Bionic features of thin biomaterial layers deposited by PLD onto titanium implants

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We report on the successful deposition by PLD method of three biomaterials, hydroxiapatite doped with zirconia (ZrO_2: HA), β-tricalcium phosphate (β-TCP) and bioglass (BG57), onto titanium substrates, for medical applications. The deposited implants have been investigated morphologically by Scanning Electron Microscopy, coupled with Energy Dispersive X-Ray Spectroscopy (EDS). The surface morphology of the implants presented roughness values very close to the ones defining the histological structure of bone. EDS spectra evidenced the absence of impurities in the deposited films. This study demonstrated that, at microscopic level, the morphology of BG57 thin films presented a superior quality as compared with ZrO_2:HA and β-TCP ones, emphasizing their capacity to cover the metallic implants, in form of thin films, making them suitable for applications in implantology.

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1. Introduction

Surface conditioning of titanium (Ti) implants is intensely debated, just as much as that of other implants, manufactured from different biomaterials. This conditioning is due to achieving a larger contact area between implants and the alveolar bone and to obtaining a relief similar to surrounding biological conditions [1, 2]. In order to achieve bionic surface features, the roughness values have to be equal or greater than the atomic dimensions of bone trabeculae. Thereby, the bionic surface acts favourably in distributing the loads transmitted by the implant to the bone, the retention in the bone tissue is better and chemical bonds between the implant and the interface are achieved [3]. Positive reactions of the surrounding tissues are thus initiated, determining a high rate of collagen synthesis (extracellular matrix) with consecutive mineralization [4].

The quality of implant surfaces influences tissular integration. The rough surfaces enable a better reticulation and bone-implant integration, which are important phenomena during the immediate postoperative stage, when blood cruor deposits and gets organised on the implant surface [5]. By penetrating and growing of bony trabeculae into superficial micro-porosities, a better spread of occlusal loads into the bone substrate is also ensured, leading to a long-term stability of the bone-implant bond [6].

The biological properties of the materials used for implant fabrication are of major importance for successful treatments and they are reflected in the tissular reaction they cause when inserted in biological systems. For this reason, the biomaterial surfaces undergo certain modifications, through a bionic coating, which, for a longer or shorter period of time, influence the reactivity of the tissues in which they are inserted.

Carbon materials, ceramics and bioglasses represent the most used bioactive/bio functional materials for a new generation of implants considered biomimmetic, reaching the ultimate level of biocompatibility, i.e. the perfect integration of a foreign structure into the human body. Because of their excellent biocompatibility properties, lack of toxicity and surface properties (which permit and intimate, rapid and high quality bond between the implant and the tissue), hydroxyapatite doped with zirconia (ZrO_2: HA), β-tricalcium phosphate (β-TCP) and bioglasses (BG57, in our case) have modernized the medical field, being recommended as the most attractive materials used in oral surgery (bone replacements), orthopaedics and dentistry. Also, these materials have been intensively studied in the last years because their excellent behaviour in prolonged contact with extracellular fluids [7, 8, 9, 10].

The main advantage of PLD method applied to these biomaterials is represented by its capacity to grow stoechiometric thin films presenting a controlled degree of crystallinity. This technique also provides the flexibility to control the morphology, phase and chemical composition of the deposited thin films. These features have an important influence over the biological properties such as

bio-resorbability or dissolution, which are processes involved in the osseointegration process of the coatings.

2. Materials and methods

2.1 Targets preparation

For the PLD experiments we used high purity nanopowders of ZrO_2: HA, β-TCP and BG57 (57% SiO_2 [8]). Aproximatively 2.5 g from each material have been pressed at ~5MPa using a Specac matrix and a hydraulic press. The obtained pellets (Φ = 20 mm, thickness = 5 mm) have been sintered in a Carbolite furnace for 6 h at 380 °C (in case of ZrO_2: HA) and 650 °C (in case of β-TCP and BG57).

2.2 PLD experiment

ZrO_2: HA, β-TCP and BG57 depositions were performed using a PLD facility equipped with a stainless steel deposition chamber and a KrF* excimer laser source, model COMPexPro 205 (λ = 248 nm, $\tau_{FWHM} \approx 25$ ns), running at a repetition rate of 10 Hz.

