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THE DETERMINANTS OF MORPHOLOGY AND PROPERTIES OF THE NANOHYDROXYAPATITE COATING DEPOSITED ON THE Ti13Zr13Nb ALLOY BY ELECTROPHORETIC TECHNIQUE

ABSTRACT

The titanium and its alloys belong at present to the most preferred and commonly applied biomaterials for load-bearing implants. The surfaces of biomaterials are subjected to modification, including the hydroxyapatite coatings deposited in order to ensure corrosion resistance and better joining between an implant and a bone through the possibility of ingrowth bone into the coating. In this paper, the morphology and properties of the nanohydroxyapatite coating deposited on the Ti13Zr13Nb flat surfaces using electrophoretic method are presented. Electrophoretic deposition at two different current values and two electrolytes (first – ethanol with nanoHAp, second – methanol with nanoHAp) was applied. The scanning electron microscopy examinations and wettability angle measurements showed an increase in the coating thickness, the surface coverage and decrease in biocompatibility with increasing voltage. The surface condition and biocompatibility of coatings were better when using methanol/nanoHAp solution as compared to the ethanol/nanoHAp one.

***Key words**: electrophoretic deposition, nanohydroxyapatite coating, titanium alloy*

INTRODUCTION

Titanium and its alloys (mainly the Ti6Al4V alloy) are commonly used for orthopedic and dental implants because of their low density, good corrosion resistance, and excellent mechanical properties [1-4]. There are some reports on possible negative effects of both alloying elements of the Ti6Al4V alloy: vanadium may provoke cytological responses and neurogenic disorders [5,6], and aluminum softens bone, damage to nerve cells and disturbance of the function of enzymes [7,8]. The alloy development is focused on non-toxic alloying elements, such as Ta, Zr, Nb, and Hf [9]. Therefore, in the recent years the Ti13Zr13Nb alloy has been examined, as it does not contain dangerous elements, and has greater strength than medical grade titanium, and one of the lowest Young modulus values, thus it is more mechanically compatible with the bone [4,8,10,11].

Many methods are used to modify the surface of metallic biomaterials to improve their mechanical and biocompatible properties [12]. The novel approach is the EPD (Electrophoretic Deposition), that is widely used to make ceramic coatings from powder suspension. This method is marked by high versatility, simplicity, need for low-cost equipment and short deposition time [13,14]. EPD leads to uniform coatings of any complex shape, and the microstructure can be designed by the simple adjustment of process parameters such as deposition time, voltage, temperature and other [15,16].

In orthopedic and dental implants equally important is their corrosion resistance [17]. The overcome to this problem may be could be the deposition of hydroxyapatite (HAp) $Ca_{10}(PO_4)_6(OH)_2$, which is the material of high biocompatibility due to it's structural and chemical similarities to inorganic part of the human bone and compatibility with surrounding tissues [18-20]. HAp coatings are often used in implants application because HAp causes better osseointegration of material, can increase bone growth thanks to its bioactivity and good biocompatibility and reduce high corrosion rate [17,20,21]. HAp coatings can be produced by several techniques: plasma-spraying [22], magnetron sputtering [23], alkaline treatment [24,25], electrodeposition [26,27] and chemical deposition [28]. Unfortunately, the main problem with commercial HAp coatings deposited by thermal spray bond techniques that their adhesion to the surface is weak and the coating becomes mechanically damaged during implantation surgery [6,29,30]. In order to increase the adhesion of the coating, the nanoHAp coating instead of microHAp is prepared. Materials in nanoscale, in many cases, possess better properties (e.g. mechanical properties) than the same material in macro scale due to the greater surface area of nanoparticles [31]. Furthermore, the nanosized hydroxyapatite coatings result in better bioactivity and better corrosion resistance [32].

MATERIALS AND METHODS

The titanium alloy Ti13Zr13Nb was investigated. The specimens of 4 mm in height and 15 mm in radius were used. The shape of the specimens showed Figure 1. The specimens were polished with abrasive paper, No. 800 as the last, then subsequently rinsed with isopropanol and distilled water for 60 min in an ultrasonic bath, oxidized in 25% nitric acid according to the ASTM 1713-08 standard for 10 min and finally rinsed with distilled water prior to deposition.

