FABRICATION AND CHARACTERISATION OF THE BIOGLASS THIN FILMS

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Abstract: *Bioglasses are among the newest class of inorganic biomaterials, based on oxides. They have been used in bone prosthesis and dental porcelain manufacturing. In this paper we report the obtaining of thin films of two bioactive glasses belonging to the* $SiO_2 - Na_2O - K_2O - CaO - MgO - P_2O_5$ *system on medical grade Ti substrates, employing pulsed laser deposition technique. These films are characterized by confocal scanning laser microscopy (CSLM) and Fourier transformation infrared spectrophotometry (FTIR).*

Keywords: *bioactive glass, pulsed laser deposition, confocal scanning laser microscopy.*

1. Introduction

The uses of bioactive glasses have been revolutionized the biomedical field in deployment as implants for humans. Many implant materials made of glasses have been used for the past three decades. In the search to improve the biocompatibility and mechanical strength of implant materials, attention has been directed towards the potential use of glasses/glasses composites. The glasses-based biomaterials have been accepted after biological evaluation through several in vivo and in vitro tests.

The bioactive materials elicit a specific biological response at the interface of the material leading to the formation of a natural bond (first shown in 1969) [1] and development of new mineralized bone tissue. Materials in this class include dense calcium phosphate ceramics, bioactive glasses (45S5 Bioglass®), bioactive glass-ceramics (Cerevital®, Wollastonite A/W glass-ceramics, machinable glass-ceramics), bioactive composites (Palavital®, stainless steel-fiber reinforced Bioglass®, polyethylene- HA mixtures, etc).

As an effect of biomechanical limitations, bioglasses, glass-ceramics, and calcium phosphate ceramics are mainly used in low or non-bearing applications. For obvious reasons, metals are mechanically suitable for load-bearing orthopaedic and dental implants. have been reported [2]. Coating the metallic implants with thin layers of bioactive material combines mechanical advantages with excellent biocompatibility. Furthermore, the coatings could protect the implants from corrosion, limiting the release of metallic ions into the body [3-6]. For chemically binding coating (orthopaedic, dental, and maxillofacial prosthetics), hydroxylapatite, bioactive glasses and bioactive-glass ceramic layers are applied.

In this work, we reported the development of bioactive coatings using a new family of

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glasses in the $SiO_2 - Na_2O - K_2O - CaO - MgO - P_2O_5$ system, employing pulsed laser ablation and deposition technique. We used a medical grade Ti substrates because titanium is the most popular choice for fabrication of orthopedic implants where high strength is required.

Moreover, the characterization of the deposits from a compositional and morphological point of view have been made.

Pulsed laser deposition (PLD) is a technique for thin film deposition since it has demonstrated the capability of growing high-quality crystalline and stoichiometric thin films [7-]. The Pulsed Laser Deposition technique is widely used to produce mono- and multi-layer thin layers in particular of materials or combinations of materials which can't be proccesed without big difficulties by other methods. Recently, coatings with great quality were obtained by PLD. The main reason for PLD progress is that materials with a however complicate composition may be transferred on a substrate without changing their stoichiometry.

2. Experimental

We used two types of glasses belonging to the system mentioned: 6P57 and 6P61, where in the glass designation the number after 6P corresponds to its silica content in wt% (table 1). The glasses were prepared using a conventional procedure. The appropriate reagents have been mixed and the mixture has been melted, broken up, frited, grinded and filtred. The powder obtained is pressed with a moulds 13 mm in diameter, Specac, Great Britanie, and then sinterised (submitted of a thermal treatment to values of increased temperatures). In this way we obtained a pill with the diameter of the cast and the thickness determined by the amount of material used, a compact and hard pill.

Table 1

Material	SiO_2	Na_2O	K_2O	CaO	MgO	P_2O_5	$\alpha(K^{-1})$
Titanium							$9.2\ 10^{-6}$
6P57	56.5	11.0	3.0	15.0	8.5	6.0	$10.8\ 10^{-6}$
6P61	61.1	10.3	2.8	12.6	7.2	6.0	$10.2\ 10^{-6}$

This pill constitutes the target which falls down laser radiation. The ablation of target material and the deposition of ablated material on a collector (substrate) took place. Thus a thin, stoichiometric bioglass film is obtained.

