Deposition of polycrystalline zinc substituted hydroxyapatite coatings with a columnar structure by RF magnetron sputtering: role of in-situ substrate heating

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Abstract. Zn incorporation into hydroxyapatite structure leads to enhanced osteointegration and antibacterial activity of deposited coatings. Radiofrequency magnetron sputtering is a physical vapor deposition technique which can be used to create thin coatings with a controlled level of crystallinity. The material state is a crucial parameter for biocoatings as it governs cell response. Bioactive Zn substituted hydroxyapatite coatings were deposited onto Ti by radiofrequency magnetron sputtering at increased substrate temperatures (100, 200, 300 and 400°C). XRD showed crystallization of the coatings at elevated substrate temperatures starting from 300°C. Cross-section transmission electron microscopy showed a polycrystalline columnar grain structure of Zn substituted coatings deposited at 400°C substrate temperature. An amorphous TiO2 sublayer of several monolayers thickness was detected in the interface between the polycrystalline coating and the Ti substrate. In-column energy dispersive X-ray analysis revealed coatings to be substoichiometric with the average Ca/P ratio being 1.5. It is established that it is possible to deposit Zn substituted hydroxyapatite in a form of a well-crystalline coating when the substrate temperature is exceeding 400°C.

1. Introduction

Extended life-expectancies combined with increasingly active lifestyles have led to many bone-related ailments including increased susceptibility to bone fracture or excessive wearing of joints. As a result, joint replacement surgeries have become omnipresent as a safe and effective way to improve the quality of life for patients suffering from joint ailments [1]. However, it has been recently reported that revision rates for total joint replacement remain unacceptably high. The problem of bacterial infection in the implantation site remains crucial as a revision surgery is associated with higher occurrence of postoperative infection-related complications [2]. Moreover, patients with revisions are having a higher chance to undergo “re-revision” that is significantly reducing a quality of patients life.
Various surface modifications methods for implants were introduced in order to increase initial fixation of the prostheses. The most frequent is a deposition of the Hydroxyapatite \([\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2], \text{HA}\) in many biomedical applications including bone grafts and joint replacements. Due to its structural and chemical similarities to human bone mineral, HA promotes the growth of bone tissue directly on its surface. In the light of demand for antibacterial coatings, HA is frequently substituted by ions of Zn, Cu, and Ag [3]. Zinc ions, for example, are well-known not only for its antibacterial properties, but they also act as an inhibitor of crystal growth. It is essential to trace element for tissue regeneration [4]. According to Fan Yang et al. [5], HA-Zn coatings enhance proliferation and differentiation of osteoblasts, which has the potential benefit of enhancing the implant osteointegration. Hence, deposition of HA-Zn as an antibacterial coating with a capability for osteointegration is important for the field of biomaterials and for the future applications in orthopedics and dental implants. In spite of remarkable properties, very little information on Zn-substituted HA (HA-Zn) is available in the literature [2].

Plasma-assisted methods such as radiofrequency magnetron sputtering (RF-MS) allow controlling crystallinity, morphology and phase composition of deposited coatings [6, 7]. The degree of crystallinity is one of the most important parameters of bioactive coatings as it governs the dissolution rate and stability of an implant. As it was previously shown in our work [8] it is possible to deposit crystalline HA-Zn coating with equiaxed grain structure. At some clinical cases, prolonged implant stability is favorable, therefore homogeneous well-crystalline HA is used in order to protect surrounding tissues from possible poisonous ions coming from the substrate.

Thus, we tempt to report our recent research data that serves to add the new knowledge in the field of physical vapor deposition of bioactive coatings. In this paper, we show a way to deposit highly-crystalline columnar-like thin HA-Zn coating when during the sputtering process a substrate heating is applied. Taking in account presented results and our previous research reports we are declaring that the RF-MS method allowed us to deposit HA-Zn coating in different crystallinity states with a prospect to manufacture multi-layer gradient calcium phosphate coating with controllable bioreorption rate.

