STUDY OF TITANIUM SUBSTRATE SURFACES COATED WITH HYDROXYAPATITE BY MAGNETRON SPUTTERING

R. M. Balestra[1], A. A. Ribeiro[1], J. C. Oliveira[2], A. Cavaleiro[2] and M. V. Oliveira[1]
[1]Instituto Nacional de Tecnologia, Divisão de Processamento e Caracterização de Materiais, Laboratório de Tecnologia de Pós, Avenida Venezuela, 82, sala 602, CEP 20.081-312, Saúde, Rio de Janeiro – RJ, Brasil.
[2]SEG-CEMUC, Departamento de Engenharia Mecânica, Universidade de Coimbra, Rua Luís Reis Santos, 3030-788, Coimbra, Portugal.
E-mail: alexandre.antunes@int.gov.br

ABSTRACT

The deposition of hydroxyapatite coatings on titanium via sputtering techniques has been quite studied on commercial dense substrates, for use as a biomaterial. In this work, porous titanium samples produced by powder metallurgy and commercially dense titanium sheet, used as control, were used as substrates, both ASTM F67 grade 2. The coatings were deposited by radio frequency magnetron sputtering using a hydroxyapatite target in argon atmosphere with different deposition times. Samples characterization was performed by Optical Microscopy, Scanning Electron Microscopy/Energy Dispersive Spectroscopy and low-angle X-ray Diffraction. Calcium phosphate coating depositions were obtained on both titanium substrates with structure similar to HA phase. The results indicated the potential of this methodology for titanium substrates with homogeneous hydroxyapatite coatings.

Keywords: Titanium, Hydroxyapatite, Magnetron Sputtering, Powder Metallurgy.

INTRODUCTION

Titanium (Ti) and its alloys have been widely used as materials for dental and biomedical applications, due to their excellent mechanical properties and biocompatibility(1). New developments in biomaterials have shown that implants with porous structure improve osseointegration because they provide space for anchoring bone cells, vascular and bone tissue ingrowth and implant stability for a long period

of time[2,3]. Porous titanium has been successfully processed by Powder Metallurgy (PM) technique, since it allows Ti parts fabrication under low temperature, avoiding undesirable reactions and contaminations[4,5].

The most widely used method for coating deposition on implants is plasma spray. This technique is widely used because it has a high deposition rate and low cost, compared with other processes[6]. Since this process utilizes high temperatures and may also cause decomposition and changes in stoichiometry and chemical properties of the coating material, as hydroxyapatite (HA)[7], for example, other techniques such as deposition by ion beam and deposition by sol-gel have also been used.

Ion beam deposition produces thin HA coatings of high density and superior adhesion[8], while sol-gel technique permits good control of stoichiometry and composition of HA. However, there may be a phase separation between the coating and substrate, causing defects[9].

Radio frequency magnetron sputtering (RFMS) is a technique, which although not used in commercial production of coatings, has been investigated and seems to be promising. This technique produces films of good adhesion, density, appropriate thickness, good smoothness, uniformity and homogeneity, both in structure and composition[10,11]. The coating also keeps stoichiometry and chemical properties similar to the target used[7].

The present work aimed to study the titanium substrate type influence on HA coating deposited by Radio Frequency Magnetron Sputtering (RFMS), for use as a biomaterial, with the purpose of optimize its biocompatibility characteristics. This material has been quite studied, but not on porous substrates produced by powder metallurgy.

MATERIALS AND METHODS

Commercially pure dense Ti sheets (DTi), from TiBrasil Ltda and porous (PTi) Ti samples, all ASTM F67 grade 2, were used as substrates. Porous Ti samples were processed by PM using Ti powder manufactured by HDH-hydrogenation-dehydrogenation process (Micron Metals/USA). Ti powders with 125-149 μm particle size range and ammonium bicarbonate as pore former additive, with 355-425 μm particle size range, were manually mixed and isostatically pressed at 350 MPa

producing PTi samples. The pore former additive elimination was conducted at 170°C/2h in a chamber furnace in air. Sintering was performed in a vacuum furnace (better than 10^{-5} Torr) at 1200°C/2h.

All substrates were cleaned by a sequence of ultrasonic bath, in order to eliminate the superficial organic impurities. Further, the DTi substrates were subjected to an acid descaling processing, according to ASTM B600-91, for removing the contaminated layer formed during the rolling process.

