Effect of micro-arc oxidation time and applied voltage on formation of strontium- and silicon-incorporated biocoatings

E G Komarova1, M B Sedelnikova1, E A Kazanceva2, Yu P Sharkeev1

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

E-mail: katerina@ispms.tsc.ru

Abstract. The study of the influence of the MAO time and applied voltage on the formation of the structure, phase and elemental compositions, and properties of Sr-Si-CaP coatings on the titanium surface were performed. It was established that the coating thickness, roughness and the average size of the structural elements (spheres and pores) grow linearly with increasing of the MAO voltage from 200 to 370 V. While, the MAO time effects only on the coating thickness. XRD revealed that the coatings deposited at the low voltages of 200-250 V have X-ray amorphous structure. Increase of the voltage to 350 V leads to the formation in the coatings of crystalline-amorphous structure with amount of crystalline monetite (CaHPO₄) phase to 35±5 wt.% The EDX microanalysis showed that maximum Ca/P atomic ratio of 0.9 and maximum contents of 1.0 at.% Sr and 1.2 at.% Si were found on the coating surface in the regions of accumulation of the monetite crystals for the coatings deposited at high voltages of 300-350 V.

1. Introduction

One of the most promising approaches in the modern biomedical materials science is to modify and functionalize the surface of metallic implants, especially from titanium and its alloys, in order to provide a new complex of the performance properties. Many surface treatment techniques including physical, physicochemical, chemical and biomimetical methods have been used to deposit the biological active calcium phosphate (CaP) coatings on the metallic implants for the improvement their osteointegration. Actual trends in the field of the biocoating deposition involve the searching of the optimal coating parameters providing the greatest mechanical and biological compatibility with bone tissue. Micro-arc oxidation (MAO), also known as plasma electrolytic oxidation (PEO) is an effective and low-cost technique for producing a porous, relatively rough and firmly adherent bioactive CaP-base coatings on the valve metal surface (e.g. Ti, Zr, Nb, Mg, etc.) [1]. MAO is the high-temperature electrochemical technology using a plasma arc discharge within an aqueous electrolyte solution [2]. The advantage of MAO process is that the coating composition can be designed by doping different specific elements from electrolytes such as calcium, phosphorus, strontium and silicon [3, 4]. For biomedical applications, Ca²⁺ and PO₄³⁻ ions in the electrolyte could enter the MAO coating during the process, so that the bioactivity potential of titanium alloys was increased [5].

Strontium (Sr), which is natural bone-seeking trace element, has been shown to enhance the osteoblast replication and differentiation and bone matrix mineralization. At the same time, Sr can
inhibit bone resorption by reducing the osteoclast differentiation and resorption activity, and inducing osteoclast apoptosis [4-7]. Silicon (Si) is known to be essential as a trace element in biological processes. In particular, it was reported [8] to have a specific metabolic role connected to the bone growth. Presence of Si at the surface of biomaterials may also enhance osteogenesis through a direct chemical mechanism and positively affect bone in-growth, osteogenesis, cell differentiation, and remodeling. Considering the beneficial effects of Sr and Si in the bone tissue, they have been widely used as doped element into CaP biocoatings via MAO method [4-7].

By varying the MAO electro-physical parameters and changing the electrolyte composition it is possible to control the properties, structure and composition of the formed coatings. The formation of Sr- and Si-incorporated CaP-based biocoatings is possible via MAO technique using aqueous electrolyte containing the Sr and Si co-substituted hydroxyapatite (HA) nano-powder as was shown in the previous studies [9, 10]. The aim of the present work was to study the effect of MAO time and applied voltage on the formation of the structure, phase and elemental compositions, and properties of Sr- and Si-incorporated CaP (Sr-Si-CaP) biocoatings on the titanium surface.

2. Materials and Methods

The experimental specimens were cut from the billets of commercially pure titanium (grade 2, Ti) with the plate-like form 10×10×1 mm by sizes. The specimens were polished with a series of increasingly finer abrasive papers up to 1200 grit. The Micro-Arc 3.0 installation with the pulsed electrical source was used to synthesize the MAO biocoatings on the Ti substrates as in the previous works [9, 10]. The Ti specimen and the titanium electrolytic bath were taken as a working and the counter electrode. To prepare the Sr-Si-CaP coatings on the Ti the aqueous electrolytes contained 30 % $\text{H}_3\text{PO}_4$, 100 g/l $\text{CaCO}_3$ and 60 g/l nano-powder of Sr and Si co-substituted HA. HA partially substituted in the cationic sublattice by Sr$^{2+}$ and in the anionic sublattice by $(\text{SiO}_4)^{4-}$ with substituents concentration of 0.5 M $(\text{Ca}_{9.5}\text{Sr}_{0.5}(\text{PO}_4)_{5.5}(\text{SiO}_4)_{0.5}(\text{OH})_2)$ was prepared by mechanochemical synthesis according to technique described in [11]. The coatings were synthesized using the pulsed anodic potentiostatic power at the fixed pulse frequency of 50 Hz and pulse duration of 100 µs. The MAO voltage was varied from 200 to 400 V with the step of 20 V, and growth time was varied to 10 min at the fixed voltage of 200 V.

