The relationship of the oxide phases on irradiated titanium surface by $Nd:YVO_4$ laser with the Ca,P deposited layer

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Keywords: Surface modification; Titanium; Laser ablation; Hydroxyapatite; Biomaterial

Abstract

The scope of this paper is focused on surface modification process by laser beam irradiation in pure metallic titanium inducing by ablation phenomenon such non stable oxides formation on the irradiated surface. The present study correlates the pulsed laser beam parameter conditions used to irradiate pure metallic titanium and its resulting crystalline phases on the surface with the deposited calcium phosphate layer on it.

Introduction

The long-term benefits of implants depend on the responses of the surrounding bone tissue inducing the osseointegration, i.e. the formation of a direct connection between the living bone and the surface of load-carrying implants. However, question arises as to how to attain better integration by modification of the implant surface in its physical chemistry characteristics. One point suggest be in agreement with many authors: the surface should be free from any contamination [1–4]. Laser processing is a new method of treating implant surfaces to produce a high degree of purity with enough roughness for good osseointegration [5]. In practical use the surface of titanium treated by laser beam will be subjected to the influences of the environment [6]. In addition, laser processing is contactless and the thermalmechanical deformation of the substrate is generally low [7].
Surfaces of pure titanium modified by a laser beam irradiation are technologically important due to the augmentation of the surface area and the biocompatibility showed by the formed meta-stable oxides [8]. Implants made of titanium have been referred to their four most important properties: prosthesis/implant system, surgical protocol, mechanical design and surface modification process [9]. The scope of the present paper is focused on this last property. Several types of surface treatment in implants are offered due to the market appeal in improvements as the osteointegration process catalysis, augmentation of the bone/implant contact surface area and corrosion resistance to the organism aggression. The present study correlates four pulsed $Nd:YVO_4$ laser beam parametric arrangements irradiating ASTM F67 metallic titanium and its resulting crystalline surfaces, following the line presented by György et al for Nd:YAG [10], with the calcium phosphate layers deposited by biomimetic process on them, according method developed by Kokubo et al. [11]. The principal discussion is related to the cause of occurrence of the non stable oxide phases by laser beam irradiation and their influence on the calcium phosphate deposited layer.

Materials 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 parameters (a) Scanning Speed—defining the irradiation exposure time point per point on the surface; and (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 laser

21st International Symposium of Ceramics in Medicine - Bioceramics 21, 2008, Búzios.
BIOCERAMICS 21. Zurich : Trans Tech Publications Ltd., 2008. v. 1. p. 565-568.

irradiation was established in four parameter conditions as showed in Table I. The analytical and characterization methods used in this study were WDXRF, SEM, XRD and FTIR.

Table I. Laser parameter configurations.

Laser Beam Parameters	**1**	**2**	**3**	**4**
Power [%]	100	100	100	100
Scanning velocity [mm/s]	500	500	100	100
Repetition rate [kHz]	35	5	35	5
Peak power [kW]	14.5	50	14.5	50
Pulse width [ns]	17	10	17	10
Average power [W]	8.6	3.8	8.6	3.8
Pulse energy [mJ]	0.24	0.56	0.24	0.56
Fluency [J/cm^2]	56	18.7	280	93.3

The crystalline structures of samples were investigated by X ray powder diffraction and the quantitative phases analysis was obtained by the phases identification and full profile adjustment methods using the programs Crystallographica Search Match [12] and Powder Cell [13] respectively. The phases considered in all refinements for the irradiated surfaces are : α-Ti, ß-Ti, TiO, Ti_2O, T_3O and Ti_6O. The phases considered in all refinements for covered surfaces by a biomimetic procedure are: $Ca_{10}(PO4)_6(OH)_2$, $Ca_{10}(PO_4)_{6-x}(CO_3)_x(OH)_{2-y}(CO_3)_y$, CaO, CaO_2, CaP_2O_6, $Ca_3(PO_4)_2$, $Ca(OH)_2$, Na_2O, Na(OH) and $NaTiO_2$.

Results

Plates of pure titanium were chemically characterized by WDXRF technique and considered as ASTM F 67 (surgical standard), according showed in the Table I.

Table II. Chemical composition of titanium plates.

Material	**N [% m/m]**	**C [% m/m]**	**H [% m/m]**	**Fe [% m/m]**	**O [% m/m]**	**Al [% m/m]**	**V [% m/m]**	**As [µg/g]**	**Mn [µg/g]**	**Ti [% m/m]**
Ti cp	0,031	0,08	0,009	0,23	0,18	0,001	-----	<10	<10	Balance
ASTM F67	0,03 max	0,10 max	0,015 max	0,30 max	0,25 max	------	------	------	------	Balance

The SEM micrographs of the irradiated surfaces with different scanning speed, repetition rate and pulse energy evidenced the ablation process occurring on all the surfaces as shown in Figure 1.