2. Materials and Methods

Custom made vacuum installation with an RF magnetron source operating at 13.56 MHz was used in order to deposit HA-Zn coatings. The HA-Zn powder was prepared by mechanochemical synthesis. The mechanochemical synthesis was carried out according to the reaction:

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6\text{CaHPO}_4 + (4-x)\text{CaO} + x\text{ZnO} = \text{Ca}_{10-x}\text{Zn}_x(\text{PO}_4)_6(\text{OH})_2 + 2\text{H}_2\text{O}, \text{ where } x = 0.4.
\]

The calcium hydrogen phosphate, calcium oxide, and zinc oxide were used in the process. The precursor powders were put in the planetary ball mill with three drums, each having a volume of 1800 mL. The process of a synthesis took 12 minutes at a room temperature. The phase composition of HA-Zn powder was confirmed by X-ray diffraction. Afterward, it was used as a precursor-powder to prepare a solid ceramic target for sputtering. The process of a target manufacturing from the calcium phosphate powder of HA-Zn is described in detail in our previous study [9]. Commercially pure (CP) Ti (99.58 Ti, 0.12 O, 0.18 Fe, 0.07 C, 0.04 N, 0.01 H wt%) was used as a substrate material. Samples were cut in the shape of plates with sizes of the 10×10×1 mm\(^3\) in order to be used as substrates for the deposition. The samples were polished in series using silicon–carbide paper up to 1200 grit. Prior to deposition, the samples were sonicated for 10 min consecutively in acetone, distilled deionized water, and ethanol. Samples were placed on the custom-made substrate holder with a built-in heater allowing to reach a temperature of ~500°C. RF-power was ramped up to the working level of 250 W in a step-wise manner (50W per 15 min) in order to ensure slow and homogeneous heat distribution along the surface of the target. Three regimes of in-situ heating were applied, being 100, 200, 300 and 400°C. The sample holder was heated in a step-wise manner with a heating rate of 50 min\(^{-1}\). The temperature of the samples was controlled by a chromel-alumel thermocouple. Pre-heated samples were moved in a position under target erosion zone by the carousel mechanism in a
vacuum chamber. The argon gas pressure (base pressure $10^{-5}$ Pa, working pressure 0.7 Pa) and the distance between substrate and target (60 mm) were kept constant. Deposition time was set to 3 hours in all sputtering cases. The average thickness of the coatings deposited at elevated temperatures, as measured by a Calotest (CSEM Instruments) were 150-200±15 nm.

Investigation of the phase composition was done by X-ray-diffraction (XRD) analysis (DRON-7, Burevestnik, Russia). The XRD experiments were carried out using the Bragg-Brentano geometry with angle $2\theta=15^\circ$–$60^\circ$, radiation source with CoKα radiation ($\lambda=1.7890$ Å) and scanning by steps of 0.01°. Phases were identified with reference to the ICDD database (card number for HA is 9-432). Phase identification was performed with a usage of the PDF-2 database, in the total profile analysis software POWDER CELL 2.4. To investigate the microstructure of the deposited HA-Zn films, transmission electron microscope (TEM) JEM 2100 (JEOL, Japan) with in-column energy dispersive X-ray (EDX) elemental composition analyzer INCA-Energy microanalyzer (Oxford Instruments, UK) was used. The distribution of Ca, P, O, Ti and Zn in the coatings was determined by EDX in three different regions across the lamella. An average content and Ca/P ratio was determined accordingly.

For the cross-section sample preparation ion thinning equipment EM 09100IS ion slicer (JEOL, Japan) was utilized which is available at the Center for Collective Use of Scientific Equipment “Nanotekh” of ISPMS SB RAS. For the preparation of thin foils for investigation in TEM samples should be pre-thinned to 100 µm before to the processing in an ion slicer by conventional grinding and polishing techniques. A final thinning is performed in low-energy and low-angle Ar-ion beam mode.

3. Results and Discussion

It is well-known that the coating deposition under elevated substrate temperatures leads to increased adatoms movement. It may result in partial crystallization of the coating and structure texturization. As it is seen in figure 1, starting from 300°C coatings recrystallization occurs with texturization and preferential orientation of HA crystals in the (002) plane. According to A. Ivanova et al. [6], the (002) plane in the HA crystals is a plane of the lowest surface energy. Therefore, HA coatings tend to grow with a (002) orientation in order to minimize the surface energy. The effect is more pronounced at the temperature of 400°C and additional growth orientation for HA crystals in the (112) plane. Thus, coatings of HA-Zn deposited on the Ti substrate under evaluated temperature starting from 300°C have a crystalline structure. At the lower substrate temperatures (100°C and 200°C), no intensity peaks corresponding to HA structure were detected.

