Calcium phosphate coatings modified with zinc– or copper–incorporation on Ti–40Nb alloy

E G Komarova[1], M B Sedelnikova[1], Yu P Sharkeev[1], A A Kazakbaeva[2], I A Glukhov[1] and M A Khimich[1,2]

[1]Institute of Strength Physics and Materials Science of SB RAS, 2/4 Akademichesky ave., Tomsk, 634055, Russia
[2]National Research Tomsk State University, 36 Lenina ave., Tomsk, 634050, Russia

E-mail: katerina@ispms.tsc.ru

Abstract. The influence of the microarc oxidation parameters and electrolyte composition on the structure, properties and composition of CaP coatings modified with Zn– or Cu–incorporation on the Ti–40mas.%Nb (Ti–40Nb) alloy was investigated. The linear growth of thickness, roughness, and size of structural elements with process voltage increasing has been revealed. It was shown that the CaP coatings have the low contact angles with liquids and, consequently, high free surface energy. This indicates a high hydrophilicity of the coatings. X–ray diffraction analysis showed that the coatings have X–ray amorphous structure. The increase of the process voltage leads to the formation of such crystalline phases as $CaHPO_4$ and β–$Ca_2P_2O_7$ in the coatings. The maximum Ca/P atomic ratio was equal to 0.4, and Zn or Cu contents was equal to 0.3 or 0.2 at.%, respectively.

1. Introduction

Materials used for implants should have not only high strength properties (yield strength, ultimate strength, fatigue strength, microhardness, wear resistance, etc.), but also low elastic properties, such as elastic modulus. Elastic modulus is an important biofunctional characteristic of implant materials. An elastic modulus of titanium and its alloys ranges from 100 to 120 GPa, which is significantly higher than that of bone tissue which ranges from 15 to 55 GPa [1]. Accordingly, the most promising research area in medical materials science is the application of β–Ti alloys with a low elastic modulus, for example, Ti–Nb or Ti–Nb–Zr systems. Thus, niobium alloyed titanium (∼ 40 mas.% Nb) could decrease the elastic modulus to 55–60 GPa [2]. To provide reliable osseointegration of bone tissue–implant interface integration, the implant surface should possess specific morphology and porosity. To solve this task, as well as to impart bioactive properties, metal surfaces are covered with bioactive calcium phosphate (CaP) coatings. There are various deposition methods for production of biocoatings on the metal implant. During the last few decades, the microarc oxidation (MAO) method is being widely used as electrical and chemical surface treatment for the formation of oxide and CaP coatings on metals [3]. Such coatings have a wide spectrum of physical and chemical properties, including high corrosion resistance, wear resistance, hardness, chemical stability in aggressive media, etc.

In addition, a serious problem in biomedicine is bacterial infection of medical implants. Bacterial infection is a result of bacteria adhesion to the implant surface and formation of a biofilm that sometimes cannot be destroyed by antibacterial drugs coming from outside [4]. Therefore, at present the investigations aimed at synthesis of biomaterials with antibacterial properties and at the study of

bactericidal properties of implanted materials and patterns of interaction of antibacterial agents with surrounding tissues of the organism are of great interest. Bactericidal and anti–inflammatory actions of implanted materials are mainly caused by the presence in their structure of certain chemical microelements possessing natural antiseptic properties. It is well known that zinc (Zn^{2+}) and copper (Cu^{2+}) in the form of free ions possess strong slowing down activity and strong antimicrobial activity against various bacteria. Zn and Cu are necessary cofactors for enzymes participating in synthesis of various components of the bone matrix [5]. In addition, Zn is an important microelement of the human body and plays an important role in various biological functions, including DNA synthesis, activity of enzymes, metabolism of nucleic acids, biomineralization, and hormonal activity. It is well known that the large Cu deficiency causes heavy skeleton disorders [6]. Addition of Zn and Cu microdosages within biocoatings will allow the directed antimicrobial activity to be obtained for a long time and the danger of growth of pathogenic microorganisms to be minimized. Incorporation of the above–indicated modifying additives will promote balancing between microelement concentrations of biocoatings and bone structures as well as improving conditions for implant adaptation to organism environments. The aim of the present work was to produce the Zn and Cu–incorporated CaP coatings on Ti–40Nb alloy by the MAO method under different process voltages and investigate their structure, composition, and physical and chemical properties.

