



MICROARC CALCIUM PHOSPHATE COATINGS MODIFIED WITH ALUMINUM OXIDE AND ZINC OXIDE NANOPARTICLES

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The aim of the work was to investigate the influence of modification using aluminium oxyhydroxide and zinc oxide nanoparticles on the properties of modified CaP coatings formed by micro-arc oxidation.

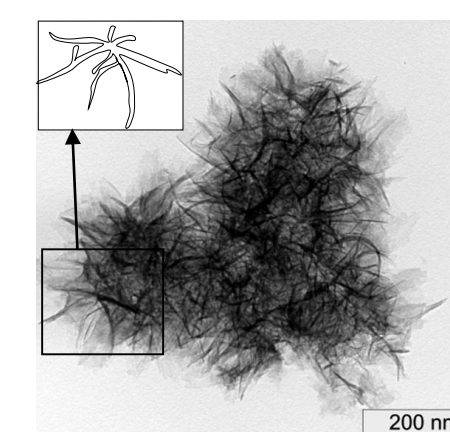
MATERIALS AND METHODS

The plates from commercially pure titanium with sizes of $10 \times 10 \times 1 \text{ mm}^3$ were used as substrates. The titanium plates were ultrasonically cleaned for 10 min in distilled water and 10 min in alcohol (Elmasonic, Germany). In order to form CaP coatings on the titanium surface the technological installation "Micro-arc-3.0" was used [4, 7]. The "MicroArc-3.0" installation was developed at the Institute of Strength Physics and Materials Science SB RAS (ISPMS SB RAS, Tomsk, Russia).

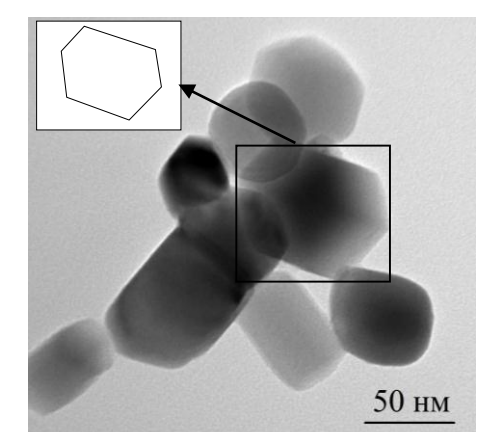
The surface of microarc CaP coatings were modified by the AlO(OH) and ZnO nanoparticles deposition using the suspension contained AlN and ZnO nanopowders. For suspension, preparing ZnO and AlN nanopowders were dispersed in distilled water by ultrasonic (US) treatment with duration range 60 min at the frequency of 18 kHz. The deposited CaP coatings on the titanium surfaces were immersed in these suspensions. Then the samples were ultrasonic treated in the suspension during 5 min. At the end of experiment, coated samples with ZnO nanoparticles were dried in air. The AlO(OH) nanoparticles obtained by heating of suspension with samples for initiation of the hydrolysis reaction.

Table 1. Coating formation parameters

Voltage of MAO	200 V
pulse frequency	50 Hz
pulse duration	100 ms
deposition duration	10 min
Electrolyte composition	$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2 + \text{H}_3\text{PO}_4 + \text{CaCO}_3$