The titanium substrates were coated by RFMS (Edwards Coating System E306A – 13.56 MHz) in argon atmosphere with 99.9999% purity and pressure in the chamber at 0.6 Pa. Hydroxyapatite with 99.9% purity, 101.6 mm in diameter and 7 mm in thickness was used as a target. Before deposition, both target and substrates were cleaned using 150 W during 15 min. The depositions were carried out at 300 W during 3 (DTi-3, PTi -3) or 5 (DTi-5, PTi -5) hours. After deposition, the samples were submitted to heat treatment at 500°C/1h in a chamber furnace (Adamal Lhomargy, Chevenard Journier System) in air, in order to improve the crystallinity of HA coatings. For assisting the coating characterizations on Ti, depositions were also performed on silicon (Si) single crystal wafers with dimensions of 10 x 10 mm using the conditions based on previous work[12].

Dense and porous Ti substrates cross-sections were prepared for Optical Microscopy (OM) and Metallography analysis. DTi mean grain size, pore morphology and PTi average porosity were determined by quantitative metallographic analysis, using Image Pro Plus 4.0 software, in about 5 random images per sample.

Titanium substrate surfaces with or without hydroxyapatite coatings were evaluated by Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS) conducted in a FEI (model Quanta FEG 450) microscopy operated at 20 kV. The coated samples were covered with a thin platinum (Pt) film in order to make them conductive.

HA-coated Si substrates were assessed by SEM/EDS using a PHILIPS (model XL30) microscopy operated at 10 kV. The samples were covered with thin gold (Au) film in order to make them conductive.

Crystalline phases identification of coatings was obtained by low angle X-ray diffractometry (XRD). X-ray data were collected in the 2θ interval from 20º to 50º, in 30s, 0.04º steps and 2º incident angle, using a PHILIPS (model X'Pert) diffractometer

with cobalt radiation monochromatized by a graphite crystal. The diffractometer was set at 40 kV and 35 mA.

RESULTS AND DISCUSSION

Macrographic images from the DTi and PTi substrates are shown in Figures 1a and 2a, respectively, both without HA coating.

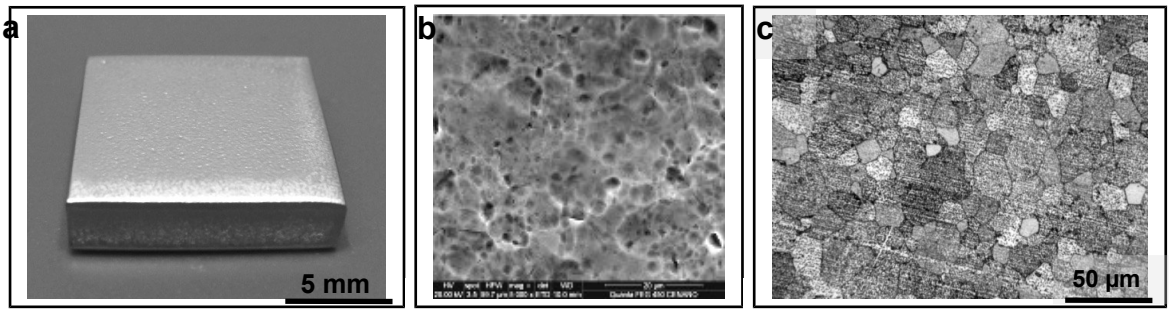

Figure 1 – DTi substrate without HA coating: macrographic (a), SEM (b), optical (c) images.

By SEM images, DTi substrate (Fig. 1b) revealed a rough topography and microstructure composed predominantly by recrystallized grains of “primary” α-Ti phase (Fig. 1c)[13]. In figures 2b and 2c, PTi substrate showed a macroporous structure consisting of closed micropores and large interconnected macropores. The closed micropores are residual pores from the sintering process and the interconnected macropores are consequence of the pore former additive elimination. In addition, optical quantitative metallographic analyses revealed that titanium dense sheet has 11.89 ± 1.93 µm α-Ti average grain size (Fig. 1c) and porous substrate (Fig. 2c) has 56.07 ± 2.31% average porosity. According to the porosity results and pore morphology, PTi substrate presented suitable porosity features for surgical implant applications[2].

