



Effect of annealing upon the structure and adhesion properties of sputtered bio-glass/titanium coatings

G.E. Stan^{a,*}, C.O. Morosanu^{a,1}, D.A. Marcov^a, I. Pasuk^a, F. Miculescu^b, G. Reumont^c

^a National Institute of Materials Physics, P.O. Box MG-7, Bucharest-Magurele, Ilfov 077125, Romania

^b Politehnica University of Bucharest, Faculty of Materials Science and Engineering, Bucharest, Romania

^c University of Lille, Laboratory of Metallurgy, Villeneuve d'Ascq, France

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ABSTRACT

Bio-glass films were deposited by radio-frequency magnetron sputtering technique onto medical grade Ti6Al7Nb alloy substrates from prepared silica based bio-glass target. A low deposition temperature was used (150 °C) and three different working pressures, followed by annealing in air at 550 and 750 °C. A quasi-stoichiometric target to substrate atomic transfer was found for Si, Ca and P, along with strong enrichment in Na and depletion in K and Mg, as evidenced by the energy dispersive microanalysis. The best results, taking into account stoichiometry and surface roughness, were obtained for the BG layers deposited at 0.3 Pa argon working pressure. The infrared spectroscopy of the as-sputtered and of the annealed films evidenced the characteristic molecular vibrations of silicate, phosphate and carbonate functional groups. The as-deposited films are amorphous and became partly crystalline after annealing at 750 °C, as evidenced by X-ray diffraction. The pull-out measurements, performed with a certified pull-test machine, gave very strong film–substrate adhesion strength values. For the non-crystalline layers, the pull-out strength is higher than 85 MPa, and decreases after annealing at 750 °C to 72.9 ± 7.1 MPa. The main objective of this work was to establish the influence of the working pressure upon the composition and morphology of the as-deposited films, and of the annealing temperature upon structure and film–substrate adhesion.

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1. Introduction

The first bio-glass (BG), known as 45S5 Bioglass[®], was reported in 1969 [1–5]. After this, various kinds of bioactive glasses and glass-ceramics with different characteristics have been developed by melting and glazing methods. Some of them are already commercialized as valuable bone-repairing materials. The prerequisite for glasses and glass-ceramics to bond to living bone is the formation of bone-like apatite layer on their surfaces in the body. This takes place for a SiO₂ content smaller than ~60 wt%, high Na₂O and CaO content and a high Ca/P ratio (between 1 and 5) [1]. Unfortunately the coating of titanium substrates with thick BG films by enameling and plasma spray techniques, usually fail due to a weak glass/metal interface and rapid dissolution in body fluids when implanted [6–8]. That is why in recent years, chemical [9–14] and laser [15–22] methods were also investigated in order to prepare adherent micrometric thin films. In comparison with hydroxyapatite films the control of composition and adhesion to

metallic substrates seems to be more difficult to accomplish in case of the BG ones. There are very few papers referring to BG coating deposited by magnetron sputtering [23]. It is widely accepted that both mechanical properties and chemical composition are important factors in the preliminary physiological bond of such implants. Low mechanical properties are the major problem that prevented the use of BG/Ti structures for load-bearing applications. The purpose of the present work is to prepare adherent magnetron sputtered (MS) bio-glass films having a structure as much as similar with that of the bio-glass target.

2. Materials and methods

2.1. Materials

The magnetron sputtering target was prepared from a bioactive glass ceramic [1,2] powder with micrometric granular size. The glass ceramic powder had the following composition (wt%): SiO₂–55, CaO–15, P₂O₅–10, K₂O–10, MgO–5, Na₂O–5. The starting reagents were: SiO₂, CaCO₃, (NH₄)₂HPO₄, K₂CO₃, MgO and NaHCO₃. The mixture of the desired composition was mechanically homogenized and heat treated at 400 °C for 10 min. The heat-treated mixture was reground and then melted at 1300 °C for 30 min and under-cooled at

* Corresponding author. Tel.: +40 724131131; fax: +40 213690177.

E-mail address: george_stan@infim.ro (G.E. Stan).

¹ Deceased.

room temperature, and the resulted powder was cold-pressed in order to obtain a 100-mm diameter MS target. Pieces of 100 mm², cut from a commercial 4 mm thick Ti6Al7Nb sheet, were used as substrates. In order to estimate the films thickness by a method based on optical transmittance measurement, parallel depositions were done on both titanium and Corning glass substrates. Prior to deposition the substrates were ultrasonically cleaned successively in acetone and ethanol for 10 min.

Post deposition, annealing in environmental air at 550 and 750 °C for 2 h with a low cooling rate (3 °C/min) was done, in order to promote the crystallization of the films and hereby decrease their dissolution rate in physiological fluids. A Nabertherm furnace—model L3/12/P320 was used.

