Bioactive coatings on 3D printed titanium implants with a complex internal structure for bone replacement

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Abstract. The micro-arc oxidation method was applied to modify the surface of 3D printed titanium implants with a complex internal structure. Two different electrolyte solutions were used for the surface modification, for which the respective working parameters of the micro-arc oxidation process were developed. Surface coatings formed with these parameters on the 3D implants have the same chemical composition and have the same surface morphology as surface coatings on 2D substrates. The measurement of the coating thickness using the X-ray microtomography demonstrates that this method is a useful tool for the thickness control of porous surface coatings at the inside and outside of the 3D titanium implants.

1. Introduction
Additive technologies, also known as additive manufacturing methods, are widely used in different industries. Especially the 3D printing process is known as one of these technologies, as well as the laser beam melting process, the layer-by-layer electron beam melting process and printing by lamination in which individual 3D structures are producible [1]. The 3D printing process is becoming more and more important, especially for medical applications. Using magnetic resonance and X-ray tomography, medical data can be obtained for the fabrication of individual 3D implants [2].

The additive technologies enable the production of individual and precisely fitting implants. Due to the additional possibility of adapting the inside of the implant with different filling patterns and thus the porosity, the integration with the bone tissue is also improved by the inside of the implant. Therefore, the development of methods and technologies for the modification and quality control of highly porous 3D tissue-engineered structures is one of the priority directions in material science and applied interdisciplinary science for the introduction of advanced regenerative technologies into clinical practice.

The formation of bioactive coatings on the surface of medical implants leads to an increase in the speed and quality of bone integration with the surgically installed implant. In addition, implants with calcium phosphate containing coatings are already being used successfully in medical practice to replace bone defects. However, the formation of such coatings on the surface of implants with a
complex shape and with a high porosity requires special methods. One of these methods for coating complex-shaped implants is the micro-arc oxidation. The aim of this work was to develop working parameters (hereinafter called as working modes) for the modification of highly porous 3D titanium implants by micro-arc oxidation, as well as to select and test a method for determining the thickness and uniformity of the coating over the entire surface of the samples.

2. Materials and methods
The 3D printed titanium test samples (fabricated by the company «LOGEEK® MS», LLC, Novosibirsk, Russia) were made of a titanium alloy and have the following dimension: high: 15 mm, diameter: 10 mm. All samples were subjected to chemical etching prior to the formation of the coatings. The coatings were formed in two different electrolytes. For the first electrolyte, the aqueous solution consists of calcium acetate \( (\text{Ca}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}, c = 15.6 \text{ g/L, purchased from Component-Reaktiv, LLC, Moscow, Russia}) \) and sodium dihydrogen phosphate dihydrate \( (\text{Na}_2\text{HPO}_4, c = 36.8 \text{ g/L, purchased from VEKTON, JSC, St. Petersburg, Russia}) \) with the addition of phosphoric acid \( (\text{H}_3\text{PO}_4, \text{ purchased from Component-Reaktiv, LLC, Moscow, Russia}) \) at a concentration of 2.5 ml/L. A supersaturated calcium oxide \( (\text{CaO, purchased from Component-Reaktiv, LLC, Moscow, Russia}) \) solution in a 10% aqueous solution of phosphoric acid \( (\text{H}_3\text{PO}_4) \) with the addition of a dispersed phase of hydroxyapatite (purchased from Fluidinova, Maia, Portugal) in an amount of up to 10 g/L was used as the second electrolyte. Hereafter, ‘MAO_1’ refers to the 3D titanium samples with the coating formed in the first electrolyte and ‘MAO_2’ refers to the 3D titanium samples with the coating formed in the second electrolyte. The coating formations were carried out on the setup “Micro-arc oxidation complex” designed in the Laboratory for Plasma Hybrid Systems, The Weinberg Research Center, School of Nuclear Science & Engineering of the Tomsk Polytechnic University (Tomsk, Russia). For the surface modification of the 3D titanium implants with the micro-arc oxidation process, a separate working mode was developed for each of the two electrolyte solutions. The working mode for the MAO_1 electrolyte solution was as follows: voltage – 350 V, voltage rise rate – 2 V/s, pulse repetition rate – 220 Hz, pulse duration 140 µs, coating formation time – 15 min. For the MAO_1 electrolyte solution, the working mode parameters are as follows: voltage – 320 V, voltage rise rate – 3 V/s, pulse repetition rate – 230 Hz, pulse duration –120 µs, coating formation time – 50 min. The temperature of electrolyte solution in both cases did not exceed 15 °C during the micro-arc oxidation process.

