Hydroxyapatite and PMMA Thin Films Synthesized by Pulsed Laser Deposition on Titanium Based Metallic Substrates

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Functionalized dental implants represent an advanced approaching in implantology, aiming to improve the biointegration and the long-term success of surgical procedures. In this article are reported the synthesis of hydroxyapatite (HA) and Poly(methyl methacrylate) (PMMA) thin films on metallic substrates – used as dental implant-type structures – by pulsed laser deposition (PLD) method. Plasma and plume evolution of ablated HA and PMMA species was registered through optical analyze by fast CCD camera. Numerical simulation performed using a simple hydrodynamic model properly reproduce this type of plasma behaviour. SEM-EDAX measurements were performed assessing the apatitic-type structure of the prepared films along with their satisfactory mechanical adhesion.

Keywords: synthetic polymer, pulsed laser deposition, hydrodynamic model

The aim of this work was to produce osteoinductive HA coatings for titanium based dental implants to be used in teeth stabilization. In the same time comparatively were obtained layers of PMMA using PLD and identical deposition parameters. Their innate similarity with the mineral compounds from bone and teeth represent the main characteristic of artificial synthetic calcium phosphates (CaP) for which they are preferred in studies and applications concerning biomedical bone-substitute thin films deposition. Poly(methyl methacrylate) (PMMA) is a transparent thermoplastic, often used as a light or shatter-resistant alternative to glass. It is sometimes called acrylic glass. Chemically, it is the synthetic polymer of methyl methacrylate.

Nowadays persist in medical applications a continuing request for materials to replace or supply the bone tissue. Such biological compatible materials include metals, ceramics and polymers [1–4]. Even some acceptable success in few particular applications materials daily used for the fabrication of bone implants were not developed for biological applications. References inferred from the interaction of biomaterials with the living tissues may help researchers and engineers to design and develop new bioactive and osteointegrative materials. Titanium (Ti) and its alloys are presently used in stomatology and orthopedy as implant materials or shape memory alloys applications [5-9]. Originally, they were directly implanted in the bone. Limitations in implant functionalization and its rather short-term stability have stimulated researchers to optimize prostheses, searching for materials more closely matching biological templates, like hydroxyapatite (HA), $Ca_5(PO_4)_3OH$ [10–12].

HA based ceramics have quite rapidly started being used widely in bone restoration and reconstruction. The thin hydroxyapatite layers herewith deposited by pulsed laser techniques, on medical metallic substrates have the role to enhance the bio-acceptance and to accelerate implant osseointegration in organism.

The concept of composite HA coating/polymer systems, combining the biological and mechanical properties of the two components, aims to reduce the cytotoxicity or inflammatory reactions of surrounding tissues.

Pulsed laser deposition, a highly performant technique as far as the chemical and physical properties are concerned (mechanical, structural, stoichiometric) it is not released for commercial use yet but it is constantly improved, tested, and attested by many research studies [13-15]. Animal experiments have shown the compatibility of nanostructured HA–PLD films with clinical implantation, evidenced by an almost twofold implant resistance due to the improved adherence to the bone tissue, compared to the bare titanium implants [16].

PLD has demonstrated capability to grow stoichiometric and high crystalline layers of complex materials, such as HA among many others [17-20].

Thin HA and PMMA layers were obtained through PLD technique on metallic titanium based substrates. Targets (HA and PMMA) and thin layers obtained were analyzed by SEM and EDAX investigations.

Experimental part

The substrate used was titanium based alloy and placed parallel with target at a 3.5 cm distance. Target preparation suppose high-purity (99.98%) polycrystalline HA powder produced by Merck (Darmstadt, Germany), the HA powder was mono-axially cold pressed at 80 MPa in the form of pellets with a hydraulic stainless steel press. The other target used was a polymer PMMA obtained from Lactic Biodegradable Polymers (Birmingham, USA).

The depositions were made on the oxygen presence at a constant pressure of 5 10^{-2} at room temperature (24 °C). The laser fluence were maintained constant at 4.5 J/cm^2.

The deposition experiments were realized on a deposition equipment schematically presented in figure 1 a) in a schematic view and b) the chamber image. Ronghly

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speaking the equipment has a pulsed laser source, a mirrors optic system and a vacuum chamber.

