Properties of CaP coatings produced by reactive RF-magnetron sputtering in a mixture of nitrogen and noble gases

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Abstract. Calcium phosphate coatings are widely used to increase the biocompatibility of metal implants. Nowadays various dopants in the structure of calcium phosphate coatings are actively studied. Nitric oxygen is known as an essential mediator of blood flow. Its presence in the structure of calcium phosphate coating can stimulate angiogenesis and promote osseointegration of the implant. This article is dedicated to the study of morphology and physico-chemical properties of the calcium phosphate coatings formed via reactive RF-magnetron sputtering of hydroxyapatite in the mixture of noble gases (Ne, Ar and Xe) and nitrogen with the same volume concentrations. There is a decrease in grain size and an increase in roughness with the growth of the atomic mass of noble gas in the mixture with nitrogen. The Ca/P ratio also decreases with the increase in the atomic mass of noble gas. Coatings formed in Ne+N$_2$ and Xe+N$_2$ gas mixtures are characterized by higher surface free energy in comparison with the ones formed in Ar+N$_2$. It allows us to suggest that the coatings formed in Ne+N$_2$ and Xe+N$_2$ are more biocompatible than ones formed in Ar+N$_2$, however, additional studies are needed to prove it.

1. Introduction
Metals are widely used in medical material science as a carcass of implants for bone defect restoration due to their suitable mechanical properties. However, the lack of biocompatibility makes it necessary to form special coatings on their surfaces. As a rule, a wide range of calcium phosphate (CaP) coatings is used to prevent unwanted contact between the metal surface and body liquids to avoid metallosis. Moreover, the chemical composition of CaP coatings is very close to the composition of human bone, thus deposition of CaP coatings increases the bioactivity of the implant.

There are lots of methods of CaP coatings deposition: plasma spraying; sol-gel, electrochemical, electrophoretic, biomimetic deposition; microarc oxidation; radiofrequency magnetron sputtering (RF-magnetron sputtering) and other methods [1].

One of the most crucial demands of CaP coatings is good adhesion. RF-magnetron sputtering provides it well. Moreover, this method also provides the possibility of CaP coating composition regulation by varying the composition of the target, the deposition parameters and the working gas [2]. Reactive RF-magnetron sputtering is provided by adding reactive gas into the chamber.

In recent years, studies of doped and substituted CaP coatings are actively carried out. Introducing the implant into the organism, almost all major systems are involved in forming its defense mechanisms: cardiovascular, nervous, etc. The use of nitric oxygen (NO) as a dopant is desirable due
to its regulatory effect on vascular tone, cell adhesion, vascular permeability, platelet aggregation, antioxidant activity, inhibition of leukocyte adhesion [3]. It is also worth noting that nitric oxide plays an important role in the regulation of blood flow, expanding or narrowing the lumen of blood vessels in accordance with the need.

Our studies demonstrate that reactive RF-magnetron sputtering of hydroxyapatite (HA) in the mixture of argon and nitrogen with different concentrations allows forming of NO-containing CaP coatings. The concentration of NO in the coating increases with the increase in the amount of nitrogen in the chamber. Biological studies revealed that the cell viability increases with the increase in nitrogen concentration in the chamber (with the increase in NO concentration in the coatings, respectively) up to 50 vol.%. The further increase in nitrogen concentration in the chamber leads to the appearance of cytotoxic properties of NO. It was shown that the optimal concentration of nitrogen in the chamber is 50 vol.%. However, in scientific literature, there is no information about the studies of the effect of mixtures of nitrogen and inert gases on the properties of CaP coatings during the process of reactive RF-magnetron sputtering.

In the work [4], CNx coatings were deposited in gas mixtures of Ne and N2, Ar and N2, as well as Kr and N2 by magnetron sputtering of the carbon target. It was revealed that the process of coating deposition in the Ne and N2 mixture is characterized by the highest amounts and energies of the plasma species due to the Penning effect. CaP coatings obtained in a mixture of the same gases are of interest to research.

