

Colorizing Ti-6Al-4V surface via high-throughput laser surface nanostructuring[☆]

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ABSTRACT

In this work, an innovative high-throughput laser surface nanostructuring process was developed to enhance the hydrophobicity and reduce the reflectivity of the Ti-6Al-4V surface using a nanosecond pulse laser. The laser textured Ti-6Al-4V surfaces exhibit combined anti-reflective, highly hydrophobic and mechanically enhanced effects. In the meantime, the anti-reflective Ti-6Al-4V surfaces show different colors when treated by different laser processing parameters. Compared with the existing ultra-short laser-based surface-texturing methods which often rely on the generation of micro-scale patterns using a focused laser spot and very fine spatial resolution, this innovative laser surface treatment method significantly increases the processing speed and reduces the production cost. This novel process will bring a new avenue for controlling the surface color, wettability and mechanical property of the important engineering surfaces.

1. Introduction

Rendering a certain metal to a different color without coating has always been an interesting research topic. It is highly desirable to controllably modify the optical property of a metal. In recent decades, fabrication of anti-reflective and colorized surfaces has been experimented by many researchers. Vorobyev and Guo demonstrated a femtosecond laser surface structuring technique that tuned highly reflective material surfaces such as gold [1], titanium [2,3], brass [3], platinum [3] and silicon [4] highly absorptive, thus creating the so-called “black metals”. Femtosecond laser structuring creates laser-induced periodic surface structure (LIPSS) consisting of laser-induced surface ripples with periodicity equal or smaller than the wavelength of laser radiation and much smaller than the effective laser spot size. The LIPSS is self-organized surface structure and its period varies with the laser fluence applied. The LIPSS has been proved to be the key for enhancing the surface anti-reflectivity owing to their unique capability of absorbing light.

Moreover, Vorobyev and Guo demonstrated the creation of colorized metals using the same technique [5]. They showed that this technique could controllably modify the optical properties of aluminum surface from UV to Terahertz range by creating the hierarchical surface structures with different experimental conditions. Huang et al. [6] and

Ou et al. [7] have also demonstrated femtosecond laser structuring methods to create LIPSS on various materials, such as gallium arsenide (GaAs), silicon (Si), brass, aluminum and stainless steel in order to increase the surface anti-reflection characteristics and blacken the surfaces. Yang et al. [8] patterned hybrid surface structures consisting of well-ordered silicon nanowires (SiNWs) with high aspect ratios decorated by silver nanoparticles (AgNPs) using a nanosecond fiber laser for realization of anti-reflective and blackened Si surfaces. The fabricated black Si surfaces exhibited a surface reflection of less than 1.0% over a wavelength range from 300 to 1200 nm.

In recent years, titanium-based alloy, especially Ti-6Al-4V, has received extensive attention due to their outstanding mechanical properties, good corrosion resistance, and moderate biocompatibility [9–12]. Various surface modification methods have been developed to enhance the surface properties of Ti-6Al-4V [13–18]. Among all the state-of-art methods, emerging laser-based surface texturing methods have demonstrated their great potential for manufacturing functional Ti-6Al-4V surface with high processing efficiency, flexibility, reduced cost, and environmental friendliness. For example, Palmieri and Belcher et al. from NASA [19–22] developed a laser ablation technique to enhance the adhesive bonding of Ti-6Al-4V surface as a replacement of conventional chemical etching and abrasive processes. Cunha et al. [23] investigated the wettability of four types of LIPSSs fabricated on

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Ti-6Al-4V using a femtosecond pulse laser. These different surface structures were created by varying laser fluence ($0.2\text{--}0.6\text{ J/cm}^2$), laser scanning speed and laser polarization. The wetting test results indicated that all of the laser treated specimens exhibit hydrophilic behavior with a contact angle of $24^\circ\text{--}76^\circ$. To produce hydrophobic or superhydrophobic Ti-6Al-4V surfaces, either long-time storage in air [24] or silane treatment [25] is needed to achieve the wettability transition after laser surface texturing. The laser textured superhydrophobic Ti-6Al-4V surfaces could find applications in the aerospace industry due to their potential capability to effectively prevent the water and ice accumulation which usually lead to malfunctioning and failure of the parts or components. In the meantime, the laser textured superhydrophobic Ti-6Al-4V surfaces have also demonstrated the potential for biological applications, such as prevention of the biofilm formation [26] and control of cell culture behavior [27].

