Laser Surface Modification for Rapid Oxide Layer Formation on Ti-6Al-4V

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The study compares and analyses the properties of the oxide layers formed on the Ti-6Al-4V surfaces treated with laser and general furnace annealing processes. The titanium alloy was subjected to different temperatures or laser powers and then immersed in the modified artificial simulated body fluid (m-SBF) solution for up to 7 days to evaluate for bioactivity. The results show that the surface of the samples exhibit different color appearances after annealing at raised temperatures or laser powers due to the different oxide layer thicknesses and phases. When the temperature and laser power were increased, the contact angle of the annealed sample would decrease gradually. Furthermore, a layer of hydroxyapatite-rich bone-like apatite was found on the surfaces of annealed samples after immersing them in the m-SBF solution for a period of time. This bone-like apatite layer can be rapidly grown on the laser annealing specimens when immersed in an m-SBF solution for only 3 days, indicating its excellent bioactivity.

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1. Introduction

Titanium and its alloy are the most commonly used materials in biomedical applications and device components because of their high strength, excellent corrosion resistance, non-toxicity and biocompatibility [1]. Three main phases including anatase, rutile and brookite are observable in the TiO_2 material. Bone implants made of titanium alloy need to be surface treated to become bioactive, and the oxide layer on the titanium alloy surface plays a key role in improving the conectivity between the surface of a medical implant and the surrounding tissues [2]. The composition ratio, topography and thickness of the TiO_2 layer affects its biocompatibility and surface biological activity. So far, there are a number of ways to prepare the TiO_2 layer, such as sol-gel, electrochemical, plasma, atmospheric furnace and laser modification methods [3-6]. The research of laser surface treatments on biomedical implants in recent years has increased noticeably. The following are some of the more recent developments: A textured Ca-P coating on Ti-6Al-4V was synthesized in a laser process and the vitro bioactivity and biocompatibility was improved [7]. Crystalline titanium oxide phases were formed and surface modifications of a Ti dental implant was applied using laser irradiation. Significant characteristics of the modified surfaces were useful for the osseointegation phenomenon [8]. With hydroxyapatite coating film through laser deposition, the coating surface morphology can provide controlled topography and higher mechanical adhesion on substrate [1, 9-11]. With surface micro-texturing of a titanium substrate applied using direct laser irradiation, the results showed that a laser process can attain desirable phase formation and better bonding strength, meanwhile an improved bone implant interface was achieved. In addition, laser surface modification was shown to be a clean and reproducible process, it also allows for better control with the microstructuring of material surfaces [12-15].

In this study, the surface morphology and oxide layer formation on Ti-6Al-4V alloy that underwent traditional furance and laser treatments were investigated and their annealed specimens were immersed in the modified artificial simulated body fluid (m-SBF) solution for up to 7 days to evaluate their bioactivity.

2. Experimental method

Commercial Ti-6Al-4V alloy was cut into plates with dimensions of 10 x 10 x 1 mm^3. These samples were polished using a tumbling method with up to 600 grades of SiC powders and then were ultrasonically cleaned with acetone and de-ionized water for 20 min. These raw samples were subjected to atmosphere heat treatment in an electric furnace at temperatures ranging from 200 to 1000 ^oC for 1 hr or they underwent the IR laser irradiation with a wavelength of 1064 nm, a pulse duration of 30 ns, repetition rate of 25 kHz, a spot size of 42 μm, scan speed of 100 mm/s, scan pitch of 2 μm and an ouput power set at 6.7 to 13.5 W, respectively. It represents that fluence value is from 19 to 39 J/cm^2. The annealed specimens were then immersed in the m-SBF for up to 7 days to evaluate their bioactivity. A surface microstructure and morphological evolution of these annealed specimens was observed using a scanning electron microscope (SEM, S-3000N, HITACHI). The compositional analysis of these samples was measured using an Energy-Dispersive X-ray Spectroscope (EDS, EX-200, Horiba). The crystalline structures of samples were investigated using an X-ray diffractometer (XRD, D8 advance, Bruker). Surface roughness measurements were obtained using an atomic force microscope

(AFM, Veeco di CP-II). Finally, the contact angle was measured using a contact angle analyzer (FTA1000, First Ten Angstroms).

