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Comparison Study on the Properties of the CaP Coatings Formed by RF-magnetron Sputtering of the Mg- and Sr-substituted β -tricalcium Phosphate and Hydroxyapatite

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Abstract—This article describes the influence of Mg and Sr substitutions in the structure of β -tricalcium phosphate and hydroxyapatite powder targets on the deposition rate of coatings formed via RF-magnetron sputtering and their properties. It was revealed that even low doses of ionic substitutions in β -tricalcium phosphate significantly affect deposition rate, morphology and physico-chemical properties of respective coatings. Similar doses of these substitutions in hydroxyapatite are not enough to influence the deposition rate, but they affect coating properties.

Keywords—calcium-phosphates, radiofrequency magnetron sputtering, ionic substitutions, thin films, implant coatings

I. INTRODUCTION

Metal implants for reconstructive surgery are usually modified with calcium phosphate (CaP) materials to increase their bioactivity and osteoconductivity. The most widely spread CaP materials used for this purpose are hydroxyapatite (HA) and β -tricalcium phosphate (TCP). Many articles are dedicated to the influence of ionic substitutions on the deposition rate of coatings and their physico-chemical and mechanical properties [1, 2]. Some of them have controversial conclusions because they were deposited under different conditions with the use of different sputtering systems. Moreover, the used targets were synthesized by different methods and characterized by various amounts of

substitutions.

In this work, we compare deposition rates and the properties of coatings formed under similar conditions, namely, the same sputtering system, the similar quantity of substitutions in sputtered targets as well as the most approximate coating deposition parameters. Respectively, the purpose of this work is to compare the influence of Mg and Sr substitutions in the composition of various sputtered targets (HA, TCP) on the deposition rate.

II. MATERIALS AND METHODS

Polished Ti (VT6) discs were used as substrates (diameter – 10 mm, thickness – 1 mm) for deposition of the CaP coatings by RF-magnetron sputtering of the Mg- and Sr-substituted β -tricalcium phosphate and hydroxyapatite. Grinding and polishing of the substrates were carried out with the use of the “Unipol-802” machine. The deposition of the coatings was performed by applying the upgraded universal magnetron sputtering system “Cathode-1M”. Six CaP-based powders were used as targets: pure hydroxyapatite (HA), Mg-substituted hydroxyapatite (Mg-HA), Sr-substituted hydroxyapatite (Sr-HA), pure β -tricalcium phosphate (TCP), Mg-substituted β -tricalcium phosphate (Mg-TCP) and Sr-substituted β -tricalcium phosphate (Sr-TCP). The number of substitutions in the composition of the sputtered targets was similar and was equal to $\sim 1.53\text{wt}\%$ for Mg and Sr in HA; $1.53\pm 0.01\text{wt}\%$ for Mg and $3.39\pm 0.09\text{wt}\%$ for Sr in TCP. Deposition processes were carried out under the following conditions: the distance between the target and the substrates was 40 mm; working pressure was 0.5 Pa; the power density was 5.26 W/cm^2 for the HA-based targets and

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4.8 W/cm² for the TCP-based targets. Sputtering of HA-based targets was carried out under the lower power density than TCP-based ones because of the technical condition of the sputtering system. In order to form the coatings with the same thicknesses for the correct comparison of physico-chemical properties of the coatings, the deposition time was 7 hours for the HA-based coatings and 21 hours for the TCP-based ones.

Optical emission spectroscopy HR2000+ (OceanOptics, USA) was used to study plasma discharge content in the wavelength range of 200-1000 nm. Coating thicknesses were studied by contact profilometry (Talysurf-5, Taylor & Hobson, UK). For this purpose, the polished Si sample was covered with Al foil to make a "step". Atomic force microscopy (Solver-HV, NT-MDT, Russia) was used to study the coating morphology. Obtained images were processed by applying the program (Nova SPM software, NT-MDT, Russia). The elemental composition of the coatings was measured by applying the energy dispersive spectroscopy method (JSM-5900LV, JEOL Ltd., Japan) at a low vacuum and an accelerating voltage of 10 kV. X-ray diffraction (XRD-6000, Shimadzu, Japan) method with the CuK α radiation at a right angle was used to measure the phase composition of the samples under study. The roentgenograms were analyzed with the use of PDF 4+ databases and the POWDER CELL 2.4 full-profile analysis program. The surface free energy (SFE) and its polar and dispersion components were calculated by the OWRK method from the water, glycerol, and dimethylformamide contact angles. The volume of each drop was 3 ml. The statistical reliability of the results was estimated using a one-way analysis of variance and the Mann-Whitney U-test (Statistica 7.0, StatSoft, USA).

