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Surface modification induced phase transformation and structure variation on the rapidly solidified recast layer of titanium

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ABSTRACT

In this study, neodymium-doped yttrium orthovanadate ($Nd:YVO_4$) as a laser source with different scanning speeds was used on biomedical Ti surface. The microstructural and biological properties of laser-modified samples were investigated by means of optical microscope, electron microscope, X-ray diffraction, surface roughness instrument, contact angle and cell cytotoxicity assay. After laser modification, the rough volcano-like recast layer with micro-/nanoporous structure and wave-like recast layer with nanoporous structure were generated on the surfaces of laser-modified samples, respectively. It was also found out that, an $\alpha \rightarrow (\alpha + \text{rutile-}TiO_2)$ phase transition occurred on the recast layers of laser-modified samples. The Ti surface becomes hydrophilic at a high speed laser scanning. Moreover, the cell cytotoxicity assay demonstrated that laser-modified samples did not influence the cell adhesion and proliferation behaviors of osteoblast (MG-63) cell. The laser with 50 mm/s scanning speed induced formation of rough volcano-like recast layer accompanied with micro-/nanoporous structure, which can promote cell adhesion and proliferation of MG-63 cell on Ti surface. The results indicated that the laser treatment was a potential technology to enhance the biocompatibility for titanium.

1. Introduction

Ti and Ti-based alloys are often used as implant materials due to their excellent mechanical properties, corrosion resistance, biocompatibility, and so on [1–5]. Previous studies have demonstrated that as the thickness of the Ti oxide layers increased, blood compatibility of these layers was obviously improved [6–8]. Other reference shows that because the Ti metal surface contains TiO_2 oxidize layer, and with tissue of liquid to do ion exchange, there is characteristic that has finer biological compatibility more than other metal [3,9]. The responses of cell and tissues at implant interfaces have been shown to be affected by the chemical properties, topography, and roughness of the implant surfaces [10,11]. Thus, numerous surface treatment methods, such as sandblast, acid etching, discharge processing, sputtering coating, hydroxyapatite coating, and anodization, are employed to enhance the surface properties of the Ti metal at present [12–18]. The fatigue and fracture behavior are mostly improved by the modification of the microstructure via various surface treatments [19]. However, these common surface treatment methods do not maintain optimal surface purity for biomedical applications [20,21]. The microstructured surfaces created by the sandblasting, large-grit, and acid-etching enhanced the osseointegration process, while smaller mass of bone tissue around the treated surfaces were observed when comparing with a smooth surface [22]. The coating qualities, such as thickness and uniformity, obtained from the coating technologies were not easily controlled [23].

Recently, a green processing technology (i.e., laser surface treatment) has been considered as a promising method to improve the surface properties of biomedical pure Ti and stainless steel implants [24–26]. The main features of laser surface treatment includes materials' surface which can be melted and vaporized in an instant refractory, non-contact processing, avoiding excessive stress caused by processing residues to prevent the normal wear of cutting tools, high superficial

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purity preservation as well as extreme regularities and uniform roughness surfaces [24,27]. Moreover, since the laser light has a good controllability of space and time, it becomes an easy-oriented and focused to its energy, power and beam. It can also be adjusted and controlled on combining with computer and auto-detection technology, which can promote a variety of flexible and automatic processing. Comparing with the electron beam, laser machining process has the advantages of processing in an air environment free from electromagnetic interference and the device is relatively simple and user-friendly. The laser beam is produced using mixture of gas like CO_2, N_2 and He, which is continuously excited by electrodes to produce a collimated photon beam.

Therefore, the green non-contact laser surface treatment can be applied on implant materials for surface modification in order to generate some functional surface properties without sacrificing any useful mechanical or biological properties. For the biomedical application considerations, the purpose of the present study is to highlight some of the major influences of laser scanning speed on the microstructure and biocompatibility of the biomedical pure Ti.

2. Materials and methods

2.1. Specimen preparations

A biomedical Grade-IV Ti bar was cut into disks (10 mm in diameter and 2 mm in thickness) and used as the substrate. The substrates were polished and ultrasonically cleaned with acetone, ethanol, acetone, and deionized water for 5 min each and then were dried in air before use. The diode-pumped solid-state (DPSS) laser with neodymium-doped yttrium orthovanadate (Nd:YVO_4) laser source system was used for the laser process. The DPSS laser system, which is divided into the host computer, laser engraving platform, another platform for composition of laser engraving laser transmitter, power supply and cooling system. Nd:YVO_4 laser light used for the solid-state laser (laser wavelength (λ) of 335 nm) at a high energy density. This system has a small writing and multi-processing capabilities. DPSS laser technology scored pattern lines on sample surface. The laser process parameters are shown in Table 1. After laser modification, the modified specimens were cleaned in ethanol for 15 min in an ultrasonic bath followed by air drying.

