Surface modification of Ti6Al4V by nanosecond laser ablation for biomedical applications

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Abstract. This paper presents the surface textured process of biometal Ti6Al4V by means of 355 nm Nd:YVO4 nanosecond laser. Our target is to create structures with sizes which favour osseointegration. In this work a pattern of parallel grooves was generated after a deep analysis of the irradiation parameters involved. Ablation modifies not only the topography but also physico-chemical properties of the metal surface. Changes in the morphology and the physico-chemical state of the laser induced groove pattern were studied by a scanning electron microscopy, X-ray diffraction and X-ray photoelectron spectroscopy, which revealed, among others, an increase of micro roughness and a oxide layer entirely formed by TiO2, which can improve biocompatibility properties of the textured surface.

1. Introduction
Metallic materials are used in orthopedics and dentistry as biomaterials for bone-replacing applications. Titanium alloy Ti6Al4V is of great choice due to its biocompatibility, high strength and corrosion resistance. Another critical factor to be fulfilled by biometals to achieve implant success is osseointegration [1, 2]. Different studies have demonstrated that the topography of the metal surface is an important factor affecting osseointegration [3, 4, 5]. Besides mechanical considerations, the process at the metal-bone interface is fully dependent on the biological interactions as a response to surface chemistry of the implant [6].

Earlier results do not completely elucidate the influence of surface roughness in osseointegration. Both random roughness and organized patterned biometal surfaces have been tested. In any case, induced surface features must be related and comparable to the size of biological entities like proteins, osteoblast cells and/or osteons [7]. Determination of the optimal topography type and dimensions is still challenging.

Laser texturing has proved to be an adequate technique for implant modification [8, 9]. Although ultrashort pulsed lasers have been increasingly used in this field, nanosecond laser technology is widely adopted in the industry for micromachining (based on time and cost effectiveness). It has been implemented over a wide range of laser sources with different combinations of wavelength, pulse duration, energy and pulse frequency [10].

The aim of this work is the analysis of irradiation parameters involved in laser surface texturing of titanium alloy Ti6Al4V in order to obtain well organised structures with sizes in a suitable range (≈ 30 µm width and ≈ 10 µm depth) for biomedical applications and the
characterisation of the possible physico-chemical alterations which are produced at the surface due to the textured laser process.

With this objective in mind, we have generated a pattern of parallel grooves by means of different combination of laser irradiation parameters. Moreover, physico-chemical characterisation of the topographies has been performed using standard surface analysis techniques. These results will allow us to establish the most adequate laser parameters in manufacturing of the biometallic surface with a high reproducibility as well as the evaluation of the effects that the physico-chemical changes induced during the ablation process produce in the material’s properties related with biocompatibility.

2. Materials and Methods

Ti6Al4V, Ti64 henceforth, in a shape of 4 mm sheet was implemented as a typical metal implant material. Samples were prepared under standard metallographic procedures. Before and after laser treatment, surfaces were ultrasonically cleaned in ethanol, acetone and distilled water.

The laser used was a Nd:YVO4 (Coherent AVIA Ultra 355-2000) at the wavelength of 355 nm and pulse duration 25 ns. The intensity profile at the laser output was near-Gaussian ($M^2 < 1.3$) and the beam diameter at $1/e^2$ intensity level was about 2.2 mm. The laser beam presents vertical polarization ($> 100 : 1$). Pulse rate, $f$, can be selected from single-shot to 100 kHz, with energy per pulse around 0.1 mJ. The maximum mean power output is 2 W at $f = 20$ kHz.

In order to improve the focalization, a convergent lens with focal length of 35 mm was used. The beam diameter, measured at the beam waist, was $32 \pm 6 \mu m$, which corresponds to an energy density of about $26 J/cm^2$. Samples were set on XYZ translation stage Newport ILS-CC. Newport MM4006 controller was used for the movement of the stages and to start/stop the laser. The focused beam was impinged normal to the surface of the sample. Customised software was applied to program the controller in any arbitrary trajectory and to synchronise the laser with sample displacement. All experiments were done in air. To modify the topography of the metal surface, the sample was precisely positioned at the waist of the focused beam using the Z-direction stage.