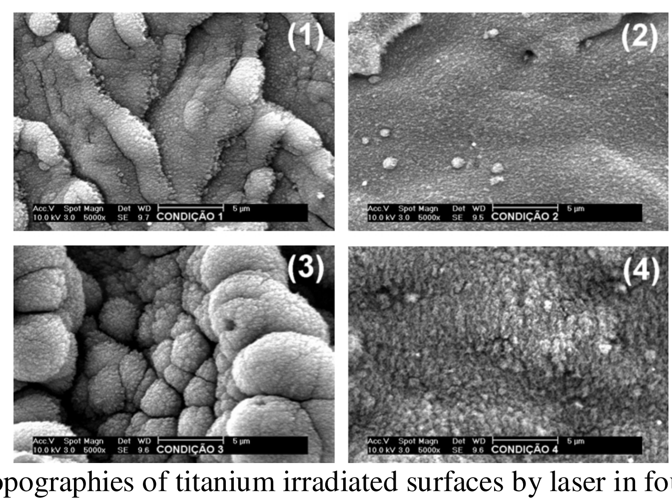

Figure 1. Topographies of titanium irradiated surfaces by laser in four conditions.

The irradiated surfaces before, Figure 2, and after covered by biomimetic procedure and heat treated at 600 ^{0}C, Figure 3, show by diffractometry and profile adjustment technique the titanium oxide phases and Ca-P phases formed respectively.

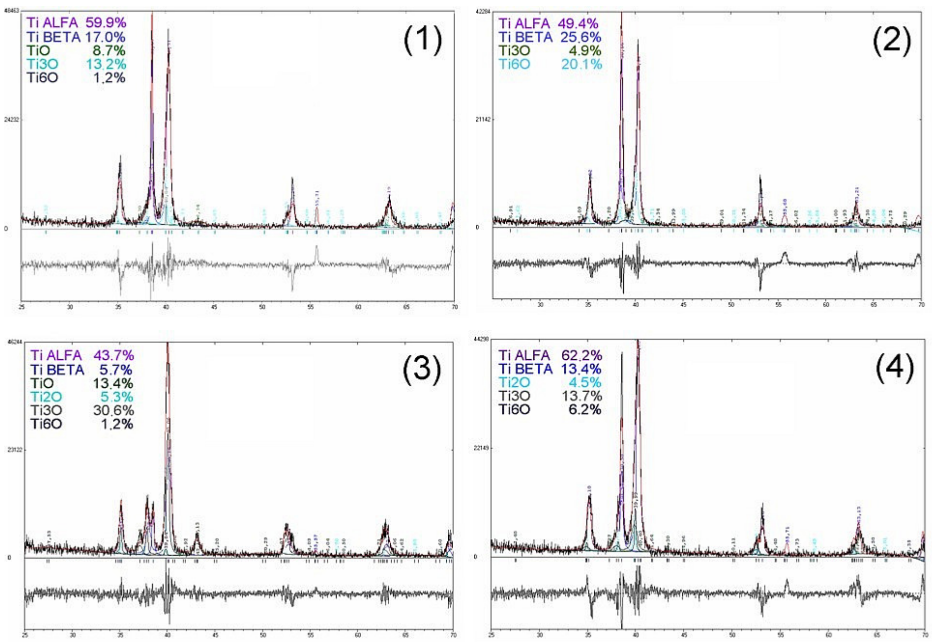

Figure 2. Quantitative phases in titanium irradiated surfaces determined by XRD and profile adjustment techniques.