The laser beam was incident on the target surface at 45 °.

The laser fluence onto the target surface was set at ~5 J/cm^2 and the number of consecutive pulses applied for all the experiments was of 10000.

High purity Ti implants (grade 2, Φ = 3 mm) have been used. Prior to introduction inside the deposition chamber, in order to eliminate the micro-impurities, the implants were successively cleaned into an ultrasonic bath (model Elmasonic X-tra 30H) in acetone, ethanol and deionised water for ~20 minutes and then blown dry in high purity (99.99999%) synthetic air jet.

The Ti implants were placed parallel to the targets, at 45 mm separation distance in front of them.

Before deposition, the targets were submitted to a cleaning process with 1000 laser pulses. During this procedure, a shutter was interposed between the target and the substrate to collect the flux of expulsed impurities and defects.

All the depositions were carried out on substrates heated at a constant temperature of 400 ℃. Thin ZrO_2:HA and β-TCP layers have been deposited in water vapours at a dynamic pressure of 50 Pa, while BG57 depositions were performed in a 13 Pa oxygen flux. The pressure inside the deposition chamber was continuously monitored usind a MKS PR4000 controller.

During the deposition process, all the targets were continuously rotated with 0.4 Hz and translated along two orthogonal axes to avoid piercing in order to insure a uniform deposition.

After deposition, ZrO_2: HA thin films were submitted to a thermal treatment in water vapours for 6 h at the same temperature applied during the experiments (400 °C).

2.3 Characterization of deposited structures

The study of thin biomaterial layers deposited by PLD has been performed using a QUANTA INSPECT F microscope, provided with a field emission gun, with a 1.2 nm resolution, coupled with an EDS, with a resolution of 133 eV at MnK.

SEM investigation of samples was conducted at different magnification orders and evidenced the characteristics of ZrO_2: HA, β-TCP and BG57 thin film depositions.

3. Results

SEM images and EDS spectra evidenced the different bionic features of thin biomaterial layers deposited on Ti implants.

3. 1. Characterisation of bionic ZrO_2: HA layers deposited on the Ti surface

In Fig. 1-3, **t**he morphology of ZrO_2: HA layer deposited on the Ti implant surface is revealed by secondary electron images (SEI).

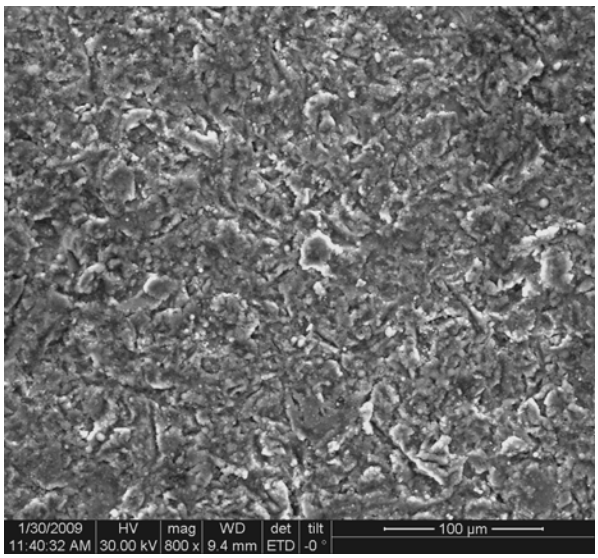

Fig. 1. ZrO_2: HA thin film deposited on the Ti implant surface. Magnification 800 X

The image does not reflect ZrO_2: HA deposits. The surface relief has the external morphology of the Ti implant.

