In-situ growth of Ca/P salt on Ti surface induced by femtosecond lasers in hydroxyapatite suspension*

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Pure Ti plate surfaces are micro-ablated by femtosecond lasers in the ambience of hydroxyapatite suspension. It is found that three-stage hierarchical surface structures are produced with various laser energies. When the laser energy is 150 μJ, a lava-like structure with a distribution of nanoholes is dispersed evenly on the laser ablated surface. While in the case of 300 μJ, the grooves-and-islands micro-patterns covered with nanoparticles are generated on the surface. Remarkably, Ca/P based substances are revealed to firmly deposit on the micro-structured surfaces. More phosphate growth is seen for the higher laser energy. Discussions suggest that the additional elements deposition could be attributed to the chemical reaction of plasma related ions in the suspension and their subsequent crystallisation on the fresh surfaces of Ti plate due to the femtosecond laser ablation.

Keywords: Ti, femtosecond lasers, phosphate, hydroxyapatite suspension
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1. Introduction

It is well known that a variety of methods have been applied to the surface treatments of Ti and its alloys to improve their biological activity such as sand blasting followed by acid etching,[1] reactive-ion etching,[2] lasers machining,[3,4] electrochemical micromachining,[5] and biomineralisation of hydroxyapatite (HA) on the surface.[6,7] To obtain a clean surface these treatments usually require rigorous pretreatment, in which some chemicals are often used, so contamination of the sample surfaces as well as the surrounding environment may occur. For the laser treatment, however, almost no chemicals are involved, which greatly reduces the environmental pollution. It was reported that a hierachical roughness can be prepared on the metallic surfaces with the irradiation of femtosecond lasers.[8−11] Therefore, this method is especially suitable for the surface modification of the bone replacement materials, which can promote the cells growth.

In this aticle, the surfaces of pure Ti plates immersed in HA suspension are micro-treated by femtosecond lasers, a layer of Ca/P salt is found to deposit on the sample surface where the hierachical roughness patterns are formed simultaneously. The underlying mechanisms are also discussed. This method can create a surface micro-pattern with Ca/P active layers to greatly improve bone cells growth on it. In addition, since no harmful substances are contained in HA suspension, this method provides a newly convenient and environment-friendly way to prepare the bioactive surfaces.

2. Experiments

In the experiment, polished pure titanium plates (10 mm×10 mm×1 mm) were adopted as the samples, and they were pasted on the bottom of an open vessel, which was mounted on a computer-controlled three-axis translation stage. Femtosecond laser pulse trains (50 fs, 800 nm, 1 kHz) were generated from a commercial Ti:sapphire amplifier system (Spectra

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Physics Inc.). After passing through a 10× microscope objective lens, femtosecond lasers were first focused on the sample surface in air ambience, and the estimated beam radius of 5 μm was formed on the target. Then HA suspension, whose formation was by ultrasonic dispersion of 2 g HA nanoparticles into 100 ml de-ionized water, was injected into the vessel to ensure the Ti plate immersed in a 2.5 mm thickness from the solution surface. In order to compensate refraction of the solution on the incident laser beam, the stage was moved 100 μm away from the laser focus along the direction of the beam propagation. The samples were scanned at a speed of 0.2 mm/s under the fixed radiation of femtosecond lasers with different energies of 150 μJ and 300 μJ. The translation is parallel to the direction of laser beam polarization, and the spatial interval between the two consecutive lines was set 50 μm.

Surface morphology of the samples was examined by scanning electron microscope (SEM, HITACHI S-4300) and atom force microscope (AFM, PSIA XE-100). And the element concentration of the samples was analysed through energy dispersive x-ray micro analyser (EDX). X-ray diffraction (XRD) analysis was conducted on an x-ray diffractometer (Philips X'pert MPD) with Cu Kα radiation ($\lambda = 0.154056$ nm), and the range of 2θ angles was from 20° to 80°.

3. Results and discussion

Surface morphologies induced by femtosecond laser irradiation with different energies of 150 μJ and 300 μJ were examined by SEM and AFM micrographs, and the results are shown in Fig. 1. At first glance, when the incident laser energy is relatively small 150 μJ, a kind of lava-like structure with random distribution of irregular nanoholes is produced on the target surface, as shown in Fig. 1(a). As the laser energy increased up to 300 μJ, an array of island-like patterns can be induced over the laser scanned region, as shown in Fig. 1(c). Their zoom-in images reveal that the two types of surface structures are covered with an amount of solid particles in the nanometer scale, which greatly improves the surface roughness. Particularly, some slurry-like substances which have a gray colour can be found to deposit in the valleys of the surface structures. It should be stressed that these deposited substances could still exist even after 30 minutes' washing by an ultrasonic cleaner, indicating that the bond force between these depositions and the microstructures is relatively high, after femtosecond laser treatments.

