



PROCEEDINGS

2020 7th International Congress on Energy Fluxes and Radiation Effects (EFRE)

Tomsk, Russia, September 14 – 26, 2020

SPONSORED BY



IEEE Nuclear and Plasma Sciences Society



Institute of High Current Electronics of the Siberian Branch of the Russian Academy of Sciences



National Research Tomsk Polytechnic University



Tomsk Scientific Center of the Siberian Branch of the Russian Academy of Sciences

Chairman

Nikolay Ratakhin

Institute of High Current Electronics, Tomsk, Russia

Co-Chairman

Andrey Yakovlev

National Research Tomsk Polytechnic University, Tomsk, Russia

Alexey Markov

Tomsk Scientific Center SB RAS, Tomsk, Russia

Program Chairman

Alexander Batrakov

Institute of High Current Electronics, Tomsk, Russia

Program Co-Chairman

Edl Schamiloglu

University of New Mexico, Albuquerque, USA

Composite Biphasic Coatings Formed by Hybrid Technology for Biomedical Applications

Alexandr Vorobyev
Tomsk Polytechnic University
30 Lenin Ave., 634050
Tomsk, Russia
alexandr.vorobyev13@gmail.com

Alexander Fedotkin
Tomsk Polytechnic University
30 Lenin Ave., 634050
Tomsk, Russia
fedotkin_sasha@mail.ru

Anna Kozelskaya
Tomsk Polytechnic University
30 Lenin Ave., 634050
Tomsk, Russia
annakozelskaya@gmail.com

Natalia Korotchenko
Tomsk State University
36 Lenin Ave., 634050
Tomsk, Russia
korotch@mail.ru

Alexander Gigilev
Tomsk State University
36 Lenin Ave., 634050
Tomsk, Russia
gigilev@mail.tsu.ru

Evgeny Shesterikov
Institute of Atmospheric Optics
V.E. Zuev SB RAS
1 Academician Zuev Sq., 634055,
Tomsk, Russia
shesterikov_e@mail.ru

Sergei Tverdokhlebov
Tomsk Polytechnic University
30 Lenin Ave., 634050
Tomsk, Russia
tverd@tpu.ru

Abstract—Calcium-phosphate (CaP) coatings were formed via combining methods of microarc oxidation (MAO) and radiofrequency magnetron sputtering (RFMS). SEM, XPS, XRD and nanoindentation methods were used to study physico-chemical and mechanical properties of the coatings. It was revealed that the upper CaP layer changes the morphology of the coatings at the microscale and increases the Ca/P ratio of biphasic coatings.

Keywords—micro-arc oxidation, RF-magnetron sputtering, calcium phosphate, coatings

I. INTRODUCTION

Usually, one technology/method is used to form biocompatible CaP coatings on the surface of medical implants.

Recently, however, there has been a tendency to form such coatings using several techniques that combine their advantages, which makes it possible to obtain coatings with improved properties.

Among the methods for the formation of calcium phosphate coatings, which are being successfully developed for clinical use, two technologies can be distinguished: microarc oxidation (MAO) and radiofrequency magnetron sputtering (RFMS). MAO is the simplest and most economical way of forming coatings with high open porosity [1]. However, in most cases, coatings formed using this method are calcium deficient [2], which does not allow stimulating successful early osseointegration enough effectively. In turn, coatings formed by the RFMS method have a high Ca/P ratio. This method is universal not only in terms of the substrate material, but also the

This work was supported by the Tomsk Polytechnic University Competitiveness Enhancement Program project VIU-School of Nuclear Science and Engineering-204/2019 and in part of magnetron sputtering was supported by the Russian Academy of Sciences (Fundamental Research Project no. AAAA-A19-119110690036-9).

target used for sputtering, which gives it greater variability compared to other methods [3].

The combination of the coatings deposition methods, namely, the deposition of thin CaP layer by RFMS on the surface of MAO-coatings, allows combining their advantages, avoiding the disadvantages, and forming coatings with the requirement properties.

