Effect of working gas on the deposition rate of CaP coatings formed by radio frequency magnetron sputtering of a hydroxyapatite target

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Abstract. This study is dedicated to the influence of the inert working gas on the deposition rate of CaP coatings formed by radio frequency magnetron sputtering of a hydroxyapatite target in Ar, Kr and Xe. The optical emission spectra of plasma, the elemental and phase composition of the formed coatings are investigated. The deposition rates of the CaP coatings formed in Ar and Kr are approximately comparable and higher than ones formed in Xe.

1. Introduction
Calcium phosphate (CaP) coatings are deposited on the metal implant surfaces in order to increase their biocompatibility. These coatings prevent unwanted contact of the metal base of the implant with body tissues. One of the promising methods of CaP coating deposition on the implant surface is radio frequency magnetron sputtering (RFMS). The coatings formed by this method are homogeneous in chemical composition and have high adhesion to the substrate.

The deposition of CaP coatings by RFMS is usually carried out in Ar. In [1, 2], the influence of the working gas on the properties of the deposited coatings with various compositions is described. However, the effect of the working gas on the properties and on the deposition rate of CaP coatings for medical purposes is not described in literature.

The study of the working gas effect on the deposition rate and physicochemical properties of CaP coatings formed by the RFMS in Ar, Kr, and Xe is the purpose of this research.

2. Materials and methods
Titanium (VT6) disks with a diameter of 10 mm and a thickness of 1 mm were used as substrates for CaP coatings deposition. They were subjected to mechanical grinding and polishing before the coatings deposition. The deposition was carried out using the upgraded magnetron sputtering system «Cathode-1M», equipped with an RF generator with a frequency of 13.56 MHz. A solid target made from pressed hydroxyapatite (HA) with an area of 224 cm² was used for sputtering. The distance between the target and the substrate was 40 mm. Working pressure was 0.3 Pa. Power density was approximately 5.2 W/cm². The deposition time was 7 hours. Ar, Kr and Xe were used as working gases.

The plasma chemical composition was studied by optical emission spectroscopy (OES). CaP coating thicknesses were measured by analyzing the side face of the substrate with CaP coating by scanning electron microscopy. The elemental and phase compositions of the coatings were investigated using energy-dispersive spectroscopy (EDS) and X-ray diffraction (XRD) analysis.
3. Results and discussion
The analysis of optical emission spectra of the plasma, carried out during the sputtering of HA in various inert gases, revealed the presence of the peaks corresponding to atomic (Ca, P, O) and molecular (CaO, PO, H₂O, OH, CaOH, H₂) ions (figure 1). This fact was explained by the elemental composition of the sputtered target. The presence of molecular water ions H₂O in the plasma spectra is associated with the decomposition of the hydroxyl group of the HA target, which also explains the presence of oxygen ions. The peaks corresponding to Ca had the highest intensity among peaks corresponding to other sputtered particles during the sputtering of HA in Xe. It should be noted that, when the HA target is sputtered in Ar, the relative intensities of the peaks corresponding to the oxygen-containing ions (O, CaO, PO, H₂O) were high compared with the other groups under study, which indicates a high content of O in a flux of sputtered particles. There was no significant difference in the thicknesses of CaP coatings deposited in Ar and Kr (2010±80 nm and 1920±30 nm, respectively). The coatings formed in Xe had a lower value of this parameter (1180±30 nm).

The study of the coating elemental compositions revealed a significant decrease in the content of O with an increase in the working gas atomic weight (table 1), which was in good agreement with the results of OES. In addition, as the atomic weight of the working gas increases, the content of Ca in the coatings increases. This also agreed with the OES results. The Ca/P ratio in the coating decreased with an increase in O content in plasma [3] since oxygen binds phosphorus atoms. Therefore, the Ca/P ratio in the coatings formed by sputtering of the HA target in an Ar and Kr were closer to the value of this parameter of the stoichiometric HA compared to coatings deposited in Xe.

Table 1. Elemental composition of the substrate and CaP coatings, at%.

| Sample | Ca     | P     | O     | Ti    | Al    | Si    | Ca/P |
|--------|--------|-------|-------|-------|-------|-------|------|
| Substrate | –      | –     | –     | 93.4±0.13 | 5.36±0.06 | 1.24±0.12 | –    |
| 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 |

The XRD analysis (figure 2) revealed the presence of the HA crystal phase (JCPDS database, file # 09-0432) in the coatings formed in Ar and Kr, which could be explained by relatively high substrate
temperatures (250°C). The temperature of coatings formed in Xe was 188°C, and the coatings were characterized by fully amorphous structure.

