Formation of bioactive coatings by radio frequency magnetron sputtering using various calcium phosphate targets and working gases

A Y Fedotkin, A I Kozelskaya and S I Tverdokhlebov
Tomsk Polytechnic University, 30, Lenin Ave., Tomsk, 634050, Russia
E-mail: tverd@tpu.ru

Abstract. The influence of working gas and the sputtered target composition on physico-chemical properties and the deposition rate of the coatings formed by radio frequency magnetron sputtering was studied. The deposition rate of the CaP coatings formed by sputtering of the HA target in Ar and Kr is greater than that of coatings formed in Xe. Strontium substitutions in the composition of β-tricalcium phosphate targets lead to the increase in deposition rate. Magnesium ones slightly decrease it.

1. Introduction
One of the most important requirements for bioactive calcium phosphate (CaP) coatings of the implants for bone regeneration is their resorption rate. The resorption rate of the coatings should correlate with the rate of new bone forming, which depends on age, activity and health of the patient. The effective ways to vary resorption rate are the use of biphasic calcium phosphate (BCP) materials and the use of substituting elements in the sputtered material. It allows not only to vary the coating solubility but also to influence its physico-chemical and biological properties.

While radio frequency magnetron sputtering, the use of various CaP targets with substituting elements and of biphasic materials targets influences not only coating properties but its deposition rate. It is a very important technological parameter. The use of the targets with the optimal chemical composition and of the sputtering parameters allows not only to improve the chemical properties of coatings but also to increase their deposition rates, and, thereby, to increase the effectiveness of radio frequency magnetron sputtering technology.

The influence of working gas on the deposition rate and on the properties of coatings formed by magnetron sputtering of various metallic and nonmetallic targets was studied in [1–4]. However, the influence of various inert working gases on the deposition rate and on the properties of CaP coating for reconstructive surgery applications have never been investigated. BCP ceramics is a mixture of the stable hydroxyapatite (HA) phase with the more soluble β-tricalcium phosphate (β-TCP) one, so designing BCP coating it is necessary to take into account the properties of HA and TCP both. The influence of Mg and Sr substitutions in HA target is already described in the literature [5, 6], but the effect of these substitutions in β-TCP on the coatings properties is not discovered. This knowledge allows to increase the deposition rate of the BCP coating and to vary its properties.

This work is a pilot study of the effect of working gas, while sputtering of the HA target, and Mg and Sr substitutions, while sputtering of the β-TCP targets, on the properties and the deposition rate of the coatings.
2. Materials and methods
Titanium discs with a diameter of 10 mm and with the thickness of 1 mm were used as substrates. The substrates were mechanically ground and polished before the coating deposition. The coatings were formed using the upgraded magnetron sputtering system “Cathode 1M” equipped with the radio frequency generator (13.56 MHz). The distance between the target and the substrate was 40 mm, and the target area was 224 cm².

The effect of working gas on the properties and the deposition rate of the CaP coatings was investigated by sputtering of pressed HA target in Ar, Kr and Xe. The working pressure was 0.3 Pa, the power density was approximately 5.2 W/cm² and the time of the deposition was 7 hour.

In order to investigate the influence of the Mg and Sr substitutions in composition of CaP targets on deposition rates of coatings formed in Ar, four various powder targets were used: β-TCP, Mg-substituted β-TCP (Mg/β-TCP, Mg = 1.53±0.01 wt.%), Sr-substituted β-TCP (Sr-β-TCP, Sr = 3.39 wt.%), and Mg- and Sr-substituted β-TCP (Mg/Sr-β-TCP, Mg = 1.18±0.22 wt.; Sr = 3.68±0.06 wt.%). The working pressure was 0.5 Pa and the power density was approximately 4.8 W/cm². The time of the deposition process was 21 hour.

Morphology, composition and mechanical properties of coatings were studied using contact profilometry, atomic force microscopy, energy dispersive spectroscopy and X-ray diffraction analysis.

3. Results and discussion
The thicknesses of the CaP coatings formed by sputtering of HA target in various working gases are different. CaP coatings deposited in Ar and Kr are characterized by a higher thickness in comparison with the coating formed in Xe. This is consistent with the results of [2, 3], in which the sputtering of TiO₂ and SiO₂ targets in various inert gases was carried out. It was shown that with an increase in the atomic mass of the working gas, a decrease in the deposition rate is observed.

The presence of Sr substitutions in β-TCP target increases the deposition rate of the coatings, however, magnesium ones slightly decrease it (table 1). When the Mg- and Sr-cosubstituted target is used, the influence of Sr has a more significant effect on the deposition rate than Mg.

The initial substrate has a smooth surface, on which there are shallow traces of polishing (figure 1(a)). CaP coatings formed by sputtering of the HA target in Ar and Kr are characterized by quasi-equiaxed grains with the size of 0.07 μm and 0.43 μm², respectively (figure 1(b), (c)). The surface of the coating formed in Xe is smooth without any grains, which indicates the amorphous structure of the coating (figure 1(d)).