3. Results and discussions

The appearance of samples can be seen in Fig. 1. After furnace or laser treatment with different annealing conditions, the surfaces of samples reveal different color appearances due to their different oxide layer thickness and phases. The SEM surface morphology and EDS results of the samples are shown in Fig. 2. It is clear that the surfaces of the as-received Ti-6Al-4V is flat and Ti, Al and V elements are present; however, after the furnace or laser treatment, the surface roughness of the samples all increased while their O and Al element peak became greater owing to the fact that the processing temperatures were higher than the pure Al melting temperature. It was observed that the laser treated sample had rougher surfaces and higher O and Al components than the furnace counterpart. It is believed that the rougher surfaces are beneficial to cell or tissue attachment for biomedical implant applications [16].

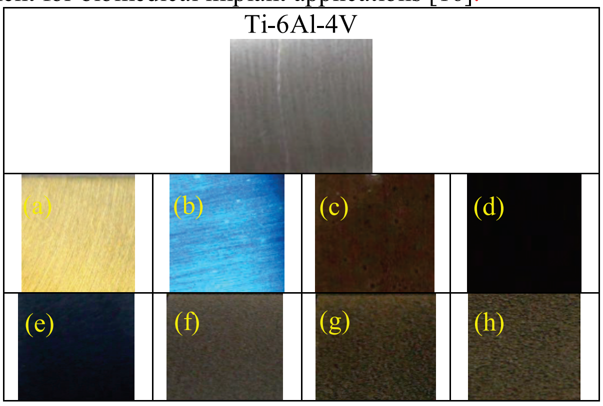

Fig. 1 Appearance of sample surfaces after furnace annealing at different temperatures (a) 300 °C, (b) 550 °C, (c) 700 °C and (d) 1000 °C; laser treatment at different output powers (e) 0.9 W, (f) 5.2 W, (g) 7.5 W and (h) 13.5 W.

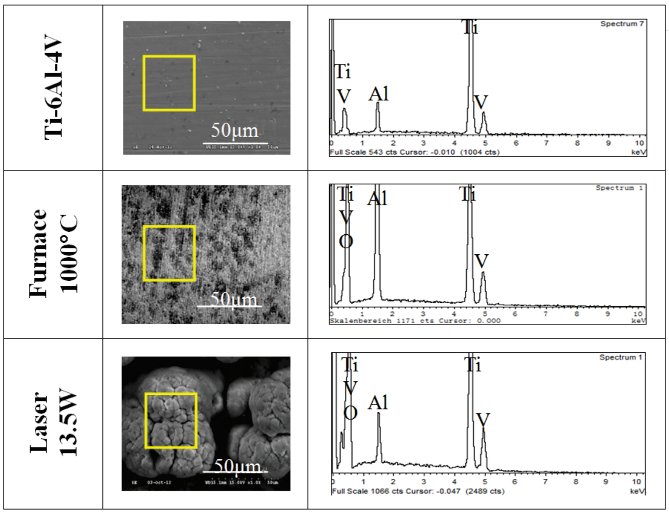

Fig. 2 SEM surface morphology and EDS results for Ti-6Al-4V specimens.

The XRD spectra of the as-received Ti-6Al-4V and the furnace annealed specimens treated at different temperature ranging from 500~1000 °C are shown in Fig. 3. It is apparent that titanium oxide peaks rise when the heating temperature is increased, while the anatase phase can be obtained at 600 °C. With the temperature reaching 700 °C, rutile becomes the main oxide phase. Fig. 4 shows the XRD patterns of the Ti-6Al-4V alloy and the annealed specimens at different laser powers ranging between 6.7 ~13.5 W. With an increase in the laser power, the titanium oxide layer grows quicker; while the rutile phase becomes the main structure when the laser power is raised to 8.5 W. Many studies [7, 8]have shown that a rutile structure is helpful for promoting the hydrophilic surface and improving the bioactivity and biocompatibility of a sample.

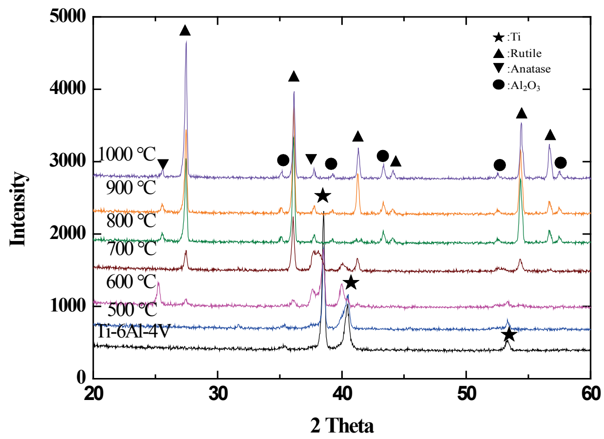

Fig. 3 XRD spectra of as-received Ti-6Al-4V and the furnace annealed specimens at different temperature ranging from 500~1000 °C.