Our study of the influence of pure inert working gas on the biological properties of CaP coatings [5] revealed that the coatings formed in Xe have the highest cell viability among the coatings formed in other gases. Presumably, the coatings formed in the mixture of Xe and N2 with the same volume concentrations will show better biological properties than in pure Xe and in the mixture of Ar and N2.

In this paper, the properties of CaP coatings formed in Ne and N2 (Ne+N2), Ar and N2 (Ar+N2), Xe and N2 (Xe+N2) gas mixtures with the same vol.% are under study.

2. Materials and methods

2.1. Coatings deposition

Deposition of CaP coatings was carried out by reactive RF-magnetron sputtering of hydroxyapatite with the use of a self-made RF-magnetron setup. Ne and N2, Ar and N2, Xe and N2 gas mixtures were used in the reactive sputtering process. Titanium (VT6) substrates were ground and polished with the use of Unipol-802 (Zhengzhou TCH Instrument Co., Ltd, Zhengzhou, China) setup. All the coatings were deposited on the substrates under the following parameters: working pressure – 0.1 Pa, power – 500 W, target area – 240.5 cm2, target-substrate distance – 45 mm, time – 3 h, inert gas/nitrogen volume ratio – 1:1.

2.2. Research methods

The morphology of the coatings was studied using atomic force microscopy (NT-MDT, Zelenograd, Russia). Energy dispersive spectroscopy JSM-5900LV (JEOL Ltd., Tokyo, Japan) was used to determine the elemental composition of coatings. The study was carried out under a low vacuum and accelerating voltage of 10 kV. X-ray phase analysis of the coatings was performed with the use of an XRD-6000 (Shimadzu, Kyoto, Japan) diffractometer with CuKα radiation. The phase composition analysis was carried out using PDF 4+ databases and the full-profile analysis program “POWDER CELL 2.4”. Coatings wettability was measured with the use of the Easy Drop (Krüss, Hamburg, Germany) setup by the sessile drop method by measuring the contact angle of wetting of a liquid with a volume of 3 mL placed on the coating surface. Contact angles were determined for water, alcohol, and formamide. Surface free energy (SFE), its polar and dispersion components were calculated by the OWRK (Owens, Wendt, Rabel and Kaelble) method. The statistical reliability of the results was determined using a one-way analysis of variance and the Mann-Whitney U-test (Statistica 7.0, StatSoft, Tulsa, USA).
3. Results and discussion

In Figure 1 the morphology of the CaP coatings under study is shown. All the surfaces are represented with an agglomeration of grains with the areas $0.067 \, \mu m^2$, $0.012 \, \mu m^2$ and $0.01 \, \mu m^2$ for the coatings formed in Ne+N$_2$, Ar+N$_2$, Xe+N$_2$ gas mixtures, respectively. Grains of the coating formed in Ne+N$_2$ are non-uniform, while the coatings formed in Ar+N$_2$, Xe+N$_2$ are characterized with quasi-equiaxed grains. The $R_d$ parameter for the coatings formed in Ne+N$_2$, Ar+N$_2$, Xe+N$_2$ is 1.03 nm, 1.47 nm and 1.91 nm, respectively. According to the obtained data, grain size decreases and average roughness increases with the increase in atomic mass of the inert gas in inert gas/nitrogen mixture.

![AFM images of the CaP coatings formed in Ne and N$_2$, Ar and N$_2$, Xe and N$_2$ gas mixtures.](image)

Table 1 represents the elemental composition of the coatings under study. Ca, P and O correspond to the composition of the sputtered HA target. Due to the low thickness of the coatings, elements corresponding to the composition of the substrate (Ti and Al) are detected. The presence of C can be explained by traces of organic solvents. According to the table, the Ca/P ratio decreases with the increase in the atomic mass of working gas.