The surface of the coatings formed by sputtering of the powder β-TCP target (figure 1(e)) is smooth and wavy, while the surfaces of the coatings formed by sputtering Mg-β-TCP, Sr-β-TCP and Mg/Sr-β-TCP targets are characterized by equiaxial grains with a size of 0.015 μm², 0.02 μm² and 0.04 μm², respectively (figure 1(f), (g), (h)).

| Coating       | Thickness, nm | Deposition rate, nm/h |
|---------------|---------------|-----------------------|
| HA(Ar)        | 2010±80       | 287±11                |
| HA(Kr)        | 1920±30       | 274±4                 |
| HA(Xe)        | 1180±130      | 169±19                |
| β-TCP         | 630±19        | 30±1                  |
| Mg-β-TCP      | 560±16        | 27±1                  |
| Sr-β-TCP      | 990±30        | 47±1                  |
| Mg/Sr-β-TCP   | 1020±31       | 49±1                  |

According to table 2, the Ca/P ratio of all coatings under study is higher than the values of Ca/P ratios of stoichiometric CaP target materials (HA=1.67, β-TCP=1.5). The value of Ca/P ratio of the HA coating formed in Xe is especially high in comparison with ones formed in Ar and Kr. It should be
noted that the presence of Mg substitutions decrease the Ca/P ratio, however, Sr substitutions increase this parameter.

**Figure 1.** AFM images of the surface of the initial substrate (a), CaP coatings formed by sputtering of the HA target in Ar (b), Kr (c) and Xe (d), as well as coatings deposited by sputtering of β-TCP (e), Mg-β-TCP (f), Sr-β-TCP (g) and Mg/Sr-β-TCP (h) targets.

**Table 2.** Elemental composition of coatings, at.%.  

| Coatings formed by deposition of HA in various inert gases | Ca | P | O | Ti | Al | Si | Ca/P |
|----------------------------------------------------------|----|---|---|----|----|----|------|
| Substrate                                               |    |   |   |    |    |    |      |
| HA (Ar)                                                 | 41.09±0.22 | 23.18±0.16 | 34.95±0.34 | 0.77±0.22 | –   | –   | 1.77±0.01 |
| HA (Kr)                                                 | 42.56±0.32 | 23.95±0.25 | 32.55±0.50 | 0.93±0.14 | –   | –   | 1.78±0.01 |
| HA (Xe)                                                 | 44.70±1.41 | 23.17±0.34 | 30.09±1.13 | 2.04±0.64 | –   | –   | 1.93±0.05 |

| Coatings formed by sputtering of various β-TCP-based targets in Ar | Ca | P | O | Mg | Sr | Ca/P |
|-------------------------------------------------------------------|----|---|---|----|----|------|
| β-TCP                                                             | 36.69±2.15 | 17.36±2.72 | 45.96±4.84 | –   | –   | 2.14±0.22 |
| Mg-β-TCP                                                          | 32.65±1.77 | 18.35±2.68 | 44.64±4.05 | 4.35±0.51 | –   | 1.80±0.17 |
| Sr-β-TCP                                                          | 35.81±7.37 | 12.76±3.10 | 48.91±7.70 | –   | 2.52±1.67 | 2.94±0.85 |
| Mg/Sr-β-TCP                                                       | 37.02±0.55 | 19.46±0.81 | 38.17±1.24 | 3.69±0.25 | 1.67±0.17 | 1.90±0.06 |

XRD analysis of CaP coatings revealed the presence of peaks corresponding to the titanium substrate and sputtered targets (figure 2). In the case of the coating formed in Xe, only peaks corresponding to the titanium substrate are observed, which indicates an amorphous structure of the coating. All the coatings formed by sputtering of the β-TCP-based targets have a crystal structure.

**4. Conclusions**

The atomic weight of inert working gas and the presence of ionic substitutions influence on the morphology, the composition of the CaP coatings, and their deposition rate. All the coatings under study have a higher than values of Ca/P ratios than stoichiometric HA and β-TCP.

The deposition rate of the CaP coatings formed by sputtering of the HA target in Ar and Kr is greater than that of coatings formed in Xe. The Ca/P ratio the coating formed by sputtering of the HA target in Xe is higher than in Ar and Kr. The coatings formed in Ar and Kr are characterized by quasi-equiaxed grains with a size of 0.07 µm² and 0.43 µm², respectively, and have a crystal structure. The surface of the coating formed in Xe is smooth, without any grains.

The presence of strontium substitutions in the β-TCP target structure increases the deposition rate, but magnesium substitutions, on the contrary, slightly decrease it. The surface of Mg-β-TCP, Sr-β-
TCP and Mg/Sr-β-TCP coatings are characterized by equiaxed grains with a size of 0.015 μm$^2$, 0.02 μm$^2$ and 0.04 μm$^2$. The addition of Mg substitutions in β-TCP target structure reduces the Ca/P ratio, Sr ones increase it. All β-TCP-based coatings have a crystalline structure.

![Figure 2](image.png)

**Figure 2.** XRD-spectra: (a) – the initial titanium substrate and coatings formed by sputtering of HA target in various inert gases; (b) – coatings formed by sputtering of β-TCP-based targets.

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