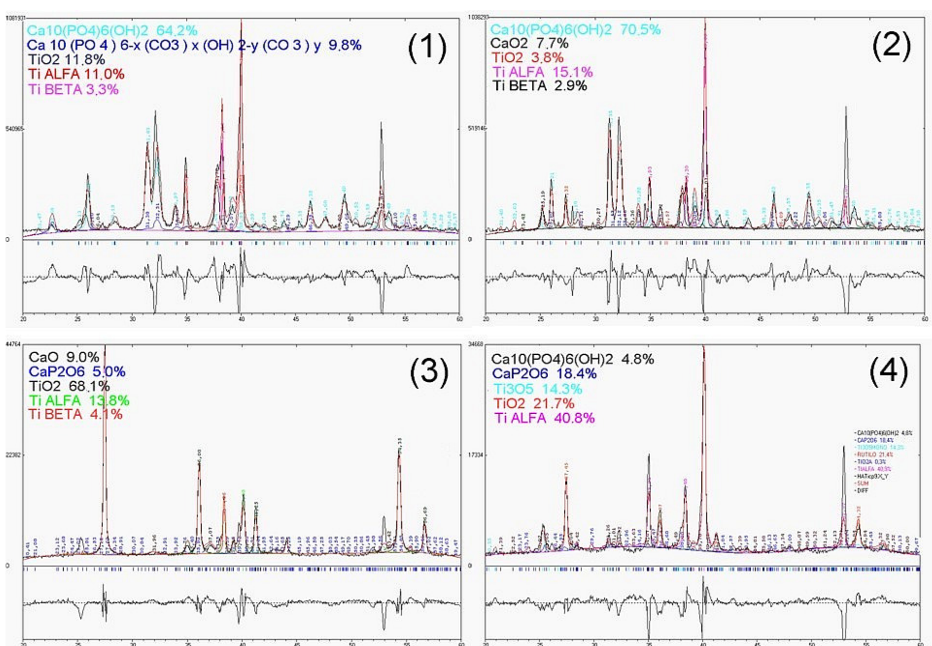

Figure 3. Quantitative phases in titanium covered surfaces determined by XRD and profile adjustment techniques.

Discussion and Conclusion

The hydroxyapatite phase occurs as major phase only in surfaces irradiated in two laser parametric conditions: 1 and 2. On the irradiated surface 4, the layer shows hydroxyapatite in its composition, but as minor phase. The irradiation condition 3 (highest fluency value) did not offer possibility to hydroxyapatite be formed in the deposited layer. These observations were confirmed by FTIR analysis as can be seen in Figure 4.

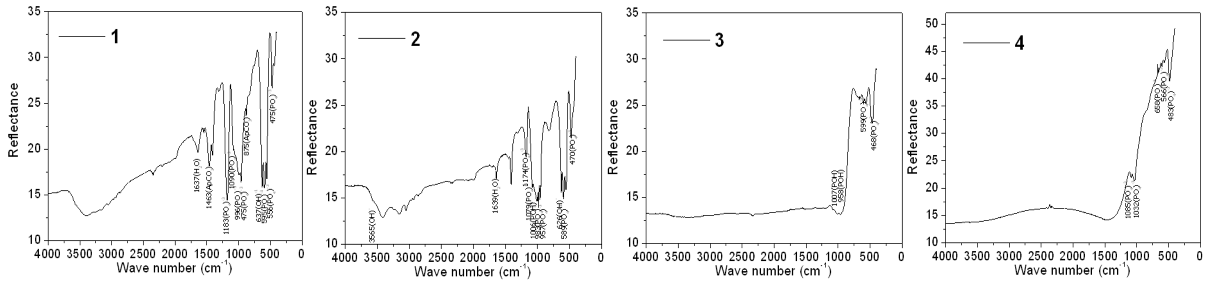

Figure 4. FTIR spectra of the four covered surfaces.

Despite the phases that have being formed, it is important to notice that the obtained morphology vary depending of the accumulated fluency (Fluency = Pulse Energy x Repetition Rate / Φ Spot x Scan Velocity). By modifying the scanning speed, repetition rate and pulse energy, the global energy delivered on the surface will change and consequently the amount of diffused atoms in the treated surface changes.

The laser-titanium interaction only undergoes thermal effects, i. e., during the process the surface heats and can be melted and vaporized creating plasma state over it. Some considerations can be done: (a) The pulsed laser Nd:YVO_4 irradiation on titanium surface with scanning velocity of 100 mm/s and 500 mm/s and repetition rate of 5 kHz and 35 kHz, under normal environment, induces meta-stable oxides formation as TiO, Ti_2O, Ti_3O e Ti_6O. Such results suggest the ablation phenomenon creates a plasma state on the surface with a consequent insulation from the environment during the irradiation process; and (b) Higher scanning velocity suggests be more favorable to hydroxyapatite formation in the biomimetic deposited layer on titanium irradiated surface (conditions 1 and 2), where it was observed the absence of Ti_2O on the irradiated surfaces.

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21st International Symposium of Ceramics in Medicine - Bioceramics 21, 2008, Búzios.
BIOCERAMICS 21. Zurich : Trans Tech Publications Ltd., 2008. v. 1. p. 565-568.