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Surface modification of Ti dental implants by Nd:YVO_4 laser irradiation

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Abstract

Surface modifications have been applied in endosteal bone devices in order to improve the osseointegration through direct contact between neoformed bone and the implant without an intervening soft tissue layer. Surface characteristics of titanium implants have been modified by addictive methods, such as metallic titanium, titanium oxide and hydroxyapatite powder plasma spray, as well as by subtractive methods, such as acid etching, acid etching associated with sandblasting by either AlO_2 or TiO_2, and recently by laser ablation. Surface modification for dental and medical implants can be obtained by using laser irradiation technique where its parameters like repetition rate, pulse energy, scanning speed and fluency must be taken into accounting to the appropriate surface topography. Surfaces of commercially pure Ti (cpTi) were modified by laser Nd:YVO_4 in nine different parameters configurations, all under normal atmosphere. The samples were characterized by SEM and XRD refined by Rietveld method. The crystalline phases αTi, βTi, Ti_6O, Ti_3O and TiO were formed by the melting and fast cooling processes during irradiation. The resulting phases on the irradiated surface were correlated with the laser beam parameters. The aim of the present work was to control titanium oxides formations in order to improve implants osseointegration by using a laser irradiation technique which is of great importance to biomaterial devices due to being a clean and reproducible process.

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Keywords: Surface modification; Titanium; Laser ablation; Dental implant; Biomaterial

1. Introduction

For over a century, researchers have been working hard so as to find the proper materials for replacement and substitution of bone tissues in the human body. Initially, the search for such composites was performed through the utilization of biological materials, as in bone grafts and transplants, which can be ranked as autogenous (donor and receptor are the same), alogenous (donor and receptor are of the same species), and xenogenous (donor is of animal origin). Due to the limitations of such biomaterials, studies have been done aiming at developing proper synthetic materials which may lead to a decrease and, eventually, to a ban of the utilization of biological materials [1].

Different surface treatments in implantable titanium devices have been put on the market in order to promote the osseointegration phenomenon, the increase of the contact area around neoformed calcified bone tissue and the corrosion resistance. The ‘‘osseointegration’’ word was coined to describe direct contact between neoformed bone and the implant without an intervening soft tissue layer [2].

By comparing with several implants surface modification processes currently on the market, such as mechanical processes (machining and abrasive sandblasting), chemical processes (acid etching and oxidation), and thermal processes (plasma spray), it has been observed that the resulting surface by laser beams irradiation, shows similar characteristics without the occurrence of contaminations since it is a clean and reproducible process, furthermore it enable a better control of the variables involved in such process.

The surface modification obtained by laser beam irradiation requires a proper relationship among the laser beam parameters, to assure the expected resulting composition,

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Table 1
Laser parameter configurations

Definitive parameters	1	2	3	4	5	6	7	8	9
Power (%)	100	100	100	100	100	100	100	100	100
Scanning velocity (mm/s)	300	300	300	500	500	500	100	100	100
Repetition rate (kHz)	35	15	5	35	15	5	35	15	5
Peak power (kW)[a]	14.5	34	50	14.5	34	50	14.5	34	50
Pulse width (ns)[a]	17	12.5	10	17	12.5	10	17	12.5	10
Average power (W)[a]	8.6	6.5	3.8	8.6	6.5	3.8	8.6	6.5	3.8
Pulse energy (mJ)[a]	0.24	0.41	0.56	0.24	0.41	0.56	0.24	0.41	0.56
Fluency (J/cm^2)	93.3	68.3	31.1	56	41	18.7	280	205	93.3

[a] Data from the equipment curves.

irradiated surface morphology and physical chemistry properties surface.

Topography and surface energy play an important role on the osseointegration process of osteoblastic cellular adhesion to the biomaterials surface [3,4]. Laser beam irradiation surface of cpTi becomes important due to the increased resulting surface area and its biocompatibility offered by both the oxides and nitretes formed.