The surface morphology (as microscope images) and the elemental composition (as energy-dispersive X-ray spectroscopy, EDS) of the coatings were analyzed using a Quanta 200 3D scanning electron microscope (FEI Company, Hillsboro, Oregon, USA) equipped with an energy-dispersive X-ray spectrometer (JSM 5900LV, JEOL Ltd., Tokyo, Japan).

Measurements of the thickness and uniformity of the coating deposition on the 3D titanium implant samples were carried out using an X-ray microtomography scanner (micro-CT), which was designed and built-up in the international research laboratory for X-Ray optics at the Tomsk Polytechnic University (Tomsk, Russia). Micro-CT micrographs of the coated samples were received by a self-build X-ray scanner utilized with a Hamamatsu microfocus X-ray source (L9181-02, Hamamatsu Photonics, Hamamatsu City, Japan) with a tube voltage of 130 kV and a current 80 µA without beam filtration [3]. A flat panel detector (Mark2430C, PRODIS.NDT, pos. Malakhovka, Ovrazhki, Moscow Oblast, Russia) was used for image acquisition [4]. The voxel (grid value in a 3D room) size is 3.21 µm, taking into account the geometric magnification of 15.42. An image acquisition time of 900 ms was set, resulting in a total scan duration of approximately 15 minutes for 1000 projections. For the reconstruction of the tomograms was performed using a standard back projections algorithm with a flat field, ring artifacts and a beam hardening correction. To analyze of 3D tomograms and to plot of the thickness distribution by size, The VGSSTUDIO MAX 3.4.5 software (Volume Graphics, Heidelberg, Germany) utilized with the module “Wall Thickness Analysis” [5].
3. Results and discussion

Figure 1 shows the macroscopic appearance as a photograph of the 3D titanium samples with the calcium phosphate coatings, as well as SEM micrographs of their microscopic surface morphology.

![Figure 1](image)

**Figure 1.** The macroscopic appearance of the 3D titanium implant samples, shown by photographs with the MAO_1 coating (a1) and the MAO_2 coating (b1), and their corresponding microscopic surface appearance shown by SEM images in different magnifications (a2, b2 and a3, b3).

Surface coatings formed in different electrolyte solutions differ in color and structure. Coatings formed with the MAO_1 are brown and coatings formed with the MAO_2 solution are gray (figure a1 and b1). As figures a2 and b2 show, the coatings cover the entire sample evenly.

Coatings produced by the micro-arc oxidation process usually have a porous structure. However, the composition of the electrolyte solution and the micro-arc working modes affect the morphology of the fabricated coatings. The surface morphology of the MAO_1 coated 3D implant sample consists of crater-like formations with a pore in the center of each crater (figure a3). On the surface of the MAO_1 coating, the number of pores in the surface area of 1000 μm² is 172.5 ± 12.6 and the average diameter of these pores is 0.82 ± 0.20.

The surface of the 3D implant sample coated with the MAO_2 solution has a rougher structure, which is caused by hollow spherical particles and hemispheres with bigger pores (figure b3). The number of the spherical particles that are situated in the surface area of 1000 μm² is 19.6 ± 2.4 with an average size of (10.71 ± 2.50) μm. In this area are pores with a number of 25.6 ± 2.3 and an average diameter of (3.76 ± 1.08) μm.