The surface and cross-sectional morphology as well as the elemental distribution and composition of the coatings were analyzed by scanning electron microscopy (SEM, Zeiss LEO EVO 50) equipped with the energy-dispersive X-ray spectroscopy analyzer (EDX, INCA, Oxford Instruments) in the “Nanotech” common use center at the Institute of Strength Physics and Materials Science SB RAS, Tomsk, Russia. The phase composition was determined with X-ray diffraction (XRD, Shimadzu XRD 6000) in the angular range of 2$\theta$=10-90° with a scan step of 0.01° using Cu Kα radiation The surface roughness was measured with a Profilometer-296 via the average roughness parameter ($R_a$).

3. Results and Discussion

Figure 1 shows pulse current density against the MAO time for the deposition of Sr-Si-CaP coatings on Ti substrates under different applied voltages. The presence of step-like pulses on the curves indicates the pulse nature of micro-arc discharges. Figure 1a shows that the current density increases with the voltage increment form 200 to 400 V. This is caused by the increase of micro-arc discharges intensity. In addition, the current density decreases with increasing of the MAO treatment time. This is due to the formation of the coating with a low electrical conductivity (dielectric CaP layer) on the Ti surface. We suppose, that the mechanism of the coating growth can be divided into two stages. In the first stage (up to ~3 min), the current density decreases intensively from 1.5 to 0.1 A/cm$^2$. It corresponds to the high coating growth under the impact of a numerous micro-arc discharges occurring as a result of a localized electric breakdown of the growing coating. In the second stage (from 3 to 10 min) the current density takes the minimum values and enters the plateau when the coating is enough thick to prevent the dielectrical breakdowns. This theory is confirmed by the regularity of the coating thickness growth at applied voltage of 200 V represented in the figure 1b.
(curve 2). It can be seen, the intensive growth of the coating thickness to 30 µm occurs in the first stage. In the second stage, the coating thickness increases by 20 µm (from 30 to 50 µm).

![Graphs of the MAO current density (a, b, curve 1) and the coating thickness (b, curve 2) against the MAO time for the deposition of Sr-Si-CaP coatings at the applied voltages of: (a) – 200, 250, 300, 350 and 400V; (b) – 200 V.](image)

**Figure 1.** Graphs of the MAO current density (a, b, curve 1) and the coating thickness (b, curve 2) against the MAO time for the deposition of Sr-Si-CaP coatings at the applied voltages of: (a) – 200, 250, 300, 350 and 400V; (b) – 200 V.

The SEM-images of the surface and cross-section of the Sr-Si-CaP coatings deposited at 200 and 350 V is presented in figure 2. It can be seen that the surface morphology of the coatings includes the spheroidal elements (spheres and hemispheres) with open pores and local particles-fragments (figure 2a,b). Previously [10] it was described that the spheres and pores formation in the MAO coatings is similar to the mechanism of the formation and collapse of electrolyte-suspension “bubble” in the channels of plasma micro-discharges. Increasing of the applied voltage from 200 to 400 V leads to an increase in the intensity of the micro-arc discharges, and as a result, the temperature inside their channels grows. In this case, the average size of spheres and pores grows in the ranges of 19.0-26.5 and 8.0-14.5 µm, respectively (figure 3a), spheres are partially destructed and the new plate-like crystals are formed inside the destroyed hemispheres (figure 2b).

The SEM images of the cross-sectional coatings show the complex porous structure including the multiple branched round and elliptic pores (figure 2c,d). With increasing of the MAO voltage the coating thickness increases linearly from 47 to 145 µm (figure 3b), pore sizes grow and large macro- pores to 50 µm in length are formed (figure 2 d). In addition, the coating average roughness increases linearly from 3.2 to 8.8 µm (figure 3b). It should be noted that the thickness and roughness curves have maximal extremum at 370 V that can be result of destruction of the coatings and structural elements under the action of high-temperature micro-arc discharges at the voltages higher than 370 V (figure 3b). Previously [12] we assumed that the increase in the voltages higher than 350 V is attended with the transformation of the micro-arc discharges in arc ones, thereby causing the sphere destruction and fragmentation. It is noteworthy, the coating morphology, roughness and sizes of structural elements do not depend on the MAO time. Thus, the MAO time effects only on the coating thickness (figure 1b).