Several studies have been published over the last years [5–10] correlating the laser parameters, the environment and the formed phases, as well as the surface morphology. However, work correlating a quantitative distribution of resulting phases and laser beam parameters on the irradiated surface of cpTi remains unclear in the literature.

The contribution of the present work is correlating the Nd:YVO_4 pulsed laser beam parameters with the quantitative distribution of the oxides and other compounds formed on the cpTi-irradiated surface.

2. Material and methods

The laser irradiation procedures were done in the Digilaser DML 100 – Violin 10 – Nd:YVO4 equipment in normal environmental atmosphere and varying the following parameters:

(a) Scanning speed—defining the irradiation exposure time point per point on the surface.

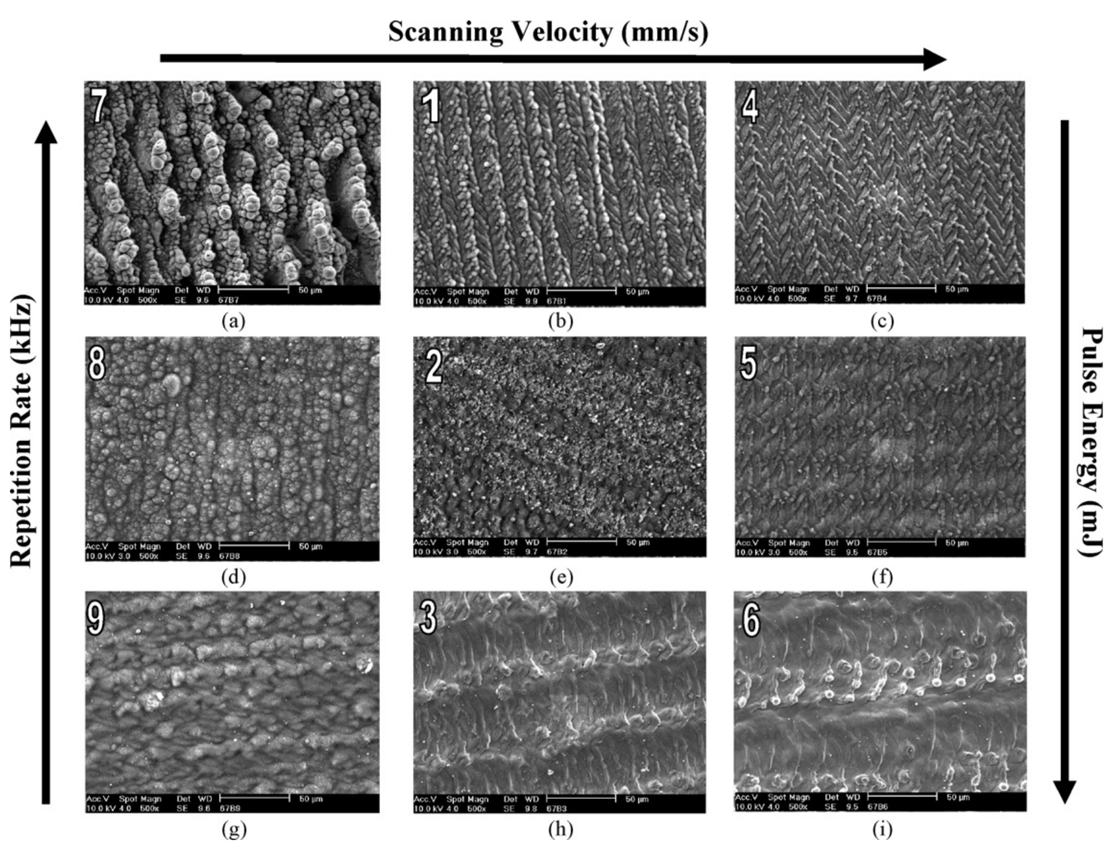

Fig. 1. SEM topographical surface images relate to laser parameters.

