# Influence of Nanoparticles Deposition Conditions on the Microarc Coatings Properties

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**Abstract.** The surface charge of biomaterials significantly contributes to such processes as protein adsorption or biofilm formation and consequently osseointegration bone tissue and implant. There are a set of methods to create a charge on dielectric biomaterials surface. One of the perspective methods of materials electrization is an introduction of the nanoparticles with appropriate biomedical properties into biomaterial. Boehmite AlO(OH) nanoparticles is perspective for the biomaterials surface modification due to its high surface area and positive charge. In this work, the investigations of microarc calcium phosphate biocoatings modified by boehmite nanoparticles on the Ti substrate were presented. A variation of the nanoparticles deposition parameters allowed producing calcium phosphate coatings with different morphology and boehmite nanoparticles size distribution. The investigations of the modified coatings by the transmission and scanning electron microscopy methods are presented in the work.

## INTRODUCTION

The problem of implant rejection and prolonged healing of bone tissue still remains topical. Despite the fact that more and more different modified implants are designed, there is no reliable solution of this problem. During the last ten years, researchers have paid attention on the implant surface charge. It is known that cell membrane surfaces are charged [1]. That is why the surface charge compatibility between implant and cells is extremely important. Calcium phosphate (CaP) coatings on bioinert substrate produced by the microarc oxidation (MAO) method are promising and proven as biocompatible material for bone implantation. Due to porous morphology and chemical composition such composite provides ideal biocompatibility, actively stimulate osteogenesis and restoration of bone tissue [2]. Nanosized aluminum oxide hydroxide (boehmite) is perspective material as sorbents, catalysts, components of composite materials, and medical materials [3]. Nanocrystalline aluminum oxyhydroxide exhibits immune stimulating properties and it is one of few compounds approved as a human vaccine adjuvant [4]. Also, boehmite has the ability to load positive charge in the aquatic environment. This makes it a promising component for the modification of CaP coatings. The previous studies have shown that the boehmite nanoparticles deposited on the CaP coatings surface changed their properties [5].

The purpose of this study was to obtain CaP coating modified by boehmite nanoparticles and investigate the base properties of such coatings.

## MATERIALS AND METHODS

Technically pure titanium VT1-0 was chosen to prepare the specimens. The specimens were in form of plates sizes of which were 10×10×1 mm$^3$. The specimens were ground with silicon-carbide paper of 120, 320, 480 and 600 grits in series. Then the samples were ultrasonically cleaned for 10 min (Elmasonic, Germany) in distilled water. In order to carry out the microarc oxidation the MicroArc-3.0 installation was developed at the Institute of Strength Physics and Materials Science SB RAS (ISPMS SB RAS, Tomsk, Russia) [2, 5–7].

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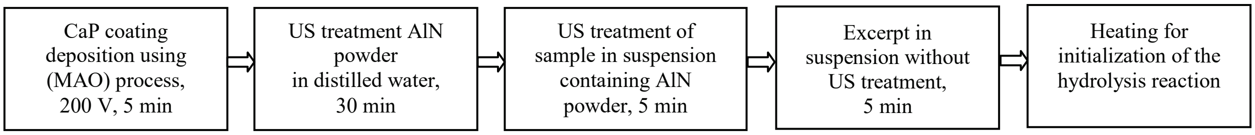



**FIGURE 1.** Scheme of the boehmite nanoparticles modification process

The CaP coatings were deposited in aqueous solution of phosphoric acid with hydroxyapatite and calcium carbonate powders in anode mode. The coating was formed under the following parameters: the pulse duration was 100 μs; the pulse frequency was 50 Hz; the deposition time was 5 min; the electrical voltage of the coating deposition process was 200 V.

The surface of microarc CaP coatings was modified by the boehmite nanoparticles deposition. The powder of aluminum nitride AlN in form of the water suspension was deposited on the microarc CaP coatings and then the hydrolysis reaction was initiated [4]. The boehmite AlO(OH) was formed as a result of the reaction:

$$AlN + 2H_2O \rightarrow AlO(OH) + NH_3.$$

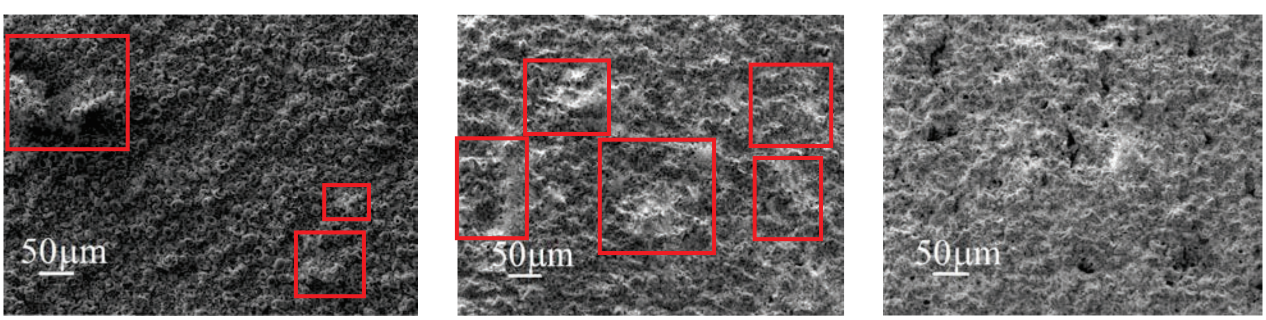
The suspension with AlN was subjected to preliminary ultrasonic (US) treatment for 30 min [5]. Then titanium specimens with CaP coating were put in the suspension and subjected to the second US treatment for 5 min. In the end of experiment the suspension with the samples was heated at the 80–90°C to initiate the hydrolysis reaction. The detailed scheme of boehmite nanoparticles deposition is presented in the Fig. 1. Three methods for introduction of boehmite nanoparticles using suspensions (AlN powder and distilled water) into microarc CaP coatings were developed. The 30 mg of AlN powder and 25 ml of distilled water were used to prepare the suspension in one of these methods. In the second method 60 mg of AlN powder and 25 ml of distilled water were used. In the last method we also used the suspension, containing 30 mg of AlN powder and 25 ml of distilled water, but the number of boehmite nanoparticles deposition on the same sample with CaP coating was increased by 5 times. For each subsequent application there was a new suspension.

The surface morphology was examined by Scanning Electron Microscope LEO EVO 50 (Shared Use Center "Nanotech"). In addition, the elemental compositions and distributions of the coatings were analyzed using energy-dispersive X-ray spectroscopy (EDX, INCA Energy 350) in conjunction with the SEM system. The phase composition was determined by X-ray diffraction (XRD, DRON 7, shared Use Center "Nanotech") in the angular range $2\theta = 5°–90°$ with a scan step of 0.01° with $CoK_\alpha$ radiation ($\lambda = 1.7890$ Å). Microstructure characterization was performed with the transmission electron microscope TEM (JEM-2100, JEOL, shared Use Center "Nanotech").

## RESULTS AND DISCUSSION

The investigation of the morphology, structure, physical and chemical properties of CaP coatings deposited by MAO method on Ti surface and modified by boehmite nanoparticles was performed.

The quantity of the AlN powder in suspension significantly affected the formation of boehmite particles and their distribution under CaP coatings surface. Figure 1 shows the SEM images of CaP coatings after introduction of boehmite nanoparticles using the first method. It was revealed that the morphology of CaP coatings after boehmite nanoparticles formation is represented by whole and partially destroyed spheroidal formations and uniformly distributed specific areas (the areas shown by red squares in Fig. 1).




(a) (b) (c)

**FIGURE 2.** SEM images of CaP coatings deposited on titanium surface modified by boehmite nanoparticles under different conditions: (a) 1 method; (b) 2 method; (c) 3 method

**TABLE 1.** Characteristics of modified CaP coatings

| No. of samples group | Parameters of AlO(OH) nanoparticles modification | Ra parameter before AlO(OH) nanoparticles deposition, µm | Ra parameter after AlO(OH) nanoparticles, µm | Aluminium content in modified CaP coatings, at % |
|---|---|---|---|---|
| 1 | Method 1<br>m(AlN) = 30 mg; | $2.20 \pm 0.32$ | $2.35 \pm 0.59$ | 2.44 |
| 2 | Method 2<br>m(AlN) = 60 mg; | $2.25 \pm 0.25$ | $2.50 \pm 0.15$ | 2.48 |
| 3 | Method 3<br>5 times nanoparticles deposition | $2.35 \pm 0.33$ | $3.15 \pm 0.20$ | 3.61 |
| 4 | CaP without nanoparticles | $2.38 \pm 0.42$ | – | – |