2.2. Surface characterization analysis of laser-modified specimens

The laser-modified specimens for optical microscopy (Olympus BX51) observation were prepared by sectioning, mounting, polishing and etching (etched with a mixture of 3 ml HF, 5 ml HNO_3, and 92 ml H_2O). A 3D profile and surface roughness measurement instrument (Surfcorder ET 4000) and a field-emission scanning electron microscopy (SEM; JEOL-6500F) were employed to analyze the surface roughness and morphologies for these laser-modified samples. Phase identification and crystallinity analysis were carried out by X-ray diffractometer (XRD, Rigaku 2200) with CuKα1 radiation operated at 50 kV and 250 mA and transmission electron microscope (TEM, JEOL-2100) operated at 200 kV. Cross-sectional view of TEM specimens was prepared by sectioning the laser-modified samples parallel to the surface to approximately 300 μm thickness. The laser-modified sample surface was stuck and then manually grinds to about ~100 μm. Ar ion beam thinning (Gatan model 691) was carefully controlled to produce an electron transparency. Wettability examination was performed using the sessile drop method using a GBX DGD-DI contact angle goniometer. Deionized water was used in the test and a contact angle measurement of an average five drops per sample was conducted.

Table 1
Different laser process parameters for biomedical grade IV pure Ti disc.

Parameters	Samples			
	LTi-1	LTi-2	LTi-3	LTi-4
Scanning speed (mm/s)	10	50	200	500
Power (W)	1	1	1	1
laser wavelength (nm)	335	335	335	335

2.3. Cell cytotoxicity assay

Prior to cell cytotoxicity assay, specimens were autoclaved at 121 °C for 15 min. To evaluate the cell cytotoxicity of laser-modified samples, each group specimens ($n = 5$) were cultured with osteoblast cells (MG-63, ATCC CRL-1427). The variations in cell morphology following various incubation periods were observed. Before cell culturing, the samples were washed sequentially in acetone (15 min) followed by ethanol (15 min) in an ultrasonic bath followed by air drying. Samples were then sterilized at 121 °C for 15 min by autoclaving. Minimum Essential Medium (MEM, Gibco) was used for MG-63 cell culture. The laser-modified samples were placed in 24-well polystyrene plates. Subsequently, the MG-63 cell suspensions with a 1×10^4 cells/ml were added to the well and cultured in an incubator at 37 °C with 5% CO_2 for 8 h, 1 day, 3 days and 5 days, respectively. After the incubation period had elapsed, 500 μl of culture medium mixed with 50 μl of 3-[4,5-dimethylthiazol-2-yl]-2,5-diphenyltetrazolium bromide (MTT) labeled solution was added to each culture well and the plate was incubated for a further 4 h to form the formazan solvent precipitates. The supernatant was aspirated and the samples covered with trypsin-EDTA for 3 min. Cells were centrifuged at 1000 rpm for 5 min and then lysed with 150 μl dimethyl sulfoxide for 10 min in 96-well plate to release the

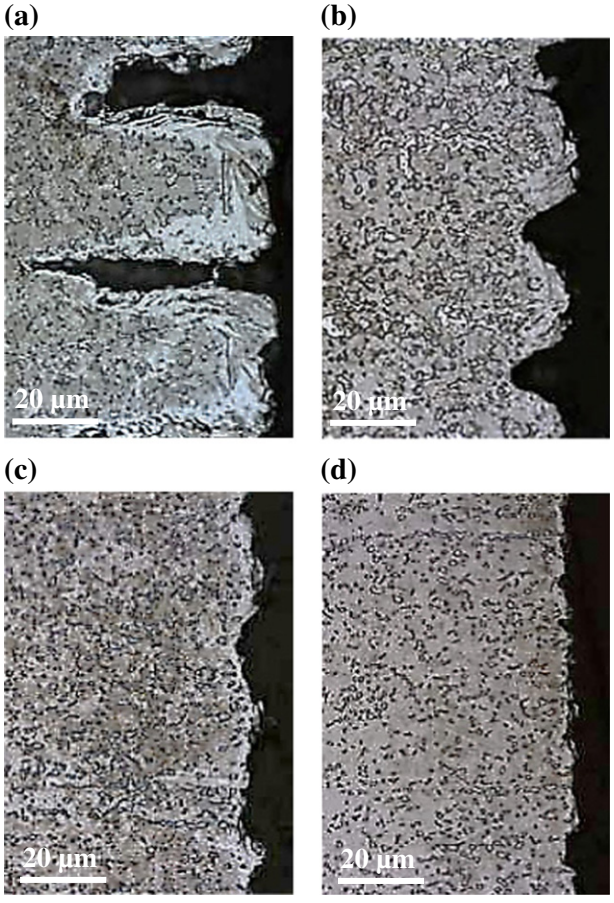

Fig. 1. Cross-sectional optical micrographs of Ti modified under various speeds of laser scanning: (a) LTi-1, (b) LTi-2, (c) LTi-3 and (d) LTi-4 samples.