![Figure 1](image1.png)

**Figure 1.** XRD diffractograms of the HA-Zn thin films deposited under 300°C and 400°C.

In figure 2 cross-section TEM of HA-Zn coating on Ti deposited under 400°C substrate temperature is presented. The coating is located between two white lines. The coating is formed by the polycrystalline state. Selected area electron diffraction (SAED) gathered from the region of the coating is represented by the bright discrete single spots and low-intensity diffusive halos. It is confirming a
polycrystalline coating’s structure. From SAED interplanar d-spacings were calculated to be 3.44; 3.16; 2.82; 2.783 which is corresponding to (002), (102), (211) and (112) crystal planes. The thin amorphous region of several monolayers in thickness is believed to be a TiO$_2$ layer and play an essential role in the coating-to-substrate adhesion according to our previous study. Coating thickness determined from the TEM images is 140±20 nm. The coating has preferential orientation and represented by a zoned structure having grains and sub-grains. In the dark-field image of the (002) which has the highest intensity various crystallites stackings and sub-grains are seen.

![Image of HA-Zn coating with TiO$_2$ layer and Ti substrate with 50 nm scale bar in (a) and (b).](image)

**Figure 2.** Cross section of HA-Zn bright (a) and dark-field images (b).

In the other region of the lamella, columnar nature of the polycrystalline coating is more clearly revealed (figure 3). In the dark-field image (figure 3 b) the columnar grains extending throughout the coating thickness are seen. The direction of the growth is clearly seen to be highly orientated and to be perpendicular to the substrate surface. The average grain width is calculated to be 30–90 nm in several different lamella regions. The grains are densely packed and are located close to each other. Observed dark-field image is obtained in (112) reflection from HA-Zn coating which has a high intensity in SAED. Moreover, this plane was clearly seen in XRD diffractograms for the substrate deposited at 400°C The amorphous interlayer is also presented in the micrograph. Note, the grains showed by the white dashed line in the bright-field image. Those grains are revealed to be consisting from smaller grains with distinct grain borders in the dark-field image.

![Image of HA-Zn coating with Epoxy and Ti substrate with 100 nm and 50 nm scale bar in (a) and (b).](image)

**Figure 3.** Cross section of HA-Zn bright (a) and dark-field images (b).
The above-mentioned region of interest (ROI) was used for EDX measurements. Indicative EDX spectra are presented in figure 4. The average Ca/P ratio gathered from the coating region is equal to 1.5 which is indicating substoichiometric HA composition. Both Zn substitution and preferential phosphate groups desorption from the coating during condensation under evaluated temperatures could play a role in the existing elemental composition.

![EDX data measured from the HA-Zn coating region of TEM lamella.](image)

Figure 4. EDX data measured from the HA-Zn coating region of TEM lamella.

In figure 5 EDX mapping of the HA-Zn coating on a Ti substrate is seen. Due to a small concentration of Zn substituents EDX analysis was not able to detect this element. However, distribution of Ca, P, Ti and O elements are in good accordance with the expected results and represents an elemental distribution as it was intended.

![EDX element mapping of the HA-Zn and Ti substrate in TEM lamella.](image)

Figure 5. EDX element mapping of the HA-Zn and Ti substrate in TEM lamella.
4. Conclusion
In-situ substrate heating during the HA-Zn coating deposition is proved to be an effective method for coatings’ structure tailoring. According to XRD data, coating crystallization occurred from 300°C substrate temperature. Coatings that were deposited at 400°C are represented by the columnar type of structure with preferential (002) orientation according to cross-section TEM. An amorphous TiO$_2$ sublayer of several monolayers thickness was detected in the interface between the polycrystalline coating and the Ti substrate in all lamella regions which contributes to the high coating to substrate adhesion level. Deposited coatings are shown to be substoichiometric with Ca/P ratio of 1.5. In-column EDX mapping indicated the presence of Ca, P, O and Ti elements distribution as it was originally intended. Thus, in-situ substrate heating is to be used for tailoring the coatings’ crystallinity state and is a prospect in the deposition of gradient multi-layer coatings.

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