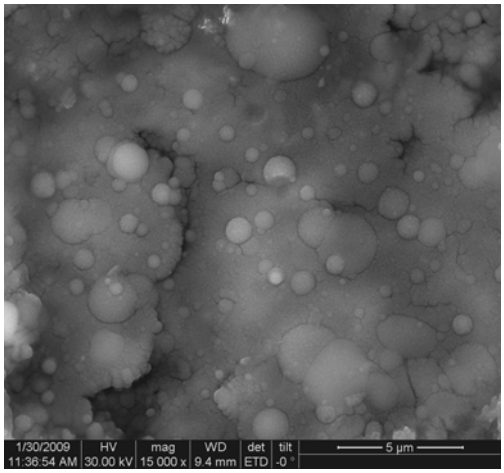

Fig. 2. SEM image of ZrO_2: HA thin film microstructure. Magnification 15000X

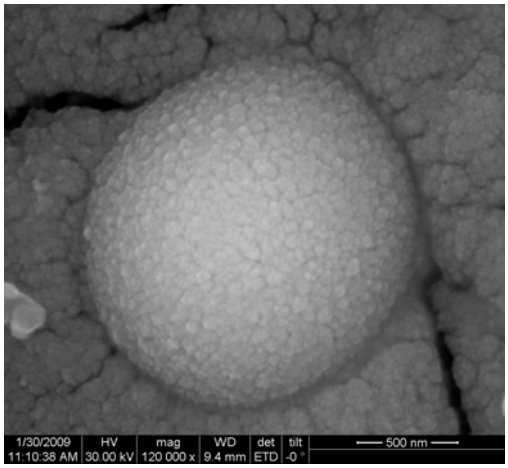

Fig. 3. Secondary electron images of the micro-structural ZrO_2: HA deposition. Magnification 120000X

In x 15,000 images the microstructure of the deposited ZrO_2:HA film can be observed.

The deposited layer is nano-structured, as the dimensions of composing particles are nanometric.

The EDS spectrum of ZrO_2: HA thin film (Fig. 4), associated to the micro-zone in Fig. 1, indicates that the sample contains Ti, Al (in the substrate) and Ca, P, O_2 and traces of Zr (in the deposited layer) only. No impurities were detected.

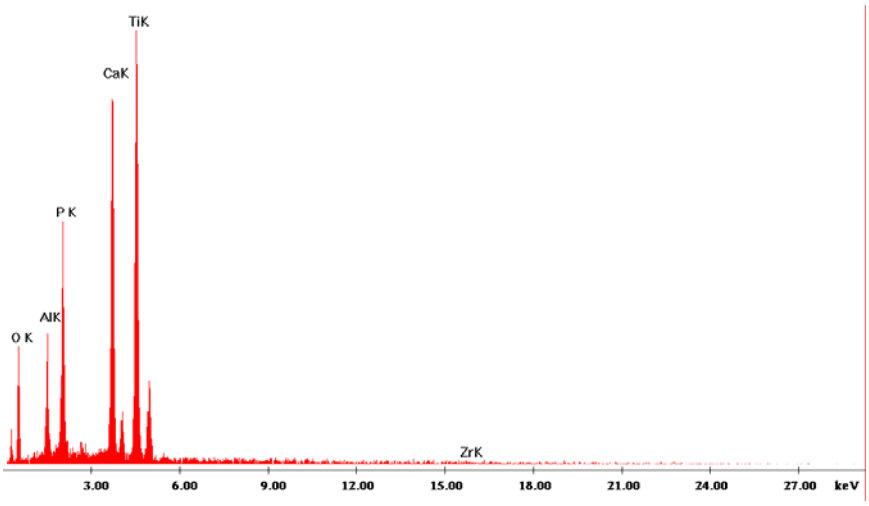

Fig. 4. EDS spectrum of ZrO_2: HA thin film

3.2. Characterisation of bionic β-TCP layers deposited on the Ti surface

The image for x 800 does not reflect the deposit of microfilm with β tricalcic phosphate, the surface relief has a coarse external morphology.