2. Materials and Methods

The Ti–40Nb alloy was produced by the method of electron arc melting with nonconsumable electrode [7]. The specimens were cut from Ti–40Nb alloy billets and their sizes were $10\times10\times1$ mm^3. Specimens were prepared with silicon–carbide papers of 120, 480, 600, 1200 grit, respectively. Then specimens were ultrasonically cleaned (Elmasonic, Germany) in distilled water and ethanol for 10 min and further dried in air. Previously it was [8] reported that to carry out MAO method for deposition of CaP coatings on specimens, the Micro–arc–3.0 technique was used. The Zn– or Cu–incorporated CaP coatings were deposited from an aqueous solution prepared from 30wt.% phosphoric acid (H_3PO_4), 6wt.% Zn– or Cu–substituted hydroxyapatite (HA), and 9 wt.% carbonate calcium ($CaCO_3$) in the anode regime [9]. Zn– or Cu–substituted HA ($Ca_{9.9}Zn_{0.1}(PO_4)_6(OH)_2$ or $Ca_{9.9}Cu_{0.1}(PO_4)_6(OH)_2$) was produced by mechanochemical synthesis in the AGO–3 planetary mill at the Institute of Solid State Chemistry and Mechanochemistry SB RAS, Novosibirsk [10]. In the previous works [3, 9] we found the optimal MAO parameters for CaP coating deposition on the Ti such as pulse frequency of 50 Hz, pulse duration of 100 μs, process duration of 10 min, and voltage in the range of 200–300 V. In this work, we used the same MAO parameters for the coating synthesis on Ti–40Nb alloy.

The surface morphology and cross–sectional structure of the CaP coatings were observed by scanning electron microscopy (SEM, LEO EVO 50, Zeiss, and Philips SEM 515) and transmission electron microscopy (TEM, JEOL JEM–2010, Japan) in the "Nanotech" center at ISPMS SB RAS, and Scientific Educational Center at NR TSU. For TEM analysis replica of CaP coating were prepared by removing the CaP particles from the substrate. In addition, the elemental composition of the coatings was analyzed by energy–dispersive X–ray spectroscopy (EDX, INCA, Oxford Instruments) in conjunction with the SEM system. The size of structural elements of the coatings is measured by the secant method according to ASTM E1382–9 and DD ENV 1071–5. The chemical composition was determined by X–ray diffraction (XRD, DRON 7, Burevestnik, in "Nanotech" center at ISPMS SB RAS) in the angular range $2\theta = 10–90°$ with a scanning step 0.03 with Co K_α radiation. The average roughness (Ra) was estimated with a Hommel–Etamic T1000 profilometer. To measure the adhesion strength of the coatings two cylinders were glued to both sides of the samples with coating and fixed in grips in order to be tested under tension (Instron–1185, Great Britain). The adhesion strength is the maximum stress required to tear the cylinder off the coating. It was measured as $\delta_A = F / S$, where F is the breakout force of coating from the substrate and S is the area of separation [8].

3. Results and Discussion

Figure 1 shows the pulse current density of MAO process against the process duration for the deposition of Zn– or Cu–incorporated CaP (Zn–CaP or Cu–CaP) coatings on Ti–40Nb under different applied voltages. The presence of steplike pulses is demonstrated by identical dependences of current densities of deposition processes as Zn–CaP as Cu–CaP coatings. This indicates the pulse nature of microplasma discharges. The substance transport in the arc and electrolyte components precipitation on the substrate occur under these discharges. Figure 1 shows that the current density increases with the voltage increment. This is caused by the increase in the microplasma discharges intensity. In addition the current density decreases with the microarc treatment time increasing. This is due to the formation of the coating with a low electrical conductivity on the surface of the specimen (dielectric CaP layer).
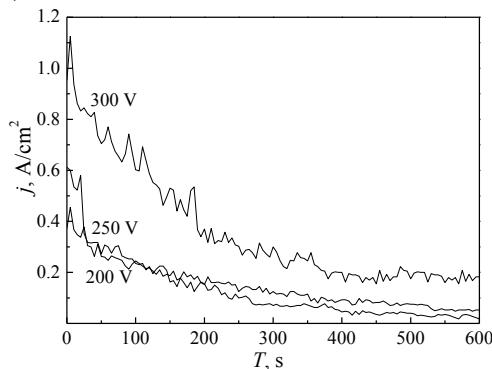

Figure 1. Current density against the process duration for deposition of Zn– or Cu–CaP coatings under different applied voltages.

