Comparative Studies of the Physical, Mechanical and Chemical Properties of Hybrid Coatings for Medical Implants

E. Kharapudchenko[a)], V. Ignatov[b)], A. Kozelskaya[c)], and S. Tverdokhlebov[d)]

National Research Tomsk Polytechnic University, Tomsk, 634050 Russia

[a)] kleine_harey92@mail.ru
[b)] ignatovvp@tpu.ru
[c)] annakozelskaya@gmail.com
[d)] Corresponding author: tverd@tpu.ru

Abstract. In the work the physical, mechanical and chemical properties of oxide and calcium-phosphate coatings formed by the microarc oxidation and radio-frequency magnetron sputtering methods, or their combination were studied. It is shown that combining the advantages of various technologies enables one to obtain a wide range of hybrid coatings used for various strategies of osteosynthesis. The calcium phosphate coatings obtained by the radio-frequency magnetron sputtering methods were chosen as coatings on cortical screws. The hybrid coatings obtained by a combination of microarc oxidation method and radio-frequency magnetron sputtering method were recommended for intramedullary implants. For extramedullary implants, the most optimal coatings are the coatings formed by radio-frequency magnetron sputtering with an intermediate TiO_2 sublayer.

INTRODUCTION

At present polytrauma is one of the main causes of death and disability of the people of active age. For this reason, the rehabilitation and recovery of the functions of the musculoskeletal system after polytrauma have become one of the key problems of modern medicine [1]. Implementation of the methods for restoring the musculoskeletal system functions is directly related to using various products and structures for osteosynthesis—medical implants.

At present, most modern implants are made of biocompatible metals (titanium, stainless steel, and zirconium) due to good biomechanical characteristics of these materials and advanced technologies for manufacturing implants from them, which are capable of providing reliable fixing of bone fragments [2]. However, the use of metal implants is associated with a risk of metallosis and, as a consequence, loosening of implanted structures and the extensive inflammation at a site of implantation. The inflammation, especially in people predisposed to oncological diseases, is extremely dangerous, as it increases the risk of developing cancer and can lead to the development of the infections [3, 4]. Therefore, the reconstructive systems and implants used in cancer patients and patients with polytrauma should contribute to the formation of optimal conditions for the regeneration of surrounding tissues without the development of inflammatory reactions. In this case, the implants in cancer patients should also remain inert to stimulating the tumor process, and ideally, have a certain anti-tumor effect by including the cytotoxic drugs in the implant structure. To improve the recovery of musculoskeletal functions, the concept was proposed based on active influence on the processes of reparative osteogenesis by application of osteoplastic materials (primarily calcium phosphates, for example, hydroxyapatite (HAP)), which stimulate the processes of remodeling and regeneration of bone tissue [5]. For this purpose, the surface of the metal implants is coated with calcium phosphate [6].

The absence of a universal technology for production of CaP coatings leads to the fact that the coatings obtained by application of different technologies have a different set of physical and chemical, and, hence, medical properties.

Physics of Cancer: Interdisciplinary Problems and Clinical Applications
AIP Conf. Proc. 1882, 020032-1–020032-4; doi: 10.1063/1.5001611
Published by AIP Publishing. 978-0-7354-1562-1/$30.00

This circumstance significantly complicates both a choice of an optimal coating for a given implant, and estimation of its clinical effectiveness. In this connection, the goal of this work is to study the physical, mechanical and chemical properties of calcium phosphate coatings obtained using radio-frequency magnetron sputtering (RFMS) of a hydroxyapatite target and microarc oxidation (MAO), and a combination of these methods; and to propose recommendations for the clinical use of implants with CaP coatings formed by these methods.

MATERIALS AND METHODS

The plates of commercially pure titanium with sizes $10\times10\times2.8$ mm^3 were used as a material of substrates.