After laser machining, samples were analysed with a scanning electron microscope (SEM) JEOL JSM 6400. Metallographic images of transverse sections were obtained by re-mounting samples at a perpendicular position to the main axis of grooves. Chemical etching with Kroll’s reagent was performed for metallographic examination. The topographical analysis was obtained by means of confocal microscopy (Sensofar PLu 2300). The crystalline structure was investigated by X-ray diffraction (XRD). Spectra were recorded with a Bruker D5000 diffractometer, Cu cathode, 40 kW, 30 mA under Bragg-Brentano geometry. X-ray photoelectron spectroscopy analysis (XPS) was performed using a Thermo Scientific K-Alpha ESCA instrument equipped with Al-Ka radiation. Charge referencing was set as C1s photo peak at 285 eV.

3. Results and Discussion

3.1. Surface structuring

Polished surfaces of metal samples were textured with a pattern of parallel grooves by overlapping single laser pits to achieve the line structure. In a previous work, the systematic procedure to select the most adequate parameters to obtain topographic characteristics in the appropriate range for biomedical applications was performed [11]. The pulse rate ($f$) was fixed at 10 kHz because, at this value, the laser delivers its maximum output power and, moreover, this high rate allows us to optimise the process, i.e., treating large areas of the metal surface in a shorter time, which is of great interest from a practical point of view.

Regarding the scan speed ($v$), the selected rage was $1 – 30 \, \text{mm} \cdot \text{s}^{-1}$. Higher values of $v$ would result in an important loss of precision in the translation stages, and, consequently, in sample micromachining. Conversely, smaller values would needlessly increase the processing time. It
was estimated that at this working $v$ range it does not cause appreciable heat accumulation in the sample surface. The degree of overlapping depends on both the pulse repetition rate and the scan speed. Otherwise, the spacing between the grooves should be taken into account to obtain a suitable periodic pattern. This value was selected by considering the maximum width of the grooves (obtained from a Gaussian fit of the groove profile) with the criterion that the overlap is 50% of the groove depth, i.e., the spacing was approximately 1 FWHM. At the maximum value of groove width, $w = 40 \mu m$, the spacing or pitch is FWHM = 1.177 $w \approx 50 \mu m$.

**Figure 1.** SEM micrograph of machined grooves in titanium alloy generated by laser irradiation in a single beam pass at $v = 25 \text{ mm} \cdot \text{s}^{-1}$, $f = 10 \text{ kHz}$ and pitch $50 \mu m$. (a) General view at 400x; (b) details of one groove at 1000x; (c) groove profiles obtained by confocal microscopy.

Figure 1 depicts SEM top view of a pattern of grooves in Ti64. In order to study the effect of scan speed on the groove depth, cross sections of samples processed at scan speed in the range $v = 1 - 30 \text{ mm} \cdot \text{s}^{-1}$ were analysed by SEM. Figure 2 shows the cross sections at $v = 25$, 10 and 5 $\text{mm} \cdot \text{s}^{-1}$. In the range $v = 10 - 30 \text{ mm} \cdot \text{s}^{-1}$, the profile of the laser machined area is smoothly wavy. However, at $v = 5 \text{ mm} \cdot \text{s}^{-1}$, the grooves become much deeper and residues debris produced during ablation remain trapped inside, which makes scan speeds below 5 $\text{mm} \cdot \text{s}^{-1}$ rather ineffective for texturing the metal surfaces. The dependence of groove sizes (depth and width) with irradiation parameters (Figure 3) shows that groove depth is the most sensible characteristic; it decreases with the scan speed while the width remains almost constant. Therefore, the analysis of the different parameters involved allows us to establish the most adequate irradiation conditions to obtain grooves with features in the range of interest: at focused beam and $f = 10 \text{ kHz}$ the optimum value of scan speed would be in the range $25 - 30 \text{ mm} \cdot \text{s}^{-1}$.