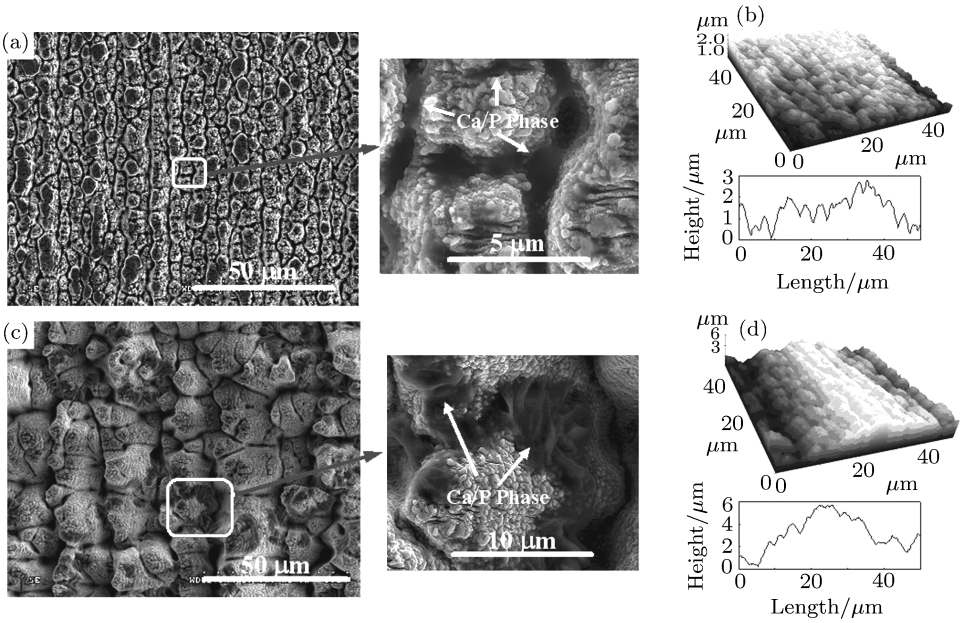


Fig. 1. Micro-patterns for Ca/P rich phase deposited on the Ti plates immersed in HA suspension, formed by femtosecond laser irradiation with different energies of 150 μJ (a) and 300 μJ (c). (b) and (d) are their AFM images with corresponding section analysis.

Besides the lava- and island-like surface structures, we can also find from their corresponding AFM images (Figs. 1(b) and 1(d)) that some grooves with a period of 50 μm generated on the sample surfaces due to the line scribing processes. The maximum roughness of the laser-treated surfaces was measured to be 2.8 μm for 150 μJ and 5.7 μm for 300 μJ. So far, we can consider the laser-treated surface structure as hierarchical stages: the first stage is the formation of microgrooves with a period of 50 μm, the second one is the formation of lava- or island-like structure, and the third one is the scattering of nanoparticles. We believe that this kind of hierarchical roughness is preferred for the osteoblasts attachment and their growth.[12]

In regard to the physics of such surface structure formation, it can be as follows: when the laser pulses strike on the sample's surface through the liquid layer of HA suspension, the target surfaces are absorbed the incident laser energy and overheated to the extreme high temperature in femtosecond scale.[13,14] Under this condition, metallic surfaces will be removed away in the form of nanoparticles, clusters, atoms, ions and electrons.[15,16] Because of the liquid surroundings, these ablated plumes from the target surfaces will subsequently collide with solution molecules, causing the liquid ionisation and then the formation of plasma. Temperatures in the plasma vary in a very large span, and the temperature gradient of the localised plasma with respect to the surrounding liquids results in the tensile thermoelastic stress and vapours generated on the sample surface.[17,18] To be exact, in our experiments, when the laser energy was 150 μJ, the laser-induced bubbles would be preferred rather than the vapour. Strikes of the shock wave generated by the burst of the bubbles would imprint craters on the melt area, leading to the formation of the lava-like surface. While for the higher laser energy of 300 μJ, the effect of laser-induced vapour can not be neglected. Then the secondary ablation by the recoil pressure of the vapour will result in the formation of the micro-islands.

