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Correlation between structural and mechanical properties of RF magnetron sputter deposited hydroxyapatite coating

A.A. Ivanova[a,b], M.A. Surmeneva[a,b], A.I. Tyurin[c], R.A. Surmenev[a,*]

[a] Research School of Chemistry & Applied Biomedical Sciences, National Research Tomsk Polytechnic University, 634050 Tomsk, Russia
[b] RASA Center in Tomsk, National Research Tomsk Polytechnic University, 634050 Tomsk, Russia
[c] NanoCenter "Nanotechnology and Nanomaterials", G.R. Derzhavin Tambov State University, 392000 Tambov, Russia

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ABSTRACT

In the present study hydroxyapatite (HA) thin films with a,b-plain and c-plain preferential orientation were prepared by means of RF-magnetron sputtering with water vapor addition into a working gas atmosphere to investigate the influence of microstructural features on mechanical performance of the coating at nanoscale. The mechanical properties of the HA coatings textured along a,b- and c-axes by nanoindentation conclusively highlight that elastic modulus, H/E ratio, H^3/E^2 parameter and percent of elastic recovery are determined by preferential orientation of the film. Nanoindentation reveals that the HA films exhibiting (300) texture possess commensurate nanohardness and lower elastic modulus compared to (002) oriented films, indicating that the former films possess higher resistance to cracking. The (002) and (300) textured coatings exhibited a nanohardness of 4.7 ± 2.0 GPa and 4.4 ± 2.2 GPa, respectively. The elastic modulus of the HA film with (300) and (002) preferential orientation was 75 ± 40 GPa and 103 ± 40 GPa, respectively. The HA coating with (300) texture showed a higher percentage of elastic recovery of 92% within unloading than that of the (002) textured film (69%).

1. Introduction

Crystallographic texture (preferred orientation) is one of the microstructural features, which significantly affects the coatings' properties [1–14]. The hexagonal hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$; HA) structure is anisotropic which determines its mechanical properties, solubility, biocompatibility and absorption activity [15–18]. The a,b-plane in the HA structure is rich in calcium ions and is positively charged, while the *c*-plane is rich in phosphate and hydroxide ions and negatively charged [18]. Apatite crystals constituting natural bone reveal preferred orientations due to highly specific biological causes, which are considered to influence on the biomechanical features of hard tissue [16,19,20].

Recent investigations demonstrate that HA with tailored surface texture influences cellular behavior due to anisotropy of the protein adsorption on different planes of hexagonal HA [16]. Molecular modelling and *in vitro* studies performed by Bhowmik group revealed that proteins with a high affinity bind to the (100) plane of HA [21]. Meanwhile, protein adsorption and desorption at nanoscale plays a crucial role in cell adhesion and biomineralization process of biomaterials [15,16,18,21]. The dynamic behavior of bone morphogenetic protein on a series of HA surface textures were investigated using molecular dynamics [15]. The authors suggest that surface-engineering approaches could be applied to directly control the texture of the HA surfaces in order to adjust the behavior of a protein adsorbed onto the biomaterial surface.

Zhuang et al. studied dense HA ceramics with the c-axis-oriented fiber-like structure and observed that the orientation degree influenced on the surface characteristics such as zeta-potential and wettability [18]. It was shown that the increase of the orientation degree along c-axis led to the change of the surface charge from negative to positive, and decrease of the surface wettability. The cell attachment efficiency was demonstrated to decrease with the increase of the orientation degree [18].

Nanoindentation study performed results by Kim et al. showed that highly c-axis oriented HA coatings prepared by pulsed laser deposition technique possessed higher values of nanohardness and elastic modulus in comparison with the randomly oriented coatings [16]. The findings of the authors indicated that c-axis textured HA film had a controlled resorption behavior and contributed precipitation of calcium phosphates from simulated body fluids. Tanase et al. established that the rate of precipitation on the c-plane of HA was faster than on the a-plane

* Corresponding author.
E-mail address: rsurmenev@gmail.com (R.A. Surmenev).

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[22]. The textured HA coating may give a new level of control of cellular behavior on the implant surface due to anisotropy of protein adsorption behavior on different faces of hexagonal HA, which is relevant for their biomedical applications [16].

The HA coating has been successfully deposited on titanium by means of RF-magnetron sputtering [6,9–14]. The effects of various deposition parameters (working pressure, working gas composition, substrate bias voltage etc.) on growth of the HA film with preferential orientation have recently been studied [9,10,13,14,23,24]. Apparently, substrate bias voltage, working pressure, working gas composition are directly correlated with ion bombardment of the growing films and played an important role on the coating texture and intrinsic structure development.

In our recent studies it was shown that the HA coatings deposited in a gas atmosphere with the addition of water vapor exhibited transformation of texture while the samples were placed near the racetrack [25,26]. It was proven that the structural changes in the coatings obtained under the racetrack were determined by negatively charged oxygen ions bombardment [27–29]. The characteristics of the deposited HA films were found to be dependent on the ion-to-atom ratio incident the substrate [14]. It was shown that, besides, the energy contribution, the momentum contribution also influenced the crystallographic texture of the deposited HA coating. Due to negative ion bombardment the structure of the HA coating is caused by momentum transfer to the growing film and anisotropy of the ion-induced resputtering of the HA crystal planes [14].