### 3.2. Surface characterisation

Changes of the morphology and the physico-chemical state of the laser induced groove pattern were studied. Morphological features created at the textured surface were shown in Figure 1 (a) and (b). They consisted of splattered material ejected from molten pool during ablation in the form of drops, clusters and pillar structure, which resulted in a characteristic microroughness inside the groove. Further analysis of these micro-structures developed inside the groove are being conducted in order to quantify the roughness of Ti64 bio-metal surfaces structured by laser, since it has been demonstrated that the creation of roughness and sub-micron features could be beneficial for cell proliferation and adhesion processes [12]. From transverse sections of
the grooves (Figure 2) it can be observed that a rib of molten material was redeposited at the top of the groove walls. The rib is part of the remelted layer of bulk material which has been produced during intense laser heating and rapid cooling, conforming the heat affected zone. This layer is about 2.5 µm and exhibits a porous texture. Grain boundaries of the original crystalline phases are no longer appreciated at the remelted zone.

**Figure 2.** SEM images of cross sections of parallel grooves obtained at \( v = (a) \ 25, \ (b) \ 10 \) and (c) \( 5 \text{ mm} \cdot \text{s}^{-1}; \ f = 10 \text{ kHz} \) and pitch 50 µm in Ti64.

**Figure 3.** Sizes of the grooves (depth and width) as a function of the scan speed.

XRD analysis of treated sample (Figure 4) do not show new crystalline structures. Typical peaks corresponding to \( \alpha \) and \( \beta \) titanium phases were detected. Changes observed in the spectra of textured surfaces are regarding to the shift and broadening of the diffraction peaks which are related to a grain refinement of the metal or a strain state caused by high cooling rates [13].

Chemical characterization of the changes induced in the remelted layer by laser texturing was performed by XPS analysis. The survey spectra of the control and laser treated samples show peaks which correspond to the principal alloying constituents: titanium and aluminium. Moreover, two other dominant peaks corresponding to carbon and oxygen were detected. Figure 5 depicts high resolution spectra of samples in Ti64. In control samples, fitted peaks for high resolution O1s spectra corresponded mainly to oxide compounds and a smaller peak which corresponds to hydroxide compounds. High resolution Ti2p spectrum shows the presence of three compounds: a dominant one assign to TiO\(_2\), and two weaker peaks for TiO and for metallic Ti. Aluminium was mainly present as oxide Al\(_2\)O\(_3\), hydroxide and metallic state. XPS analysis of laser treated samples reflects a significant increase of the oxygen content at the surface of the samples. This increase could probably be a consequence of the surface oxidation during
laser structuring under a non-controlled atmosphere. Laser irradiation induced an oxide layer entirely composed of TiO$_2$, a highly stable protective surface film, which makes titanium one of the most corrosion-resistant metals [14]. Furthermore, Ti and Al metallic peaks are not longer detected; this shows the growth in thickness of the oxide layer, as it was described in previous works [15, 16]. XPS also indicates a major rise of OH compounds after laser treatment. This surface enrichment of polar compounds could positively contribute to the surface hydrophilicity [17].

4. Conclusion
The study of the micromachining process of Ti6Al4V by means of 355 nm Nd:YVO$_4$ nanosecond laser was presented. The surface was textured under a groove pattern with an appropriated
set of parameter, i.e. \( f = 10 \text{ kHz} \), \( v \) in the range \( 25 \text{–} 30 \text{ mm} \cdot \text{s}^{-1} \) and pitch is 50 \( \mu \text{m} \), in order to obtain surface features in the range of \( \approx 30 \mu \text{m} \) width and \( \approx 10 \mu \text{m} \) depth which is reported to be suitable for biomedical applications. SEM analysis of transverse section samples revealed the presence of a thin layer of remelted material throughout the groove topography. This layer exhibited a micro-roughness and porous structure which maximise the exposure surface and, consequently, could be beneficial for cell adhesion and proliferation. A grain refinement of original crystal structure and consequently an induced residual strain in those layers could be appreciated. Regarding to the surface chemistry, XPS analysis reflected an increased surface oxidation in addition to a growth in OH which could positively contribute to the surface hydrophilicity by laser surface modification. Those findings could improve corrosion and biocompatibility properties of the metal.

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