Deposition of calcium phosphate coatings using radio frequency magnetron sputtering of substituted β-tricalcium phosphate targets

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Abstract. The influence of magnesium and/or strontium substitutions on the deposition rate of β-TCP was investigated. Pure β-TCP, Mg-β-TCP, Sr-β-TCP and Mg/Sr-β-TCP targets were used for the coating formation. It was shown that strontium substitutions in the structure of β-TCP target increase the deposition rate of coatings. Magnesium substitutions, on the contrary, decrease this parameter. It makes it possible to increase the deposition rate of coatings formed by radio frequency magnetron sputtering without any negative effect on coatings properties. It was demonstrated that all coatings formed by radio frequency magnetron sputtering of β-TCP targets were calcium-rich. The methods of AFM and SEM revealed that coatings under study were characterized by various morphologies. Magnesium-containing coatings (Mg-β-TCP and Mg/Sr-β-TCP) had the lower value of nanohardness than other ones. All coatings were characterized by the higher value of surface free energy than titanium substrate. The coatings formed by sputtering of β-TCP, Mg-β-TCP, Sr-β-TCP had approximately the same value of this parameter.

1. Introduction

Implants, produced on the basis of metals and their alloys, are common in the reconstructive surgery and used for bone defect treatment. In particular, titanium meshes are used in craniofacial surgery for the reconstruction of the bone tissue structure [1]. Regeneration of the skull bones injuries allows avoiding serious pathologies, such as enophthalmos and diplopia [1]. The essence of surgical operation is the removal of damaged bone tissue and its subsequent replacement by a titanium mesh. The mesh structure of the implant makes it possible for the surgeon to adapt its shape to the individual trauma features of the patient. Moreover, it allows growing of the bone tissue into the implant. This process increases the stability of its fixation [2, 3].

The use of titanium for the implant is due to its mechanical strength. However, the use of metal implants is connected with the risk of the metallosis occurrence and, as a consequence, loosening of implanted structures and the development of extensive inflammation at the site of implantation [4]. Various coatings, which are not rejected by the organism and avoid the unwanted contact of the metal implant base, are used [4].
There are many various ways of forming biocompatible coatings on the metal implant surface, namely, plasma spraying, a sol-gel method, electrochemical, electrophoretic and biomimetic deposition, microarc oxidation, radiofrequency magnetron sputtering etc. [5].

One of the most important requirements for coatings on titanium mesh is theirs high adhesion strength. Therefore, the deposition of coatings was carried out using radiofrequency magnetron sputtering (RFMS). Advantages of this technology include high adhesion strength and better control of chemical composition of deposited coatings by varying the chemical composition of the sputtered targets, chamber pressure and discharge parameters [6].

It is widely known that the type of CaP material, used for the coating deposition, affects the deposition rate [7]. β-tricalcium phosphate (β-TCP) was chosen for our study because of its high deposition rate and good biological properties. Four various types of targets based on apatitic β-TCP were studied. The first one was pure β-TCP. The second one was Mg-substituted β-TCP (Mg-β-TCP) with the content of the magnesium substitution of 1.53±0.01 wt.%. The third target was Sr-substituted β-TCP (Sr-β-TCP) with the content of the strontium substitution of 3.39±0.09 wt.%. The latter one was Mg- and Sr-substituted β-TCP (Mg/Sr-β-TCP), which contained magnesium and strontium substitutions of 1.18±0.22 wt.% and 3.68±0.06 wt.% respectively.

The purpose of our work was to investigate the influence of ionic substitutions on the deposition rate of β-TCP and coatings properties.

2. Materials and methods

2.1. Production of targets
Four different types of targets were manufactured in Riga Technical University (Prof. Janis Locs) using wet chemical precipitation method.

2.2. Coating deposition
All coatings were deposited using the upgraded magnetron sputtering system «Cathode 1M» equipped with the radio frequency generator (13.56 MHz). The preliminary pressure in the chamber was 10⁻³ Pa, and working pressure (Ar) was 0.5 Pa. The distance between the sputtered target and surfaces was 40 mm. The discharge power was 1.5 kW, and the reflected one was 400 W. The deposition time was 21 hour.

2.3. Profilometry
The evaluation of thickness and roughness of coatings was carried out using contact profilometer TalySurf-5 (Taylor & Hobson, UK). Coatings were deposited on silicic substrates in order to determine their thickness. Part of the substrate was covered with a mask to obtain a "step".

2.4. Atomic Force Microscopy (AFM)
The surface structure of the samples was studied by atomic force microscopy using the Solver-HV setup (NT-MDT, Russia).

2.5. Scanning electron microscopy (SEM) and Energy-dispersive X-ray spectroscopy (EDX)
The morphology of the coating surface and their chemical composition were studied using scanning electron microscope QUANTA 200 3D (FEI, USA) equipped with energy-dispersive X-ray spectroscope JSM-5900LV (JEOL Japan). Thin gold film (~30 nm) was deposited on the coatings using SC7640 (Quorum Technologies Ltd, UK) magnetron sputtering system.

2.6. Coating Wettability
The wetting contact angle of the calcium phosphate coatings was determined using the "Easy Drop" (Krüss, Germany) setup. Water and dimethylformamide (DMFA) were used as wetting liquids. The
volume of each drop of liquid was 2 ml. The calculation of the surface free energy (SFE) was carried out by the OWRK method (the method of Owens, Wendt, Rabel and Kaelble).

2.7. Nanoindentation test
The mechanical properties of the coatings were tested using a NanoScan-4D nano-hardness tester (FSBI TISNCM, Russia). The maximum load on the indenter was 5 mN.