Even though some outstanding surface functionalities have been achieved on Ti-6Al-4V surfaces using the existing laser texturing techniques, low process throughput and high production cost are two major disadvantages for the previous research work. The authors' research group previously developed an innovative high-throughput laser surface nanostructuring process [28,29]. In this paper, this method was used to enhance the hydrophobicity and reduce the surface reflectivity of the Ti-6Al-4V surface. The laser textured Ti-6Al-4V surface exhibits three combined surface characteristics: (1) colorized and highly anti-reflective; (2) highly hydrophobic; and (3) mechanically enhanced. This innovative method will bring a new avenue for controlling the surface color, wettability, and mechanical property of important engineering surfaces.

2. Experiments

2.1. Materials

The specimen materials used in this research work is an important engineering metal alloy, Grade 5 Ti-6Al-4V alloy, which has been widely used for a range of applications in the aerospace, marine, power generation and offshore industries. The Ti-6Al-4V specimens have been furnished in the form of as-annealed (annealing temperature $700\text{--}785^\circ\text{C}$) and ground square sheets with a dimension of $25\text{ mm} \times 25\text{ mm} \times 3.8\text{ mm}$. The as-received specimens have an average grain size of $\sim 2\text{ }\mu\text{m}$, according to literature [30,31].

2.2. High-throughput laser nanostructuring process

During the high-throughput laser nanostructuring process, the specimen was first treated by a high-energy nanosecond pulse laser confined with water using a large spatial increment and a fast processing speed. Then the laser textured surface was immersed in a chlorosilane reagent as shown in Fig. 1. Laser surface treatment employs a 1064 nm Nd:YAG nanosecond laser. The laser was directed to the surface using a 3-axis galvanometer laser scanner. During the laser treatment, the specimen was submerged in deionized water, thereby confining the laser-induced plasma to achieve an enhanced texturing effect. In this study, a fixed laser power of 3.38 W was used. The scanning speed and pitch were set in the control software that ensured a 50% spot overlap between two successive laser pulses. The Ti-6Al-4V specimens were laser treated using different laser power intensities ranging from 0.6 to 8.4 GW/cm². During the second step, the laser textured specimen was immersed in ethanol solution with 1.5% volume percentage cholosilane reagent [$\text{CF}_3(\text{CF}_2)_5(\text{CH}_2)_2\text{SiCl}_3$], also known as FOTS, at room temperature for $\sim 3\text{ h}$. After the chemical immersion treatment, specimens were then cleaned and dried at 80°C in a vacuum oven for 1 h.