III. RESULTS AND DISCUSSION

Optical plasma spectra study revealed that plasma discharges are represented with working gas ions (Ar) and atomic (Ca, P and O) and molecular (CaO, PO, OH, H₂O, CaOH) particles of sputtered targets (Fig. 1). Spectra corresponding to the sputtering of HA-based targets are characterized with the higher intensity of target particles peaks in comparison with TCP-based spectra. HA, Mg-HA and Sr-HA spectra contain an intensive peak corresponding to H₂. Presence of molecular hydrogen is explained by hydroxyapatite decomposition, while β -tricalcium phosphate doesn't contain hydrogen, so the spectra obtained while sputtering of TCP, Mg-TCP and Sr-TCP don't have this peak. CaO and PO are the most intensive peaks among ones corresponding to target particles. Plasma compositions are represented by predominantly oxygen-containing particles. Chemical bonds in oxygen-containing particles are strong: oxygen is the second most active oxidizing agent after fluorine. For example, the energy of Ca-Ca chemical bond is 0.16 eV, while the Ca-O bond energy is 4.9 eV [3].

According to our study of deposition rates of coatings formed by sputtering of TCP powder targets [4], it can be assumed that the used concentration of Mg and Sr ionic substitutions into TCP target significantly affect deposition rate (Table I). At the same time, similar concentrations of these substitutions in HA target don't cause statistically reliable differences in the deposition rate of coatings. This phenomenon

can be explained by the difference in the crystal lattice of HA and TCP. In the works [4, 5], computer modeling of the crystal lattices of TCP and HA is given. The significance of ionic substitutions effect on the lattice is proved by the experimental study of ionic yield into 0.9 wt.% NaCl solution. Sr substitutions increase the ionic yield of lattice elements, while Mg ones decrease this parameter. Ozeki et. al. [6] claim that the deposition rate of CaPs depends on lattice energy, which is also connected with their solubility. According to our experimental results, the amount of Mg substitutions in Mg-HA was not enough to cause a change in these parameters. This suggestion is proved by [7], where there was revealed no significant differences in lattice parameters of pure HA and Mg-substituted HA. The amount of Mg substitutions was 1%, which was close to the group Mg-HA studied in this work. It seems that incorporation of Sr into TCP causes larger changes in lattice parameters than into HA one because HA contains a larger cation site compared to TCP [8].

This assumption explains why a similar amount of Sr in TCP and HA increases the deposition rate of TCP-based coatings and doesn't affect the deposition rate of HA-based ones.

The initial Ti substrate is characterized by the presence of shallow traces caused by grinding and polishing (Fig. 2a). Coatings formed by sputtering of HA target are characterized by spherical grains with an area of 0.010 μm^2 (Fig. 2b). There are small grains of 0.005 μm^2 on the surface of CaP coating formed by the sputtering of Mg-HA (Fig. 2c). The coating formed by sputtering of the Sr-HA (Fig. 2d) target is characterized by complex shape agglomerates consisting of grains with an area of 0.018 μm^2 . There was revealed no structural elements on the surface of coatings formed by sputtering of TCP (Fig. 1e). Ion substituted TCP-based coatings are represented with grains of 0.017 μm^2 and 0.001 μm^2 for Mg-TCP (Fig. 2f) and Sr-TCP (Fig. 2g), respectively.

TABLE I. THICKNESSES AND DEPOSITION RATES OF COATINGS FORMED BY RF-MAGNETRON SPUTTERING OF TCP AND HA-BASED POWDER TARGETS.