Calculation of the texture coefficient carried out according to [4] revealed that the preferential orientation of the coatings formed in Ar and Kr was (002). According to [5], this HA plane is characterized by the lowest surface energy value. The coatings formed in Ar were characterized by a mixed structure with preferential orientations (002) and (102).

![Figure 2. XRD-spectra of the initial substrate and deposited coatings.](image)

4. Discussion

Sputtering of a multicomponent target in various working gases is a complex process that is influenced by many factors. The threshold energy for sputtering of particle \( E_{\text{th}} \) for each pair of sputtered atom/bombarding ion and the surface binding energy \( U_s \) are ones of the most significant factors affecting sputtering process. The ratio of these parameters is a function of the ratio of masses of the sputtered particle \( M_2 \) and of the bombarding ion \( M_1 \) and can be calculated according to equation [6]:

\[
\frac{E_{\text{th}}}{U_s} = 1.9 + 3.8(M_2/M_1)^{-1} + 0.134(M_2/M_1)^{1.24}
\]

Due to the fact that the same HA target was sputtered in all gases, \( U_s \) can be accepted as unknown constant for all sputtering processes. It follows from the above that the change in \( E_{\text{th}} \) can be estimated using \( E_{\text{th}}/U_s \). Accepting \( M_1 \) as a constant, \( E_{\text{th}}/U_s \) depends on \( M_2 \) (figure 3a). It follows from the graph that an increase in the atomic mass of the working gas leads to an increase in the ratio \( E_{\text{th}}/U_s \) and, consequently, in \( E_{\text{th}} \). Moreover, the increase in working gas atomic weight increases the difference in \( E_{\text{th}} \) between Ca and O, as well as P and O.

Another important parameter affecting sputtering of HA is the ability of bombarding particle to transfer its energy to the sputtered one. The coefficient \( \gamma \), characterizing the part of energy transferred during the elastic collision of particles, is calculated by the equation [7]:

\[
\gamma = \frac{4M_1M_2}{(M_1+M_2)^2}
\]

As in the case of the \( E_{\text{th}} \), the coefficient \( \gamma \) depends on \( M_2 \). The dependence of \( \gamma \) on \( M_2 \) when sputtering of HA target in various working gases is presented in figure 3b.

On the one hand, the decrease in the working gas atomic weight leads to the increase in \( \gamma \) and to the decrease in \( E_{\text{th}} \) for Ca and P, which causes the increase in coating deposition rate. On the other hand, the decrease in working gas atomic weight decreases \( E_{\text{th}} \) of O more significantly. According to [3], the presence of 1% oxygen in the chamber reduces the sputtering yield of the target by 60%. EDS-analysis revealed the decrease in the content of O in the coating compositions with the increase in working gas atomic weight. According to OES data, the increase in working gas atomic weight also leads to the decrease in oxygen-containing ions content in discharge plasma. These results correlate well and allow us to suppose that the decrease in working gas atomic weight leads to the increase in O content in the
sputtered particles flux, which, in its turn, reduces the coating deposition rate. The authors of [1, 2] claim that the coatings deposition rate increases with a decrease in working gas atomic weight. This increase is caused by the decrease in sputtered particles scattering with the decrease in working gas atomic weight [1].

![Figure 3. The dependence of ratio E₀/Uₙ (a) and the energy transfer coefficient (γ) (b) on M₂.](image)

Results of this study allow us to suppose that not only the sputtered particles scattering affects the deposition rate of the coatings. Thus, the closeness of deposition rates of the coatings formed in Ar and Kr can be explained by the effect of a variety of competing processes.

5. Conclusion
Coatings formed in Ar and Kr are characterized by similar values of deposition rate, which exceed the deposition rate of the coatings formed in Xe. The ratio Ca/P in the coatings formed in Xe significantly exceeds the value of this parameter in stoichiometric HA. Formed in Xe CaP coatings are amorphous, in contrast to the coatings formed by sputtering of HA target in an Ar and Kr.

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