Table 2
Crystalline structures of identified phases in the irradiated structures

Phase	Crystalline system	Space group	Cell parameters (Å)	ICSD number
α-Ti	Hexagonal	*P*63/*m m c*	$a = b = 2.95$, $c = 4.686$	76,144
β-Ti	Cubic	I*m*-3*m*	$a = b = c = 3.3111$	44,391
TiO	Cubic	F*m*-3*m*	$a = b = c = 4.1766$	28,955
Ti_3O	Trigonal/rhombohedral	*P*-3 1*c*	$a = b = 5.1411$, $c = 9.5334$	24,082
Ti_6O	Trigonal/rhombohedral	*P* 3 1*c*	$a = b = 2.95$, $c = 4.686$	17,009

(b) Repetition rate—defining the pulse quantity irradiated point per point by time unit.

The wavelength, focus position, number of passes and distance between scanning lines were remained constants. The peak power, average power, pulse width and pulse energy, were varying as a function of the repetition rate whose values were gathered from the equipment manufactor's guide. After a pilot study, the laser irradiation was established in nine parameter conditions as showed in Table 1.

The irradiated samples were characterized by scanning electron microscopy (SEM-Phillips XL-30 microscope) operating at 20 kV using (×500) magnification.

The crystalline structures of samples were investigated by X-ray powder diffraction (Seifert XRD 3000 TT diffractometer) and the quantitative phases analysis was obtained by Rietveld refinements [11] using the program GSAS [12]. The phases considered in all refinements are listed in Table 2.

3. Results and discussion

The SEM micrographs of the surface of all samples obtained with different scanning speed, repetition rate and pulse energy are displayed in Fig. 1. It can be observed in all accumulated fluencies a fast melting and solidification process occurring on the samples surface. Despite the phases