Sample	Thickness, nm	Deposition rate, nm/h
TCP	630±19	30±1
Mg-TCP	560±16	27±1
Sr-TCP	990±30	47±1
HA	1045 ± 5	149±1
Mg-HA	912 ± 114	130±16
Sr-HA	873 ± 80	125±11

All the coatings under study are characterized by a lower content of oxygen in comparison with respective targets (Table II). It is caused by the scattering of this element on the way from target to substrate. It is interesting to note that the amount of Mg and Sr in the coatings formed by the sputtering of ion-substituted TCP is higher than in targets. There is no significant difference between HA-based targets and coatings. TCP-based targets have a lower value of Ca/P ratio in comparison with respective coatings, while HA-based ones have the opposite trend. Mg substitutions decrease the Ca/P ratio in TCP-based coatings, while Sr substitutions increase this parameter. Ca/P of HA-based coatings doesn't depend on the presence of Mg and Sr substitutions.

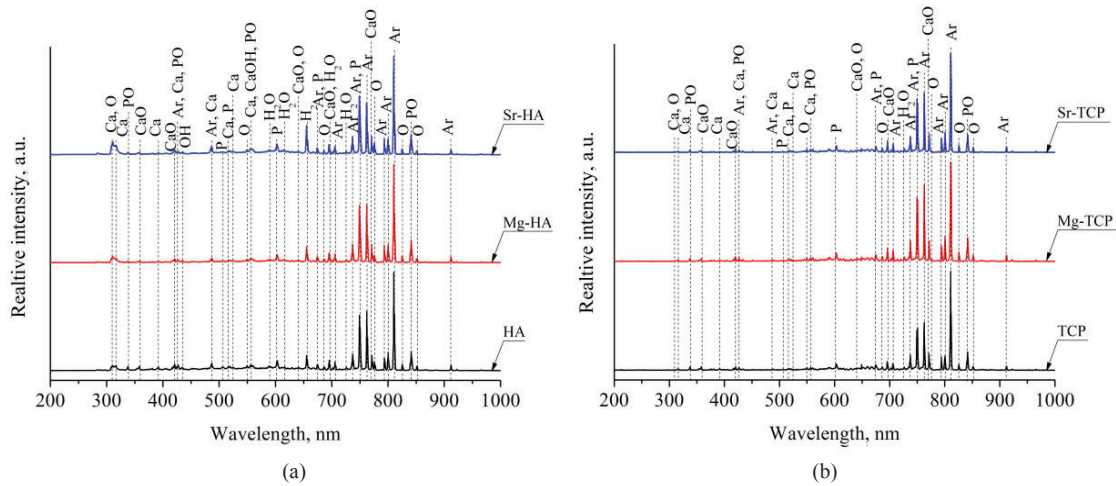


Fig. 1. Optical emission spectra of plasma discharges obtained during the sputtering of HA-based (a) and TCP-based targets (b).

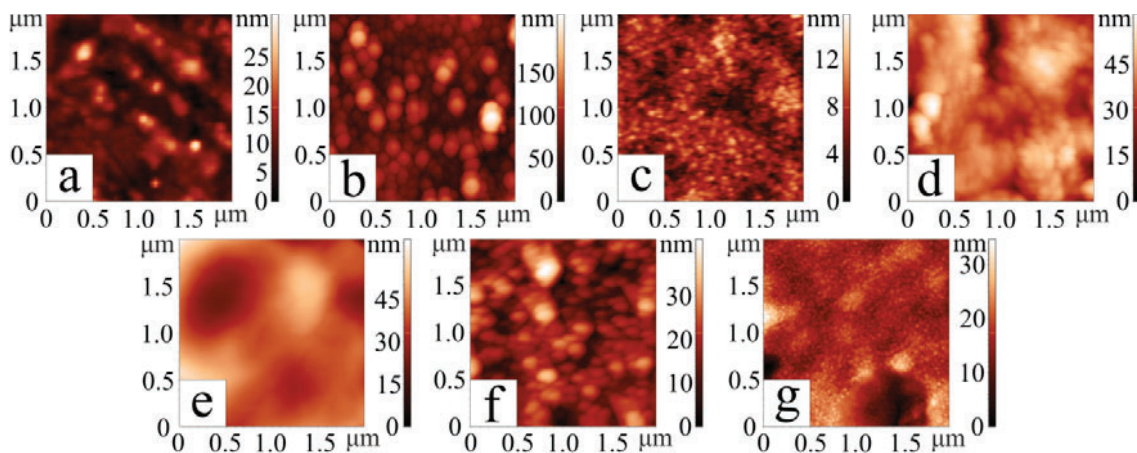


Fig. 2. AFM-images of the initial substrate (a), the coating formed by sputtering of pure HA (b), the coatings formed by sputtering of Mg- and Sr-substituted HA (c and d, respectively), the coating formed by sputtering of pure TCP (e), the coatings formed by sputtering of Mg- and Sr-substituted TCP (f and g, respectively).