The figure 4 shows the XRD patterns in the angular range 2θ=25-55° for the Sr-Si-CaP coatings deposited at the MAO applied voltages of 200, 250, 300 and 350 V. It can be seen that the XRD patterns of the coatings formed at 200-250 V include the diffused halo indicated the X-ray amorphous phase in the coatings and weak broad reflexes of single monetite (CaHPO₄) phase. With increasing of the applied voltage from 300 to 350 V the number of reflections from different crystallographic planes of CaHPO₄ phase increases and the reflection intensity increases on the XRD patterns. Thus, the increase of the MAO voltage leads to the coating structure transformation from X-ray amorphous state into the amorphous-crystalline state with amount of crystalline CaHPO₄ phase to 35±5 wt.%.
Figure 2. SEM-images of the surface (a, b) and cross-section (c, d) of the Sr-Si-CaP coatings deposited at 200 V (a, c) and 350 V (b, d).

Figure 3. Graphs of the size of spheres and pores (a), the thickness and roughness (b) of the Sr-Si-CaP coatings against the MAO applied voltage.

In the previous work [12] it was reported that the formation of crystalline phase in the coatings is associated with the growth of the micro-arc discharge temperature (>2000 K). The identified CaHPO₄ phase in the coatings crystallizes in the triclinic system with the following lattice parameters: \( a=6.8871 \text{ Å} \); \( b=6.9649 \text{ Å} \); \( c=6.6167 \text{ Å} \). These XRD results are in the agreement with the SEM results.
indicating the incorporation of spheroidal structural elements in the coatings that can be in the X-ray amorphous state and the presence of plate-like crystals in the coatings formed at the higher voltages potentially corresponding to the crystalline CaHPO$_4$ phase (figure 2a, b).

![XRD patterns of Sr-Si-CaP coatings deposited at applied voltages of 200, 250, 300 and 350 V.](image)

**Figure 4.** XRD patterns of Sr-Si-CaP coatings deposited at applied voltages of 200, 250, 300 and 350 V.

The EDX microanalysis of Sr-Si-CaP coatings revealed the different amounts of Ca, P, O, Ti, Sr and Si elements throughout the coating surface and cross-section in dependence on the MAO voltage (table 1). It can be seen for the coating surface, with increasing of the applied voltage the Ca amount increases, Ti and P amounts decrease, and O, Sr and Si amounts are constant. While for the coating cross-section, the Ca, P, Sr and Si amounts increase, O amount decreases, and Ti amount is constant with increasing of voltage. These behaviors can be associated with increase in the intensity and temperature of the micro-arc discharges leading to the increase of the reactive capacity of the all electrolyte components including Ca-containing compounds. Also, increase in the MAO voltage leads to the partial recrystallization of the X-ray amorphous phase of the coatings into the crystalline CaHPO$_4$ phase as shown above by XRD (figure 4). As a result, the Ca/P atomic ratio increases from 0.3 to 0.6 on the coating surface and equals to 0.3 in the cross-section of all type coatings (table 1).

The EDX grey-level mapping showed that the Ti, P, Ca, Sr and Si elements are distributed homogeneously throughout the surface of Sr-Si-CaP coatings deposited at the low voltages of 200–250 V. An increase in the voltage from 300 to 350 V leads to the localization of calcium and phosphorus in the areas of the plate-like crystals accumulation (figure 5).

**Table 1.** Quantitative elemental composition of Sr-Si-CaP coatings.

| Elements | Number of the elements on the coating surface, at.% | Number of the elements in the coating cross-section, at.% |
|----------|-----------------------------------------------|--------------------------------------------------|
|          | 200 V  | 300 V  | 350 V  | 200 V  | 300 V  | 350 V  |
| Ca       | 5.4±0.2 | 8.0±0.5 | 9.1±0.5 | 4.5±0.3 | 7.1±0.4 | 7.8±0.4 |
| P        | 20.7±0.3 | 19.7±0.6 | 18.9±0.2 | 13.7±0.2 | 23.2±0.7 | 22.6±0.7 |
| O        | 59.4±0.4 | 60.3±1.5 | 61.9±0.5 | 67.6±0.9 | 54.9±1.1 | 55.2±2.2 |
| Ti       | 13.3±0.5 | 10.6±1.3 | 8.8±0.8 | 13.3±0.8 | 13.4±1.0 | 13.2±1.5 |
| Sr       | 0.8±0.1 | 0.8±0.1 | 0.8±0.1 | 0.5±0.1 | 0.9±0.1 | 0.8±0.1 |
Table 3. Elements concentration in Sr-Si-CaP coatings deposited at 350 V; the element’s concentration is marked by white color.

| Element | Concentration |
|---------|---------------|
| Si      | 0.5±0.1       |
| Ca      | 0.6±0.1       |
| Sr      | 0.6±0.1       |
| Si      | 0.3±0.1       |
| Ca      | 0.5±0.1       |
| Sr      | 0.5±0.1       |

**Figure 5.** SEM image (a) and EDX grey-level maps of the Ca, Sr and Si distribution (b-d) throughout the surface of Sr-Si-CaP coatings deposited at 350 V; the element’s concentration is marked by white color.