A KrF* excimer laser source (λ=248 nm, τ_{FWHM} =7ns) was used for deposition. The energy per laser pulse was 400 mJ, while a fluence of 5.7 Jcm^{-2} was set for each deposition. The films were grown in low pressure (13 Pa) oxygen on Ti grade 4 (99.6%) substrate chemically etched. The chamber was evacuated down to a residual pressure of 10^{-4} Pa prior to every deposition. During deposition, the substrates were held at a constant temperature 400°C. The target-substrate distance was 4 cm. Every film took 5000 subsequent laser pulses at 10 Hz repetition rate to deposit. To avoid drilling, the target was rotated with a frequency of 0.4 Hz during multipulse irradiation.

The films obtained were characterized by confocal scanning laser microscopy (CSLM) and Fourier transformation infrared spectrophotometry (FTIR). The roughness and topography of the bioglass surface were investigated by CSLM and their composition by FTIR.

The deposition were realized in Laser-Surface-Plasma Interaction Laboratory (LSPI) at National Institute for Laser, Plasma and Radiation Physics –INFLPR- Bucharest. For Fourier Transform Infrared Spectroscopy analysis we used a Perkin Elmer BX Spectrum-Pike, spectral resolution 4 cm^{-1}, S/N ratio 20000:1. The spectra were taken in the reflectance mode, at INFLPR Bucharest.

The assessment of topography and uniformity of the bioglass layer is made using the CSLM method, which is also recommended for many studies about an interaction of human osteoblasts with bioactive materials. This investigation process is based of sequential exploration of the sample by a laser beam and acquirement of resulting interaction effects between light and material for surface or spatial imaging. The resolution is much improved because the confocal microscope eliminates optical influence from neighbor domains. For nondestructive investigation of specimens by CSLM was used a Leica TCS SP system equipped with a He-Ne laser having 633nm wavelength and a set of PL Fluotar (10X, 40X, numerical aperture NA 0.7) objectives, at Center for Microscopy-Microanalysis and Information Processing, University “Politehnica”- Bucharest. The images were obtained from this system by performing in reflection mode. Data processing and displaying were made by Leica software designed for an independent Graphic Station.

3. Results and discutions

Laser fluence was varied in (4-8) J/cm^2 and we observed that for 5.5-6 J/cm^2 we obtained best compromise between structural fidelity and uniformity of bioglass thin films on the titanium substrate. Therefore we used on 5.7 J/cm^2.

The analyses performed by FTIR show (fig.1) the molecular bindings SiO_2 into powders and films and demonstrate that PLD deposition maintains these bindings. Also we can see that don’t appear suplimentar peaks due to the impurities.

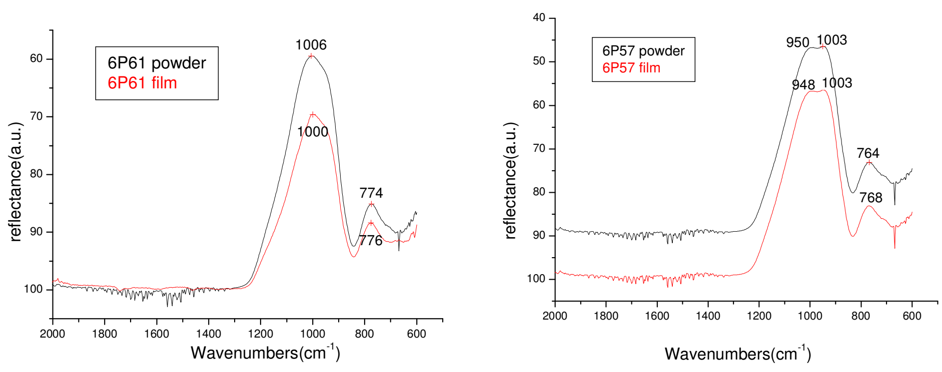
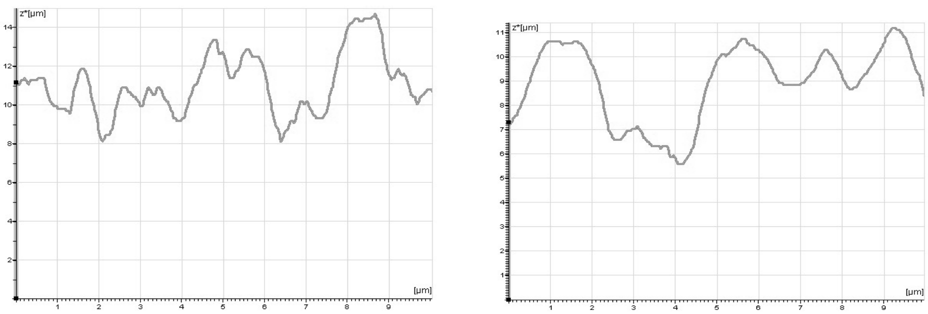