In our experiments, analyses through XRD and the selected area EDX were used to identify the alternation of elements and crystal structures on the sample surface ablated by femtosecond laser pulses, and the obtained results are depicted in Fig. 2. The EDX measurements shown in Fig. 2(a) reveal that the chemical elements on the laser irradiated surfaces include Ti, Ca, and P elements. Because no elements of Ca and P are found on the sample without laser-treatment, we can deduce that the deposited substances on the structured surfaces of the Ti plates should be Ca/P rich phase. The additional Ca and P elements on the femtosecond laser-treated surface seem to be larger for higher incident energy, and the atom ratios of Ca/P are 0.91 for 150 μJ and 0.87 for 300 μJ. On the other hand, some peaks are seen clearly from the XRD patterns in Fig. 2(b), which can be identified as $Ca_3(PO_4)_2$ for the case of 150 μJ and $CaHPO_4$ for the case of 300 μJ. This means that the depositions on the structured surfaces are in fact the Ca/P based crystalline substances. With increasing femtosecond laser energy, the relative height of the resultant crystalline peaks will become larger, which implies that the more Ca/P salts will be synthesised during femtosecond laser treatment and deposition on the sample surfaces. The steady growth of calcium phosphate salts on the Ti plate surfaces will benefit to the promotion of bone cells, and subsequent improvement of the biological activity of the sample surfaces.

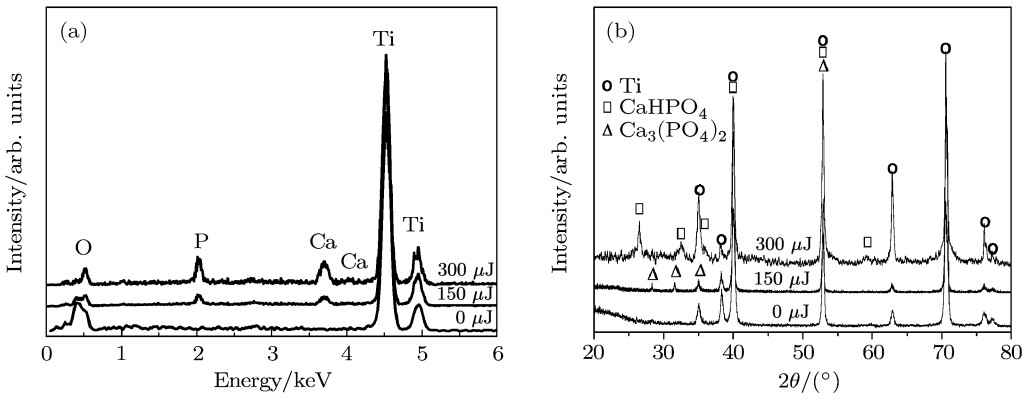


Fig. 2. EDX spectra (a) and XRD pattern (b) of the samples under different femtosecond laser energies.

Here it should be mentioned that the chemical analysis of the sample immersed in HA suspension for 20 minutes but without undergoing any laser treatments is also illustrated in Fig. 2 for comparison. Clearly, femtosecond laser irradiation and the induced surface microstructures could be mainly responsible for the firm deposition of additional elements.

In fact, during the femtosecond laser ablation processes shown in Fig. 3 (a), the induced plasmas and their temperature fields not only play an important role in the formation of micro-patterns on the target surfaces, but also have great influence on the elements and ions in the surrounding medium. Before laser irradiation, the components of HA suspension includes many different particulates such as Ca^{2+}, H^+, PO_4^{3-}, OH^-, and nano HA particles etc. However, when the focal femtosecond laser pulses are directed into the solution to produce high-temperature plasmas, particles such as HA, PO_4^{3-} and OH^- are readily decomposed or ionised into the forms of Ca^{2+}, P^{5+}, O^{2-}, H^+, PO_4^{3-}, HPO_4^{2-}, $H_2PO_4^-$ in the different temperature regions, depending on the plasma temperature. On the other hand, as an active metal, a layer of dense oxide layer is always formed on the surface of Ti plates, which can protect the internal atoms from oxidisation. As shown in Fig. 3(b), the surface layer of the sample will be removed under the femtosecond laser irradiation, keeping the Ti atoms with broken bond and positive charges exposed to the surrounding medium. Thus a high surface activity is achieved. As the plasma temperature decreases gradually to the environmental level, the active surface firstly reacts with the anions in the medium. The possible reaction processes are given by

$$\mathrm{Ti}^+ + \mathrm{PO}_4^{3-} \longrightarrow [\mathrm{PO}_4 \cdot \mathrm{Ti}]^{2-}, \quad (1)$$

$$\mathrm{Ti}^+ + \mathrm{HPO}_4^{2-} \longrightarrow [\mathrm{HPO}_4 \cdot \mathrm{Ti}]^{-}, \quad (2)$$

$$\mathrm{Ti}^+ + \mathrm{H_2PO}_4^{3-} \longrightarrow [\mathrm{H_2PO}_4 \cdot \mathrm{Ti}], \quad (3)$$

$$\mathrm{Ti}^+ + \mathrm{O}^{2-} \longrightarrow [\mathrm{O} \cdot \mathrm{Ti}]^{-}. \quad (4)$$