The formation of calcium phosphate coatings by microarc oxidation was carried out using the bipolar microarc oxidation setup (Tomsk Polytechnic University). The formation of calcium phosphate coatings by microarc oxidation was performed in an electrolyte solution based on phosphoric acid (H3PO4) with density ρ = 1.0824 g/ml to which CaO powder (30 g/l) and hydroxyapatite powder (20 g/l) were added. The coatings were formed during 15 min under the action of pulsed current having the following characteristics: pulse time is 50 s; pulse repetition frequency is 50 Hz; initial current density is 0.2 A/mm^2; final voltage is 150 V (dense coatings), 170 V (porous coatings). The formation of oxide coatings was carried out using the bipolar microarc oxidation setup in the mode of arc oxidation (AO). The TiO_2 coatings were formed during 15 min under the action of pulsed current having the following characteristics: the pulse time is 50 s; the pulse repetition frequency is 50 Hz; the initial current density is 0.01 A/mm^2. The formation of calcium phosphate coatings by radio-frequency magnetron sputtering of a hydroxyapatite target was performed using the setup developed at Tomsk Polytechnic University (TPU) under the following technological modes: the preliminary pressure in a chamber is 7×10^{-3} Pa, the working pressure Ar is 5×10^{-1} Pa, the RF power is 2 kW, the duration of spraying is 8 hours, the distance between the target and the samples is 35 mm. Argon (Ar) with 99.99% purity was used as the working gas for sputtering the HAP target. Preheating of the samples before sputtering was not carried out.

A quantitative study of the morphological characteristics (mean pore diameter, pore size distribution, etc.) was performed using the Image J 1.38 software package (National Institutes of Health, USA). The chemical composition of the surface was studied using the method of energy dispersive analysis (EDS) (EDS analysis system Genesis 4000, S-UTW-Si (Li) detector). The values of nanohardness H and elastic modulus E of the films were determined using a NanoTest 600. The adhesion properties of calcium-phosphate coatings to a titanium substrate were studied in accordance with the recommendations of GOST R 52641-2006 "Standard Test Method for Testing for Shift of P-Calcium and Metal Coatings" [7]. The studies were carried out at a traverse speed 2.5 mm/min using an Instron 3369 test machine (Instron, England). *In vitro* studies were performed according to ISO 23317 [8]. Biological activity of calcium-phosphate coatings was studied by holding samples with coatings in a liquid that simulates human body fluid (SBF) for 4 weeks.

RESULTS AND DISCUSSION

The studies of the morphology of coatings using contact profilometry and SEM showed that numerous craters with an average diameter of 1.6±0.8 μm, which are the centers of the interaction between the acid and the metal surface of the model implant, are observed on the initial surface of the titanium substrate after electrolytic etching (Fig. 1a). The calcium-phosphate coatings formed by the microarc oxidation method have a complex spatial organization. The surface is formed by spherulites with an average diameter of 2.8±1.6 μm, at the top of the spherulites there are pores with an average diameter of 2.0±0.3 μm (Fig. 1b). The surface of the implants obtained by the microarc oxidation method is the most developed of all the studied groups, with an average value of the roughness parameter Ra = 1.6±0.4 μm.

Figure 1c shows the surface of titanium after electrochemical oxidation. Electrochemical oxidation of implants leads to the formation of numerous pores and spherulites on their surface with an average size of 0.6±0.3 μm.

The homogeneous and smooth calcium-phosphate coatings on the surface of titanium substrates are formed using the HFMR method (Fig. 1d). The average roughness (Ra parameter) of such coatings is 0.95±0.5 μm. The hybrid coatings formed by a combination of microarc oxidation and RF magnetron sputtering methods, as well as oxidation and RF magnetron sputtering are shown in Figs. 1e and 1f, respectively. The surface of the former is characterized by pores with an average size of 2.5±1.5 μm. Such coatings have a sufficiently developed surface roughness R_a = 1.7±0.6 μm. In turn, the hybrid coatings formed by the method of oxidation and RF magnetron sputtering have the lowest roughness R_a =0.91±0.2 μm among the coating groups under study.