Figure 2 shows SEM–images of cross–sectional structure of the Zn– and Cu–CaP coatings deposited under different oxidation voltages. It is seen that the coatings have gradient structure with many pores. With increasing the oxidation voltage, the thickness and sizes of pores increase. Further SEM investigations showed that the surface morphology of the Zn– and Cu–CaP coatings is identical and represented by the structural elements of spheroidal form with pores (Figure 3, a, d). The same surface morphology with spheres and pores were obtained for CaP coatings on the Ti in the previous works [3, 9]. The process of spheres and pores formation on the coating surface is similar to the process of formation and collapse of electrolyte–suspension "bubble" in the area of microplasma discharges.
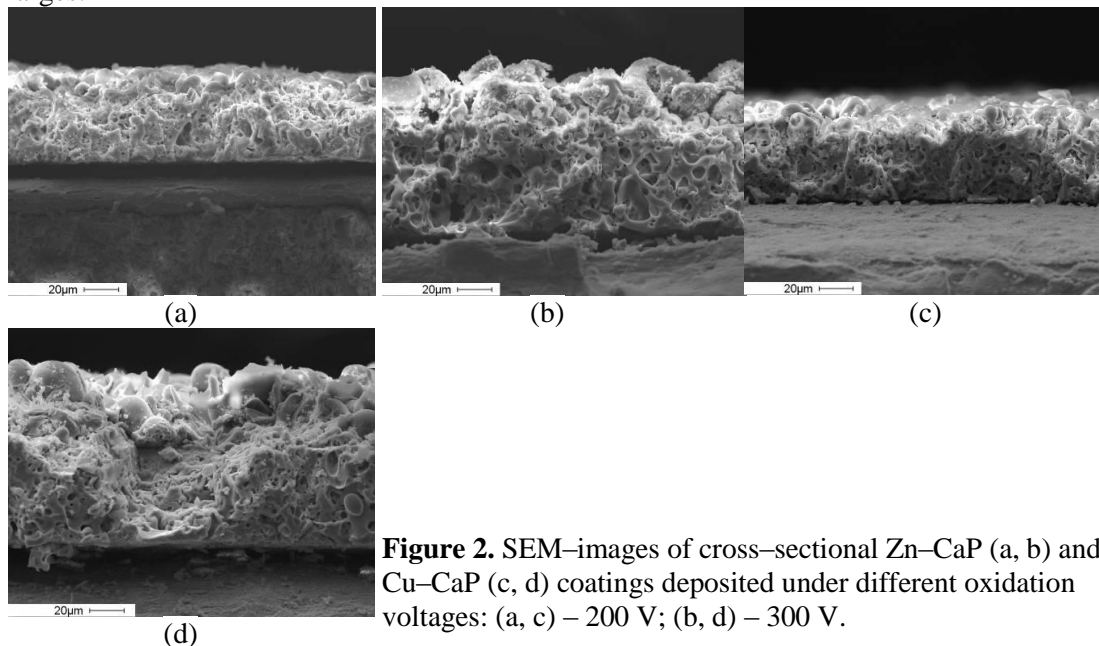

(a)   (b)   (c)

(d)

Figure 2. SEM–images of cross–sectional Zn–CaP (a, b) and Cu–CaP (c, d) coatings deposited under different oxidation voltages: (a, c) – 200 V; (b, d) – 300 V.