The combination of anions with the Ti surface will result in the further deposition of Ca^{2+}, H^+, and etc. Their reactions are described as follows:

$$\mathrm{Ca}^{2+} + [\mathrm{PO}_4 \cdot \mathrm{Ti}]^{2-} \longrightarrow \mathrm{Ca}\,[\mathrm{PO}_4 \cdot \mathrm{Ti}], \quad (5)$$

$$\mathrm{Ca}^{2+} + [\mathrm{HPO}_4 \cdot \mathrm{Ti}]^{-} \longrightarrow \mathrm{Ca}\,[\mathrm{HPO}_4 \cdot \mathrm{Ti}]^{+}, \quad (6)$$

$$\mathrm{Ca}^{2+} + [\mathrm{O} \cdot \mathrm{Ti}]^{-} \longrightarrow \mathrm{Ca}\,[\mathrm{O} \cdot \mathrm{Ti}]^{+}. \quad (7)$$

$$\mathrm{H}^+ + [\mathrm{PO}_4 \cdot \mathrm{Ti}]^{2-} \longrightarrow \mathrm{H}\,[\mathrm{PO}_4 \cdot \mathrm{Ti}]^{-}, \quad (8)$$

$$\mathrm{H}^+ + [\mathrm{HPO}_4 \cdot \mathrm{Ti}]^{-} \longrightarrow \mathrm{H}\,[\mathrm{HPO}_4 \cdot \mathrm{Ti}], \quad (9)$$

$$\mathrm{H}^+ + [\mathrm{O} \cdot \mathrm{Ti}]^{-} \longrightarrow \mathrm{H}\,[\mathrm{O} \cdot \mathrm{Ti}]. \quad (10)$$

As the reaction occurs, the phosphate and calcium ions accumulated on the surface of Ti becomes increased, and a layer of calcium phosphate salts will be eventually generated on the sample surfaces, as shown in Fig. 3(c). In the case of 150 μJ, the metallic surface is obtained at the lower energy and the material removed becomes slight. Moreover, the plasma formed by the reaction between the ejected materials and the ambient medium exhibits a relatively low temperature and a small volume. As a result, the amount of ions and particles affected by the plasma gets smaller and so is the deposition of Ca/P salts on the structured surfaces. While the case of 300 μJ can supply higher energy to the deposition of the ions and particles. Due to the complexity of the laser–matter interactions in the solution ambience, the specific chemical reaction process on the surface of Ti plate and the influence of the incident laser energy on the formation of products deserve further study.

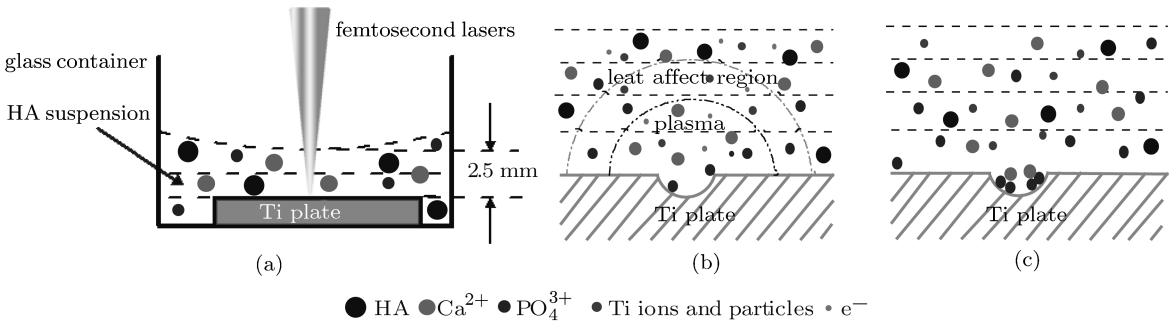


Fig. 3. Schematic of Ca/P deposited on the surface of pure Ti plates immersed in HA suspension under femtosecond laser irradiation.

4. Conclusions

A three-stage hierarchical micro-pattern was generated on the surfaces of the pure Ti samples in HA suspension ambience under the femtosecond laser irradiation. When the laser energy was 150 μJ, a kind of lava-like structure with randomly distributed irregular nanoholes are dispersed on the sample surfaces. While the laser energy was increased to 300 μJ, the groove-and-island patterns were formed on the sample surfaces. At the same time, plasma generation in the suspension by femtosecond laser pulses led to the reaction between the specific ions and the chemical active Ti surface during ablation processes. As a result, Ca/P -based substances had a steady *in-situ* growth on the laser-ablated surfaces. Furthermore, the higher incident laser energy would increase the Ca/P deposition, which might improve the biocompatibility of the metallic devices for the interventional treatments.

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