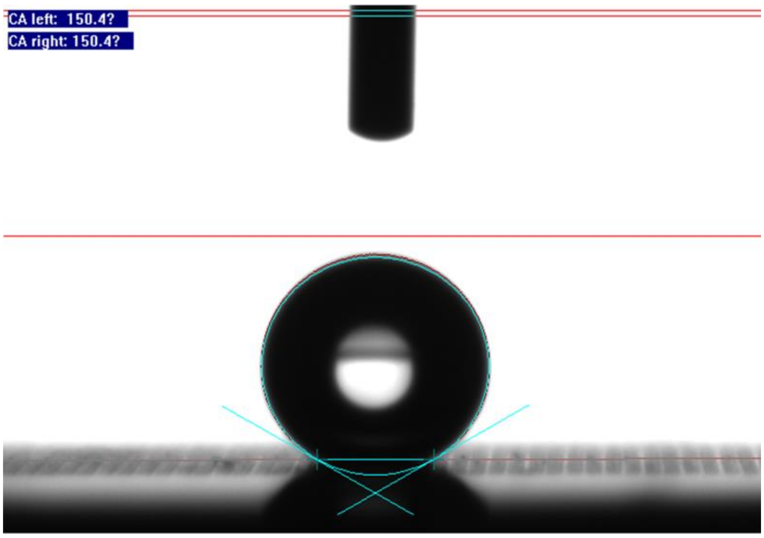


Fig.4 Measurement of contact angle

Fig.5 shows the evolvement of water contact angle with time for line patterned samples with various spaces. Before the laser treatment, all surfaces were hydrophilic because the contact angle of polished titanium surface was 77.8 °. Directly after laser processing, the contact angles decreased greatly and all surfaces became more hydrophilic. This behavior was well pronounced one day after the laser treatment. Because the spaces between lines were different, the changes of contact angles were also different and the minimum contact angle was less than 20 °.

One day later, the contact angles increased gradually to reach above 100 ° (except △ =100μm), and the maximum contact angle reached about 150 °. But the contact angles did not always increase with time. During a special period, all of the contact angle curves showed some fluctuations, the total tendency of contact angle decreased first and then increased again, and the fluctuation degree was different for different patterns with different spaces. This phenomenon is likely induced by the chemical reaction between sample material and air or due to the environmental influence.

Beyond this special period, no major change of the contact angle was observed in the following days, all of the contact angles (except for △ =100μm) increased above 130 ° and became stable in a certain range, and the maximum contact angle of line patterned sample reached 157.2 °. The change tendencies of contact angles with time were different for the line patterned samples with different spaces, therefore, the final contact angles were also different. On the whole, the space was smaller, the final contact angle was bigger. So in order to obtain desired hydrophobic surface by laser texturing, the laser processing parameters must be set reasonably.

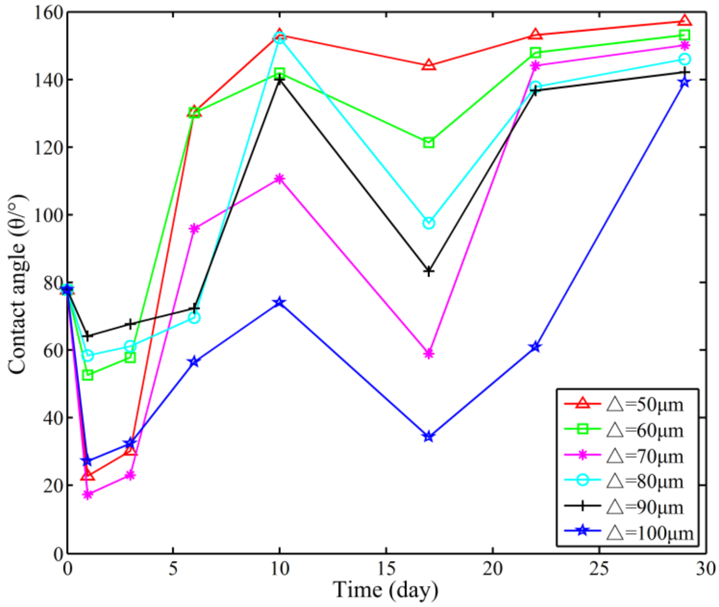


Fig.5 Evolvement of the contact angle with time for various Ti samples with line pattern