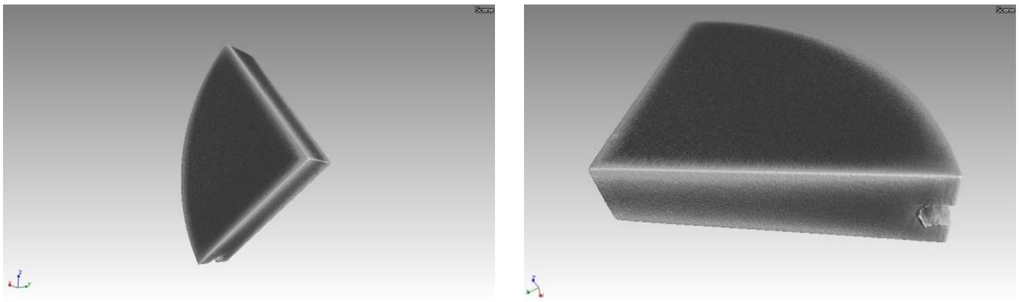


Fig. 1. The shape of Ti13Zr13Nb specimens

Electrophoretic deposition (EPD) was carried out in a two different suspensions prepared by dispersing: I) 0.1 g of HAp nano-powder in 100 mL of methanol (pure for analysis 96%) and II) 0.1 g of HAp nano-powder in 100 mL of ethanol (anhydrous 99.8%). The commercial nanopowder (MK Nano Canada) had a particle size about 20 nm. The suspensions of HAp were obtained by ultrasonic dispersion for 60 min.

The scheme of the electrophoretic equipment showed Figure 2. The Ti13Zr13Nb specimens were used as the cathodes to receive the coating, the anode was Pt electrode. The distance between the two metallic electrodes was set at 20 mm. Electrophoretic deposition was performed at room temperature. The constant time 4 min and charging voltage 15 V or 25 V were applied.

The specimens after EPD were thermally treated in a tubular furnace in a high vacuum atmosphere at 550 ^{o} C for 60 min and cooled to room temperature.

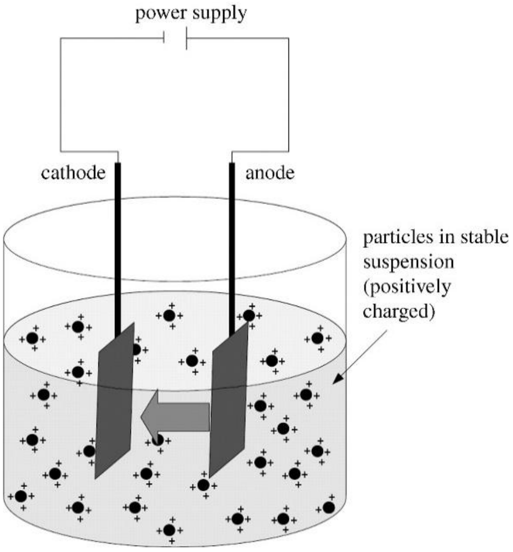


Fig. 2. Scheme of the electrophoretic deposition [14]

The surface and cross-section examinations were performed by ultra-high scanning electron microscopy with the Nanonivea JEOL equipment. The chemical compositions of coatings were measured with the EDS equipment, constituting the SEM part. The thickness coatings of the specimens were examined by SEM Microscopy at an angle of 45. The height was determined from the relation sin (45). The biocompatibility of coatings was characterized by the measurements of the wettability angle using distilled water drop at room temperature with the Contact Angle Goniometer ZEISS.

RESULTS AND DISCUSSION

Results shown in Figs. 3-6 demonstrate the appearance of nanohydroxyapatite coatings on specimen surfaces. Nanohydroxyapatite coating formed in both solutions used and both voltage values. The increase in voltage reduced the quality of the nanoHAp coating, in particular in the case of I suspension (nanoHAp/ethanol).

Fig. 7 presents the cross-sections of the nanoHAp coatings. The thickness of the coating increased significantly with increasing voltage.

Fig. 8 demonstrates the values of the wettability angle of the nanoHAp coatings. The contact angles were significantly smaller for coatings obtained in I suspension (nanoHAp/methanol) than in II suspension (nanoHAp/ethanol).

Figs. 9 and 10 present characteristic spectra of elements obtained by the EDS technique. Only Ti element is observed in the spectrum corresponding to the nanoHAp coating.