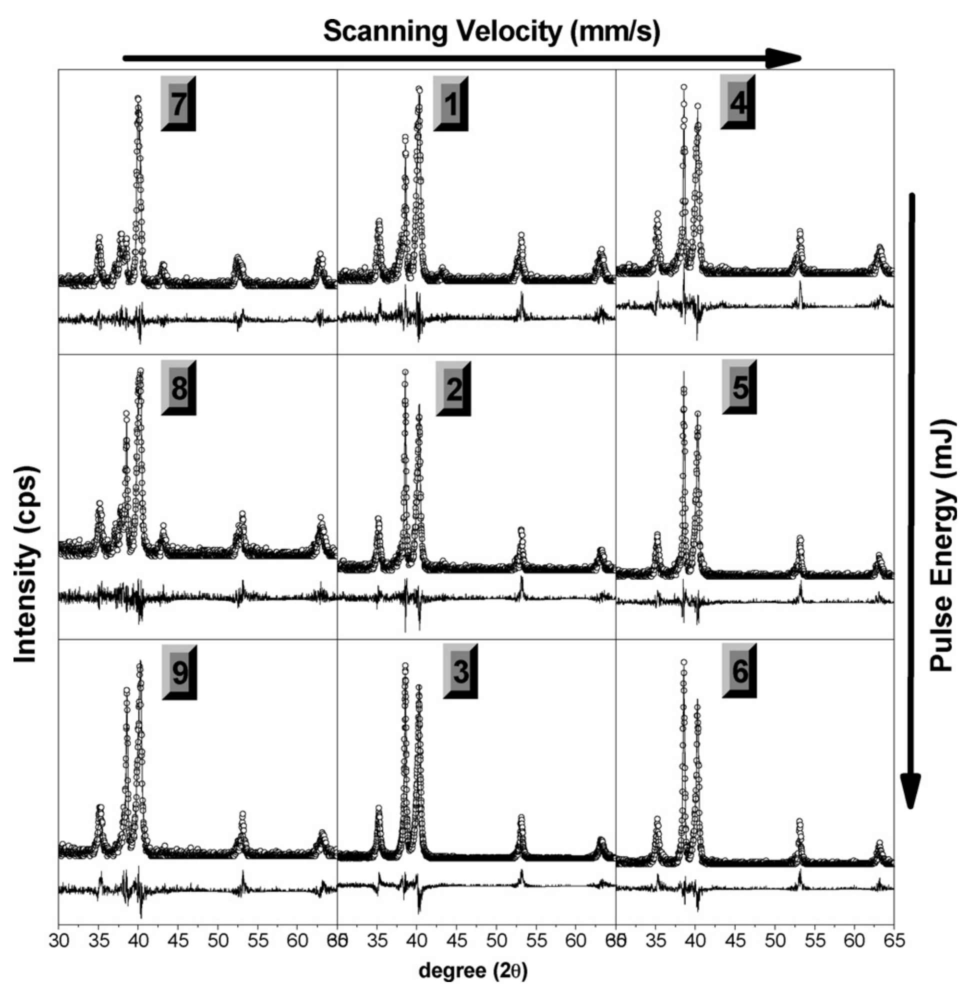

Fig. 2. Irradiated surfaces XRD spectra after Rietveld refinements.

that have being formed, it is important to notice that the obtained morphology vary from a high roughness surface (Fig. 1a) to a more smooth one (Fig. 1i), depending of the accumulated fluency through.

The influence of repetition rate for samples obtained with the same scanning speed must be considered. Fig. 1a, d and g shows the SEM of samples surfaces obtained with scanning speed equal to 100 mm/s. As it can be observed, the increases of repetition rate correspond to a rougher surface.

Considering samples obtained with the same pulse energy and repetition rate (Fig. 1a–c, for example), conclusion can be drawn considering the scanning speed increases, i.e., the lower the scanning speed the higher the rough surface will be.

Fig. 2 presents the final graphics after Rietveld refinements for all samples; the Bragg peak positions of the considered phases in the refinements were not presented to allow a better view. In all samples, peaks are slightly moved from their standard position due to the high residual stress developed during very fast heating and cooling process resulting from laser ablation. However, although the uncertainty in the discrepancy factors of Rietveld refinements are in some cases high, it can be stated that the obtained phases percentages are in a good approach and in agreement with others authors, as will be discussed later.

Fig. 3 shows the phases percentage obtained by Rietveld refinement. By analyzing the phase's percentage against fluency, some conclusions can be drawn. As respectively