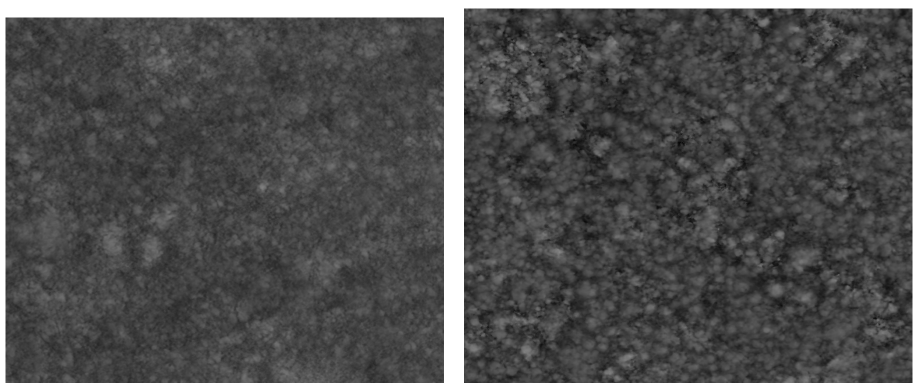
Fig.1 *FTIR spectra of powder and film 6P61*

The surface profile (fig.2) and the topographic analyses (fig.3) by CSLM show the uniformity of layers obtained by PLD and also the maintaing topography of titan substrate:



a) b)

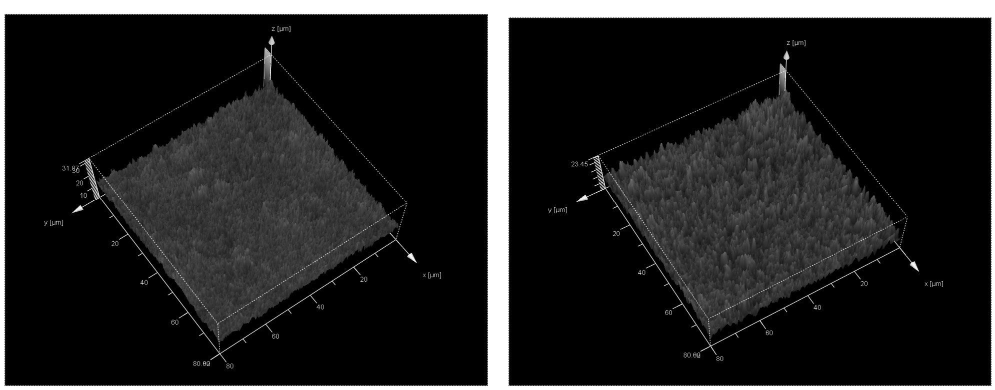
Fig.2 *Profile of surface on arbitrary 10 μm length for a) 6P57 and b) 6P61*



a) b)