Meanwhile, it is well established that the coating structure primarily affects its mechanical properties. Due to non-equilibrium deposition process the sputtered films possess different structure compared with bulk materials. The film characteristics such as crystallographic texture and presence of compressive stress influence on the plastic deformation process and, thus, the film nanohardness, which have been confirmed elsewhere [5–8]. The mechanical properties of the coating on the surface of metallic implant determine the stability of such devices *in vivo*. Thus, microstructural control targeted at preferentially oriented HA can provide tailored resorption and mechanical behavior of the coating. A major goal of this study is to investigate the microstructural and mechanical performance of differently textured HA thin films deposited by RF-magnetron sputtering in water vapor containing atmosphere.

2. Materials and Methods

The HA films were deposited by means of a custom-made setup with RF-power generator (COMDEL, 13.56 MHz). The detailed description of the equipment is given elsewhere [14,25]. An RF power density of 2.0 W/cm^2 was employed for the sputter deposition. The distance from a substrate holder to a target was approximately 40 mm. The base pressure in the vacuum chamber was better than 8×10^{-4} Pa. The working pressure was kept at 4.0×10^{-1} Pa during deposition. Pure titanium (Ti, grade 2) plates 1.5 mm thick were used as substrates (10 mm × 10 mm). The titanium plates were chemically etched in acid solution containing HF (48%) and HNO_3 (66%) dissolved in the distilled water with the ratio 1:2:2.5 in volume. After acid-etching the samples were ultrasonically washed in ethanol followed by deionized water for 10 min at room temperature. Resulted roughness (Ra) measured by atomic-force microscopy of the treated Ti plates was of 0.41 ± 0.08 μm. The HA coatings were deposited with the addition of water vapor into working gas atmosphere with a proportion of partial pressures of Ar/H_2O equals to 9:1. In order to control the flow of the gas mixture during deposition, the installation is equipped with a three-channel system to allow the inflow of the working gases. This latter system consists of inflow-regulating valves (automatic inlet valves) with built-in electronic control blocks. In automatic mode, the gas flow changes automatically such that the pressure in the chamber is maintained at the desired level. It is assumed that electron collisions with water molecules in the chamber induce water dissociation into ions (such as O^{2+}, H_2O^{2+}, O^+, and OH^+) which may affect the coating deposition rate [14] and provide additional OH-groups for HA formation. In order to provide more uniform distribution of the coating thickness, the substrate holder was moved by circular and arc rotation. The details of the substrate rotation and geometrical description of the applied vacuum chamber are described elsewhere [14]. The samples were located on the substrate in the radial direction from the center of the substrate holder in such a way that one part of the specimens was located in the center of the substrate holder (Sample A); another part of the samples was positioned under the target erosion zone (Sample B).

X-ray diffraction analysis was done using a series D8 Advance Bruker diffractometer with a CuKα X-ray tube. Imaging was carried out in the form of θ–2θ scans (Bragg-Brentano configuration) with generator current voltage of 40 mA and 40 kV, respectively. The step size 2θ was 0.05° and the measurements were conducted within the range of 10° to 60°. The diffractograms were analyzed using the program EVA. The HA (#09-0432) and titanium (#44-1294) patterns from the International Center for Diffraction Data (ICDD) database were used as references for data interpretation. From the intensity data, the preferred orientation of crystallites in thin films was evaluated by the texture coefficient (TC) according to the equation published elsewhere [30,31]. The density of the deposited coatings was determined using X-ray reflectometry (XRR) using D8 Advance Bruker (Bruker AXS GmbH, Karlsruhe, Germany) equipped with a scintillation detector and CuKα radiation. The samples were scanned from 0.3° to 6° with a step size of 0.01°. The Parratt's method was used to determine the critical angle of the total reflection. The elemental composition of the deposited HA coating has been analyzed by means of X-ray photoelectron spectrometer (XPS) VG Scienta. Analysis was performed by applying AlKα radiation with energy of 1486.6 eV, power of 200 W and voltage of 10 kW, angle of photoelectron escape relative to the surface of 45°, and research area of 250 × 1000 mm^2. Photoelectron spectra were treated by subtracting a linear background and using the peak area for the most intense spectral line of each detected elemental species to determine the atomic concentration (at. %).

The coating microstructure was studied by Transition Electron Microscopy (TEM) using thin specimens prepared by Ar ion thinning (equipment EM-09100IS, Jeol) using conditions which minimize structural changes in the samples (accelerating voltage of 6 kW, angle of incoming ion beam 2–4°). TEM was carried out on the JEM 2100 (Japan) at an accelerating voltage of 200 kW and with a resolution capability of 1.4 Å. Nanoindentation tests were performed using a Nanotriboindenter TI-950 (Hysitron Inc., USA) equipped with a Berkovich tip [32]. The nanohardness (H) and the reduced modulus (E) of the coatings were obtained using the indentation curves according to the Oliver and Pharr method [33]. Load–displacement curves with the load ranging from 100 μN to 500 μN were obtained to determine the penetration depth (h), elastic modulus (E) and nanohardness (H) of the composites as a function of the applied load. The following loading-unloading sequence was performed at each peak load: the loading to maximum load for 5 s, hold segment for 2 s to minimize the creep effect, complete unloading for 5 s. In total 100 indentations were performed for each studied sample. Based on statistical analysis, some outliers were excluded from further analysis, which resulted in 10 indentations corresponding to the same loading values. The indentations points were spread over several separated areas of the surface avoiding any interference between them. Then the obtained data were averaged and standard deviations of the measurements were calculated. A multiple range test (Fisher's correlation coefficient) at a 95% confidence level was performed in order to investigate differences in the mechanical properties between two groups of the samples.