The change trends of contact angles with time for grid pattern and spot pattern are shown in fig.6 and fig.7. Immediately after laser processing, the contact angles of grid pattern and spot pattern decreased less than 40° and 50°, respectively. One day later, the contact angles increased gradually to reach values above 90°, and the maximum value was about 120°. However, in a following special period, the contact angle curves also fluctuated the same as that of line patterned sample, the reason of which is also similar to the explanation for line patterned case. Beyond above special period, for samples with grid pattern, only samples with spaces of 50μm and 60μm showed the final contact angles larger than 90°, and the maximum contact angle reached 153°. Samples with spot pattern finally showed hydrophobic with contact angles higher than 90° (except for △=90μm and △=100μm), and the maximum contact angle reached 132.5°. It can be derived that the surface wettability of titanium can be changed by laser processing so as to obtain hydrophobic surface, and the pattern type and processing parameters have great influences on the surface wettability.

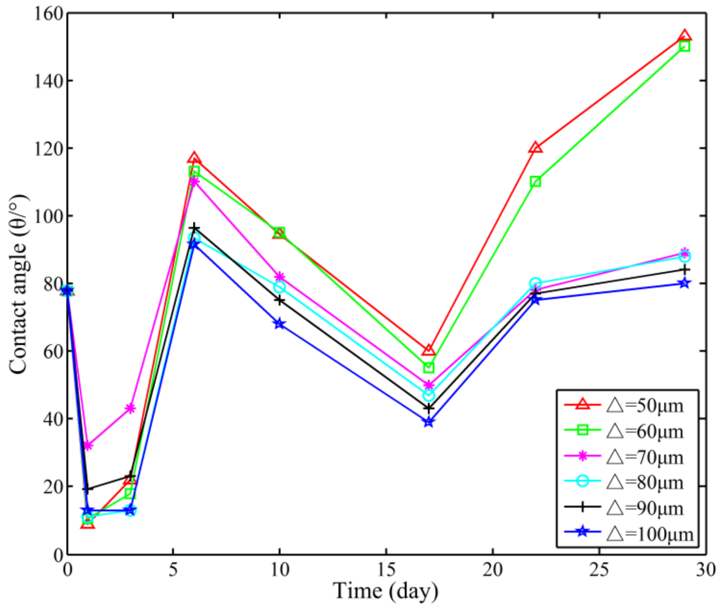


Fig.6 Evolvement of the contact angle with time for various Ti samples with grid pattern

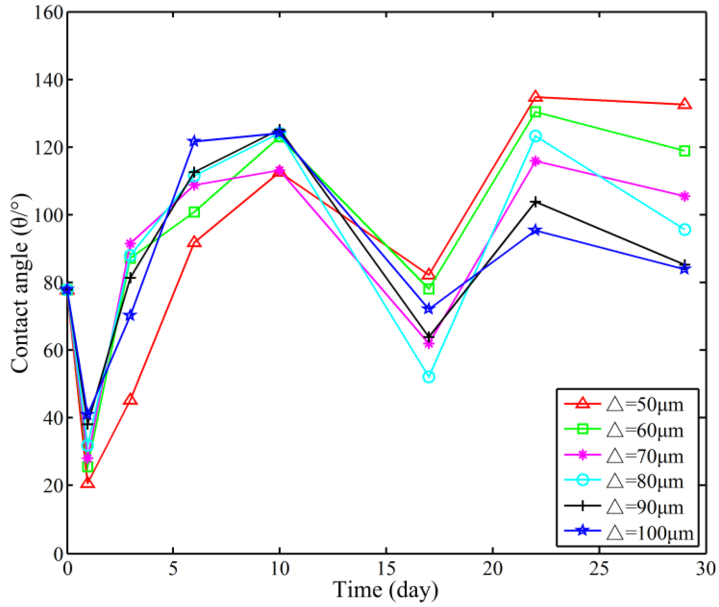


Fig.7 Evolvement of the contact angle with time for various Ti samples with spot pattern