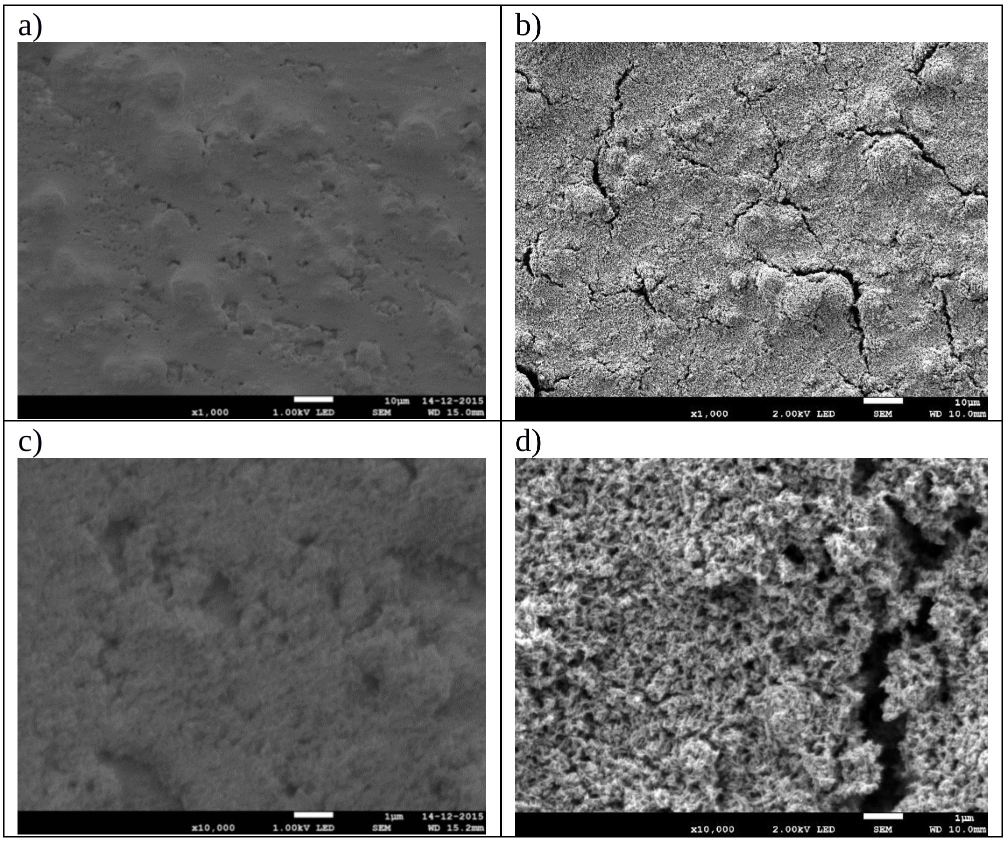


Fig. 3. Comparison of nanoHAp coatings on Ti13Zr13Nb obtained from EPD 15 V and I suspension: a), c) before heat treatment; b), d) after heat treatment (different magnification rates)