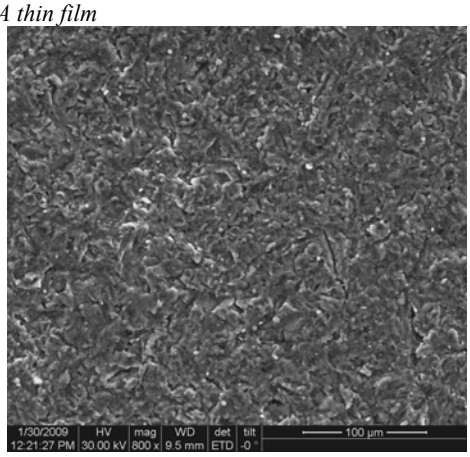

Fig. 5. The sample's surface is not specific to deposits of β tricalcic phosphate. Magnification 800X

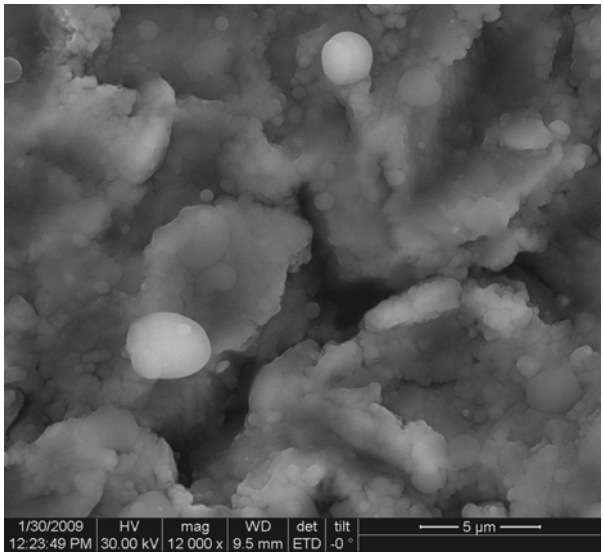

Fig. 6. The examined surface becomes characteristic of a layer deposited on the sample. Magnification 12000X

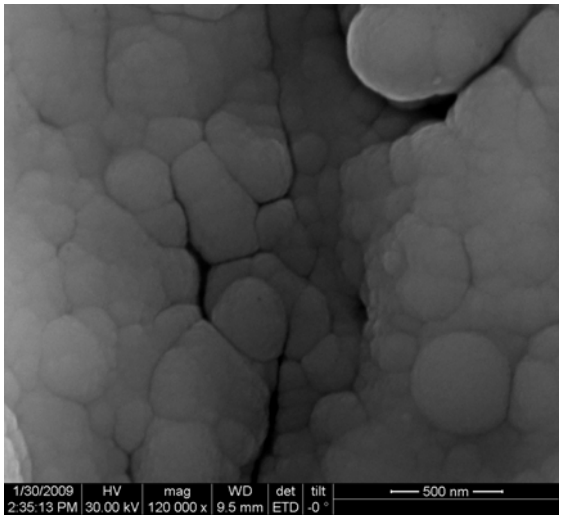

Fig. 7. The microstructure of β-TCP deposited thin film. Magnification 120000X

SEM images in Fig. 6-7 emphasise the even and thin layer covering the coarse segments in the implant relief, the external surface becoming microstructural by means of the β tricalcic phosphate film deposits.

EDS spectrum of β-TCP thin film (Fig. 8), associated with the micro-zone in Fig. 5, evidenced the presence of Ti, Al (in the substrate) and Ca, P, O_2 (in the deposited layer) only. No impurities were detected.