TEM image of AlO(OH) nanoparticles



TEM image of ZnO nanoparticles

RESULTS AND DISCUSSION

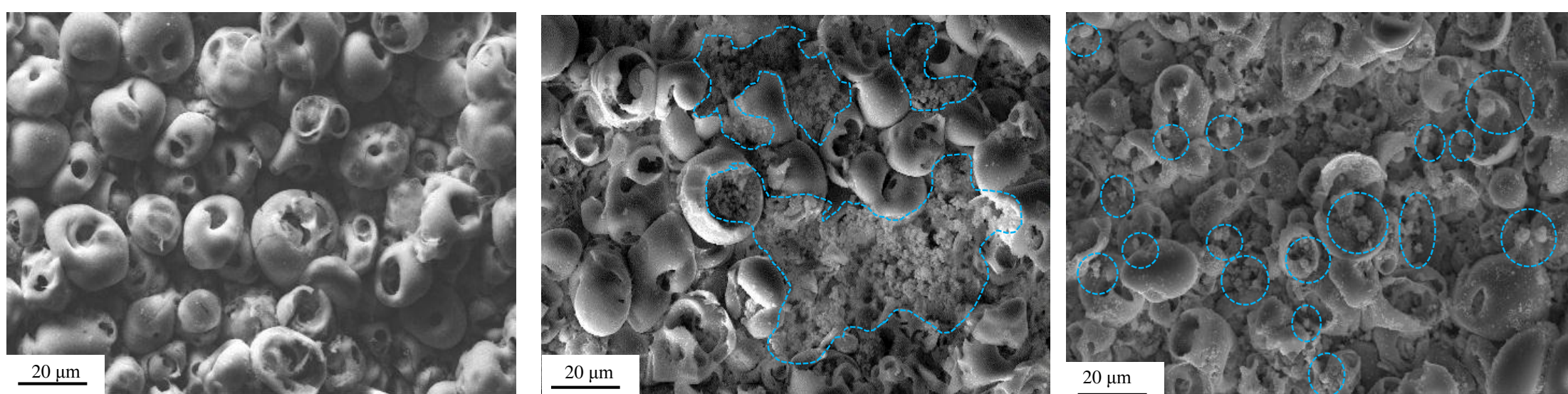


FIGURE 1. Typical SEM micrographs of coatings deposited on the Ti (a, c) at 200 V and modified by AlO(OH) (b) and ZnO (c) nanoparticles.

The SEM images of the CaP coatings morphology are shown in figure 1. The surface of deposited CaP coatings on the titanium substrate before modification has homogeneous structure represented with porous spheroidal formations (Fig. 1a). Such structure of formed coating is due to the features of the MAO. Average roughness (R_a) of such coating equal $3.2 \mu\text{m}$.

After modification aluminum oxyhydroxide nanoparticles agglomerations were found on the coating surface (fig.1 b, outlines with blue dotted lines). Roughness parameter R_a of modified coating increased from 3.2 up to $4.7 \mu\text{m}$ when the AlO(OH) nanoparticles were deposited (Table 1). The coating modified with zinc oxide contains spherical agglomerates of ZnO nanoparticles up to $10 \mu\text{m}$ in size (fig.1 c, outlines with blue dotted lines).

It should be noted that zinc oxide nanoparticles, in contrast to aluminum oxyhydroxide nanoparticles, do not form large areas up to $100\text{-}200 \mu\text{m}$ in size on the surface of CaP coatings (fig. 1c). These morphological changes in the coatings with ZnO nanoparticles inevitably lead to an increase in surface roughness by R_a from 3.2 to $4.9 \mu\text{m}$.

EDX analysis performed on the samples with CaP coatings showed presence of O, Ca, P, Ti, Al and Zn (Table 1). The Ca/P atomic ratio in these coatings is equal to 0.3 for all types of CaP coatings. Moreover, zinc in the coating contains more than aluminum in the coating with AlO(OH) at equal concentrations of the used powder in the suspensions. This is due to the large number of dense agglomerates zinc oxide nanoparticles.

SUMMARY

The research of the morphology, elemental composition and corrosion properties of the CaP coatings deposited by the MAO method and modified by AlO(OH) and ZnO nanoparticles was performed.

The CaP coatings have homogeneous porous surface and developed internal pore structure. The ZnO nanoparticles adding to coating leads to forming dense ZnO nanoparticles agglomeration of $8\text{-}10 \mu\text{m}$ in sizes on the coatings surface. After modification AlO(OH) nanoparticles agglomerations areas with sizes up to $100 \mu\text{m}$ were found on the coating surface.

It was established that the coatings modified with aluminium oxyhydroxide (AlO(OH)) nanoparticles have high corrosion resistance properties. The corrosion potential of CaP coating doubled after AlO(OH) nanoparticles adding from 0.12 to 0.24 mV . At the same the corrosion potential of CaP coating with ZnO nanoparticles decreased to 0.05 mV . Thus, it was shown, that due to the special structure of the AlO(OH) nanoparticles the modified CaP coatings exhibited high corrosion resistance.