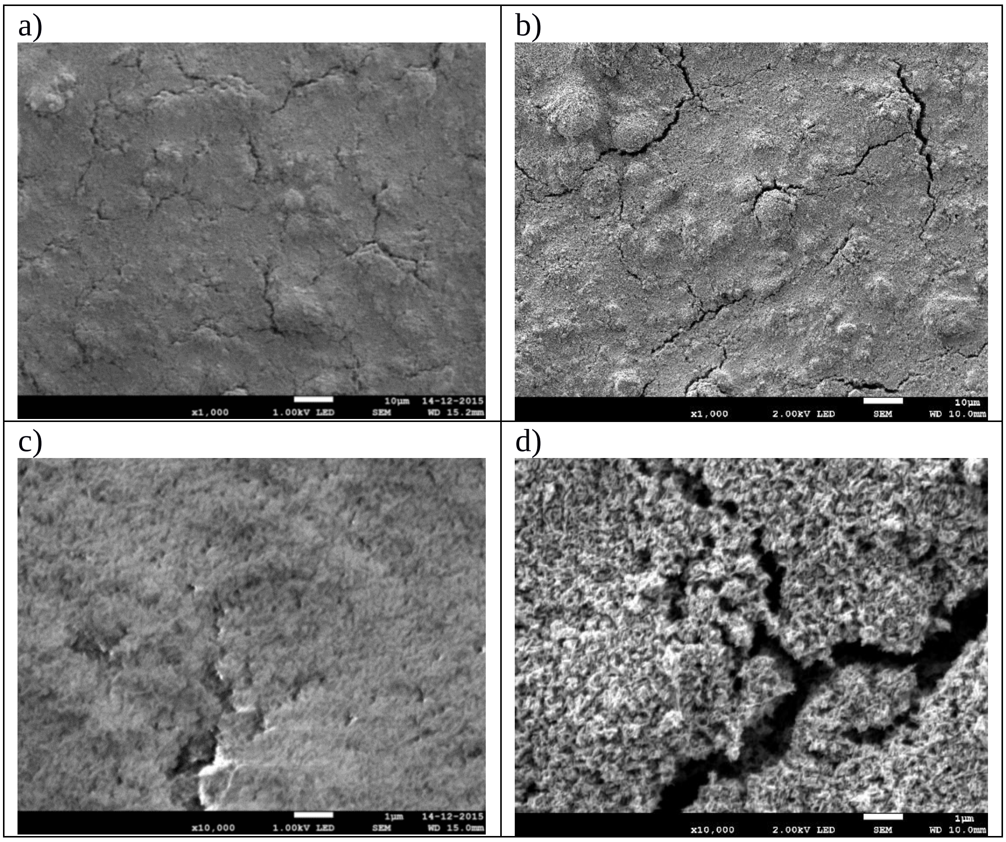


Fig. 4. Comparison of nanoHAp coatings on Ti13Zr13Nb obtained from EPD 25 V and I suspension: a), c) before heat treatment; b), d) after heat treatment (different magnification rates)

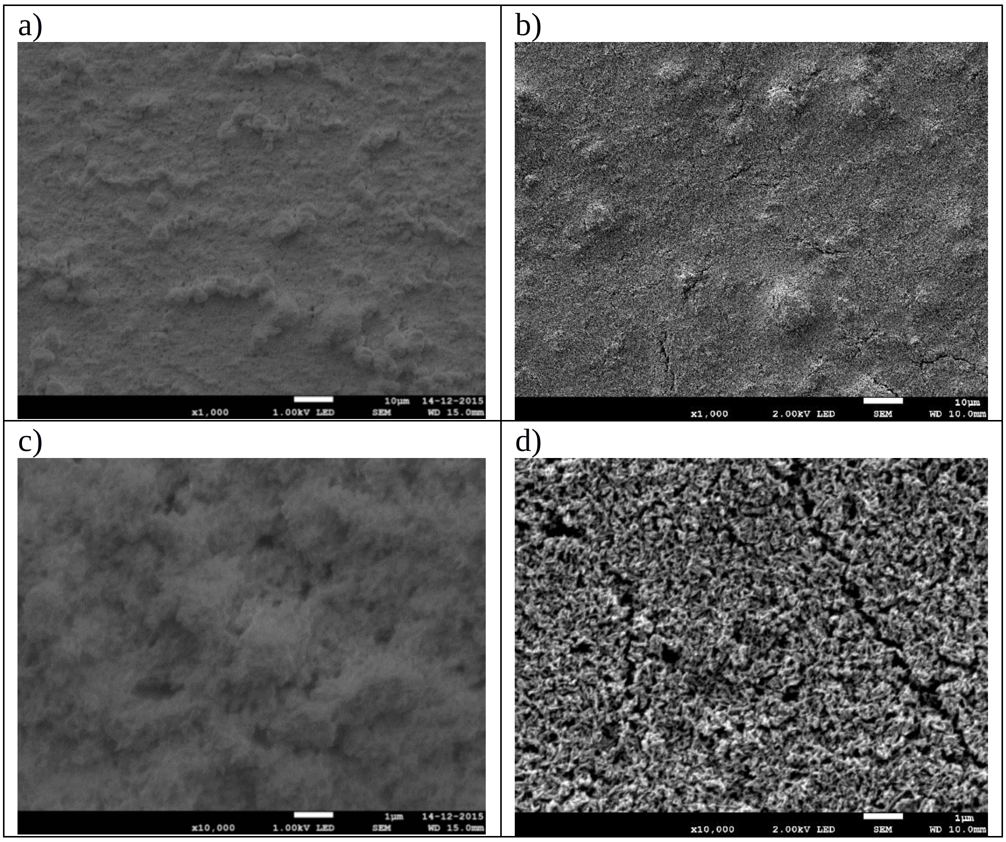


Fig. 5. Comparison of nanoHAp coatings on Ti13Zr13Nb obtained from EPD 15 V and II suspension: a), c) before heat treatment; b), d) after heat treatment (different magnification rates)