The surface roughness values of samples before and after laser processing are shown in table 1. After laser treatment, the surface roughness increased significantly. The surface roughness of grid patterned sample was bigger than that of line patterned sample, and the surface roughness of line patterned sample was bigger than that of spot patterned sample. For the same microstructure, surface roughness decreased with the space between lines or spots increasing because the interaction of splashing and solidification is more serious when the space is smaller. And the final contact angle globally increased with the surface roughness increasing. Therefore, the effect of surface morphology on wettability can be attributed to the change of surface roughness.

In order to see the influence mechanism of surface roughness on material's wettability, experiments were also conducted with materials such as austenitic stainless steel (AISI 316L), Al6061 and tungsten carbide [22]. After laser processing, the dual scale structures could be seen on the all textured surfaces of these samples, which presents a micron scale structure with superimposed submicron features. The CA measurements of austenitic stainless steel (AISI 316L), Al6061, and tungsten carbide before and after laser processing were 54 °and 165.8 °, 76 °and 160 °, 75 °and 147 °, respectively. These results indicate that the hydrophobicity is not material dependent and that the hydrophobic behavior of the sample surface is primarily caused by dual scale surface structure. In addition, a more pronounced dual scale structure also results in higher contact angles, indicating higher hydrophobicity. When the scan was performed in two directions at 90◦, pockets were formed, which contributed to the formation of the air pockets under the water surface, thus possibly increasing the stability of the heterogeneous water-air-solid interface. The detailed reason that the dual scale structure affects the surface wettability greatly can be referred to ref. [22]. Formation of the dual scale structure leads to the change of surface roughness, therefore, the effect of surface morphology on wettability is essentially induced by the dual scale structure.

As we know, the surface roughness does not change over time, so an influence of the surface chemistry seems more reasonable to explain such a change of surface wettability with time, the following section will analyze the surface chemical composition of titanium before and after laser treatment in order to find out the reason for the change of surface wettability with time in detail.

Table 1 Surface roughness and contact angle before and after laser treatment

Pattern type	Smooth	Line		Grid		Spot	
Space(mm)	none	0.05	0.1	0.05	0.1	0.05	0.1
Roughness(μm)	0.07	6.49	5.18	6.69	6.49	0.35	0.21

Contact angle(°)	77.8	157.2	139.5	153	89.1	132.5	83.8

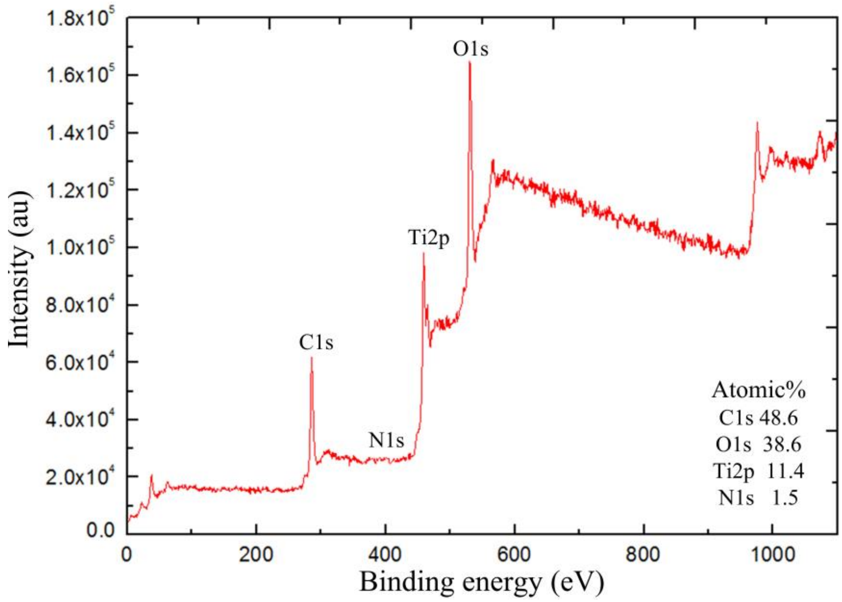
3.3 Analysis of surface chemical composition