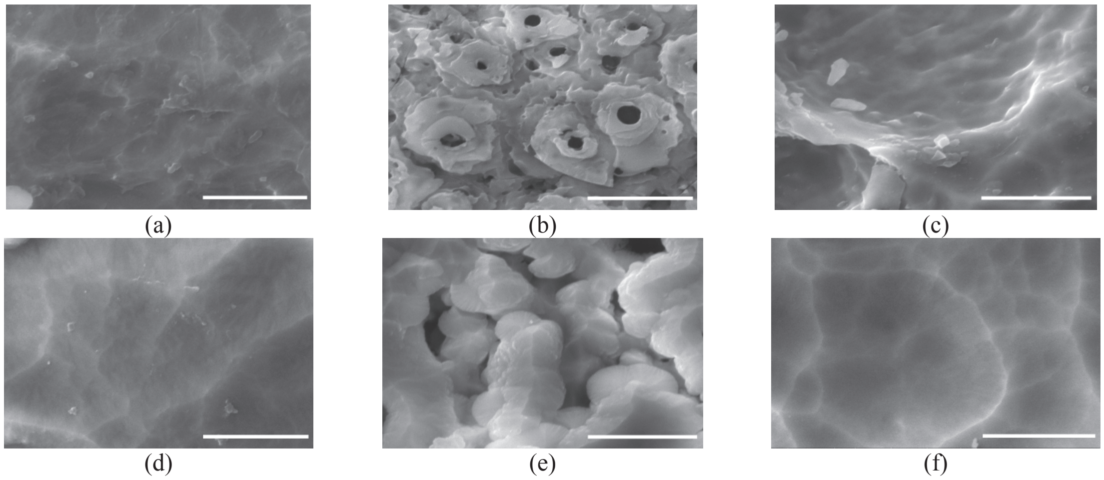

FIGURE 1. SEM images of the Ti substrate (a) and CaP coatings created by MAO (b), AO (c), RFMS (d), MAO + RFMS (e) and TiO_2 + RFMS (f) methods. Scale bar 5 μm

The investigations of the mechanical properties of various types of coatings showed the following results (Table 1). The coatings obtained by the RFMS method have the highest adhesion strength 445.8±5 MPa. The strength of an adhesive bond depends on a thickness of a film. Usually the thinner the film is, the higher the bond strength with a substrate. This is due to the determining effect of a substrate, which is more pronounced in thin films. The thickness of the RFMR coatings is 1±0.1 μm. The thin coatings formed by RF magnetron sputtering have high adhesion strength and can be used as coatings for cortical screws. MAO coating have the lowest adhesion strength 30.6±1.6 MPa. The thickness of the coatings obtained by this method is four times greater than the thickness of the RFMS coatings and is 4±0.4 μm. The combination of MAO and RFMS techniques allows obtaining the coatings with sufficiently high adhesion strength 415.1±4 MPa. It should be noted that multilayer coatings consisting of several thin layers are stronger than single layers having the same thickness.

TABLE 1. Physico-mechanical properties of the calcium-phosphate coatings

	Ti	**Ti+MAO**	**Ti+RFMS**	**Ti+MAO+ RFMS**	**Ti+TiO_2**	**Ti+TiO_2+ RFMS**
Thickness, μm	–	4±0.4	1±0.1	5±0.5	0.8±0.2	1.8±0.3
h_{max}, μm	0.320	0.592	0.232	0.432	0.297	0.245
***H*, GPa**	5.16±2.63	1.56±0.29	8.8±2.21	3.14±1.8	5.14±0.98	8.02±1.41
***E*, GPa**	159±51	36±12	154±30	68±25	145±18	134±18
Adhesion strength, MPa	–	30.6±1.6	445.8±5	415.1±4	250.5±8	104.5±5

TABLE 2. In vitro evaluation for apatite-forming ability of CaP coatings

Method		**Ca, at %**	**P, at %**	**Ca/P**	**O, at %**	**Ti, at %**
RFMS	Before SBF	35.33	14.86	2.37	39.91	9.80
	After SBF	34.69	14.47	2.39	39.87	10.97
MAO	Before SBF	8.07	21.9	0.36	46.94	23.09
	After SBF	10.26	23.53	0.43	47.19	19.02
MAO + RFMS	Before SBF	32.43	5.52	5.87	36.89	25.16
	After SBF	25.81	16.61	1.55	42.10	15.49

