The Elasticity of Calcium Phosphate MAO Coatings Containing Different Concentrations of Chitosan

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Abstract. Calcium-phosphate coatings were formed on the commercially pure titanium by the method of microarc oxidation (MAO) from the electrolyte, which additionally contains 2.5-15 wt.% solution of chitosan. The surface morphology, wettability and elasticity of the formed coatings were investigated. It is shown that the addition of chitosan to the electrolyte composition increases porosity and elasticity of the coatings.

1. Introduction

In traumatology, implants made on the basis of titanium and its alloys, capable of withstanding mechanical loads during operation, are widely used. However, low wear and corrosion resistance of metal implants in a corrosive liquid medium of the human body, contribute to the release of metal ions into the body [1]. To prevent the release of metal ions into the human body, as well as to increase the biocompatibility and reduce the time of treatment, various coatings are deposited to the surface of titanium implants. The latter must combine biological activity and high mechanical strength. As a rule, calcium phosphate materials, in particular hydroxyapatite, are used as biocompatible coatings. Hydroxyapatite has a chemical composition similar to that of bone tissue and provides a high biocompatibility of the implant with the body.

Another important property of coatings for implants is their developed porosity. With the introduction of such implants into the body, the bone tissue grows into the pores of the coating. This ensures the strength and long-term fixation of an implant, its normal functioning in the human body. As presented in a number of studies, porous bioceramics has a high biocompatibility, supporting bone growth in the implant [2,3].

One of the most commonly used methods for deposition of porous calcium phosphate coatings on titanium implants is the microarc oxidation method (MAO), which is a process of anodic oxidation with high plasma voltage [4,5]. One of the drawbacks of calcium phosphate coatings formed by the MAO method is their low elasticity. In addition, with increasing coating thickness, adhesion strength significantly decreases [6], which causes the destruction and detachment of the coating as a result of significant flexural deformations to which the elastic implant undergoes, both during implantation and during operation.

To increase elasticity of the electrolytically deposited calcium-phosphate coatings, the authors of this work used an electrolyte containing chitosan solution. Chitosan is a biodegradable, biocompatible and non-toxic polysaccharide, which in recent years has been considered as one of the most promising materials for biomedical applications [7–10].
Thus, the purpose of this work is to study the influence of chitosan on elasticity of the calcium phosphate coatings formed by the MAO method.

2. Materials and methods
The samples of the commercially pure titanium with sizes 60×20×0.5 mm³ were used as a material of substrates. Preparation of the surface of the samples before coating 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 calcium phosphate coatings by the microarc oxidation method using the setup created 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, additionally containing 2.5-15 wt.%, by weight of chitosan solution obtained when dissolving dry powder chitosan in acetic acid with the concentration of 4.5%. The coating was formed at voltage of 190 V with a voltage rise rate of 3 V/s, with a pulse repetition rate of 50 Hz and a pulse duration of 9.7 ms for 20 minutes. The process was conducted at a temperature of 15°C.

The thicknesses and the roughness of the CaP coatings was determined using Talysurf 5-120 contact profilometer (Tailor-Hobson, England).

The study of the surface morphology of the coatings was performed using scanning electron microscopy (SEM) using a JEOL-6000 electron microscope.

The diameter measurement and counting of the number of pores in the obtained images was carried out using the Image J 1.38 software package (National Institutes of Health, USA).

The elasticity of the coatings was investigated using Bend instrument (Gradient Techno, Russia) according to ISO 1519:2011. The smallest diameter of the rod, bending around which did lead to mechanical destruction or detachment of a coating was taken as the value of elasticity index. The values obtained from the results of 5 measurements for each of the studied groups were taken as the value of the elasticity index.

The wettability of each CaP coating was studied using an EasyDrop device (Krüss, Germany) with the ‘sit’ drop method by measuring the contact angle of a 3 µL liquid drop one minute after placing it on the sample surface. To avoid surface contamination, contact angle measurements were carried out immediately after surface modification.

3. Results and discussion
The studies of morphology of coatings using SEM showed that the surface of the calcium phosphate coating formed by the MAO method without the addition of a polymer has a complex spatial organization. On the surface, there are numerous craters at the top of which pores with an average diameter (0.3 ± 0.2) μm are located (Fig. 1, a). The surface roughness of such coating is Ra = 0.8 ± 0.2 μm. Adding a polymer to the electrolyte composition leads to an slight increase in the number of pores in the coatings, while the pore size does not change (Table 1). It should also be noted that the average roughness also does not change (Table 2).

The thickness of the coatings is up to 15 microns μm for all coatings.

The studies of measuring wettability of coatings showed that addition of a polymer to the electrolyte composition leads to an increase in the wetting angle. Moreover, with an increase in the mass content of the polymer from 2.5 wt.% to 15 wt.%, hydrophobicity of the coatings increases (Table 3).
Figure 1. SEM images of calcium phosphate coatings formed on Ti substrates by MAO methods in electrolytic solution without chitosan addition (a) and with the addition of 2.5% wt. chitosan (b), 5% wt. chitosan (c), 10% wt. chitosan (d) and 15% wt. chitosan (e). The contact angles of CaP coatings are shown in the inserts.

Table 1. Elasticity, number and diameter of pores of the CaP coatings (means ± standard deviations).

|               | Elasticity, mm | Pores/µm²   | Diameter of pores, µm |
|---------------|----------------|-------------|-----------------------|
| CaP           | 7              | 2.4±0.2     | 0.3±0.2               |
| CaP + 2.5 wt.% chitosan | 1              | 2.6±0.4     | 0.6±0.3               |
| CaP + 5 wt.% chitosan | 1              | 3.5±0.1     | 0.7±0.3               |
| CaP + 10 wt.% chitosan | 1              | 3.6±0.3     | 0.7±0.3               |
| CaP + 15 wt.% chitosan | 1              | 2.8±0.3     | 0.8±0.3               |
Table 2. Roughness of the CaP coatings (means ± standard deviations).

|                | CaP       | CaP+2.5 wt.% chitosan | CaP+5 wt.% chitosan | CaP+10 wt.% chitosan | CaP+15 wt.% chitosan |
|----------------|-----------|------------------------|---------------------|----------------------|----------------------|
| \( R_a \)      | 0.8±0.2   | 0.9±0.2                | 0.8±0.2             | 0.9±0.2              | 0.8±0.1              |
| \( R_z \)      | 2.5±0.5   | 2.5±0.3                | 2.8±0.5             | 3.1±0.5              | 2.9±0.4              |

Table 3. Contact angles of CaP coatings (means ± standard deviations).

|                | CaP       | CaP+2.5 wt.% chitosan | CaP+5 wt.% chitosan | CaP+10 wt.% chitosan | CaP+15 wt.% chitosan |
|----------------|-----------|------------------------|---------------------|----------------------|----------------------|
| Contact angle, ° | 14.7±2    | 39.2±1                 | 41.1±0.7            | 53.3±0.5             | 59.7±2               |

4. Conclusions
The calcium phosphate coatings are formed on titanium substrates by MAO using electrolytes containing various chitosan concentrations. It is shown that the addition of chitosan to the calcium phosphate electrolyte contributes to an increase in the elasticity and slight increase of the coating porosity. All coatings formed by MAO from electrolytes containing a polymer are characterized by the same elasticity. With increasing of a polymer concentration in the electrolyte, an increase in the wetting angle of the surface of the formed coatings is observed.

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