Quantitative EDX microanalysis inside the local regions of accumulation of the crystals throughout the coating surface revealed the highest concentration of Ca (figure 5b) and the maximum Ca/P atomic ratio equal to ~0.9. This result confirms that these crystals can correspond to the CaHPO₄ phase (Ca/P=1.0). Also, it was revealed that with increasing of the applied voltage the Sr and Si concentrations in the regions of crystal accumulation increase to 1.0 and 1.2 at.%, respectively (figure 5c,d).

4. Conclusion

Thus, the study of the influence of the MAO time and applied voltage on the formation of the structure, phase and elemental compositions, and properties of Sr-Si-CaP coatings on titanium surface were performed. It was established that the coating thickness, roughness and the average size of the structural elements (spheres and pores) grow linearly with increasing of the MAO voltage from 200 to 370 V. While, the MAO time effects only on the coating thickness. XRD revealed that the coatings deposited at the low voltages of 200-250 V have the X-ray amorphous structure. Increase in the voltage to 350 V leads to the formation in the coatings of crystalline-amorphous structure with amount of the crystalline monetite (CaHPO₄) phase to 35±5 wt.%. The EDX microanalysis showed that the maximum Ca/P ratio of 0.9 and maximum contents of 1.0 at.% Sr and 1.2 at.% Si were found on the coating surface in the regions of accumulation of the monetite crystals for the coatings deposited at the high voltages of 300-350 V.

Acknowledgments

The work has been financially supported by the Fundamental Research Program of the State Academies of Sciences for 2013-2020, direction of research III.23. Authors wishing to acknowledge assistance or encouragement from Dr. M.V. Chaikina (ISSCM SB RAS, Novosibirsk, Russia), V.V. Chebodaeva, M.A. Khimich and A.I. Tolmachev (ISPMS SB RAS, Tomsk, Russia).

References

[1] Sharkeev Yu P et al 2014 Biocomposites based on calcium–phosphate coatings, nanostructured and ultrafine–grained bioinert metals, their biocompatibility and biodegradation (Tomsk: Publishing House of Tomsk State University)

[2] Gnedenkov S V, Sharkeev Y P, Sinebryukhov S L, Khrisanfova O A, Legostaeva E V, Zavidnaya A G, Puz’ A V, Khlusov I A and Opra D P 2016 Corros. Rev. 34 65

[3] Zhang Z, Sun J, Hu H, Wang Q and Liu X 2011 J. Biomed. Mater. Res. B Appl. Biomater. 97B 224
[4] Yan Y, Sun J, Han Y, Li D and Cui K 2010 Surf. Coat. Tech. 205 1702
[5] Nan K, Wu T, Chen J, Jiang S, Huang Y and Pei G 2009 Mater. Sci. Eng. C 29 1554
[6] Dang Y, Song W, Chang B, Han T, Zhang Y and Zhao L 2016 Int. J. Nanomed. 11 1003
[7] Liu W, Cheng M, Wahafu T, Zhao Y, Qin H, Wang J, Zhang X and Wang L 2015 J. Mater. Sci. Mater. Med. 26 203
[8] Pietak A M, Reid J W, Stott M J and Sayer M 2007 Biomater. 28 4023
[9] Sedelnikova M B, Komarova E G, Sharkeev Yu P, Tolkacheva T V, Khlusov I A and Sheikin V V 2017 AIP Conf. Proc. 1882 020062
[10] Komarova E G, Sedelnikova M B, Sharkeev Yu P, Kazakbaeva A A, Glukhov I A and Khimich M A 2017 J. Phys. Conf. Ser. 830 012101
[11] Chaikina M V, Komarova E G, Sharkeev Yu P, Bulina N V, Prosanov I Yu 2016 AIP Conf. Proc. 1760 020009
[12] Sharkeev Y, Komarova E, Sedelnikova M, Sun Z M, Zhu Q F, Zhang J, Tolkacheva T and Uvarkin P 2017 Trans. Nonferrous Met. Soc. China 27 125