In order to further study the effect of chemical composition on surface wettability, XPS was used to analyze the spectra of Ti2p, C1s, O1s and N1s for titanium before and after laser treatment (>30 days after laser treatment), and the results are shown in fig.8. Before laser treatment, the titanium surface exhibited a carbon content of 48.6%, after laser processing, the carbon content increased to 60.7%, 58.7% and 52% for line pattern, grid pattern and spot pattern, respectively. The result indicates that a change in the surface chemistry was clearly induced by laser processing and the carbon content increased.

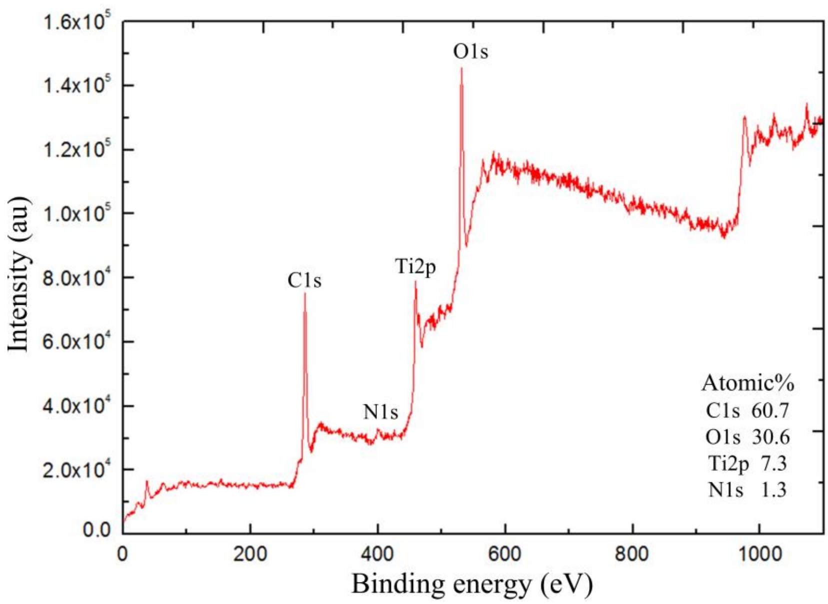
Based on the previous research, the increased carbon content mainly results from the accumulation of carbon. It can be attributed to the generation of new hydrophobic functional groups such as -CH3 or graphite carbon produced by laser ablation on the surface, both of which are hydrophobic, and also the decomposition of carbon dioxide in air during laser processing [23]. Decrease in titanium content indicates formation of titanium oxides. However, it is worth noting that titanium oxide is not hydrophobic in itself. Furthermore, it is evident from the spectral data that the accumulation of carbon on the surface possibly has an additional effect on the hydrophobic behavior of the surface [22], therefore, the surface wettability is closely related to the change of surface chemical composition after laser processing, especially carbon content.

To further investigate the change of carbon before and after laser treatment, XPS analysis for C1s also has been carried out and the results are shown in fig. 9. After laser treatment, there was some graphite C generated on all three types of microstructures' surfaces in different degree. Especially for the line patterned sample surface, the occurrence of (CH3)2-C*=O further improved the hydrophobicity of the surface on the basis of graphite C existence, which resulted in a higher contact angle.