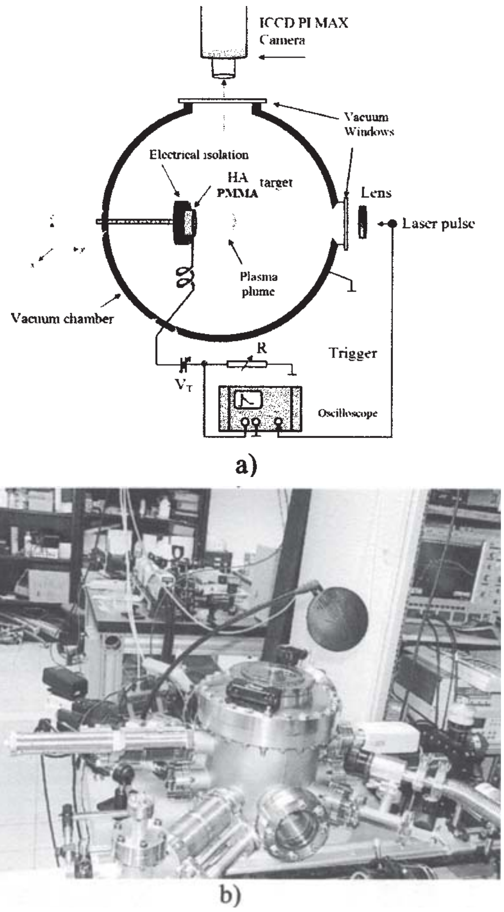

Fig. 1 The experimental setup used for HA and PMMA thin layers deposition a) schematic set up and b) deposition chamber image [15]

An important problem that appears during the laser ablation process and the complex Oxygen increase is the formation of oxide blanks inside the layer and layer-substrate interface. To avoid this problem a solution can be the RF discharge (radiofrequency).

For HA and PMMA thin layers formation pulses number varied between 2000 and 3000. The growth layers were analyzed through scanning electrons microscopy (SEM) and chemical analyze (X-ray determination - EDAX).

Results and discussions

In figure 2 the evolution of the non-dispersed optical emission of plasma produced by laser ablation of HA and PMMA targets is presented. These images evidence a splitting of the plasma plume in two main structures with distinct dynamics and velocities.

Thin superficial HA and PMMA layers were obtained on metallic substrate (titanium based alloys) through pulsed laser deposition in order to improve his corrosion resistance and biocompatibility. Using EDAX equipment the targets chemical composition was analyzed before and after the laser beam interaction.

Mass and atomic percentages of O, Ca and P in HA case and O and C in PMMA case were followed to observe the influence of the laser effect on targets. Chemical analyses were performed on obtained thin layers after PLD and some amounts of C, O and Ca were investigated to determine the process transfer success. The results are presented in table 1 and 2 for targets analyses.

Concerning the HA target a ratio of 1.79 between Ca:P of the surface is observed, table 1, which is in range of general HA types. The polymeric material presents a ratio of 3.6 O at one C by atomic percentage point of view.

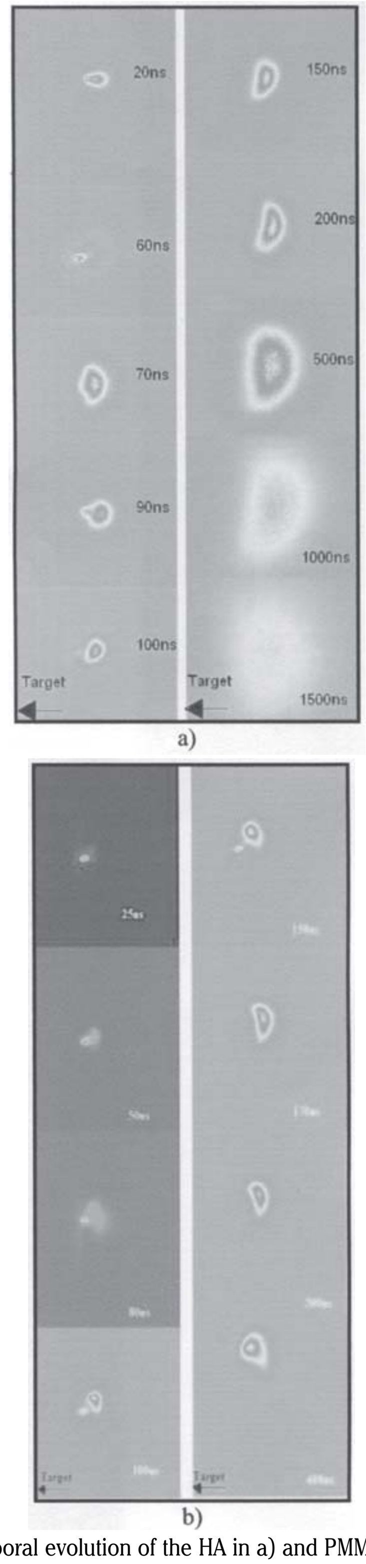

Fig. 2 Temporal evolution of the HA in a) and PMMA in b) plasma plume emission recorded by the ICCD camera (20 ns gate)

Table 1
CHEMICAL COMPOSITION OF HA AND PMMA POLYMER USED AS TARGETS IN PLD TECHNIQUE

Material	Chemical element	wt %	at%
HA	O	44.4451	64.80262
	Ca	38.83118	2.,602
	P	16.72371	12.59538
PMMA	O	82.73127	78.2445
	C	17,26873	21.7555

The laser beam affected surfaces are presented through SEM microscopy, at low gun filament tension supply, in figure 3a for HA and b for PMMA.