| Sample  | C       | O       | Al      | P       | Ca      | Ti      | Ca/P    |
|---------|---------|---------|---------|---------|---------|---------|---------|
| Ne+N$_2$| 4.93±1.26 | 29.36±1.34* | 5.5±0.25* | 1.33±0.11* | 2.01±0.12* | 56.87±0.75* | 1.52±0.15* |
| Ar+N$_2$| 5.08±0.77 | 24.85±1.83 | 6.2±0.28 | 0.92±0.25 | 1.09±0.13 | 61.86±0.88 | 1.21±0.17 |
| Xe+N$_2$| 5.93±0.8 | 25.09±2.57 | 6.27±0.34 | 1.47±0.19* | 1.28±0.14* | 59.96±1.65* | 0.89±0.14* |

* significant difference with Ar+N$_2$ group, p<0.05.

XRD-analysis (not shown in the article) of the samples revealed that all the coatings under study are characterized with an amorphous structure. The only peaks found in the XRD-spectra were corresponding to the substrate material. This result corresponds to the study of the properties of the coatings formed in Ar+N$_2$ mixtures with different volume ratios. At the same time, the study of coatings formed in pure Ne and Ar revealed a few peaks corresponding to crystalline HA [6]. It can be concluded that the presence of nitrogen in the chamber decreases the coatings crystallinity up to amorphous condition.

Table 2 represents the wettability of the coatings under study. The coatings formed in Ne+N$_2$ and Xe+N$_2$ have a better wettability for water and alcohol but worse for formamide in comparison with the coatings formed in Ar+N$_2$. Total SFE and its polar component of these coatings are also higher than these parameters calculated for the coatings formed in Ar+N$_2$. It can be suggested that the coatings formed in Ne+N$_2$ and Xe+N$_2$ have better biocompatibility than ones formed in Ar+N$_2$ because the high polar component of SFE stimulates cell adhesion [7].
Table 2. The contact angle of wetting with various liquids ($\theta_w$ – contact angle of wetting with water, $\theta_a$ – contact angle of wetting with alcohol, $\theta_f$ – contact angle of wetting with formamide) and SFE ($\sigma$) of CaP coating with its components ($\sigma^D$ – dispersive component, $\sigma^P$ – polar component).

| Sample      | $\theta_w$, deg. | $\theta_a$, deg. | $\theta_f$, deg. | $\sigma$, mJ/m² | $\sigma^D$, mJ/m² | $\sigma^P$, mJ/m² |
|-------------|------------------|------------------|------------------|-----------------|------------------|------------------|
| Ne+N₂       | 59.4±3.14*       | 10.3±2.63        | 34.2±2.64*       | 50.19±1.20*     | 3.85±0.29*       | 46.33±0.91*      |
| Ar+N₂       | 71.7±0.95        | 7.9±0.37         | 25.3±1.88        | 34.40±0.24      | 6.71±0.07        | 27.66±0.18       |
| Xe+N₂       | 58.5±1.07*       | 3.8±2.15*        | 35.3±2.09*       | 45.57±0.77*     | 5.30±0.25*       | 40.28±0.52*      |

* significant difference with Ar+N₂ group, $p<0.05$.

4. Conclusion
Calcium phosphate coatings were produced on titanium substrates by reactive magnetron sputtering of hydroxyapatite in the mixture of noble gases and nitrogen: Ne+N₂, Ar+N₂ and Xe+N₂. The type of inert working gas in the mixture with nitrogen significantly affects the properties of CaP coatings. An increase in the atomic mass of inert working gas decreases grain size and Ca/P ratio but increases the average roughness of the coatings. The XRD study of CaP coatings revealed only the peaks corresponding to titanium substrates. It can be suggested that the presence of nitrogen in the chamber decrease coating crystallinity up to amorphous state. The coatings formed in Ne+N₂ and Xe+N₂ have higher values of total SFE and its polar component in comparison with ones formed in Ar+N₂. Summing up, properties of the CaP coatings produced by reactive RF-magnetron sputtering in the gas mixture can be changed by varying the noble gas.

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