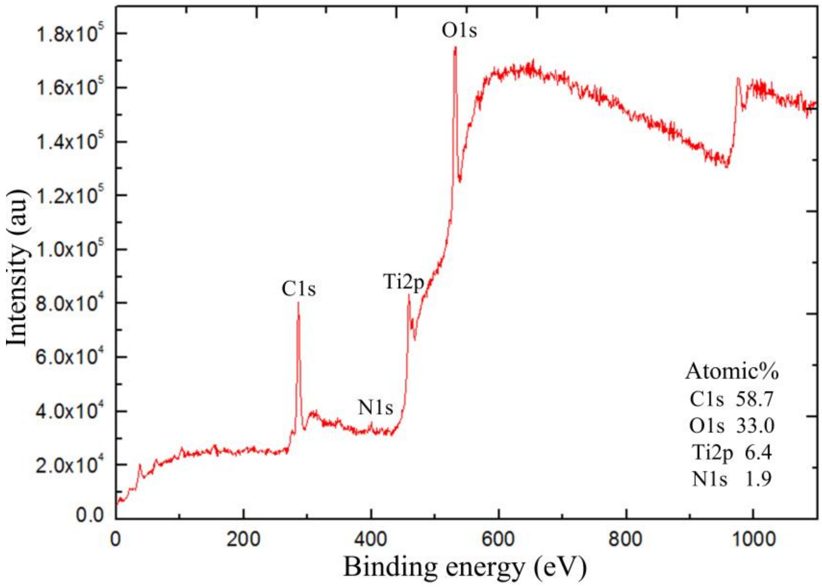
The results of XPS analysis indicate that the surface chemical composition changes with time after laser treatment, while the surface morphology does not change over time. So the influence of surface chemical composition on wettability will continue from the beginning of laser processing to the stabilization of surface chemical composition, by contrast, the influence of surface morphology on wettability is formed directly after laser treatment and will not change with time. Thus, after laser treatment, the modification of surface wettability over time is due to the change of surface chemical composition. Generally speaking, surface morphology and surface chemistry are considered to be the most possible influencing factors for laser-induced modification of surface wettability.