3. Results and discussion
The study revealed that the presence of strontium substitutions in the β-TCP structure increase the deposition rate of coatings. Magnesium substitutions, on the contrary, decrease this parameter. The deposition rate from each target in decreasing order was Mg/Sr-β-TCP (48.6±1.5 nm/h) > Sr-β-TCP (47.1±1.4 nm/h) > β-TCP (30±0.9 nm/h) > Mg-β-TCP (26.7±0.8 nm/h).

According to Ozeki and coauthors [7], materials with a low density are characterized by the high deposition rate. This was demonstrated using Sigmund theory of sputtering. The influence of magnesium and strontium substitutions in the β-TCP structure on the material density was investigated previously [8]. Strontium substitutions decrease the density of β-TCP, magnesium ones increase this parameter [8].

The β-TCP structure is characterized by the hexagonal lattice. The parameters of the unit cell of pure β-TCP are a=b=10.4380 Å, c=37.4016 Å; α=β=90 ° and γ=120 °. According to [9], magnesium substitutions reduce the a-parameter to 10.3375 Å, and the c-parameter to 37.175 Å at a concentration of magnesium substitutions of 10.5 mol%. It leads to an increase in the density of the material. Strontium substitutions increase the unit cell size causing the decrease in density. Authors explain this result by the difference in size of substituting and substituted ions. Thus, it can be concluded that magnesium and strontium substitutions influence the β-TCP density and cause the change in the material deposition rate.

The characteristics of coatings were measured using the SEM and AFM technologies. The wettability of samples was measured using contact angle method. The study results are shown in figure 1. The initial surface of the titanium sample is smooth with shallow scratches from polishing. The average surface roughness (Ra) of the sample is 0.157±0.009 μm. AFM studies revealed the granular structure of the sample surface (figure 2A). Figure 2B shows the surface of the coating formed by sputtering the β-TCP target. There are irregularities in the surface of the coating with Ra is 0.402±0.026 μm. Research at higher magnification did not reveal any structure. The coating formed by sputtering of the Mg-β-TCP target, which is shown in figure 2C, is characterized by a wavy surface. The average surface roughness is 0.399±0.010 μm. The coating structure is non-uniform grains. The coating deposited by sputtering of the target based on β-TCP with the Sr substitutions (Sr-β-TCP) also has a wavy surface with the roughness of which is 0.326±0.065 μm. It should be noted that the structure of coatings formed by sputtering the targets of Mg-β-TCP and Sr-β-TCP differs significantly. Thus, the grain size of the coatings formed by sputtering of strontium-substituted targets is significantly smaller than the grain sizes of the coatings that were formed by sputtering of the Mg-β-TCP target. Coatings formed by sputtering of Sr-β-TCP targets consist of grains of spherical shape. The wavy surface of coatings formed by sputtering of Mg/Sr-β-TCP has an average roughness of 0.161±0.017 μm.

Moreover, calcium phosphate coatings are characterized by higher wettability than polished Ti (figure 1). Their surface free energies were calculated based on the contact angle of surfaces. β-TCP, Mg-β-TCP and Sr-β-TCP samples have the highest value of SFE (77.7±2.1, 74.2±1.8 and 76.7±2.7 mN/m respectively). The value of this parameter for Mg/Sr-β-TCP sample is lower than other groups of coatings (64.3±0.7 mN/m) with polished Ti having the lowest value of SFE (42.8±0.3 mN/m). These data agree well with the values of roughness measurements: the largest value of SFE corresponds to the maximum roughness of the SFE and vice versa. It is well known that microtopography and the surface roughness are closely associated with the SFE value and, hence, with the value of surface wettability. The rough surface has a large contact area of the liquid with the solid
as compared to the smoother one. In turn, an increase in the area of actual contact leads to a proportional increase in the surface free energy of the rough surface compared to the smoother surface.

![Image of SEM and AFM images](image_url)

**Figure 1.** SEM (on the left) and AFM (on the right) images of the samples surfaces and their contact angles images (inserts): A – polished titanium, B – β-TCP, C – Mg-β-TCP, D – Sr-β-TCP; E – Mg/Sr-β-TCP.

Tests of mechanical characteristics revealed that magnesium dopes decrease coatings nanohardness. No other differences between other groups of coatings were found. All coatings are harder than polished Ti. The values of nanohardness of polished Ti, β-TCP, Mg-β-TCP, Sr-β-TCP and Mg/Sr-β-TCP are 3.5±0.4, 10.7±1.1, 8.7±1.3, 10.0±2.7 and 5.3±0.6 GPa respectively.

According to data obtained by EDX method, ratios Ca/P in targets and coatings differ significantly. Their values are presented in figure 2. This difference can be explained by the fact that argon ions...
transfer more energy to calcium atoms than to phosphorus ones because of the smaller difference in 
masses of bombarding and sputtered particles. Thus, all coatings, formed by $\beta$-TCP targets sputtering, 
are calcium rich compared to targets.

![Figure 2. Ratio Ca/P in targets and coatings.](image)

4. Conclusion
The properties of $\beta$-TCP, Mg-$\beta$-TCP, Sr-$\beta$-TCP and Mg/Sr-$\beta$-TCP coatings and its deposition rate 
were investigated. It was shown that strontium substitutions in the structure of $\beta$-TCP increase the 
deposition rate of coatings. Magnesium, on the contrary, decreases this parameter. Thus, it should be 
concluded that ionic substitutions in the $\beta$-TCP structure are a promising technology helping to 
overcome the main disadvantage of the RFMS without worsening of coatings properties.

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