The estimates of the nanohardness and modulus of elasticity of the coatings showed that the RFMS coatings have a maximum value of nanohardness 8.8±2.21 GPa and modulus of elasticity 154±30 GPa. Such a combination of mechanical properties characterizes the CaP coatings obtained by RF magnetron sputtering as a hard and at the same time elastic material, which is a favourable factor for the implants operating under load. The coatings formed by microarc oxidation have the lowest (of the presented types of coatings) value of nanohardness 1.56±0.29 GPa and the modulus of elasticity 36±12 GPa, which is due to their high porosity. Magnitude of nanohardness and modulus of elasticity of hybrid (MAO + RFMS) coatings has intermediate values and is 3.14±1.8 and 134±18 GPa, respectively. For extramedullary implants, for which high mechanical properties are primarily important, the most optimal coatings are the coatings formed by radio-frequency magnetron sputtering with an intermediate TiO_2 sublayer. In addition, in the case of dissolution of a thin calcium-phosphate layer, the oxide sublayer acts as a protective layer that is also bioinertic. According to the results of the energy dispersive analysis MAO coatings have calcium deficient composition both before and after the exposure of the samples to SBF (Table 2). In contrast, the RFMS coating is characterized by calcium saturated compositions, which after exposure to SBF almost do not change. The hybrid coatings obtained by a combination of microarc oxidation methods in electrolyte solution and radio-frequency magnetron sputtering of a hydroxyapatite target (MAO + RFMS) are characterized by the highest value of Ca/P ratio—5.87. The values of ratio Ca/P after exposure of samples to SBF is close to the norm (1.55). Therefore, this type of coating will contribute to osseointegration of the implant, which allows us to recommend them for intramedullary implants.

SUMMARY

In the work the physical, mechanical and chemical properties of oxide and calcium-phosphate coatings, formed in various modes of microarc oxidation and radio-frequency magnetron sputtering were studied. As a result of the studies, the coatings with optimal characteristics for extramedullary and intramedullary implants and intramedullary screws were chosen. It is shown that radio-frequency coatings are characterized by high adhesion to substrates, high elasticity, and spatial homogeneity. These features suggest the use of these coatings on cortical screws. Hybrid coatings obtained by a combination of microarc oxidation method and radio-frequency magnetron sputtering method have optimal physical and mechanical properties. In addition, the chemical composition of these coatings (relative to Ca/P) after exposure to SBF is the closest to the norm, which will contribute to good osseointegration. The latter allows us to recommend these coatings for intramedullary implant. For extramedullary implants, for which high mechanical properties are primarily important, the most optimal coatings are the coatings formed by radio-frequency magnetron sputtering with an intermediate TiO_2 sublayer. The conducted research has shown that combining the advantages of various technologies allows one to obtain a wide range of hybrid coatings used for various strategies of osteosynthesis.

ACKNOWLEDGMENTS

The research is carried out at Tomsk Polytechnic University within the framework of Tomsk Polytechnic University Competitiveness Enhancement Program and grant (VIU-316/2017).

REFERENCES

1. *Damage Control Management in the Polytrauma Patient*, edited by H.-C. Pape, A. B. Peitzman, M. F. Rotondo, and P. V. Giannoudis (Springer, Switzerland, 2017), p. 338.
2. R. J. Narayan, *Materials for Medical Devices* (ASM Int., 2012).
3. T. Bald, T. Quast, J. Landsberg, et al., Nature **507**, 109–113 (2014).
4. T. E. Rayes, R. Catena, S. Lee, et al., PNAS **112**(52), 16000–16005 (2015).
5. S. V. Dorozhkin, Biomatter **1**(2), 121–124 (2011).
6. S. I. Tverdokhlebov, V. P. Ignatov, I. B. Stepanov, D. O. Sivin, and D. G. Petlin, Engineering **4**, 613–618 (2012).
7. *Standard Test Method for Testing for Shift of P-Calcium and Metal Coatings*, GOST RF No. 52641–2006.
8. *Implants for Surgery-In Vitro Evaluation for Apatite Forming Ability of Implant Materials*, FDIS I.S.O. No. 23317 (2007).