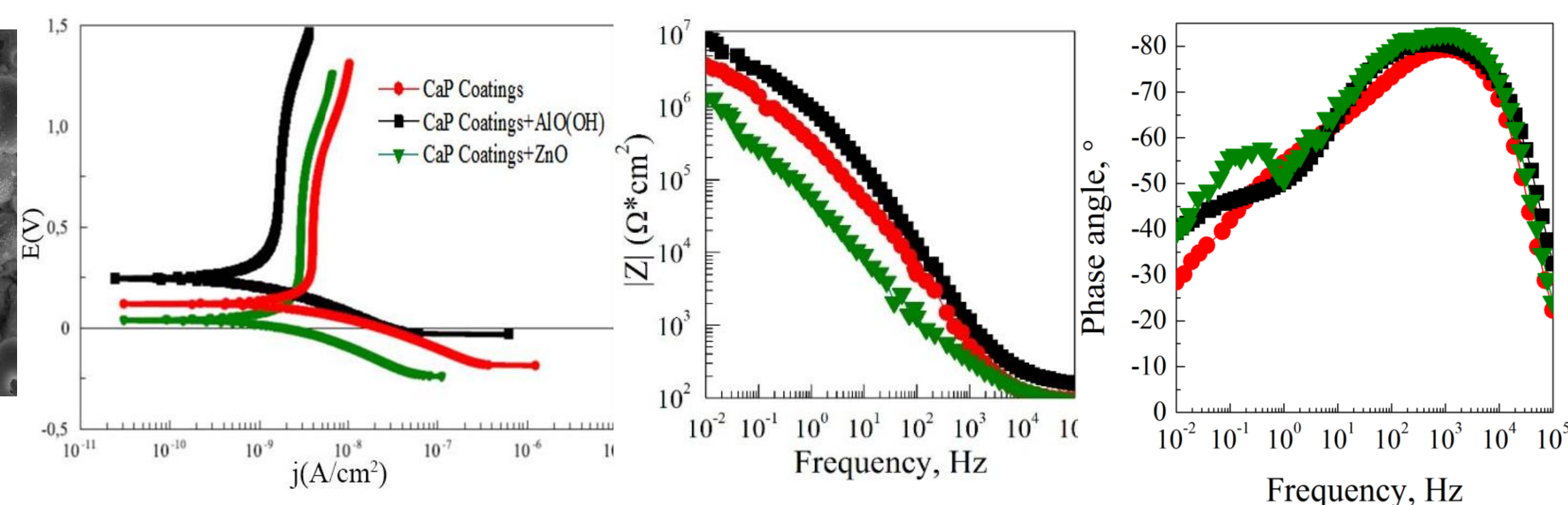


FIGURE 2. Potentiodynamic polarization curves obtained in Ringer solution (a); Impedance modulus versus frequency (b) and phase angle theta versus frequency (c) dependencies obtained in Ringer solution.

Analysis of the polarization curves of the obtained coatings indicates a significant effect of the AlO(OH) introducing into coating on the protective characteristics of the coating.

The corrosion potential of CaP coating doubled after AlO(OH) nanoparticles adding from 0.12 to 0.24 mV . At the same the corrosion potential of CaP coating with ZnO nanoparticles decreased to 0.05 mV . The higher value of the corrosion potential of coating modified by AlO(OH) is explained by the presence of some area of AlO(OH) nanoparticles agglomerations (since the defect area was more than 100 mm^2).

Note that the presence of two time constants (two inflections on the plot of the phase angle (θ) versus frequency (Fig. 2 c) indicates the presence of two layers - the lower non-porous layer and the upper porous layer. After the introduction of aluminum oxyhydroxide nanoparticles into the CaP coating, the corrosion current density (j_c) decreases to $1.1 \cdot 10^{-9} \text{ A/cm}^2$, and the polarization resistance (R_p) increases to $1.6 \cdot 10^7 \Omega \text{ cm}^2$. This indicates an increase in the corrosion resistance of coatings as a result of their modification by nanoparticles of aluminum oxyhydroxide. The current density (j_c) and corrosion potential (E_c) decrease after the introduction of zinc oxide nanoparticles into the biocoating. However, the specific polarization resistance (R_p) in this case increases from $2.4 \cdot 10^6$ to $3.1 \cdot 10^7 \Omega \text{ cm}^2$.