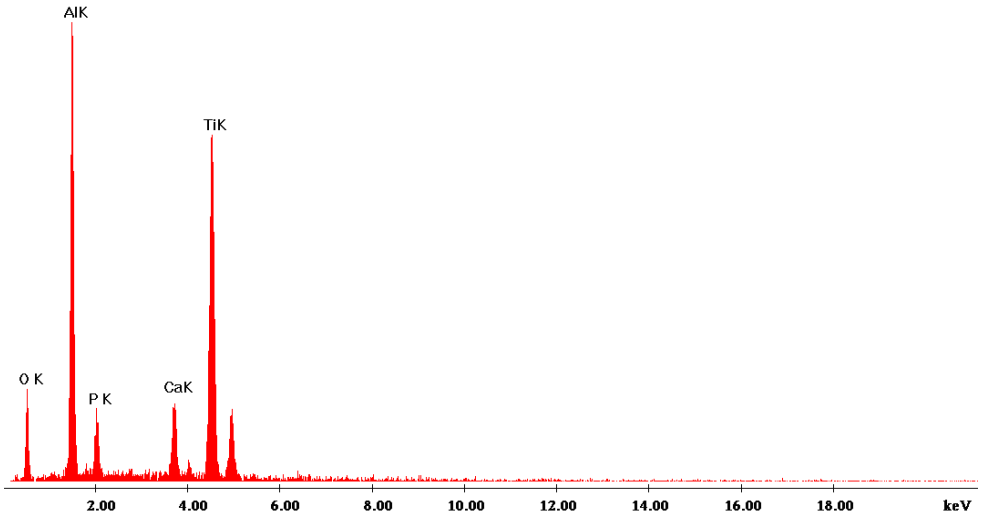

Fig. 8. EDS spectrum of β-TCP thin film

3.3. Characterisation of BG57 bionic layers deposited on the Ti surface

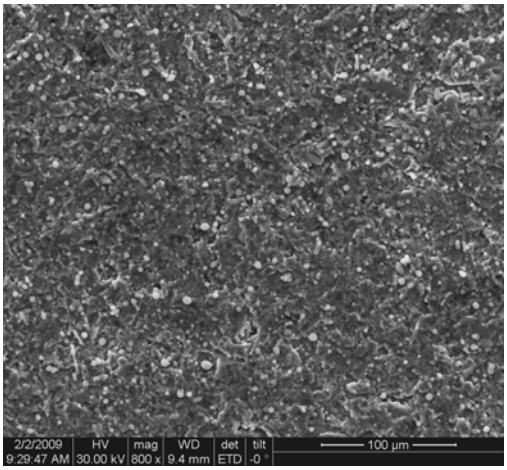

Fig. 9. The microstructure of the deposited BG57 film is not characteristic. Magnification 800X.

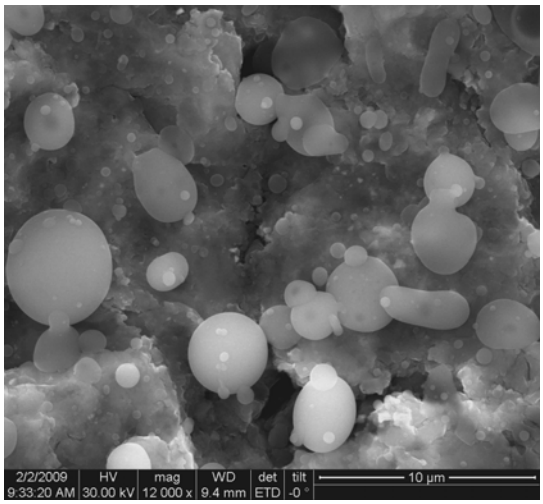

Fig. 10. Granular aspect, with particle agglomerations. Magnification 12000X

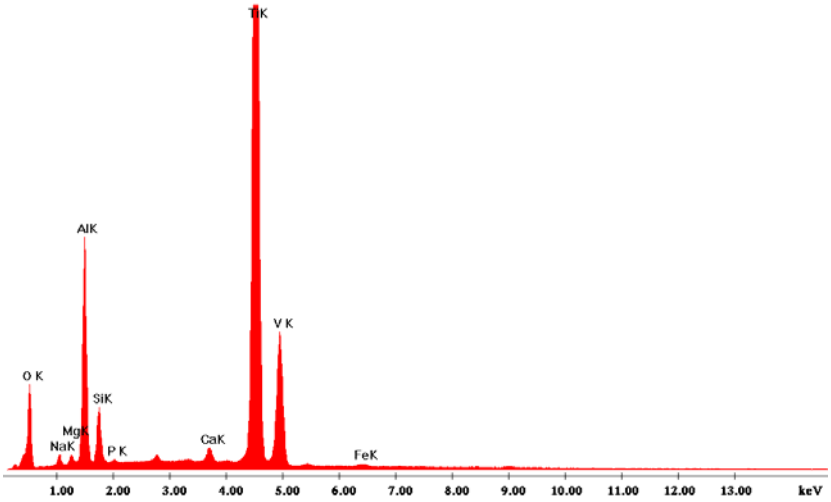

Fig. 12. EDS spectrum of BG57 thin film.