2.3. Surface characterizations

Water contact angle (WCA) for the laser textured surfaces was

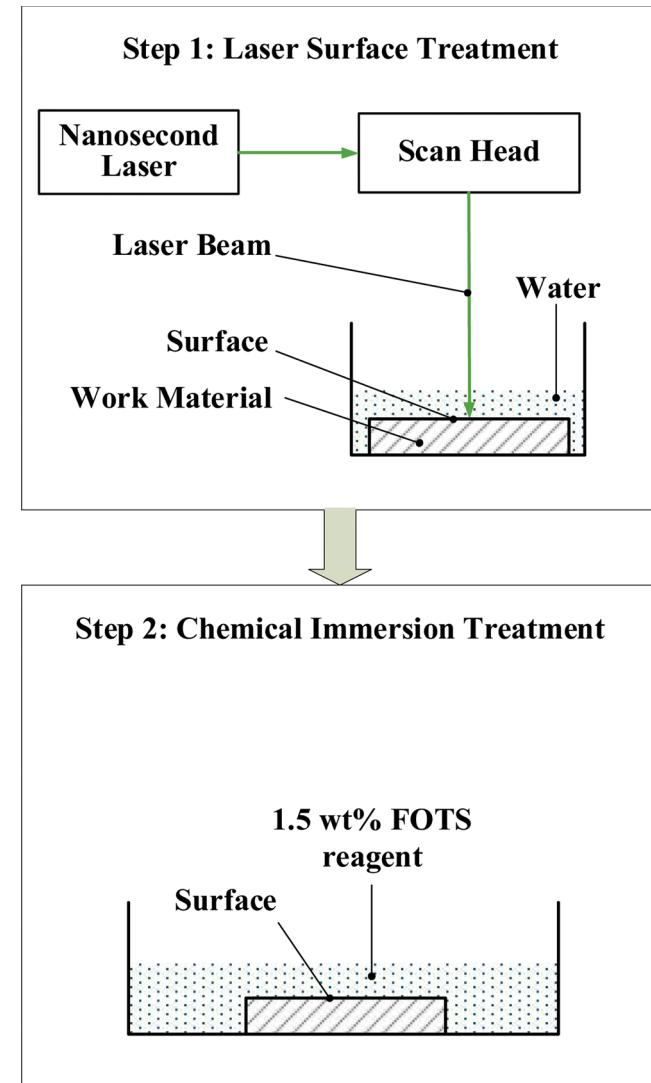


Fig. 1. Schematic of the high-throughput laser surface nanostructuring process.

measured by the wettability test using a contact angle goniometer (Rame-Hart model 100) coupled with a high-resolution CMOS camera (6–60 \times magnification, Thor Laboratories). For each WCA measurement, a micropipette (Eppendorf Research 0.5–10 μL) was used to form a still water droplet with a volume of 4 μL on the surface, and its optical shadowgraph was obtained using the CMOS camera. The optical shadowgraph was quantitatively analyzed using ImageJ software to determine the WCA for each measurement. Five WCA measurements were performed at various locations on each specimen surface, and the average value of measurement results was obtained.

The spectral reflectance of the specimen processed by the high-throughput laser nanostructuring process was measured using a UV-VIS-NIR spectrometer (USB4000 & FlameNIR, Ocean Optics Co.) with normal incidence. The UV-VIS-NIR spectrometer measures the reflectance of the specimen surface in the wavelength range of 450–1670 nm. An integrating sphere was connected to the spectrometer for reflectance data collection. Before reflectance measurement, calibration of the reflectance scale was performed by measuring the incident flux remaining in the sphere after reflecting from a standard reference material. Then the specimen was placed against the entrance port for the actual reflectance measurement. OceanView® software was utilized to process and visualize the spectral reflectance measurement results. Each specimen surface was measured four times at various locations, and the averaged spectral reflectance was obtained.

The Vickers microhardness of the laser textured surfaces was examined by micro-indentation tests using a commercial digital micro-indentation tester (LECO LM 100). The untreated and laser treated Ti-6Al-4V surfaces with various laser power intensities were indented nine times at various locations using a 200 gf load, and the averaged value of all measurements was reported. The surface microstructure was examined using a scanning electron microscope (SEM, Hitachi S-4800). The surface chemistry was analyzed by X-ray Photoelectron Spectroscopy (XPS) using a Kratos Axis Ultra high-performance system. Before the identification of each peak, the whole recorded wide-scan spectrum was aligned with the binding energy of C 1s. Core level spectrum analysis was done for specific elements to get detailed distribution of different chemical groups.

3. Results and discussions

3.1. Surface reflectance and colorization effect

For the laser textured Ti-6Al-4V surfaces, the spectral reflectance for the untreated and mechanically ground Ti-6Al-4V specimens falls 28%–33% within the visible spectrum, 33%–42% within the IR-A spectrum, 42%–52% within the IR-B spectrum as shown in Fig. 2. Using a laser power intensity from 1.3 to 8.4 GW/cm², the high-throughput laser nanostructuring process significantly reduced the spectral reflectance to 6%–8% within the visible spectrum, 6%–10% within the IR-A spectrum, 10%–14% within the IR-B spectrum.

The significant reduction of surface reflectance demonstrates the strong capability of the developed laser nanostructuring method for altering the optical properties of metal surfaces.