Can be observed the follows left by laser bean on the ceramic and polymer surfaces for different amplification powers.

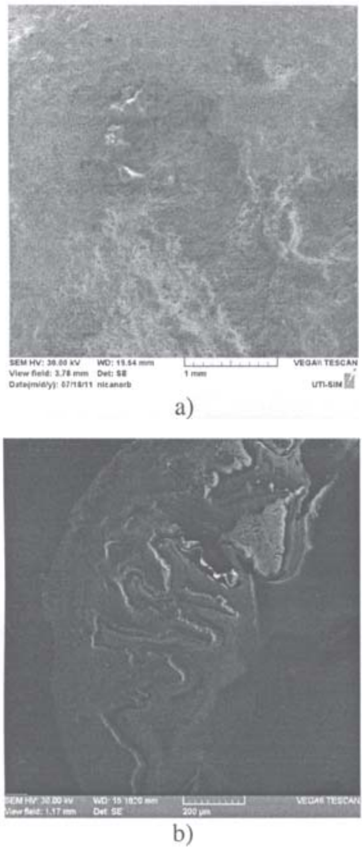

Fig. 3 SEM images of HA in a) and PMMA in b) surface after laser ablation

In table 2 is presented the ratio of Ca:P which is 1.87 (by atomic percentages) still in range of hydroxyapatite with very small modifications of general percentages after the laser beam applications. The small increase of calcium percentage is correlated with loss of oxygen element during the laser ablation.

The results present a ratio of 3.4 O:C in the ablated surface of polymer case which is near the target ratio and the modification put on oxygen percentage change also. In both cases the surface does not seems to be affected from chemical point of view after the impact of laser beam with target and the material ablated suppose to behave similar and to have very small chemical modifications.

The layers surface structures obtained after pulsed laser ablation are presented, in a) for HA and in b) for PMMA, in figure 4. Images were done at 2500x using a SE detector

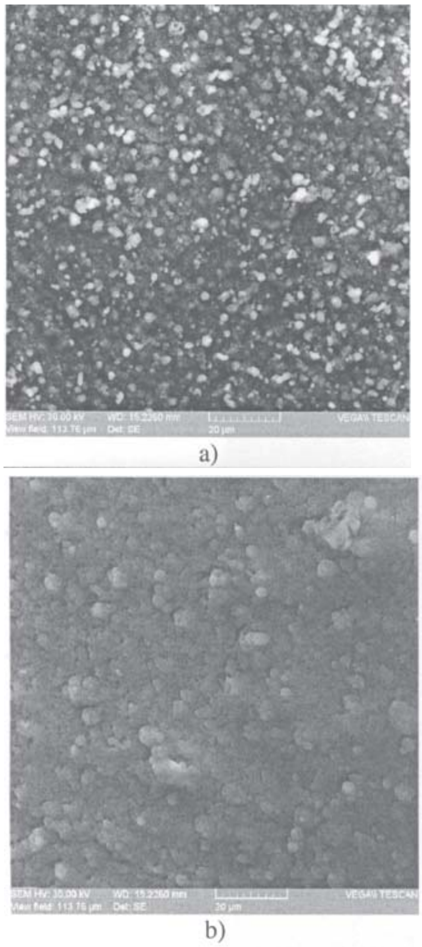

Fig. 4 SEM images of HA in a) and PMMA in b) thin layers obtained through PLD technique on titanium based metallic support

and a low power supply of lamp filament. The layers present good properties without peelings, cracks, agglomerations or other defects. In both cases the obtained layer morphologically is made from different particles based on a nanometric layer and on top with micrometer size particles.

Chemical analyze of growth layers on titanium based substrates is presented in table 3 for HA and PMMA targets as well.

In HA case a), the ratio Ca:P modify to 1.90 that represent a small modification of the percentages with the increase of calcium and decrease of phosphorus based on the processes in material plume between target and substrate and between plume and substrate at contact.

In polymer case the ratio between oxygen and carbon is 2.52 based on decrease of oxygen element with the increase in the same time of the carbon percentage.

From the ratio modifications suffered by both materials under pulsed laser deposition can be appreciate that the thin superficial layers obtained on metallic substrate are modified forms of HA and PMMA polymer.