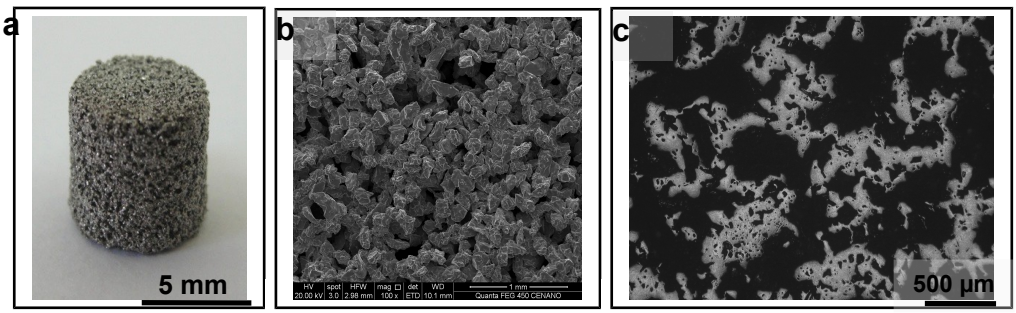

Figure 2 – PTi substrate without HA coating: macrographic (a), SEM (b), optical (c) images.

Figures 3 and 4 present SEM images and EDS spectra from Si substrates coated with HA at different times. In Figure 3a, the coating deposited for 3 h showed bubbles, detachments and thickness of about 280 nm, according to previous work[12]. On the other hand, the coating deposited for 5 h (Fig. 4a) did not show bubbles and detachments, indicating a uniform and smooth surface with some protrusions and thickness of about 410 nm. This morphological difference between the coatings should be due to an alteration in the state of hydroxyapatite target during depositions. Further, P and Ca peaks in Figure 3b are more intense than those in Figure 4b, which confirm the higher thickness of coating with 5 h deposition time.

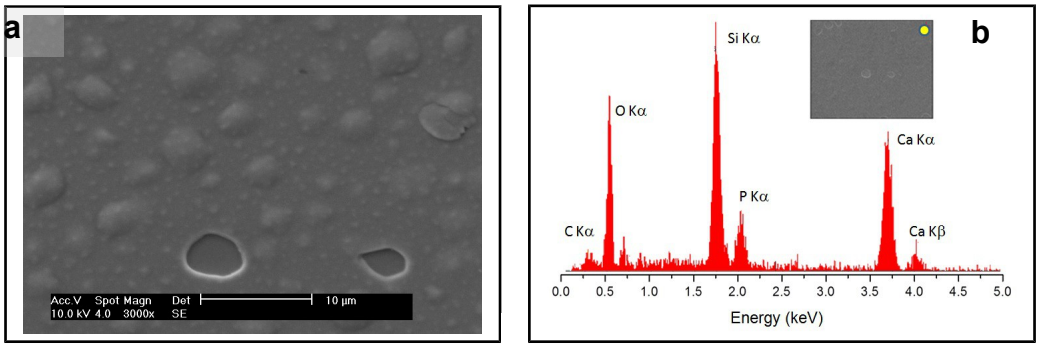

Figure 3 – Si substrate coated with HA for 3 h deposition time: SEM image (a), EDS spectrum (b).

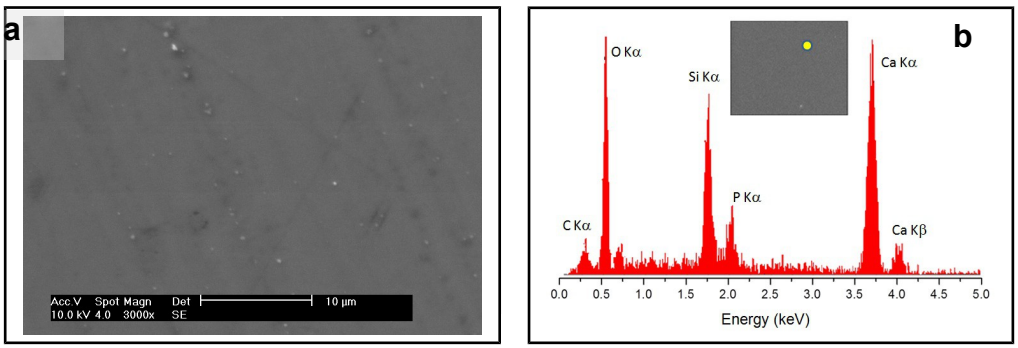

Figure 4 – Si substrate coated with HA for 5 h deposition time: SEM image (a), EDS spectrum (b).