The Ti-6Al-4V surfaces treated by the high-throughput laser nanostructuring process appear to be purely black at all viewing angles using a laser power intensity of 8.4 GW/cm², indicating that their optical absorption has been significantly increased. The enhanced absorptance of the laser nanostructured Ti-6Al-4V surface can be attributed to the trapping of light inside the holes and cavities on the surface and the Fresnel angular dependent reflection [3]. These absorption mechanisms lead to the broadband high absorption in the visible and

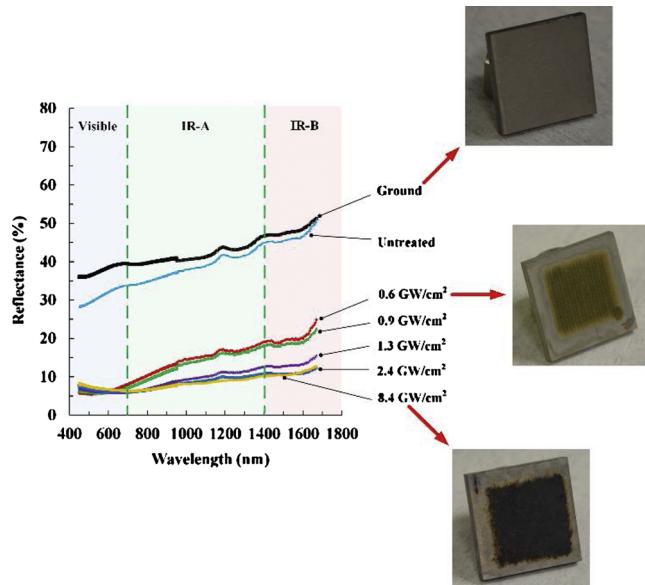


Fig. 2. Spectral reflectance measurement results for Ti-6Al-4V surfaces treated by the high-throughput laser nanostructuring process. In accordance with International Commission on Illumination (CIE) classification, the spectrum of this reflectance measurement is subdivided into a visible spectrum from 450 nm to 700 nm, an IR-A spectrum from 700 nm to 1400 nm, and an IR-B spectrum from 1400 nm to 1670 nm.

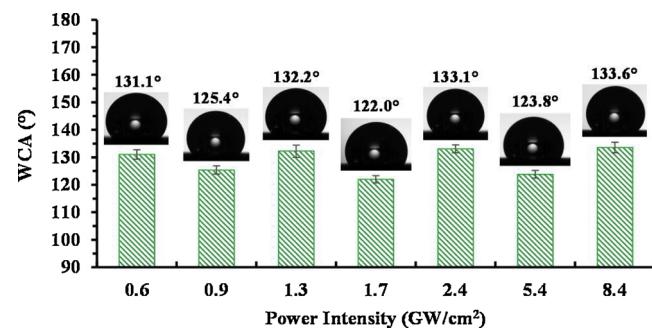


Fig. 3. WCA measurements of Ti-6Al-4V surfaces treated by the high-throughput laser nanostructuring process with different laser intensities.

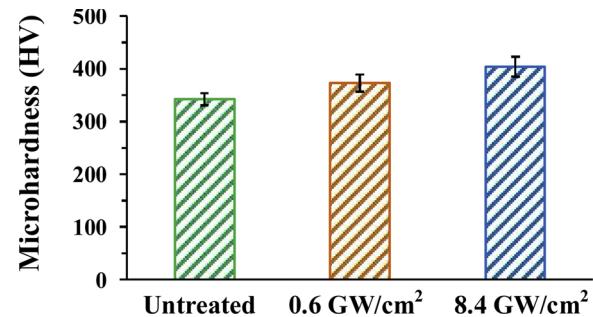


Fig. 4. Vickers microhardness measurements of Ti-6Al-4V surfaces treated by the high-throughput laser nanostructuring process.