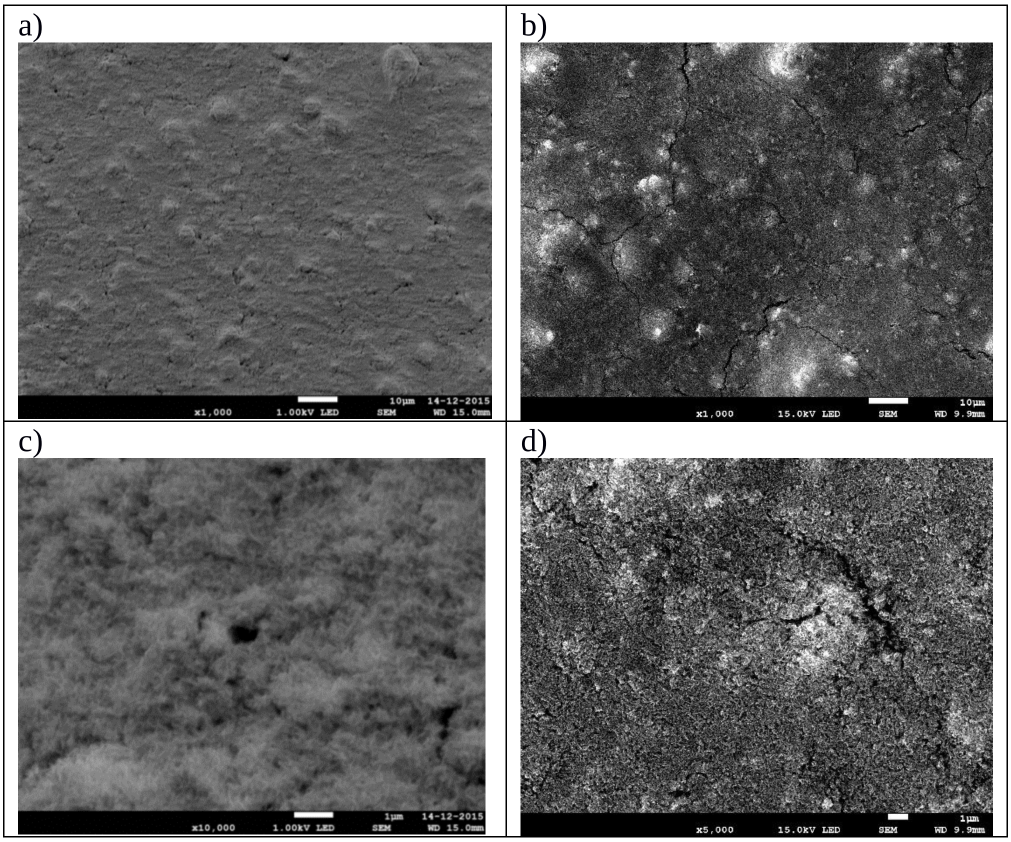


Fig. 6. Comparison of nanoHAp coatings on Ti13Zr13Nb obtained from EPD 25 V and II suspension: a), c) before heat treatment; b), d) after heat treatment (different magnification rates)