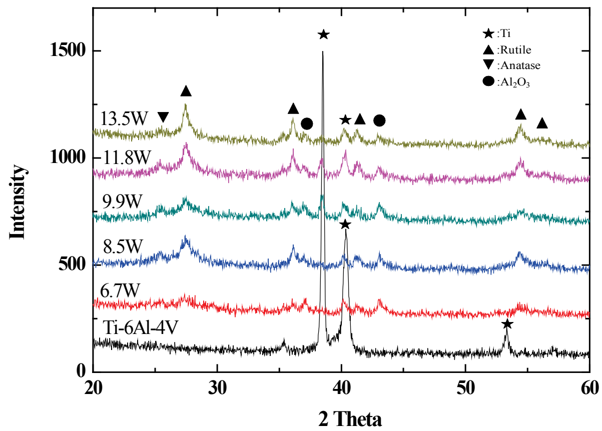

Fig. 4 XRD spectra of as-received Ti-6Al-4V and the laser annealed specimens at different output powers ranging from 6.7 ~13.5 W.

The contact angle of the specimens with m-SBF droplets are shown in Fig. 5. The contact angle of the as-received Ti-6Al-4V alloy is 81°. This value is reduced for a better hydrophilicity with the increase of furnace annealing temperatures or laser output power. For the furnace sample annealed at 700 °C, the angle drops sharply. The contact angle of the specimens subject to laser treatments also decline sharply. From the XRD results in Fig. 3, the main titanium oxide layer phase of the samples annealed at the temperatures higher than 700 °C and the laser treated counterparts is the rutile phase. It is apparent from the experiments that the laser treated samples can obtain rougher and more opened titanium oxides enriched surfaces (Fig. 2) than the furnace. Therefore, a better hydrophilicity performance can be achieved by laser treating the samples.

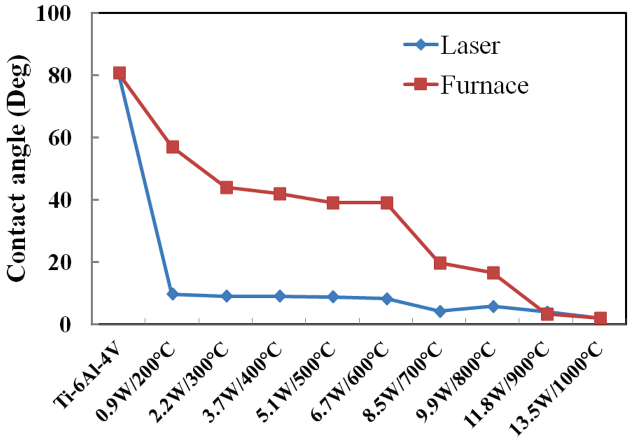

Fig. 5 Contact angle of the specimens with m-SBF droplets.

The as-received Ti-6Al-4V, 1000 °C furnace annealed and 13.5 W laser treated samples were immersed in m-SBF for 3, 5 and 7 days to evaluate their bioactivity and their surface morphology can be seen in Fig. 6. From these tested samples, it is clear that the 13.5 W laser treated sample has a better calcium (Ca) and phosphorus (P) inducibility than the 1000 °C furnace annealed counterpart (Fig. 7). This is due to the fact that the 13.5 W laser treated sample has rougher and more opened surfaces than its 1000 °C furnace annealed counterpart, and hence provides a larger and more bioactive surface upon which to induce the Ca^{2+} and $PO4^{3-}$ ions in the m-SBF. When the time of immersion in the m-SBF was increased, a Ca-P enriched deposition gradually formed on the surfaces of the samples and a bone-like apatite layer appeared. Crystalline HA was found on the 13.5W laser treated surfaces after only 3-days of immersion in the m-SBF (Fig. 8), which indicates that it has a more favourable bone-like apatite inducibility than the other samples, and a more favourable biocompatible performance is expected for biomedical implant applications.