near infrared spectra, resulting in the structural black color. However, by using a lower laser power intensity of 0.6 GW/cm², it is surprising to see that the laser nanostructured surface appears to be brownish, which is quite different from that using a higher laser power intensity. The color change induced by this laser nanostructuring method when using different laser power intensities is attributed to the total surface reflectance as a function of wavelength [5]. It should be noticed that the reflectance of the laser nanostructured surface drops significantly over the entire measured wavelength range compared to those of the ground and untreated surfaces. The reflectance drop appears to be more pronounced as the wavelength decreases, which shows a nearly square root dependence of reflectance on wavelength. Thus this spectral dependence will induce different absorption intensities at different color wavelength ranges, thus leading to the appearance of different surface colors. The color change of the laser-nanostructured surface by using different laser power intensities reveals that this method can also be utilized for colorizing the metal surface. As previously discussed, many existing researchers have attempted to colorize the metal surfaces using ultra-short laser surface texturing methods [5–7]. These methods often rely on the generation of micro-scale patterns using a focused laser spot (30–50 μ m) and very fine spatial resolution, resulting in extremely low throughput in treatment of macroscale metal surfaces. However, the novel laser nanostructuring method developed in this work significantly improves processing efficiency by using a large laser line spacing and a fast processing speed, which will lead to a breakthrough in process throughput rendering practical treatment of macroscale metal surfaces.

3.2. Wettability

The relationship between the laser processing parameters and the resultant surface wettability was experimentally determined as shown in Fig. 3. Immediately after laser texturing process, the surfaces exhibited superhydrophilicity, and it was difficult to record the accurate contact angle due to lacked accuracy. After the chemical immersion process, the high-throughput laser nanostructuring process produced consistent hydrophobic surfaces on Ti-6Al-4V with WCA ranging from