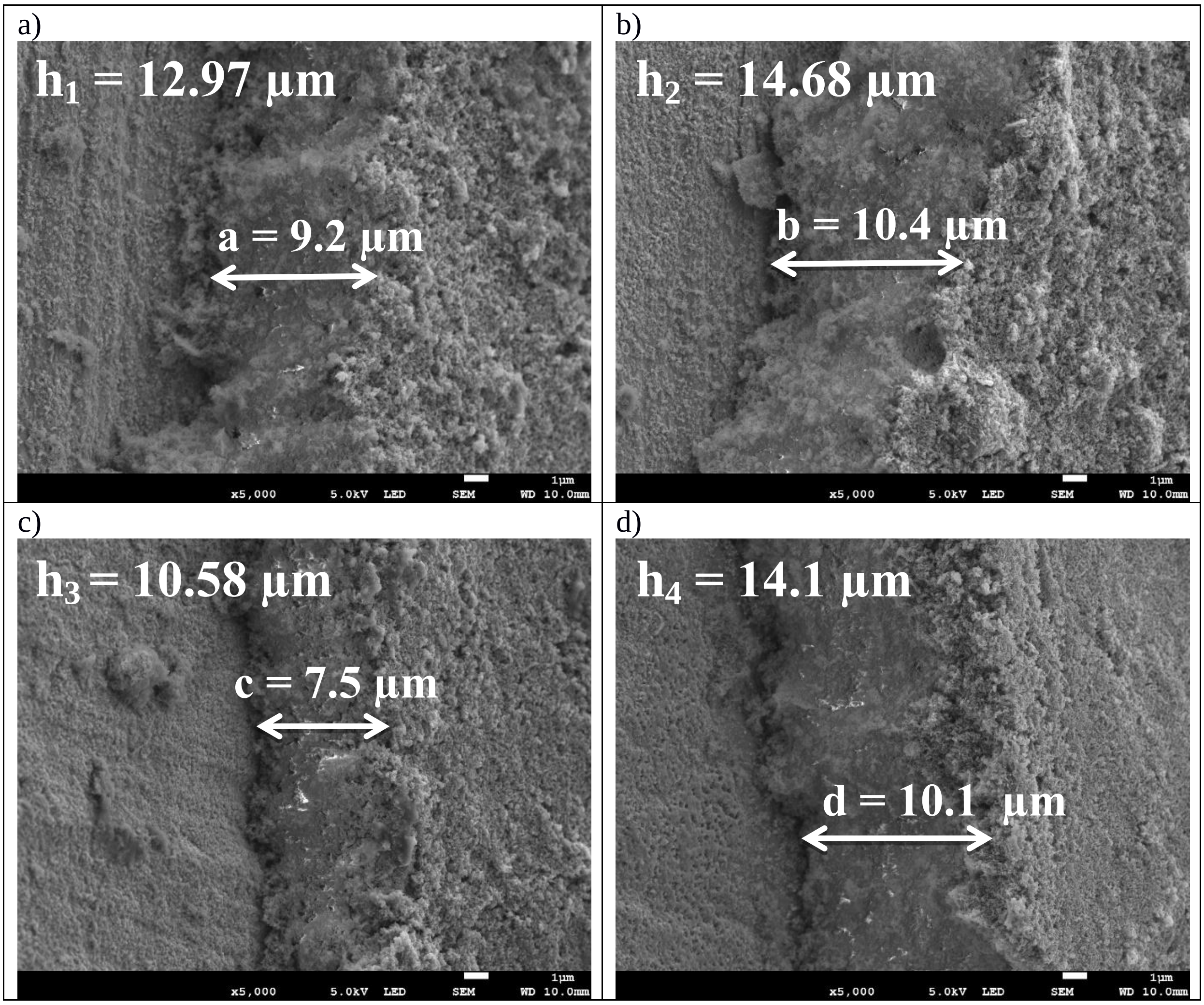


Fig. 7. The cross-section of the nanoHAp coatings obtained from: a) EPD 15 V, I suspension; b) 25 V, I suspension; c) 15 V, II suspension; d) 25 V, II suspension