Table 1 shows the elemental composition of the coatings, which corresponds to the composition of the utilized electrolyte solutions and consists of the elements carbon (C), oxygen (O), phosphorus (P) and calcium (Ca). Aluminum (Al) and titanium (Ti) are present in the elemental composition measurements of the coatings due to the substrate consisting of titanium alloy.

The Ca/P ratio in the applied surface coatings is 0.89 ± 0.05 for the MAO_1 coating and 0.37 ± 0.04 for the MAO_2 coating. These determined Ca/P ratios are in accordance with coatings formed on flat substrates, which were reported in references [6]. These results prove the finding of the optimal micro-arc oxidation working modes, whereby the physico-chemical properties of the coatings on the 3D titanium implant samples are comparable with known coatings on flat structures.
Table 1. Elemental composition of the formed coatings obtained by EDS, at%.

| Sample  | C         | O           | Al         | P         | Ca         | Ti         |
|---------|-----------|-------------|------------|-----------|------------|------------|
| MAO_1   | 4.79 ± 1.01 | 50.58 ± 1.59 | 1.00 ± 0.14 | 1.89 ± 0.23 | 1.69 ± 0.15 | 40.07 ± 2.85 |
| MAO_2   | 19.62 ± 0.89 | 46.34 ± 1.94 | 0.43 ± 0.14 | 16.25 ± 0.28 | 6.02 ± 0.80 | 11.35 ± 1.01 |

Figure 2. X-ray microtomograms of the scanned implant sections of the calcium phosphate containing surface coatings MAO_1 (a1-a2) and MAO_2 (b1-b2).

Figure 3. Layer thickness distribution in the region of interest with a size of 2.5 × 2.5 × 1.5 mm for the surface coatings MAO_1 and MAO_2 on the 3D titanium implant samples.

The thickness and heterogeneity of the coatings on the 3D titanium implant samples were determined by X-ray microtomography (figure 2). This method provides information about the internal structure of the highly porous and complex-shaped 3D samples with calcium phosphate coatings and visualizes them with high-definition images. Figure 2 shows that both the inside and outside of the 3D titanium
implant samples are covered with a calcium phosphate coating. For the MAO_1 coating, the thickness is in the range from 0.12 µm to 116.08 µm and for the MAO_2 coating, the thickness is in the range from 0.12 µm to 63.37 µm. The lowest value for the measured coating thickness represents the lower sensitivity limit of the utilized X-ray microtomography device.

Figure 3 summarizes the results of the X-ray microtomography as thickness distribution diagram for the surface coatings MAO_1 and MAO_2 on the 3D titanium implant samples in the region of interest with the size of 2.5 × 2.5 × 1.5 mm over the count of voxels with a size of 3.21 µm. As the result, the average thickness of the MAO_1 coatings is (33.01 ± 15.75) µm, while for the MAO_2 coatings the average thickness is (13.39 ± 7.17) µm. Figure 2 and 3 demonstrate that the MAO_1 coatings have a higher layer thickness distribution and less heterogeneity compared to the MAO_2 coatings.

4. Conclusions
As a first result, the required parameters of the micro-arc oxidation for the modification of 3D printed titanium implants were determined. The applied working modes for two different electrolyte solutions to form calcium phosphate containing surface coatings make it possible to obtain coatings that are chemically similar to those on flat titanium implant samples. The results of the elemental composition analysis and the obtained Ca/P ratios are in agreement with the actual literature in this research field. Layer thicknesses and the heterogeneity of the formed surface coatings on the 3D titanium implant samples with a complex internal structure were successfully investigated applying the X-ray microtomography method. The MAO_1 coatings have a higher layer thickness distribution and less heterogeneity compared to the MAO_2 coatings. Coatings formed via the MAO_1 electrolyte solution having a thickness in the range of 0.12 µm to 116.08 µm and average thickness of (33.01 ± 15.75) µm. The thickness of the coatings formed via the MAO_2 electrolyte solution is in the range from 0.12 µm to 63.37 µm with an average thickness of (13.39 ± 7.17) µm.

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