Table 2

CHEMICAL COMPOSITION OF HA AND PMMA POLYMER OF TARGETS AFTER IRRADIATION WITH THE LASER BEAM ON THE SURFACES PRESENTED IN FIGURE 2

Material	Chemical element	wt %	at%
HA	O	44.18322	64.61925
	Ca	39.54738	23.08979
	P	16.2694	12.29096
PMMA	O	72.73127	77.2445
	C	27.26873	22.7555

Table 3

ChEMICAL COMPOSITION OF HA AND PMMA POLYMER THIN LAYERS OBTAINED THROUGH PLD TECHNIQUE ON METALLIC SUBSTRATE

Material	Chemical element	wt %	at%
HA 1	Ca	71.03099	66.01769
	P	28.96901	34.58231
PMMA	O	67.33152	68.56025
	C	20.00179	27.12985

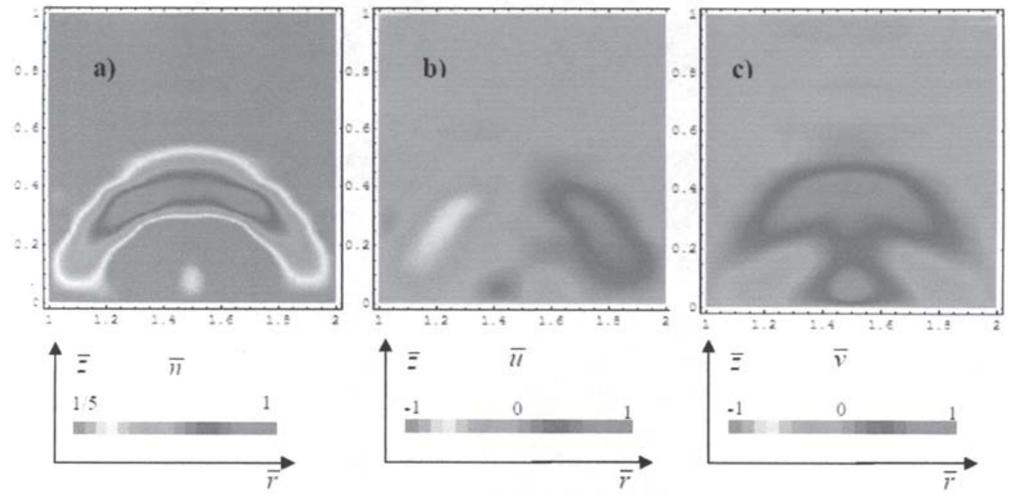

Fig. 5 a-c: Numerical two-dimensional contour curves of the normalized density, n (fig. 5a), normalized radial velocity u (fig.. 5b) and axial velocity υ (fig. 5c) at the normalized time $t = 0.5$

Numerical simulations

A simple model of plasma expansion at the early stages of its evolution is proposed (results from ref. 15 can be also considered) by assuming four particular hypotheses.

Firstly, the plasma spatial evolution has axial symmetry and it is solved in the cylindrical coordinate system induced in the region above the target surface (the z-axis coincides with the laser beam axis and is directed along the outer normal to the target surface).

Secondly, the plasma is in the state of local thermo-dynamical equilibrium and satisfies the quasi-neutrality condition.

Thirdly, the expansion is described in the approximation of a non-viscous non-thermo-conducting gas.

At last, we suppose that the release of energy by thermal radiation is neglected and the ideal gas equations of state are considered. In such circumstances, the two-dimensional gas dynamics is described by the usual hydrodynamic equations system with adequate limit and boundary conditions [15] lead to the numerical solutions represented in figures 6 a-c. Thus, in figures 5 a-c, the two dimensional contour curves of the normalized density n and normalized velocities u and υ , respectively, are plotted for the normalized time $t = 0.5$.

Despite of the crude approximations, some features of the expansion process are well highlighted. Undoubtedly, the most important are the generation of two plasma structures (fig. 5 a), the symmetry of the normalized speed field with respect to the symmetry axis of the spatial-temporal Gaussian (fig. 5 b) and the shock waves and vortices at the plume periphery for the normalized speed field (fig. 5 c). These observations are in agreement with the experimental plasma images at various stages of evolution (fig. 2).

Conclusions

Using a pulsed laser deposition simple as function but complicated as processes for a physic deposition method, layers from targets of HA and PMMA polymers were obtain on titanium based substrates in order to improve their corrosion resistance and biocompatibility properties. Chemical analyses using an EDAX detector were performed on targets before and after laser impact and also on thin layers obtained after deposition. Tests follow the analyze of chemical modifications during the pulsed laser deposition method of targets and of the layers.

Microstructural analyze presents the laser beam effects on targets surface and also the general aspect of the thin layers on top of the metallic materials. The thin layers are characterized by nano and micro formations of materials with different chemical compositions, between them and also comparative with the targets, based most of the time on the materials plume evolution and interaction with the substrate.

The numerical simulations reproduce well this type of plasma behavior, using a simple hydrodynamic model.

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