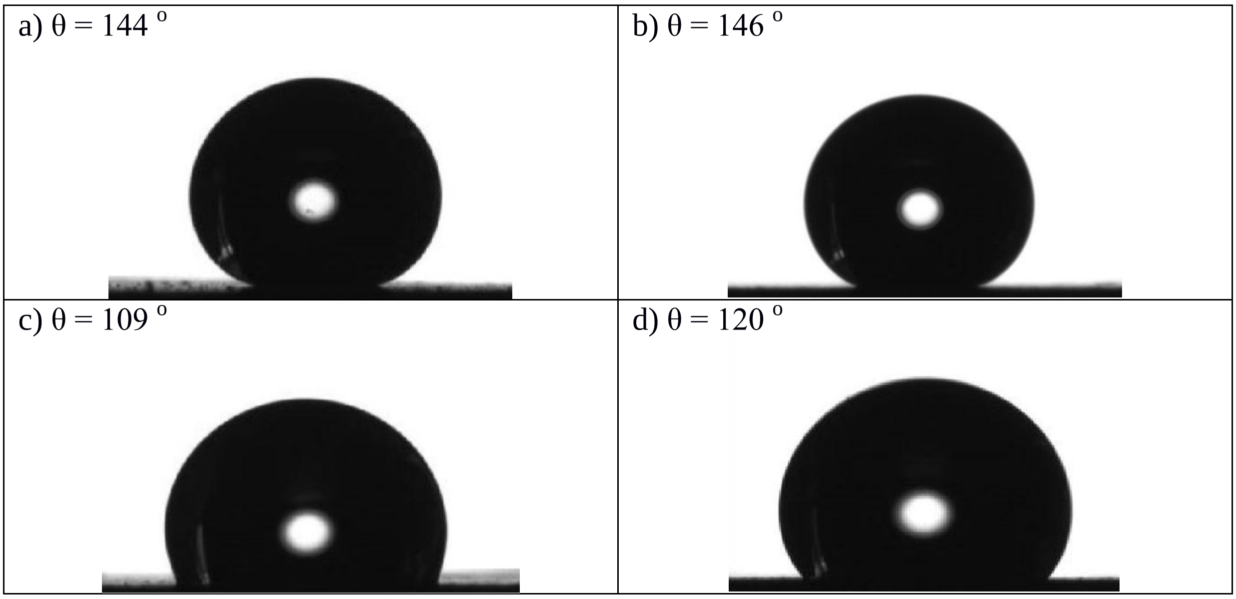
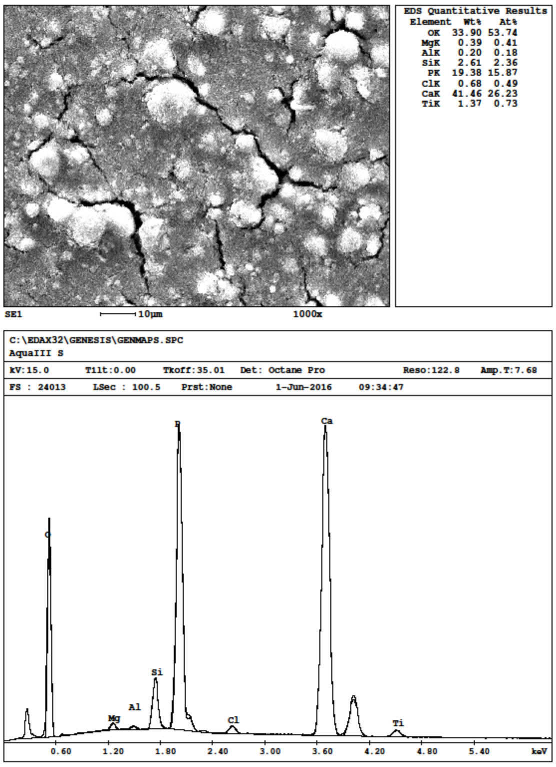


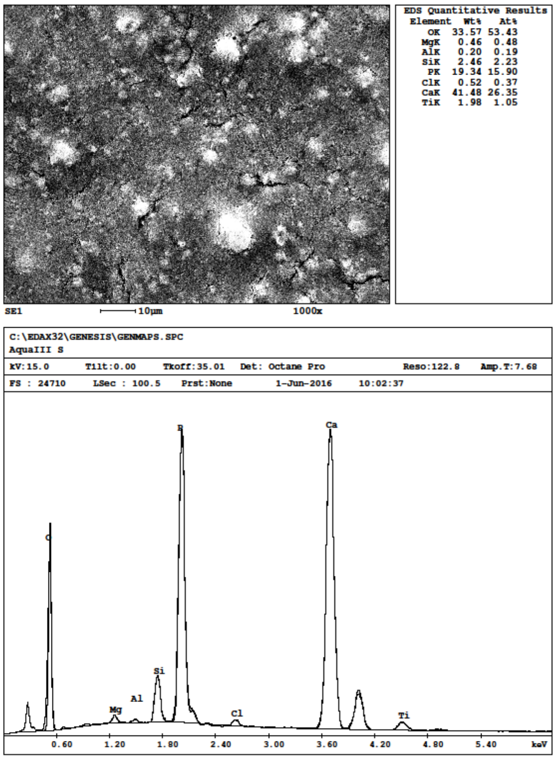
Fig. 8. The wettability angle of the nanoHAp coatings: a) EPD 15 V, I suspension; b) 25 V, I suspension; c) 15 V, II suspension; d) 25 V, II suspension



EDS Quantitative Results

Element	Wt%	At%
OK	33.90	53.74
MgK	0.39	0.41
AlK	0.20	0.18
SiK	2.61	2.36
PK	19.38	15.87
ClK	0.68	0.49
CaK	41.46	26.23
TiK	1.37	0.73

Fig 9. EDS examination of the nanoHAp coating obtained from I suspension.