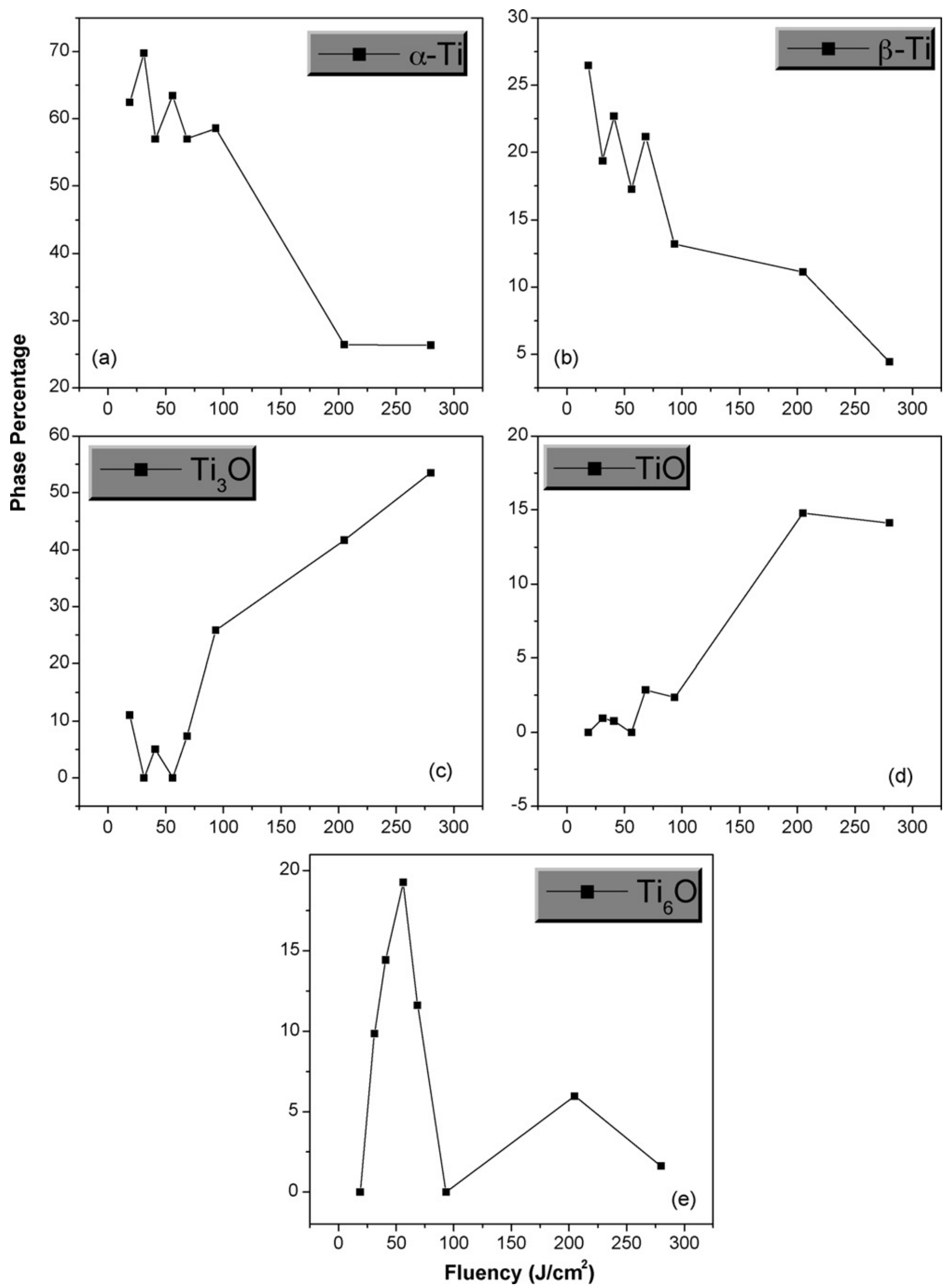

Fig. 3. Irradiated surface phase's percentage by Rietveld analysis.

observed in the Fig. 3a and b, α-Ti and β-Ti had decreased by increasing fluency. In the other hand, Fig. 3c and d indicated an opposite behavior for TiO and Ti_3O phases, indicating that increasing fluency caused an increase in the oxidation state of metallic Ti. For intermediate Ti oxidation state (Ti_6O—Fig. 3e), a maximum phase percentage obtained for fluencies close to 50 J/cm^2 occurred. These results are not surprisingly as one can expect that increasing the energy delivered at surface in normal atmosphere will increase the oxidation state of metals.

As observed in the XRD patterns of samples (Figs. 2 and 3), depending on the laser parameters set, different phases are formed on metal surface. By modifying the scanning speed (mm/s), repetition rate (kHz) and pulse energy (mJ), the global energy delivered on the surface may be varied and the amount of diffused atoms in the treated surface depends upon the repetition rate [13,14]. The laser-titanium interaction only undergoes thermal effects, but during the laser pulse the surface is heated and can be melted and vaporized creating plasma state on its surface. As a result, diffusion mechanism from species close to the irradiated area (especially oxygen and nitrogen) into the hot titanium getter will take place. The very fast heating and cooling processes lead to a non-equilibrium phenomena [15,16] where the thermochemical reaction rate constants have a Arrhenius-type temperature dependence and also depend on other parameters such as a wavelength, power, polarization, time of irradiation, consistency of the environment gaseous atmosphere, focusing details, etc.

The presence of Ti_6O and Ti_3O is due to oxygen ordering in the hexagonal α-Ti and can be explained by oxygen diffusion in the α-Ti initial lattice. Some researchers [8,16,17] have showed that the higher accumulated fluency, the higher degree of oxidation, i.e., with a high oxygen diffusion, samples will trap more oxygen in the melted phase. The characteristic peaks of TiO_2 (rutile and anatase) were not observed, indicating that the maximum fluency used in our work (280 J/cm^2) was not enough to form the high titanium oxidized phase. This result is in agreement with Pérez del Pino et al. [7], which has obtained rutile and anatase phase only with fluencys above 294 J/cm^2.