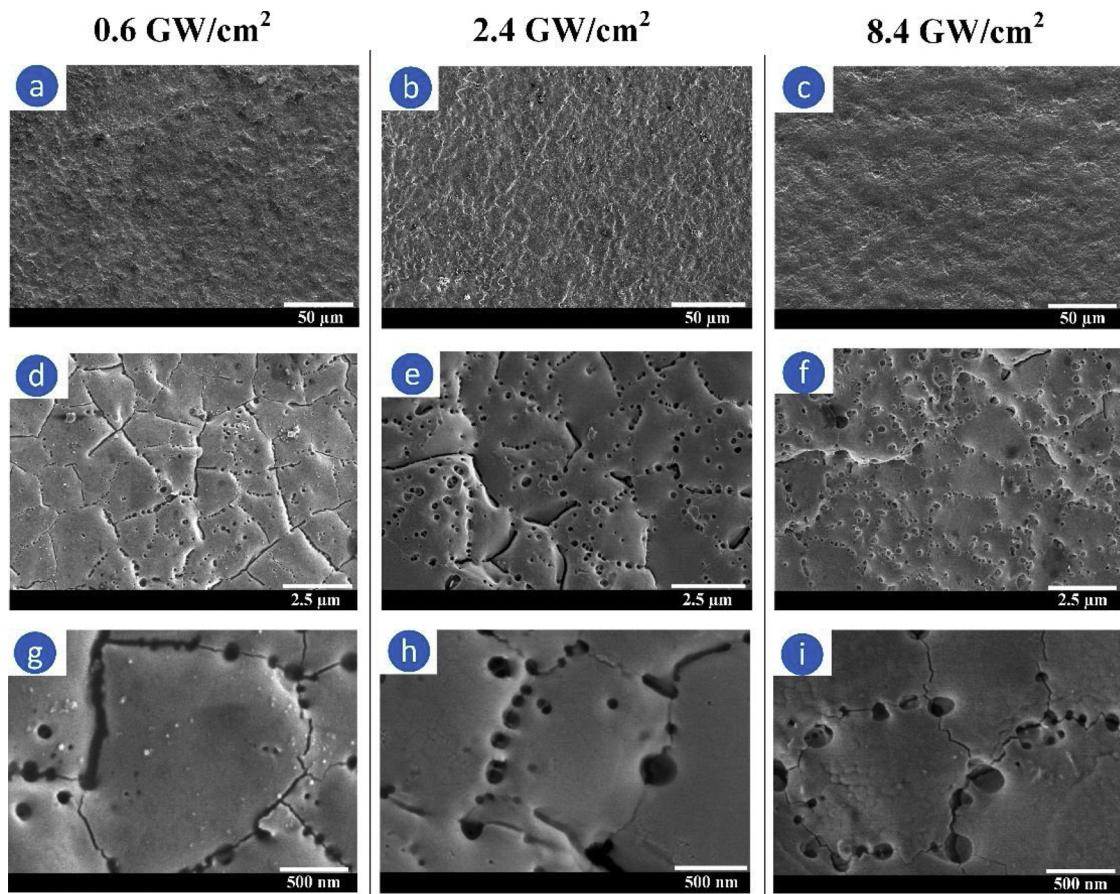


Fig. 5. SEM micrographs of Ti-6Al-4 V surfaces treated by the high-throughput laser nanostructuring process: (a–c) under a low magnification of $500\times$ using laser power intensity of $0.6\text{ GW}/\text{cm}^2$, $2.4\text{ GW}/\text{cm}^2$ and $8.4\text{ GW}/\text{cm}^2$; (d–f) under a medium magnification of $10,000\times$ using laser power intensity of $0.6\text{ GW}/\text{cm}^2$, $2.4\text{ GW}/\text{cm}^2$ and $8.4\text{ GW}/\text{cm}^2$; (g–i) under a high magnification of $50,000\times$ using laser power intensity of $0.6\text{ GW}/\text{cm}^2$, $2.4\text{ GW}/\text{cm}^2$ and $8.4\text{ GW}/\text{cm}^2$.

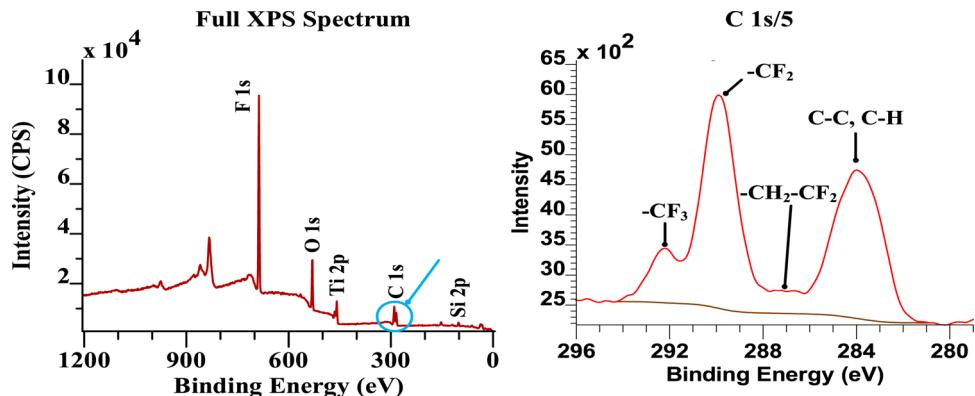


Fig. 6. Full XPS spectrum and core elemental XPS spectrum of carbon element on the Ti-6Al-4 V surface treated by the high-throughput laser nanostructuring process using a laser power intensity of $0.6\text{ GW}/\text{cm}^2$.

120° to 135° using various laser power intensities ranging from 0.6 to $8.4\text{ GW}/\text{cm}^2$. It can be found that varying laser power intensity does not significantly alter the WCA for these hydrophobic Ti-6Al-4V surfaces. These results indicate that the developed high-throughput laser nanostructuring process is very robust and can provide a wide laser operation window which produces consistent hydrophobic Ti-6Al-4V surfaces. The WCA achieved using this method is quite comparable to some of the results in the existing literature [24]. Thus this laser nanostructuring process has been proved to an efficient method for enhancing the surface hydrophobicity

3.3. Microhardness

The microhardnesses of the untreated Ti-6Al-4V surface and the Ti-6Al-4V surfaces treated using different laser power intensities are shown in Fig. 4. The microhardness of the untreated surface was $342.2 \pm 11.5\text{ HV}$. Through the high-throughput laser nanostructuring process, the surface microhardness of all surfaces processed by different laser power intensities were increased. Using a laser power intensity of $8.4\text{ GW}/\text{cm}^2$, the surface microhardness was enhanced up to $403.9 \pm 18.7\text{ HV}$ with an 18.0% increase. The microhardness

improvement achieved using this laser nanostructuring method is comparable to the enhancements of surface mechanical strength of Ti-based alloys using the existing state-of-art laser texturing methods [32–37]. Therefore, this novel laser surface nanostructuring method can be used to effectively enhance the surface mechanical strength and improve the surface wear resistance.

