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Nanometer Crystalline Coatings of Hydroxylapatite: Surface Characterization by Grazing Incidence X-ray Diffraction from Synchrotron Radiation

A. Mello[(1)*], B.R.Pujada[(1)], E.O.Lopez[(1)], A. M. Rossi[(1)]

[1]Centro Brasileiro de Pesquisas Físicas (CBPF), Rio de Janeiro, RJ, Brazil, mello@cbpf.br;

Abstract – An opposing RF magnetron sputtering approach was successfully applied for growing Hydroxylapatite (HAP) crystalline thin-coatings at room temperature on silicon and titanium substrates. The surface structural information of these biocompatible coatings at nanometer scales was obtained by grazing-incidence X-ray diffraction (GIXRD) with synchrotron radiation. The GIXRD spectra were obtained by fixed incidence theta angles at 0.25, 0.5, 0.75 and 1 degree for a structural profile analyses with reduced substrate interference. The GIXRD results have shown that all the principal peaks are attributed to a crystalline HAP. Previous tests of biocompatibility indicate these nanometer coatings for medical applications.

Hydroxylapatite (HAP) thin coatings on biocompatible metals have been extensively studied in connection with medical implants [1]. Conventional sputtering techniques have shown some advantages over the commercially utilized plasma spray method. However, the as-sputtered coatings are usually amorphous, which can cause serious adhesion problems, when post-deposition annealing is needed [2]. In this work we have utilized an alternative magnetron sputtering system based on an opposing geometry to prepare thin and adherent HAP coatings on single crystal silicon and titanium substrates. It was found out that under chosen experimental conditions the as-sputtered HAP coatings are phase-pure and crystalline with excellent results from biocompatibility experiments with osteoblasts cells [3,4]. Nevertheless, good conventional X-ray diffraction spectra of HAP coatings could only be made for thick layers (~1μm), avoiding a better understanding of the HAP surface at nanoscales [5].

The grazing-incidence X-ray diffraction technique (GIXRD) was performed in the Brazilian Synchrotron Light National Laboratory (LNLS) and has provided the necessary photon density for the structural profile analyses of HAP nano coatings at different depths, over the coating surface. The thickness calibration was obtained by X-ray Specular Reflectivity (XRR). In addition, all the X-ray analysis were performed with synchrotron radiation operating at the energy of 9000eV and the wavelength of λ = 1,377Å. For GIXRD the incidence angle θ was fixed in θ=0.25, 0.5, 0.75 and 1 degree. The HAP coatings were also analyzed by optical microscopy with an in-situ Fourier Transform Infrared Spectroscopy (FTIR) (RigaKu IR-Prestige).

The HAP coatings are highly crystalline as shown in our previous works [3-5], but at low coating thickness (Fig.1) and shallow X-ray analyses the picks have larger linewidths suggesting smaller crystals at surface when compared with thicker coatings [3,4]. Although the GIXRD patterns are typical of a polycrystalline material, strongly preferred orientation of growth along the (100) and (002) family planes are observed in HAP coatings on Si(001) and titanium. The FTIR results (Fig.2) confirmed that all coatings are pure-phase HAP. Among other calcium phosphates the OH^- band at 3572 cm^-1 could be elected the HAP *fingerprint* in our coatings.

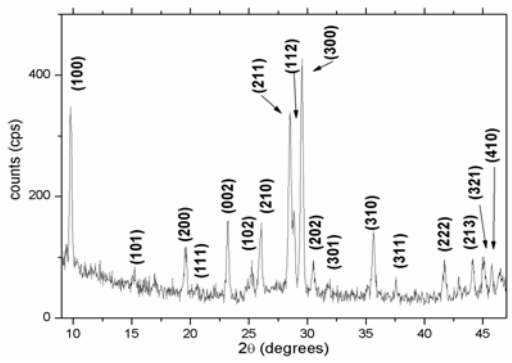

Figure1: GIXRD diffraction pattern of an as-sputtered 66nm hydroxylapatite coating, on Si(001) substrate.Incidence angle theta = 0.5°

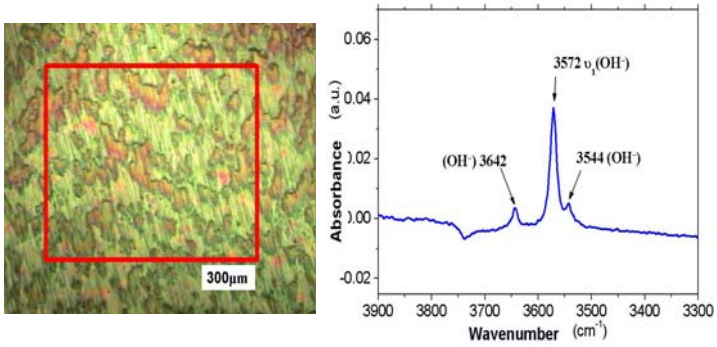

Figure2: a) optical image of an acid etched titanium substrate coated with a 300nm nanometer HAP layer; b) in situ FTIR spectrum obtained for the rectangle area showing the fingerprint of a highly crystalline HAP: sharp Infrared oscillation modes for the OH^- groups.

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