DTi-3, DTi-5, PTi-3 and PTi-5 samples exhibited dense and uniform coatings without detachments, as shown in Figures 5a, 6a, 7a, 8a, respectively. DTi-3 coating (Fig. 5a) presented a microstructure similar to small sphere-like drops dispersed on

the surface, whereas PTi-3 coating (Fig. 7a) revealed one like “egg threads” and protrusions similar to globular shape. In Figure 6a, DTi-5 coating showed a smooth microstructure similar to Si substrate with 5 h deposition time (Fig.4a), where the roughness observed on surface substrate has not been much changed (Fig. 1b). For PTi-5 sample (Fig. 8a) the coating exhibited a globular microstructure with globules dispersed throughout surface. These observations indicated that the surface type and deposition time have significant influence on coating microstructure.

EDS maps of all samples, which are not displayed in the present work, revealed Ca and P presence throughout the investigated zone (30.48 μm x 26.57 μm). In addition, P and Ca peaks in Figures 6b and 8b are more intense than those in Figures 5b and 7b, respectively, which suggests a higher thickness of coatings with 5 h deposition time. The thickness of coatings on Ti substrates should be indirectly estimated by comparison with HA-coated Si substrates, which values are described above.

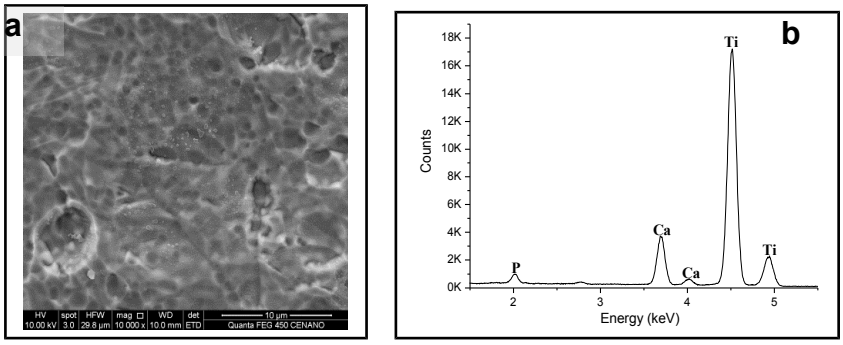

Figure 5 – DTi substrate with HA for 3 h deposition time: SEM image (a), EDS spectrum (b).

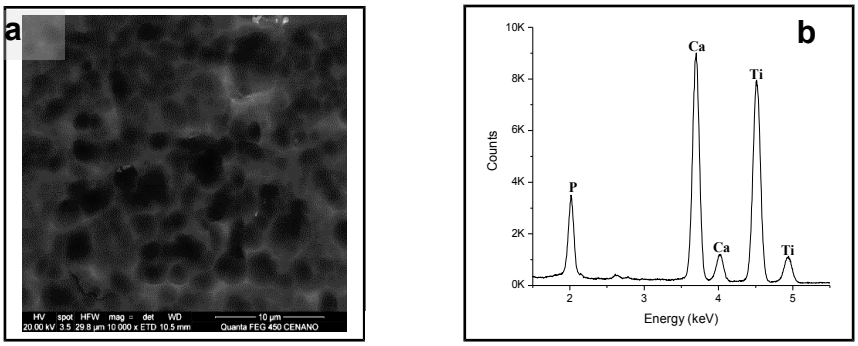

Figure 6 – DTi substrate with HA for 5 h deposition time: SEM image (a), EDS spectrum (b).

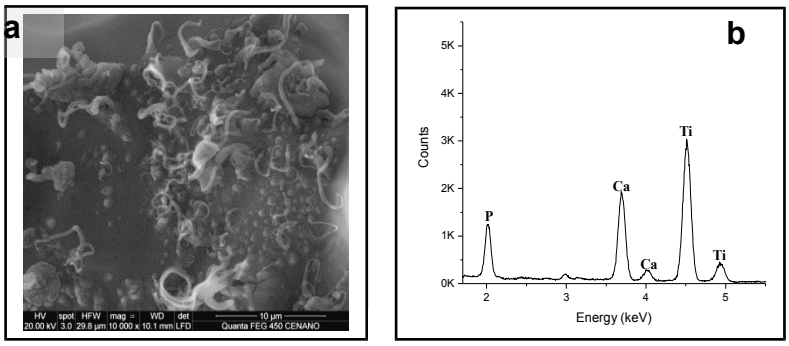

Figure 7 – PTi substrate with HA for 3 h deposition time: SEM image (a), EDS spectrum (b).