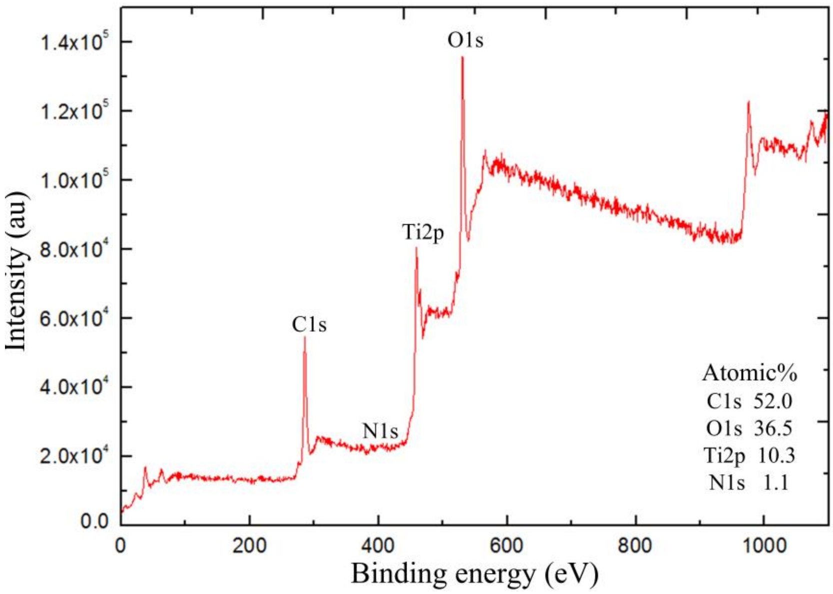
(a) Untreated titanium



(b) Line pattern

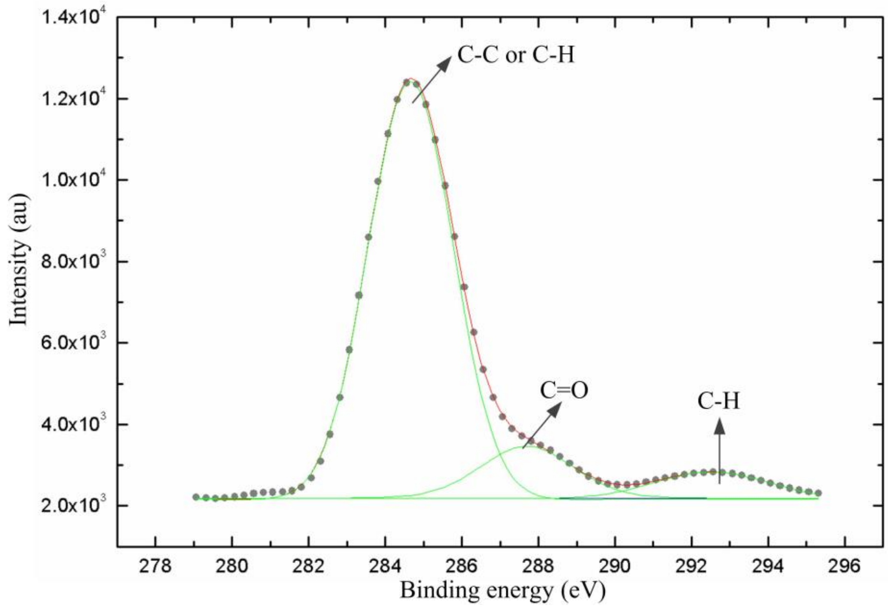


(c) Grid pattern

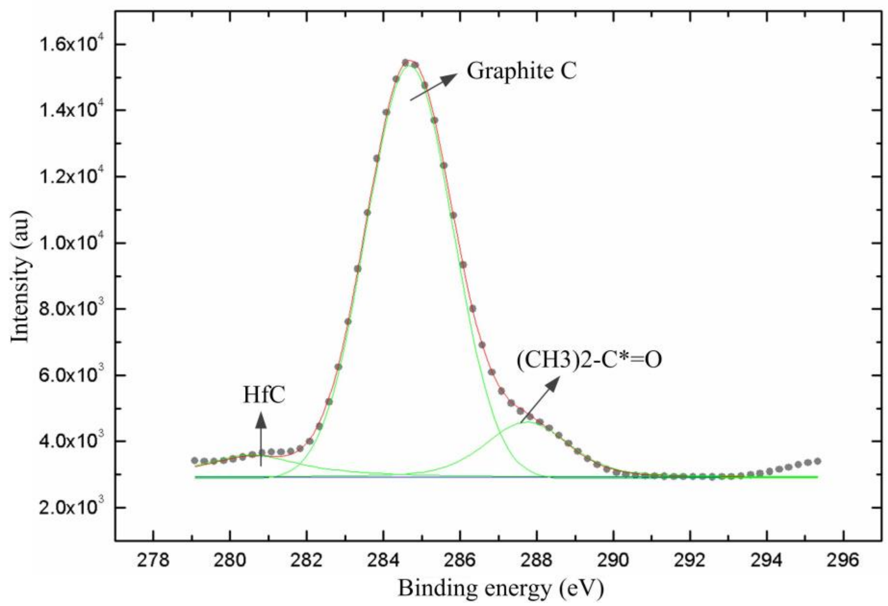


(d) Spot pattern

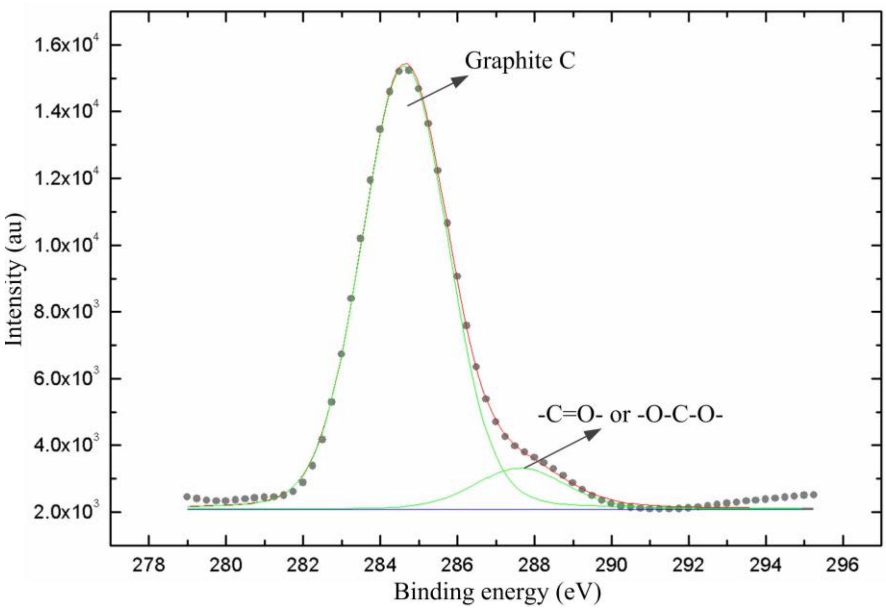
Fig.8 XPS spectra of titanium before and after laser treatment