II. MATERIALS AND METHODS

Composite coatings were formed on titanium substrates with a diameter of 10 mm and a thickness of 2 mm. Preparation of the samples surface before deposition included cleaning in an ultrasonic bath in distilled water and chemical etching in an aqueous solution of nitric and hydrofluoric acids taken in volume ratios of HN: HF: H₂O = 1: 2.5: 2.5, at temperature of 15-20 °C for 10-15 seconds, followed by neutralization in a 1% aqueous solution of sodium hydroxide and repeated washing with distilled water. The formation of CaP coatings by the MAO method using the setup developed in National Research Tomsk Polytechnic university was carried out in a saturated solution of CaO in 10% H₃PO₄ with the addition of hydroxyapatite with a dispersion phase with a particle size of up to 70 μm. The coating was formed at voltage of 320 V with a voltage rise rate of 3 V/s, with a pulse repetition rate of 200 Hz and a pulse duration of 100 μs for 15 minutes. The process carried out at a temperature of 15 °C. After coating formation, the samples were washed in distilled water and dried in an oven at a temperature of 120 °C for 30 minutes.

The deposition of the upper layer was carried out by sputtering of the powder targets of the following composition: pure β-tricalcium phosphate (β-TCP), pure hydroxyapatite (HA), Mg-substituted β-tricalcium phosphate and Mg-substituted hydroxyapatite (Mg-β-TCP, Mg-HA, Mg

substitutions concentration was 1.53 ± 0.01 wt.%), Sr-substituted β -tricalcium phosphate and Sr-substituted hydroxyapatite (Sr- β -TCP, Sr-HA, Sr substitutions concentration was 3.39 ± 0.09 wt.%).

Powder targets used to form CaP coatings by the RFMS were placed in hexagonal crucible with an area of 230 cm^2 and a depth of 0.6 cm. The volume of the sputtered powder was constant in all cases and was approximately 138 cm^3 . The preliminary pressure in the chamber was 10^{-3} Pa , and the working pressure (Ar) was 0.5 Pa. The distance between the sputtering target and the surfaces was 40 mm. The power density was approximately 4.8 W/cm^2 . The deposition time of coatings formed by RF-sputtering of targets based on HA was 7 hours, and for coatings based on β -TCP it was 21 hours.

III. RESULTS AND DISCUSSION

The formed composite coatings consist of two layers: the lower thick layer formed using the MAO and the upper thin layer formed by the RFMS. The thickness of each layer of the composite coatings is presented in Table I. As can be seen from the analysis of the data that the deposition rate of the upper CaP layer strongly depends on the material of the sputtered target and ionic substitutions. Thus, the coatings formed by sputtering of β -TCP-based targets has a lower deposition rate compared to the coatings formed by sputtering of HA-based ones. K. Ozeki et. all in [4] observed a clear correlation between the deposition rate of the coatings and their solubility. It was shown that the more soluble the respective target material was, the higher the deposition rate of the formed coatings. Thus, less soluble hydroxyapatite was characterized by a lower deposition rate than more soluble β -TCP. However, in the present work, we observed the opposite trend.

The addition of Sr to the composition of the sputtered β -TCP target increases its deposition rate, and, conversely, Mg substitution contributes to a slight decrease in it. The different deposition rates of the coatings are due to the influence of magnesium and strontium substitutions on the crystal structure of the β -TCP powder targets. Theoretical calculations [5] showed that strontium substitutions lead to an increase in the volume of the unit cell, which causes an increase in the deposition rates of the Sr- β -TCP target. The decrease in the unit cell volume caused by magnesium substitutions, on the contrary, leads to a slight decrease in the deposition rate of the Mg- β -TCP target.

TABLE I. THE THICKNESSES OF THE STUDIED COATINGS.