The measurements of the structural elements (spheres and pores) sizes showed that the histograms of the element size distribution have unimodal character for all coatings (Figure 3, b, c, e, f). The size of structural elements depends substantially on the MAO parameters, in particular, on the applied voltage. Zn– and Cu–CaP coatings start to form at the initial process voltage of 200 V. In this case, the average sizes of spheres and pores for both coatings are 17.7 and 4.4 μm, consequently (Figure 3, a–c). The increase in the MAO voltage to 300 V leads to the growth of spheres and pores to 25.9 and 7.2 μm, respectively, and to the destruction of some structural elements. In this case, the plate–like crystals of the new substance are formed on the surface of fragments and hemispheres (Figure 3, d).
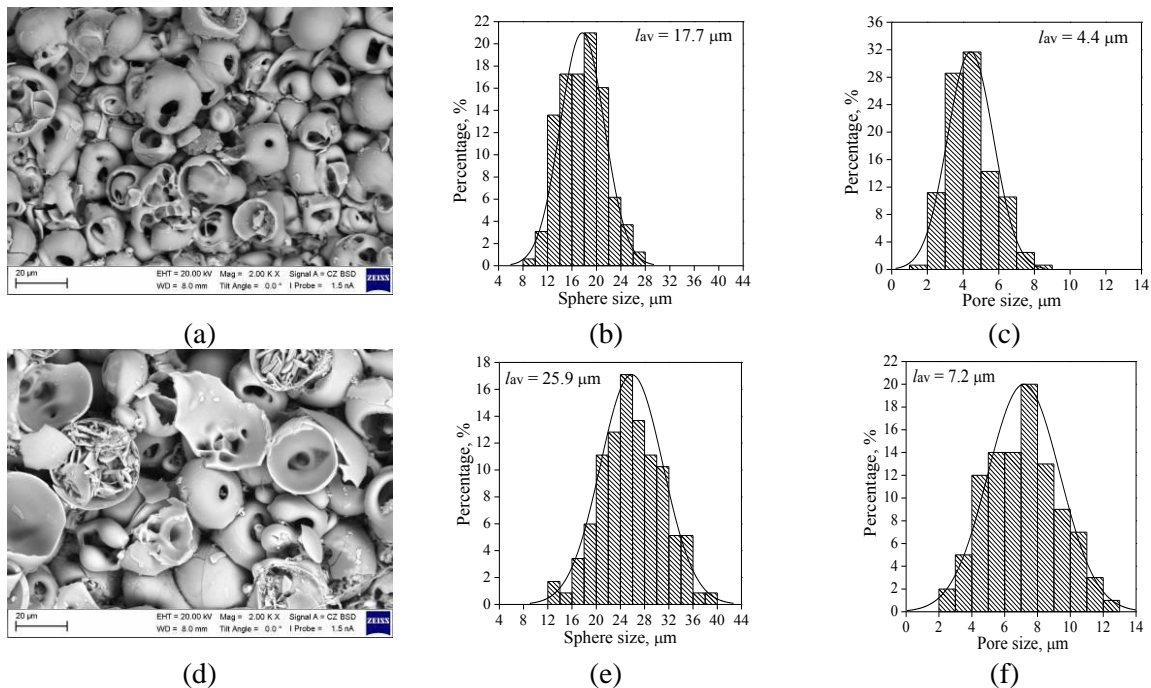

Figure 3. SEM–images (a, d) and histograms of structural element distribution by sizes (b, c, e, f) for Zn– or Cu–CaP coatings deposited under oxidation voltages: (a–c) – 200 V; (b–f) – 300 V.

It was found that with increasing of the process voltage the thickness and roughness of the Zn–CaP and Cu–CaP coatings increase linearly from 50 to 110 μm and from 3 to 6 μm, respectively (Figure 4, a). Khlusov et al [11] reported about novel concepts of "niche–relief" and "niche–voltage" for stem cells and supposed that the average roughness in the range of 2.5–5.0 μm is optimal for successful stem cells adhesion to the coating surface and their further differentiation into the bone tissue. Also, Sammons et al [12] reported that the microporous rough surfaces improved osseointegration of the implants. The change in the surface morphology, topography and thickness of these coatings under increase of the process voltage is connected with increasing of microplasma discharge intensity. However, such important characteristic of the coatings as the adhesion strength to substrate has a low values and decreases from 10 to 4 MPa with increasing of the process voltage (Figure 4, b). This is due to the increase in the coating thickness and size of pores. Unfortunately, it is faulty adhesion for medical applications because according to the ISO 13779–4, for medical devices the adhesion strength of coatings to substrate must be not less than 15 MPa. In this regard, to increase the coating adhesion, the surface was preliminary treated before the coating deposition using sandblasting and subsequent chemical etching [8]. Such pretreatment allows to increase the adhesion strength twice.