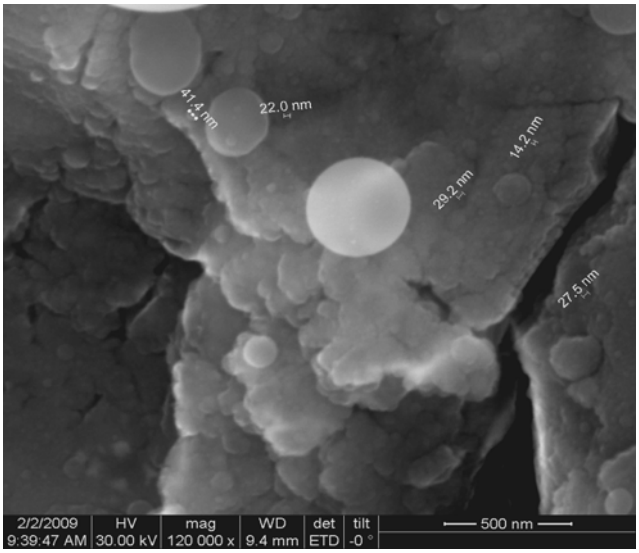

Fig. 11. SEM micrography of BG57 thin film evidencing the presence of 14 nm – 25 nm sized particles. Magnification 120000X.

EDS spectrum of BG57 thin film (Fig. 12), associated to the micro-zone in Fig. 9, evidenced the presence of Ti, Al, V (in the substrate) and Si, Ca, P, Na, Mg, Fe and O_2 (in the deposited layer) only. No impurities were detected.

The morphology of the bioglass layer deposited on the Ti surface is emphasized by large magnifications. The bioglass film completely covers the coarse segments in the implant's surface relief.

4. Discussion

SEM investigations of ZrO_2:HA thin layers obtained by PLD method revealed an uneven deposition determined by surface roughness, slight discontinuities of the deposition, with pore sizes between (5-10) μm. The morphology of the surface layer is granular, with agglomerations of submicron sized particles.

SEM examinations of thin β-TCP layers evidenced an uneven deposition of the biomaterial, determined by surface roughness, with discontinuities and slight porosities in the coatings, with pore sizes between (10-20) μm. The morphology of the surface layer is granular, with agglomerations of sub-micron sized particles. The deposited layer of β-TCP is not well emphasized and is not characteristic, the surface relief resembling to that of the Ti under layer.

SEM investigation of thin BG57 films revealed an uneven deposition showing pores in the treated surface, with sizes in the (5-10) μm range. The morphology of the surface layer is granular, with agglomerations of sub-micron sized, round-shaped and smooth particles, with a glassy (drop-shaped) aspect and an average diameter of 5 μm. These particles are evenly distributed on the bioglass film. It has a nanostructured aspect, with grain sizes of ~14 nm - 25 nm.

The surface morphology of the Ti implants deposited by PLD presents roughness values in the (5-20) μm range. Thus for the thin biomaterial layers, a bionic surface is achieved, with values resembling to the one characteristic to bone histological structure: bone lamellae present sizes in the (3-7) μm range, osteocytes have sizes between (10-20) μm, osteoblasts present sizes in the (50-100) μm range [11], which are biological elements active in bone formation. Cellular components of blood have sizes close to the values specific for the implants' surface roughness. Flow and humectation by biological fluids are thus achieved implant level, while contact between the implant and these fluids may determine bone-formation physiological reactions in surrounding tissues.

5. Conclusions

The biomaterial-metal interface has several roles: to change the topography of the metallic surface, in order to increase the roughness, and consequently of the active surface, to protect it against corrosion, to form an activated micro layer which favors the initiation of reactions for the interface between surface molecules, deposited by PLD, and bone.

Microscopically, the properties of bioglass are remarkable. These are amorphous materials that are successfully used as covering material for metallic implants, to significantly enhance their biocompatibility.

Acknowledgements

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