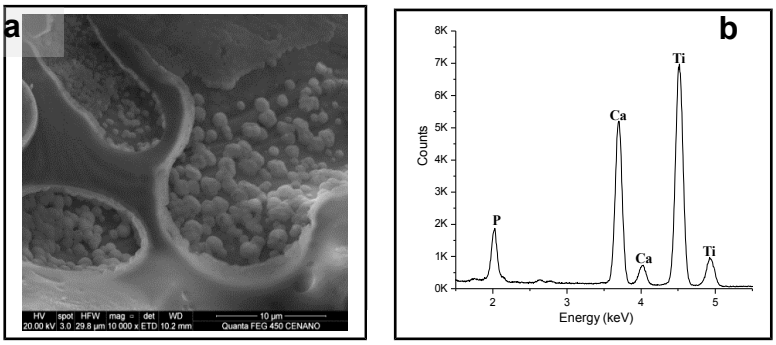

Figure 8 – PTi substrate with HA for 5 h deposition time: SEM image (a), EDS spectrum (b).

Figure 9 shows XRD diffractograms of Si and DTi substrates coated with HA at different times. In Figure 9a, for HA-coated Si substrates, the diffractograms indicated a low crystallinity coatings composed by hydroxyapatite, calcium oxide (CaO) and calcium phosphate ($Ca_2P_2O_7$) crystalline phases. However, the coating with 5 h deposition time presented more intense HA peaks than those obtained with 3 h deposition time. For DTi substrates (Fig. 9b), the diffractograms indicated amorphous HA coatings for both deposition times and showed Ti peaks and a peak around to 35º with high full width at half maximum, which is not coincident with CaO peak observed in the HA-coated Si substrates (Fig. 9a). This behavior should be the result of a more P quantity deposition in relation to Ca, which decrease free Ca amount in the coatings and prevent CaO formation.

The sputtering process can also produce amorphous coatings, because it is critical to maintain the integrity of HA coatings, controlling the heat-treatment temperatures and heating environment results in conversion of amorphous coatings to HA coatings of different crystallinity degrees. In addition, changes in the most

intense XRD peaks between postdeposited heat-treated HA coatings and HA target suggest differences in structural orientation of the crystals[14].

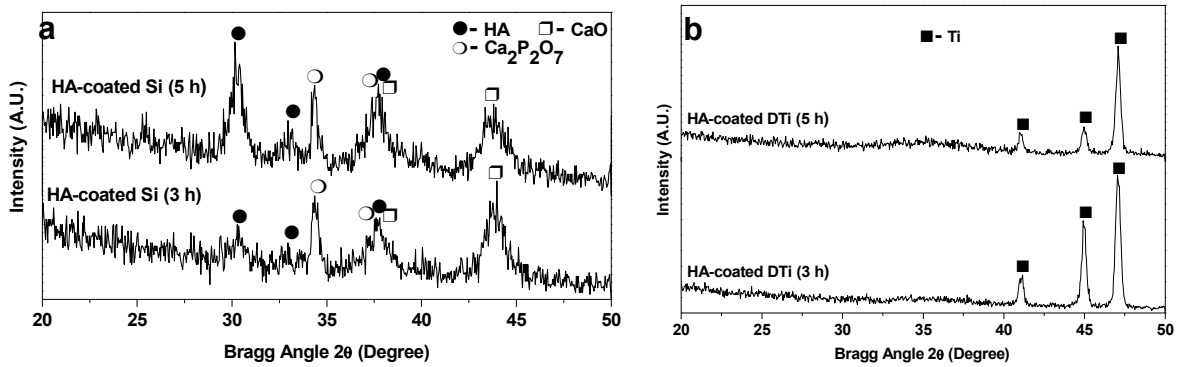

Figure 9 – XRD diffractograms: HA-coated Si (a) and HA-coated DTi (b).

In relation to HA-coated PTi substrates, the XRD analyses were hampered because of interconnected porosity. However, SEM/EDS analyses showed that it is possible to deposit a continuous coating on macroporous surface by RFMS.

CONCLUSIONS

Powder metallurgy technique processed porous Ti substrate with suitable interconnected porosity for surgical implants. RFMS process successfully produced dense and uniform coatings without detachments on DTi and PTi substrates. SEM/EDS images revealed different morphologies of HA coatings, indicating that the substrate type and deposition time have significant influence on coating microstructure. Although XRD results presented amorphous coatings on Ti substrates, the HA-coated Si substrates are composed by HA, CaO and $Ca_2P_2O_7$ crystalline phases. In addition, the coating on Si substrate with 5 h deposition time exhibited HA peaks with more intensity. Based on such results, RFMS revealed potential for coating porous Ti substrates fabricated by PM.

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