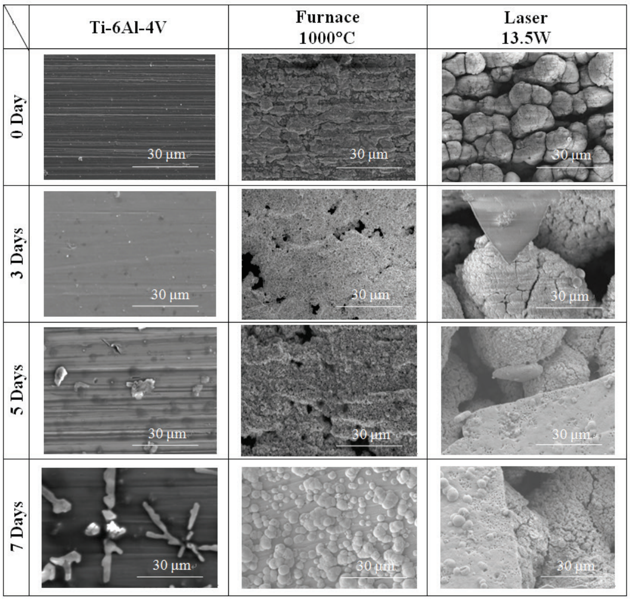

Fig. 6 The SEM surface morphology of samples after 0, 3, 5 and 7 days immersion in the m-SBF.

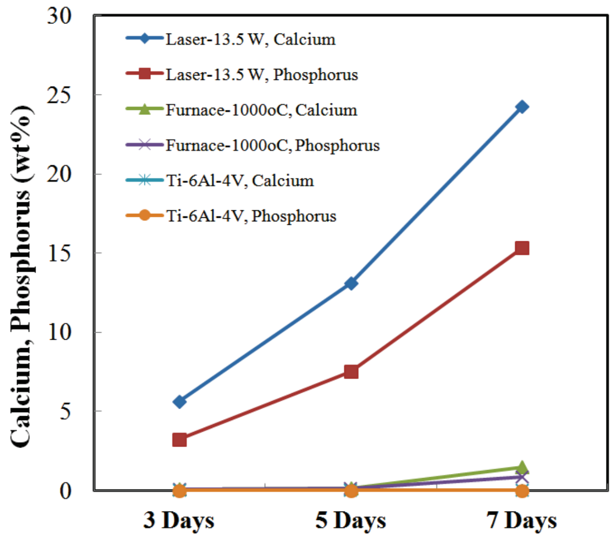

Fig. 7 The relationship between the Ca and P composition on the sample surfaces and the immersion period of time.

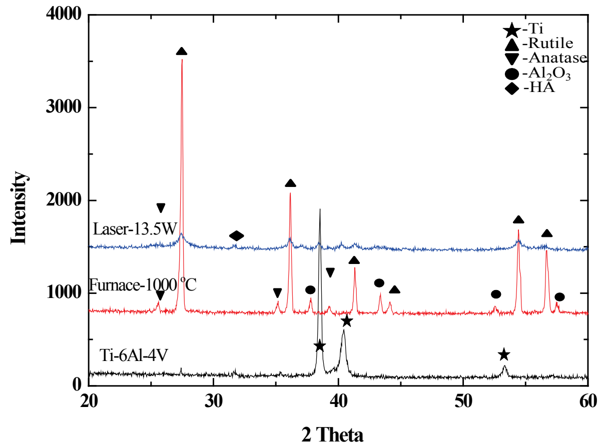

Fig. 8 XRD spectra of the as-received Ti-6Al-4V, 1000 °C furnace annealed and 13.5 W laser treated sample surfaces after immersing in the m-SBF for 3 days.

4. Conclusions

The oxide layer on the Ti-6Al-4V surfaces grew greatly after it was subject to furnace annealing at high temperatures or Nd-YAG laser treatments. The rutile phase was found to be the main oxide structure on the sample surfaces when the furnace annealing temperature reached 700 °C or the laser processing power was increased to 8.5 W. Due to the rougher and more opened titanium oxides enriched surfaces, the laser treated samples were found to have a more hydrophilic surface and a more favourable Ca and P inducibility to form bone-like apatite structures in the m-SBF. The crystalline HA spectra can be observed on the 13.5W laser treated sample surfaces after they were immersed in the m-SBF solution for only 3 days, which indicates its effective bioactivity for biomedical implant applications.

Acknowledgments

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