EDS Quantitative Results

Element	Wt%	At%
OK	33.57	53.43
MgK	0.46	0.48
AlK	0.20	0.19
SiK	2.46	2.23
PK	19.34	15.90
ClK	0.52	0.37
CaK	41.48	26.35
TiK	1.98	1.05

Fig 10. EDS examination of the nanoHAp coating obtained from II suspension.

Presented results give an evidence that titanium alloy Ti13Zr13Nb can be subjected to an electrophoretic deposition process to obtain nanohydroxyapatite coatings. The coating surface (Fig. 3–6) shows the impact of electrophoretic deposition parameters on the quality of the coating. Fig. 3–6 show that for both types of electrolyte, the increase of voltage increases the quantity of powder nanohydroxyapatite agglomerates formed on the surface, but the number of cracks and their size as well. Fig. 3, 5 and 6 demonstrate that the cracks appear only in the coating subjected to the high-temperature treatment. The only exception is shown in Fig. 4; the cracks appear in the coating before and after the high-temperature treatment.

The occurrence of cracks is probably associated with the coating thickness. The coating deposited in suspension II at 25 V of voltage is the thickest of all the coatings obtained in the study. Fig. 5 and 6 show that the use of the suspension II significantly increases the quality of the coating as proved by less the number of the powder agglomerates of nanoHAp and minimal cracks in the coating. Nevertheless, with the increase of the voltage also with the used electrolyte II, the number of cracks increases.

The use of ethanol and methanol as electrolytes in the electrophoretic process was investigated in the past [32-35]. There are only a few reports of the use of the two electrolytes with the same electrophoretic deposition parameters of nanohydroxyapatite for the titanium alloy [36], but none for the Ti13Zr13Nb alloy. Rojaee et al. [32] in their study with nanoHAp powder deposited by an electrophoretic method with a use of methanol as an electrolyte clearly proved that the coating obtained by EPD method in this solvent was characterized by better mechanical properties and homogeneity.

Fig. 7 shows the cross-section of the nanoHAp coatings obtained from all EPD parameters. One of the main advantages of electrophoretic deposition process is a possibility to obtain coatings with designed parameters such as thickness and homogeneity. Many studies have shown that it is possible to obtain hydroxyapatite or nanohydroxyapatite coating with thickness 3.71 µm to 35 µm and more [1,19,33,37]. It is clear that the hydroxyapatite ceramic is a brittle material and with the increasing thickness of the coatings the susceptibility to brittle cracking would increase. Here the coating of a thickness between 10.58 µm to 14.68 µm was obtained, similar to that reported in [37] and characterized by good mechanical properties and bioactivity [37].

Fig. 7 shows that voltage increases the thickness of the coatings in both electrolytes used (I and II suspension). Obtained coating thicknesses are thicker in the case of suspension I compared to the suspension II. The smallest thickness of the coating is obtained at 15 V in methanol. The smallest thickness is associated with no appearance of cracks even after the high-temperature treatment. The highest thickness of the coating is obtained at 25 V in ethanol, and in this case, many cracks on the coating before after the high-temperature treatment appear.

Fig. 8 shows the wettability angle of the nanoHAp coatings obtained at all EPD parameters. The obtained values are in the range 109^o – 146^o and are considerably smaller for coatings obtained in II suspension. Previous studies have shown that it is possible to obtain hydroxyapatite coating with wettability angle of 5^o to 105^o, which would have good biological properties [38-40]. With the increase of the wettability angle, the biological properties decrease. In this study, the obtained coatings are hydrophobic which indicates weak biological properties. Fig. 8 shows that the wettability angle increase with increasing voltage and the wettability angles are considerably lower for coatings obtained in methanol electrolytes.

The EDS analysis shows the presence of only Ti alloy element on the nanohydroxyapatite coating obtained from both kind of the suspension (I and II). The EDS analysis confirmed the presence of the nanohydroxyapatite coating on titanium alloy surface.

CONCLUSIONS

The nanohydroxyapatite coatings deposition by electrophoretic technique on titanium alloy Ti13Zr13Nb surface is a relatively easy to process, which may be controlled by parameters such as the voltage value and a solvent type in the electrolyte.

The coatings obtained in methanol as the electrolyte are characterized by better homogeneity, they are thinner and possess fewer cracks, and they demonstrate a smaller angle wettability compared to that in ethanol.

In both electrolytes, the increase of the voltage reduces the coating quality, increases the thickness and the angle of wettability.

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