Results of XRD analysis showed that the Zn–CaP and Cu–CaP coatings deposited under the process voltages of 200–250 V are in the X–ray amorphous state (Figure 5). Low intensive reflexes corresponding to the β–calcium pyrophosphate (β–$Ca_2P_2O_7$) and monetite ($CaHPO_4$) phases are presented in XRD patterns. With increasing the oxidation voltage to 300 V the intensive crystalline

monetite phase forms in the coatings. Monetite exhibits osseoinductive properties like other acid calcium phosphates, which "etches" bone apatite and induces desorption of specific osteoinductive BMP–type proteins [13]. In addition, monetite dissolves easily in the body fluids and transforms into hydroxiapatite at subsequent mineralization. The XRD results are in agreement with the SEM results. Figures 3 and 4 illustrate that the plate–like crystals are typical for monetite crystals.
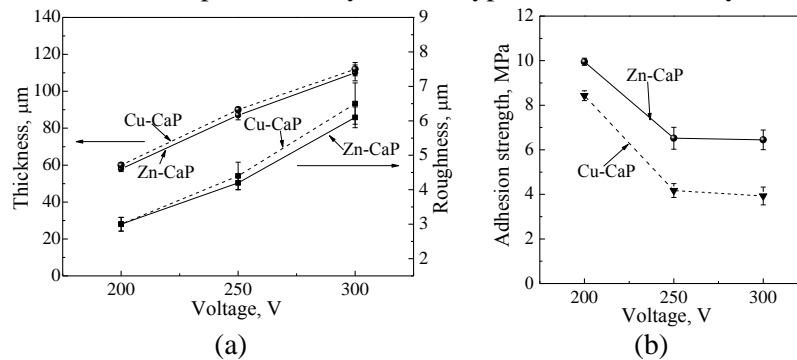

Figure 4. Graphs of thickness and roughness (a), and adhesion strength (b) of Zn–CaP and Cu–CaP coatings against the applied voltages.

Figure 6 shows bright–field (BF) and dark–field (DF) TEM–images with selected–area diffraction (SAD) patterns for particles of Zn– or Cu–CaP coatings. The TEM–study reveals the amorphous structure of coatings. It was observed in the SAD–patterns with two diffusion halos (Figures 6, c, f). It confirms the XRD results (Figure 5) indicating the X–ray amorphous structure.
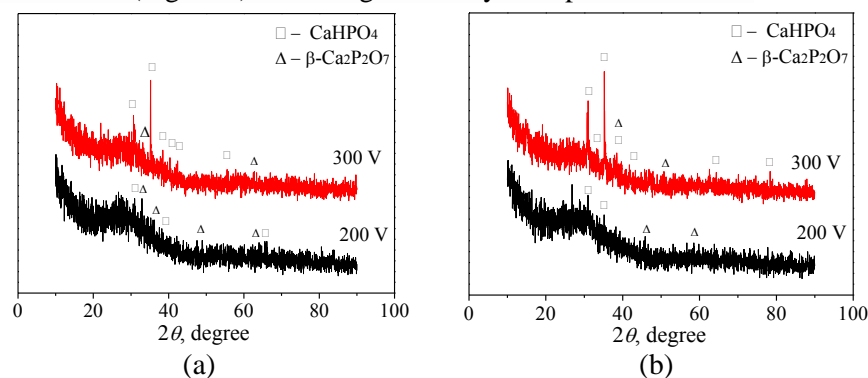

Figure 5. XRD–spectra of Zn–CaP (a) and Cu–CaP (b) coatings deposited under different process voltages.

The EDX microanalysis performed from surface and cross–sectional profile of Zn–CaP and Cu–CaP coatings revealed the elemental composition with the following elements: Ca (5.7–9.8 at.%), P (15.8–25.2 at.%), O (51.2–63.3 at.%), Ti (5.8–9.8 at.%), Nb (2.2–4.2 at.%), Zn or Cu (0.1–0.4 at.%). The larger amount of Ti than Nb in the coatings can be connected with predominant Ti content in amorphous state. The EDX results showed that the maximum Zn and Cu incorporation of 0.3 and 0.2 at.% corresponds to the coatings deposited under oxidation voltage of 250 V. With increasing the process voltage and consequently the temperature in the microplasma discharge region, the process of Ca^{2+} ion deposition from the electrolyte is intensified and the Ca/P ratio increases [3]. The maximum Ca/P ratio of 0.5 is obtained for both coatings deposited under the process voltage of 300 V.