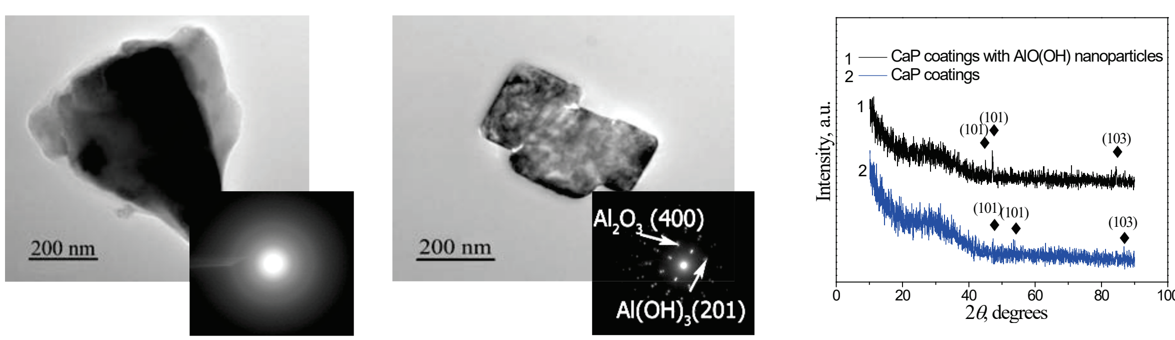
The size of the areas was up to 130 µm. Elemental analysis of such coatings demonstrated that Al content was equal 2.44 at %. Roughness parameter $R_a$ of modified coating increase from 2.20 to 2.35 µm when the AlO(OH) nanoparticles were deposited (Table 1).

CaP coatings modified by AlO(OH) nanoparticles using the second method are presented in Fig. 1b. The increase in the AlN mass to 60 mg led to the increase of specific areas quantity in the CaP coatings and their more uniform distribution (Fig. 1b). In this case, the roughness $R_a$ of coating changes from 2.25 to 2.50 µm (see Table 1). The results of EDX spectroscopy demonstrated that the Al content was 2.48 at %.

The CaP coating shown in Fig. 1c was modified by boehmite nanoparticles five times (the third method). The fivefold modification allows producing porous CaP coating covered by boehmite nanoparticles. The maximum value of $R_a$ parameter of 3.15 µm (Table 1) was detected for such coating. Aluminium content in modified CaP coating was also maximum (3.61 at %).

The coating samples numbered with 2 and 3 (Table 1) were selected for TEM study. As seen in Fig. 2a, the coating samples numbered with 2 had amorphous structure. The diffusion halos were observed in the selected-area diffraction (SAD) patterns (see insert in Fig. 2a). After fivefold boehmite nanoparticles deposition the fragments with crystalline structure were found in the coating (see Fig. 2b). Also, the reflexes corresponding to aluminum hydroxide ($Al(OH)_3$) and aluminum oxide ($Al_2O_3$) were observed in SAD pattern of the coatings modified by boehmite nanoparticles five times (Fig. 2b).

The results of XRD analysis confirmed the X-ray amorphous structure of the microarc CaP coatings modified by AlO(OH) nanoparticles (Fig. 2c). The diffuse halo corresponding to amorphous phase of CaP coating was observed in typical XRD spectra of the coatings produced under the all regimes of boehmite nanoparticle deposition. Reflexes corresponding to Ti were observed in XRD spectra of the modified CaP coatings on Ti substrate. With increasing of the AlN powder mass any changes in XRD patterns of modified CaP coatings were not found. Also, XRD analysis of microarc CaP without boehmite nanoparticles showed the amorphous state and reflexes of titanium substrate (Fig. 2c).




(a) (b) (c)

**FIGURE 3.** BF-TEM images and SAD-patterns (a, b) for CaP coatings samples number 2 and 3; (c) typical XRD spectra of CaP coatings with AlO(OH) nanoparticles and without it: ♦—Ti

These results can be explained by the poor crystalline of boehmite. In some literature it is called pseudoboehmite, but this name is not defined [8]. Crystallographic studies of researchers [9–11] indicate that there is no structural difference between boehmite and pseudoboehmite.

## SUMMARY

Modification by boehmite nanoparticles parameters as quantity of AlN powder and number of boehmite deposition significantly influence on the microarc CaP coating morphology. It was established that the increase of quantity of AlN powder till 60 mg provides the more uniform formation of boehmite nanoparticles on CaP coatings surface, but the content of Al was 2.48 at % in this case. The fivefold modification by AlO(OH) leads to forming porous CaP coating with the highest roughness of $R_a$ = 3.15 μm and Al concentration of 3.61 at %.

The coating structure of the samples after preliminary US treatment for 30 min of suspension with 30 and 60 mg of AlN powder before and after deposition of boehmite nanoparticles is in the X-ray amorphous state. Reflexes corresponding to titanium are observed in XRD spectra of such coatings. AlO(OH) nanoparticles are undetected in these coatings. The increase of the number of boehmite modification to five leads to the formation of the aluminum hydroxide and aluminum oxide on modified CaP coating surface. Thus, the multiple US treatment of CaP coating in the presence of boehmite nanoparticles promotes an increase of the aluminum content in the coating. The resulting aluminium oxide is a stable and strong compound, which can affect the crystallinity of some fragments in coating [12].

Subsequent investigations will focus on determining the influence of boehmite nanoparticles deposition conditions on the charge of the CaP coating surface. It will allow us to establish the optimal method of boehmite nanoparticles deposition.

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