Sample	The thickness of the MAO-coating, μm	The thickness of the upper coating, μm
MAO	35 ± 1.7	—
MAO+ β -TCP	35 ± 1.5	0.7 ± 0.1
MAO+Mg- β -TCP	35 ± 1.5	0.6 ± 0.1
MAO+Sr- β -TCP	36 ± 1.5	1.0 ± 0.1
MAO+HA	36 ± 1.0	2.4 ± 0.1
MAO+Mg-HA	34 ± 0.5	1.1 ± 0.1
MAO+Sr-HA	36 ± 1.0	1.3 ± 0.1

In the case of sputtering targets of Sr- and Mg-substituted HA, both substitutions lead to a decrease in the deposition rate. A decrease in the deposition rate of the HA target upon the addition of Sr was also observed by Boyd in [6].

SEM revealed that the initial surface is smooth with shallow polishing marks oriented in the same direction (Fig. 1a).

The surface of CaP coatings formed by a combination of two methods of MAO and RFMS is the same at the macro level and is represented by structural elements of a spheroidal shape (spherulites) with through pores (Fig. 1). The size of spherulites varies from 7 to 20 microns. Spherulites are destroyed and fragmented during the formation of CaP coatings, due to the action of high-temperature microplasma discharges, and microcracks are formed (Fig. 1d). Dendrite crystallites are observed along the edges of the spherulites (Fig. 1c) on the samples with composite coatings formed by the MAO method with the subsequent deposition of a thinner layer using an RF-sputtering of the target from HA. The formation of crystallites is apparently due to the high temperature in the vacuum chamber. AFM studies have shown that, at the micro level, the coating structure is quasi-equiaxed grains with an area of $5 \mu\text{m}^2$ (Fig. 1a). The deposition of a thin CaP layer formed by sputtering of the target from HA onto the MAO surface results in the formation of smaller rounded crystallites with an area of 0.3 to $0.5 \mu\text{m}^2$. The upper layer of composite coatings formed by sputtering of the Mg-HA target consists of equiaxed grains with an area of $0.1\text{-}0.2 \mu\text{m}^2$ located on the surface of the initial elements of the MAO coating (Fig. 1c). Sputtering of the Sr-HA target onto the surface of the MAO coating leads to the formation of elongated grains whose size is from 1 to $2.5 \mu\text{m}^2$ (Fig. 1d).

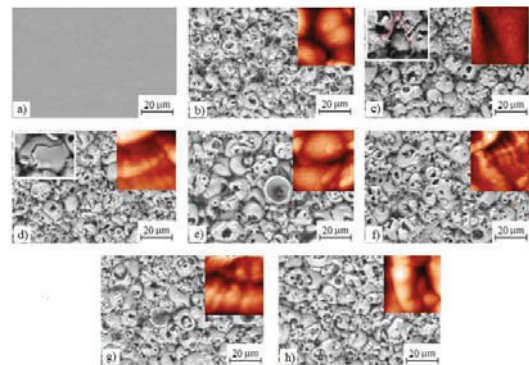


Fig. 1. SEM images of composite coatings formed on the surface of titanium substrates (a) using the MAO method (b) and a combination of the MAO and RFMS of the targets from HA (c), Sr-HA (d), Mg-HA (e), TCP (f), Sr- β -TCP (g), and Mg- β -TCP (h).

The formed layer obtained by sputtering of the β -TCP target is an elongated grain with an area of 0.3 to $0.5 \mu\text{m}^2$ laid in layers on the surface of the MAO coating, repeating its original relief. Quasi-equal-shaped grains with an area of $1.7 \mu\text{m}^2$ are visible on the surface of coatings formed by a combination of the MAO methods and RF magnetron sputtering of a target from Mg- β -TCP. Grains of a similar shape and a smaller area ($1 \mu\text{m}^2$) are marked on the surface of the coatings whose upper layer is formed by sputtering of the target from Sr- β -TCP. Such developed morphology of the surface of all obtained CaP coatings has a high osteoinduction, enhances proliferation and mechanical adhesion between the implant biomaterial and natural bone, ensuring the mechanical stability of the implant [7, 8].