3.4. Microstructural analysis

The microstructure of Ti-6Al-4V surfaces treated by the high-throughput laser nanostructuring process using different laser power intensities was examined by SEM as shown in Fig. 5. It can be found that using a laser power intensity ranging from 0.6 GW/m^2 to 8.4 GW/m^2 , the laser nanostructured surfaces show an isotropic texture without any obvious lay pattern when examined at lower magnification.

However, using higher magnification, it is indicated that the laser nanostructured Ti-6Al-4V surface consists of microscale surface ripples dispersed with nanoscale pores. This type of surface structure significantly reduces the surface reflectance via light trapping in these pores and the Fresnel angular dependent reflection [3]. Due to this absorption mechanism, the laser nanostructured Ti-6Al-4V surface could exhibit low surface reflectance which leads to the structural colors in the visible spectrum. In addition, the surface color change induced by this laser nanostructuring method is also closely related to the surface micro/nanostructure. It should be noted that the nanoscale pores dispersed on the laser nanostructured surface become larger when increasing laser power intensity. It is well known that the colors contained in the visible spectrum correspond to different wavelengths. In the meantime, the light absorption capability at different wavelength of the nanostructured surface is highly dependent on the size of the surface features. Therefore, the significant difference of the surface feature size when using different laser power intensities could potentially contribute to the color change induced by this laser nanostructuring process. The experimental results indicate that this laser nanostructuring process has strong capability of producing various surface colors by modifying the experimental conditions.

In the meantime, the SEM images taken at a higher magnification indicate that the laser-induced nanoscale pores exhibit a higher density along the grain boundaries. There is not a clear explanation for this phenomenon at this moment and further investigation is essentially needed to elucidate the underlying mechanism.

3.5. Surface chemistry analysis

Detailed XPS analysis was conducted for the Ti-6Al-4V surface treated by the high-throughput laser nanostructuring process using a laser power intensity of 0.6 GW/cm^2 as shown in Fig. 6. Elements of C 1s, O 1s, Ti 2p, Si 2p and F 1s were observed in the full spectrum survey on the top surface. The distinct peaks of fluorine and silicon were originated from the FOTS cholosilane reagent used during the chemical immersion treatment. For the element of C 1s, the presence of $-\text{CF}_2-$ and $-\text{CF}_3$ groups, confirms the occurrence of surface fluorination in the specimens during the chemical immersion treatment. The surface fluorination induced by $-\text{CF}_2-$ and $-\text{CF}_3$ groups with low binding energy groups are believed to efficiently reduce the surface energy and lead to an enhancement of surface hydrophobicity [38,39]. In the meantime, no chlorine signal was observed in the XPS full spectrum survey although there is chlorine in the FOTS reagent. It is hypothesized that the chlorine elements in FOTS cholosilane reagent reacted with metal oxide and dissolved in the chemical solution. During the chemical immersion treatment process, it is believed that surface chemical etching and fluorination occur at the same time between the laser-textured metal surface and the chlorosilane reagent. It is also believed that HCl generated during the CIT phase is the source of etching effects, aiding in the generation of surface nanostructures.

4. Conclusions

An innovative high-throughput laser surface nanostructuring process that can be used to effectively control the color and wettability of important engineering alloys was developed in this work. Experimental results indicate that the laser nanostructured Ti-6Al-4 V surfaces exhibit combined colorized, highly hydrophobic and mechanically enhanced effects. This novel method does not only efficiently modifies the surface functionalities but also increases the processing speed and reduces the production cost compared with the existing ultra-short laser-based surface-texturing methods, thus providing a new methodology for fabrication of multi-functional engineering surfaces. Future work will further investigate the mechanism of the surface color change. This task could be completed by measuring the spectral response of the colorized surface to the light at specific wavelength using the spectrophotometry technique.

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