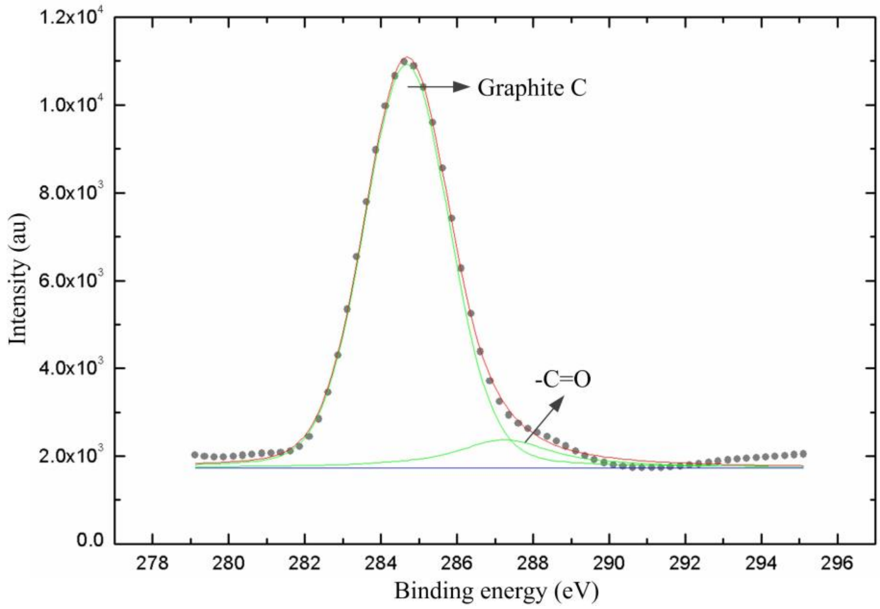
(a) Untreated titanium



(b) Line pattern



(c) Grid pattern



(d) Spot pattern

Fig.9 XPS spectra for the carbon peak before and after laser treatment

4. Conclusions

In order to study the modification of surface wettability by laser treatment, three kinds of microstructures with different spaces between lines or spots have been processed on titanium surfaces by nanosecond laser irradiation. Several conclusions can be obtained as follow.

(1) Compared with traditional mechanical processing methods, three different types of microstructures including line pattern, grid pattern and spot pattern were processed by nanosecond laser high efficiently and high precisely with almost no mechanical deformation

and the smallest machining errors.

(2) The results of contact angle measurement show that the contact angle of polished surface is 77.8° before laser irradiation, which means hydrophilic. Directly after laser treatment, the contact angle decreases greatly and the surface changes to be more hydrophilic. And then the contact angle increases over time. Finally, the maximum contact angles for three microstructures with line pattern, grid pattern and spot pattern are 157.2°, 153° and 132.5°, respectively. Therefore, the surface wettability can be improved and changes from hydrophilicity to hydrophobicity and even superhydrophobicity by laser texturing. Additionally, the final contact angles of surfaces with different microstructures and their corresponding surface roughnesses have a proportional relationship globally.

(3) Through XPS analysis, it can be found that the influence of surface chemical composition on wettability will continue in a certain period since laser treatment begun, while the effect of surface morphology on wettability is pronounced immediately after laser treatment and will not change with time. Therefore, the modification of surface wettability with time is due to the change of surface chemistry, during the change process of which the accumulation of carbon plays a critical role in the improvement of surface hydrophobicity. Overall, surface morphology and surface chemistry codetermine the laser-induced modification of surface wettability.

Acknowledgments

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