TABLE II. ELEMENTAL COMPOSITION OF THE POWDER TARGETS AND THE COATINGS, AT. %.

Sample	Ca	P	O	Mg	Sr	Ti	Al	Ca/P
Ti control	–	–	–	–	–	90.27±0.42	9.73±0.42	–
TCP powder	16.00±0.00	13.2±0.03	70.26±0.07	0.32±0.03	0.22±0.01	–	–	1.21±0.01
TCP coating	36.69±2.15	17.36±2.72	45.96±4.84	–	–	–	–	2.14±0.22
Mg-TCP powder	15.15±0.05*	13.14±0.02*	70.12±0.05*	1.38±0.00*	0.21±0.01	–	–	1.15 ± 0.01*
Mg-TCP coating	32.65±1.77†	18.35±2.68	44.64±4.05	4.35 ± 0.51†	–	–	–	1.80±0.17
Sr-TCP powder	16.23±0.02*	12.52±0.03*	70.27±0.07	0.11±0.01*	0.87±0.02*	–	–	1.30±0.01*
Sr-TCP coating	35.81±7.37	12.76±3.10	48.91±7.70	–	2.52 ± 1.67†	–	–	2.94±0.85
HA powder	13.80±0.24	8.65±0.49	77.54±0.70	–	–	–	–	1.60±0.07
HA coating	15.98±0.07	12.12±0.06	69.50±0.16	–	–	2.22±0.12	0.18±0.03	1.32±0.01
Mg-HA powder	11.85±0.40*	9.02±0.31	78.20±0.04	0.93±0.13*	–	–	–	1.32±0.09*
Mg-HA coating	14.02±0.75†	12.18±0.68	71.30±1.75†	1.35±0.45†	–	0.80±0.05†	0.35±0.13†	1.15±0.01†
Sr-HA powder	11.50±0.39*	8.64±0.12	79.38±0.47*	–	~0.47*	–	–	1.33±0.04*
Sr-HA coating	14.49±0.09†	12.41±0.08†	70.38±0.47†	–	0.46±0.02†	2.10±0.48	0.17±0.05	1.17±0.01†

* significant difference between pure and substituted powders ($p < 0.05$);

† significant difference between pure and substituted coatings ($p < 0.05$).

The XRD-study of powder targets (not shown in the paper) revealed that spectra corresponding to ion substituted TCP-based are characterized with a slight shift of characteristic peaks ($0.19 \pm 0.03^\circ$ to higher angles for Mg-TCP and $0.06 \pm 0.03^\circ$ to lower ones), which indicates successful incorporation of substitutions into the lattice [4]. The Sr-TCP spectrum contains a small HA peak. Mg and Sr substitutions

decrease characteristic peaks on $0.33 \pm 0.04^\circ$ and $0.21 \pm 0.04^\circ$, respectively. Mg also causes the appearance of peaks corresponding to whitlockite ($\text{Ca}_{2.5}\text{Mg}_{0.41}(\text{PO}_4)_2$). According to XRD-spectra of coatings, Mg and Sr substitutions decrease the crystallinity of coating formed by sputtering of ion-substituted TCP- and HA-based coatings. Crystalline orientation (002) is

the most energetically beneficial in comparison with other ones for all the coatings under study [9].

IV. CONCLUSION

A comparison of CaP coatings formed by RF-magnetron sputtering of TCP- and HA-based targets was carried out. Mg and Sr substitutions significantly affect the deposition rate of TCP-based coatings, however, the same amount of these substitutions don't influence this parameter of TCP-based coatings. Nevertheless, Mg and Sr substitutions in the structure of TCP- and HA-based coatings affect their morphology and physic-chemical properties. Mg substitutions decrease the Ca/P ratio of TCP-based coatings, Sr ones increase this parameter. Both substitutions decrease the crystallinity of all the coatings under study.

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