4. Conclusion

Thus, the investigations of the morphology, structure, and properties of Zn– and Cu–CaP coatings on Ti–40Nb alloy formed by MAO method in electrolyte based on substituted HA under different applied voltage in the range of 200–300 V were performed. It was found that the thickness and roughness of

the coatings, and the average size of the structural elements (spheres and pores) grow linearly with increasing the MAO voltage. In this case, the coating adhesion strength to substrate decreases. It was established by the XRD that the coatings deposited under voltages of 200–250 V have X–ray amorphous structure. Increase of the voltage to 300 V leads to the formation in the coatings of crystalline phases such as $CaHPO_4$ and β–$Ca_2P_2O_7$. The EDX analysis showed that maximum contents of 0.3 at.% Zn or 0.2 at.% Cu were found in the coatings deposited under the voltage of 200–250 V. Maximum Ca/P ratio of 0.5 was obtained for both coatings deposited under 300 V.
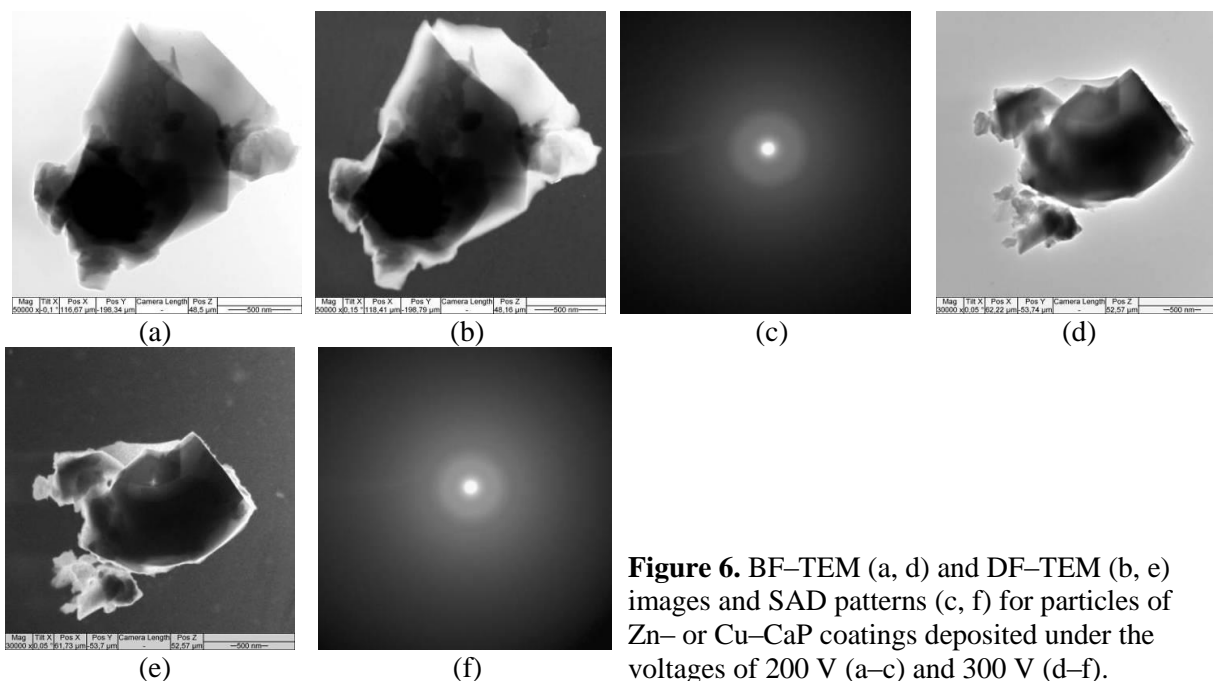

(a)　　　(b)　　　(c)　　　(d)

(e)　　　(f)

Figure 6. BF–TEM (a, d) and DF–TEM (b, e) images and SAD patterns (c, f) for particles of Zn– or Cu–CaP coatings deposited under the voltages of 200 V (a–c) and 300 V (d–f).

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