Table II presents the elemental composition of CaP coatings of the studied samples. The presence of aluminum is due to the composition of the Ti-6Al-4V substrate. The composition of the coatings corresponds to the composition of the CaP electrolyte and sputtered targets and is represented by the following elements Ca, P, O. In the case of the formation of the upper layer by sputtering of Sr- and Mg-substituted targets from HA and TCP, Sr and Mg elements are present in the coatings (Table II).

It should be noted that coatings formed by the MAO method are calcium-deficient and characterized by the ratio Ca/P = 0.33.

Deposition of the upper layer using RFMS leads to an increase in the Ca/P ratio of the coatings under study. In this case, the Ca/P ratio of CaP coatings formed by sputtering of the Sr- and Mg-substituted targets is lower compared to coatings formed by sputtering of the pure HA and the β -TCP targets. In addition, it can also be seen from Table II that, when sputtering Sr and Mg-substituted targets, the amount of Mg in the coatings is higher than Sr. Apparently, this is due to the fact that not all sputtered Sr atoms reach the substrate due to their larger atomic mass (88) compared to Mg (24).

TABLE II. THE ELEMENTAL COMPOSITION OF THE STUDIED CAP COATINGS OBTAINED BY THE XPS METHOD

Sample	The content of elements in the coating (at.%)							
	O	Ca	P	Ti	C	Sr	Mg	Ca/P
MAO	61.45±0.64	5.95±0.34	17.59±0.19	3.65±0.30	11.36±1.43	-	-	0.33
MAO+HA	54.88±0.84*	17.94±0.60*	14.65±0.50*	-	12.54±0.48	-	-	1.22
MAO+Sr-HA	57.67±1.84*	17.11±0.48*	17.01±0.49	-	7.69±2.77	0.52±0.04*	-	1.00
MAO+Mg-HA	59.96±1.99	13.38±0.44*	17.44±0.62	-	7.88±2.91	-	1.34±0.28*	0.76
MAO+ β -TCP	59.35±0.97††	15.13±0.10††	16.24±0.35††	-	9.28±1.37†	-	-	0.93
MAO+Sr- β -TCP	58.29±2.53	13.23±0.81††	19.00±1.29††	-	9.03±4.67	0.45±0.06*	-	0.69
MAO+Mg- β -TCP	62.81±0.49††	8.52±0.08††	18.34±0.31*	-	7.43±1.19*	-	2.89±0.37††	0.46

* significant differences with MAO ($p < 0.05$);

† significant differences between groups of the X- β -TCP and X-HA coatings, where X is Mg or Sr ($p < 0.05$).

XRD analysis showed that the coatings under study are completely amorphous, except for coatings formed by a combination of MAO methods and RF-sputtering of the HA and the Sr-HA targets. There are peaks of the crystalline HA phase on the X-ray diffraction patterns of these coatings.

The study of the mechanical properties of the coatings found that the value of the elastic modulus of CaP coatings formed by the MAO method is lower compared with the composite ones (Table III).

TABLE III. THE MODULUS OF ELASTICITY OF THE CAP COATINGS UNDER STUDY.

Coating	E_{rr} , GPa
MAO	15.4 ± 3.8
HA	21.3 ± 3.7
Mg-HA	29.8 ± 6.8
Sr-HA	36.6 ± 9.5
β -TCP	25.6 ± 5.8
Mg- β -TCP	17.4 ± 3.2
Sr- β -TCP	19.5 ± 4.1

All the obtained CaP coatings have a lower elastic modulus close to the value of the elastic modulus of the human bone (13.7 GPa) [9] in comparison with the implants without coatings made from pure Ti (138.2 GPa). The use of such composite coatings will provide better mechanical compatibility with bone due to a greater reduction in intrinsic residual stresses in the implantation zone [10].