The presence of cubic β-Ti can be explained in terms of growth in symmetry of the hexagonal α-Ti during heat propagation. The quenching process provided by the fast cooling will allow β-Ti stabilization. The formation of cubic TiO could also be related to the β-Ti. TiO present a cubic structure almost similar with the β structure. One can infer that oxygen atoms will diffuse to the melted β-Ti to form TiO, being the latter lattice bigger than the former due to oxygen incorporation. Accordingly discussed before, it is important to note that the highest TiO concentration (Fig. 3d) is related to samples with lowest β-Ti concentration (Fig. 3b).

Despite the high number of parameter influencing the control of phases and morphologies obtained at titanium surfaces, the accumulated laser fluency (Table 1) seems to be the more sophisticated. The accumulated energy per unit area (fluency) can be calculated as:

$$F = \frac{E_p f}{DV}$$

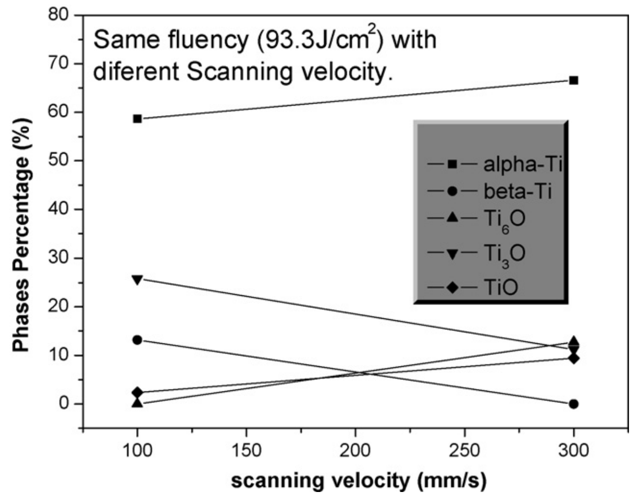

Fig. 4. Phase's percentage obtained by Rietveld analysis for samples irradiated with same Fluency (93.3 J/cm^2). Samples 9 and 1 were obtained by using scanning velocity equal to 100 and 300 mm/s, respectively.

where E_p is the pulse energy, f the repetition rate, D the spot diameter and V is the scanning velocity. However, the same accumulated laser fluency can be reached by using different laser parameters. Samples 1 and 9 present the same accumulated fluency, but as it can be observed at Table 1, these samples were irradiated with different pulse energy, repetition rate and scanning velocity of the laser beam. Fig. 4 shows the phase's percentage for samples 1 and 9, where the modified surfaces were obtained by using scanning velocity of 300 and 100 mm/s, respectively. As it can be observed, even surfaces modified with same accumulated fluency, the samples present different surface phases distribution. It was noticed that increasing the scan velocity would decrease the percentage of titanium oxides phases with high oxidation state, i.e., TiO and Ti_3O. These results indicated that fluency could not be taking into account by itself. In fact, accumulated fluency give the total energy distributed by area in the metal surface, but the way this energy is delivered, i.e., pulse energy, repetition rate and scanning velocity, will affect the laser-assisted oxidation kinetics. As explained by L. Nánai et al. [16], metal surface oxidation is a multi-sequence process culminating with species incorporation onto metal. The results discussed in our work corroborate to the idea that laser irradiation has some crucial effects on the chemical processes taking place on the metal surface oxidation being not purely thermal with laser serving only as one extensive heat source.

4. Conclusions

The accumulated energy per unit area (Fluency) could not be taking into account by itself; the velocity in which this energy is delivered on the surface has influenced the oxidation state of metal being irradiated. The laser beam irradiation is a clean and reproducible process, furthermore it enable a better control of the variables involved in such process where the implant surface does not interact with any other materials for its modification and improve the implant surface with significant characteristics which may help the osseointegation phenomenon, such as morphology, surface roughness, formation of some compounds that facilitate the wetting and the physical chemistry properties surface.

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