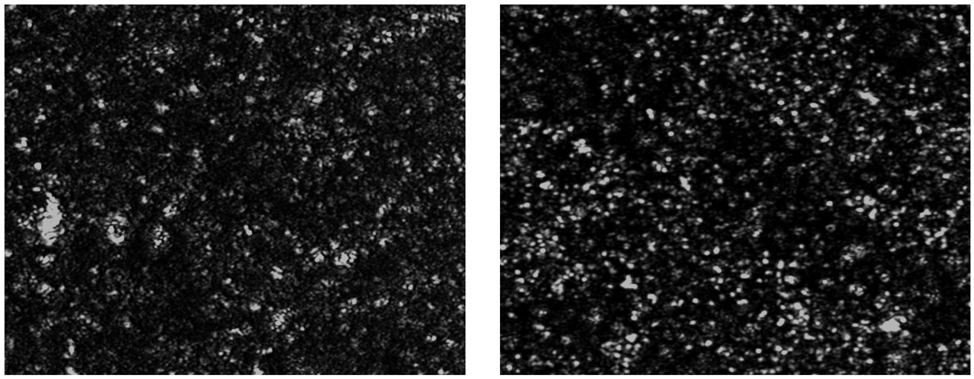
Fig.3 *Surface topography, zoom 1, 10 X objectiv, for a) 6P57 and b) 6P61.*

3D images of thin films show the formation of a structure with a special configuration: conic protuberances with 20-30 μm maxim height (fig.4). This thing is good, because the film biocompatibility is proportional with film surface and surface obtained is big, then the biocompatibility is big too.



a) b)

Fig. 4 *CLSM image 3D, zoom 3.12, 40X objectiv, for a) 6P57 and b) 6P61.*



a) b)

Fig.5 *CLSM image, zoom 3.12, 40X objectiv, for a) 6P57 and b) 6P61.*

Using a special software, we processed the images 2D (fig.5) and we could determine the radius of the particles: 200-250 nm both in 6P57 and 6P61 bioglasses.

Also, for exploring the spatial characteristics of the surface contours in a statistical manner, we used image 3D (fig.4) and we obtained the corresponding histograms (fig.6). Height histogram shows the statistical distribution of the z-heigts of all the points in the image. We can see a Gaussian distribution, still an evidence for surface uniformity.

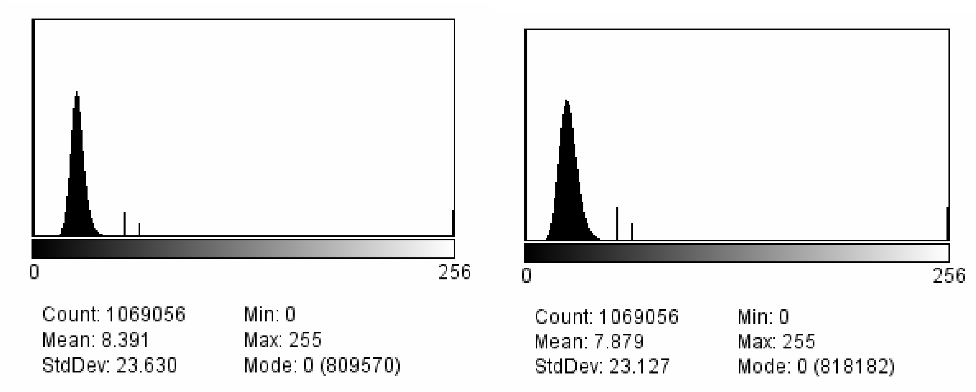


Fig.6 *Histograms on 1mm x 1mm, 10X objective, for 6P57 and 6P61.*

4. Conclusions

In conclusion, we demonstrated that is possible to obtain uniform bioactive glass thin films by PLD. Our films is composed mainly of macroscopic particles directly emitted from the target and their deposition are make with conserving the target stoichiometry. Once again, the versatility of PLD technique have been confirmed.

As future development, we will test the bioglass films obtained, in simulated body fluid solution, for to validate their bioactivity. We will analyse their capability, when they are in contact with body fluids, to stimulate the growth of hydroxylapatite on their surface. Also we will study the influence on this bioactivity by variable chemical compositions and film morphology related to different experimental conditions.

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