IV. DISCUSSION

The physicochemical and the mechanical properties of biphasic CaP coatings formed using hybrid technology are investigated.

It was found that the deposition of the upper calcium phosphate layer by RFMS occurs at different rates depending

on the composition of the sputtered target. It was revealed that the deposition rate is affected by ionic substitutions in the composition of the sputtered target. The deposition of the thin CaP layer by the RFMS method on the surface of the MAO-coatings changes their morphology at the micro level, while no changes were revealed at the macro level. Coatings formed using the hybrid technology are characterized by a higher Ca/P ratio. The studied coatings are amorphous. The elastic modulus of composite coatings exceeds the corresponding value of the MAO-coatings.

ACKNOWLEDGMENT

This work was supported by the Tomsk Polytechnic University Competitiveness Enhancement Program project VIU-School of Nuclear Science and Engineering-204/2019 and in part of magnetron sputtering was supported by the Russian Academy of Sciences (Fundamental Research Project no. AAAA-A19-119110690036-9).

REFERENCES

- [1] C. Wang, F. Wang, and Y. Han, "Structural characteristics and outward-inward growth behavior of tantalum oxide coatings on tantalum by micro-arc oxidation," *Surf. Coatings Technol.*, vol. 214, pp. 110–116, Jan. 2013.
- [2] X. Shi *et al.*, "Corrosion resistance and biocompatibility of calcium-containing coatings developed in near-neutral solutions containing phytic acid and phosphoric acid on AZ31B alloy," *J. Alloys Compd.*, vol. 823, p. 153721, May 2020.
- [3] M. A. Surmeneva *et al.*, "Effect of silicate doping on the structure and mechanical properties of thin nanostructured RF magnetron sputter-deposited hydroxyapatite films," *Surf. Coatings Technol.*, vol. 275, pp. 176–184, Aug. 2015.
- [4] K. Ozeki, Y. Fukui, and H. Aoki, "Influence of the calcium phosphate content of the target on the phase composition and deposition rate of sputtered films," *Appl. Surf. Sci.*, vol. 253, no. 11, pp. 5040–5044, Mar. 2007.

- [5] A. I. Kozelskaya et al., "Radio frequency magnetron sputtering of Sr- and Mg-substituted β -tricalcium phosphate: Analysis of the physicochemical properties and deposition rate of coatings," *Appl. Surf. Sci.*, vol. 509, p. 144763, Apr. 2020.
- [6] A. R. Boyd, L. Rutledge, L. D. Randolph, and B. J. Meenan, "Strontium-substituted hydroxyapatite coatings deposited via a co-deposition sputter technique," *Mater. Sci. Eng. C*, vol. 46, pp. 290–300, Jan. 2015.
- [7] J. Zhi Chen, Y. Long Shi, L. Wang, F. Ying Yan, and F. Qiang Zhang, "Preparation and properties of hydroxyapatite-containing titania coating by micro-arc oxidation," *Mater. Lett.*, vol. 60, no. 20, pp. 2538–2543, Sep. 2006.
- [8] V. Karageorgiou and D. Kaplan, "Porosity of 3D biomaterial scaffolds and osteogenesis," *Biomaterials*, vol. 26, no. 27. Elsevier BV, pp. 5474–5491, Sep. 01, 2005.
- [9] J. L. Arias, M. B. Mayor, J. Pou, Y. Leng, B. León, and M. Pérez-Amor, "Micro- and nano-testing of calcium phosphate coatings produced by pulsed laser deposition," *Biomaterials*, vol. 24, no. 20, pp. 3403–3408, Sep. 2003.
- [10] Y. C. Chai et al., "Current views on calcium phosphate osteogenicity and the translation into effective bone regeneration strategies," *Acta Biomaterialia*, vol. 8, no. 11., pp. 3876–3887, Nov. 01, 2012.