2.2. Deposition procedure

The films were deposited by radio-frequency magnetron sputtering (1.78 MHz), in argon atmosphere. The target to substrate distance was set to 30 mm. The working chamber was evacuated to a base pressure of 10⁻³ Pa, and then back-filled with high purity (99.9995%) argon at a 40-sccm flow rate. The target pre-sputtering was done for more than 30 min, under the same conditions as the deposition. Prior to deposition, the substrates were etched for 10 min at a 0.4-kV DC bias voltage in argon plasma produced by a wolfram plasmatron, in order to remove the thin oxide layers and other impurities which might persist after the ultrasonic cleaning. The deposition pressure was varied by modifying the diffusion pumping speed, and the influence upon the films structure was studied. Three deposition pressures were used: 0.16 Pa (sample indicative—BG-a), 0.22 Pa (sample indicative—BG-b), and 0.3 Pa (sample indicative—BG-c). The depositions were carried out for 1 h, using a 1.78-MHz generator at a constant and low RF power (DC_{bias} target value of 44 V) in order to avoid the overheating of the target surface. The substrates were not heated during deposition and their temperature (around 150 °C) was only dependent on plasma self-heating.

2.3. Characterizations

The layer thicknesses were estimated from optical spectroscopy transmittance in the non-absorbance and low absorption region, by the Swanepoel procedure [24], using the films deposited on glass substrates. The transmittance measurements were performed using a PerkinElmer UV-VIS-NIR Lambda 90 spectrophotometer in the wavelength range from 300 to 800 nm.

The influence of the deposition pressure upon the surface morphology was investigated by scanning electron microscopy (SEM) using a FEI Quanta-FEG 400 microscope.

In order to test the stoichiometry of the target to substrate transfer during the sputtering, chemical composition analysis was performed by energy dispersive microanalysis (EDS), with a Princeton Gamma-Tech, Inc., attachment. The heat-treated BG films were examined for their surface morphology by environmental scanning electron microscopy (ESEM), using a Philips XL30 unit, equipped with a Sapphire-UTW EDAX detector.

Fourier transform infrared spectroscopy (FTIR) was used for analyzing the functional groups present in the bio-glass film. The

Table 1
Deposition pressure and film thickness.

Sample	Ar pressure [Pa]	Thickness [nm]
BG-a	0.16	980
BG-b	0.22	810
BG-c	0.30	750

analyses were performed with a PerkinElmer BX Spectrum spectrometer, in attenuated total reflection mode (ATR) using a Pike-MIRacle diamond head of 1.8 mm diameter. The spectra were recorded in the range 4000–400 cm⁻¹, with a resolution of 4 cm⁻¹.

The structure was investigated by X-ray diffraction (XRD) using a BRUKER D8 ADVANCE diffractometer, in parallel beam setting, with monochromatised Cu K_{α1} incident radiation. In order to enhance the signal coming from the film, the patterns were recorded in grazing incidence geometry at 2° incidence angle.

The adhesion strength at the substrate–film interface was measured by pull-test method, using a certified adhesion tester—PATHandy model (maximum pull force = 6.3 kN), equipped with a 2.8-mm diameter stainless steel test elements (stubs). The test elements were glued onto the film's surface by a cyanoacrylate one-component Epoxy adhesive, E1100S. The stub surface was first polished, ultrasonically degreased in acetone and ethanol and then dried in nitrogen flow. After gluing, the samples were placed in an oven for thermal curing (130 °C/h). The pull force was smoothly increased until fracture occurred.

3. Results and discussions

The film's thicknesses decrease as the working pressure increases (Table 1). The decrease of the deposition rate with the Ar pressure is due to the shortening of the mean free path of the sputtered particles. Increasing the sputtering pressure, the sputtered particles suffer more collisions while traveling from the target to substrate, and some of the sputtered particles are back-scattered towards the target. This resulted in a decrease of the deposition rate due to scattering.

The EDS results reveal a quasi-stoichiometric transfer for Si, Ca and P, while the concentration strongly increases for Na, and decreases for K and Mg. One can notice a monotonous enrichment in Ca and P, and depletion in K, Na and Mg by increasing the working pressure (Table 2). The elemental percentages obtained by EDS were converted in oxides in order to be compared with the target composition.

It is well known that the Ca/P molar ratio is of great interest for the biological reactivity of such structures. As proved by Hench's studies [1–5], the bioactivity of a glass-ceramic is favored by a SiO₂ content lower than 60 wt% and a Ca/P molar ratio lying between 1 and 5. Thus, taking into account the overall composition of the films versus the working pressure (Table 2) we can conclude that the most promising layer was obtained at the highest working pressure (0.3 Pa). This is the main reason why we have investigated in the followings the effect of various annealings only upon the BG-c type films.

An additional reason in favor of the BG-c structure was the observation that the surface morphology becomes rougher with

Table 2
Chemical composition in oxides and Ca/P molar ratios of the BG target powder and of the as-deposited films.

Sample	Working pressure [Pa]	SiO ₂ [wt%]	CaO [wt%]	P ₂ O ₅ [wt%]	K ₂ O [wt%]	Na ₂ O [wt%]	MgO [wt%]	Ca/P molar ratio
Target	–	55	15	10	10	5	5	1.89
BG-a	0.16	58.9	8.4	9.6	4.5	15.8	2.8	1.11
BG-b	0.22	58.3	10.5	11.6	2.6	14.4	2.6	1.13
BG-c	0.30	55.5	17.0	12.6	2.0	11.0	1.9	1.70

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