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Surface engineering in formation of modern multilayer structures — biofunctional hydroxyapatite coatings produced by pulsed laser ablation and glow discharge nitriding multiplex method

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Abstract. Biocompatible coatings produced on the basis of the chemically extracted natural hydroxyapatite (HAp) from the animal bones were deposited using multiplex method comprising glow discharge nitriding (GDN) of the titanium alloy substrate and pulsed laser deposition (PLD) of HAp on the formerly fabricated titanium nitride layer (TiN). The TiN interlayer plays an important role improving adhesion of HAp to substrate and preserves the direct contact of the tissue with metallic substrate in the case of possible cracking of HAp coating. Surface morphology of deposited layers, crystallographic texture and residual stress were studied in relation to the type of laser applied to ablation (Nd:YAG or ArF excimer), laser repetition, temperature of substrate and atmosphere in the reactive chamber.

Keywords: hydroxyapatite, pulsed laser deposition, glow discharge nitriding.

1. Introduction

Many kinds of special materials are currently used in bone surgery. Recently, biodegradable materials for bone tissue have been developed to respond the requirement [1]. Biomaterials are either modified natural or synthetic materials, which find application in wide spectrum of medical implants and prosthesis for repair, augmentation or replacement of natural tissues. Some well-known examples of the clinical use of biomaterials are total joint replacement, vascular grafts and heart valves. For this purpose synthetic materials have to be used which possess suitable mechanical and wear properties, and show optimal tissue response [1,2]. Artificial bone substitutes have been constructed from many sorts of metals, ceramics, and polymers. A radical innovation in the implant production was the introduction of the synthetic hydroxyapatite (HAp), $Ca_{10}(PO_4)_6(OH)_2$ which is a calcium phosphate compound similar to the bone mineral phase, comprising about 45% by volume and 65% by weight of human cortical bone. Hydroxyapatite has also found clinical application as a genetic bone graft material, and much attention is being given to the development of the porous HAp for tissue guiding with the prospect of application as bone graft in revision joint fracture repair and spinal fusion procedures. However, the load bearing implants cannot be entirely made of HAp because it is a brittle ceramic material [3,4]. However, to take profit of HAp bioactive properties in spite of its problems of brittles as a bulk material, it can be applied as coating on the surface of metallic implants [4–7]. Among the different HAp deposition methods, the pulsed laser deposition (PLD) technique, firstly demonstrated in HAp deposition application in 1992 [8], yielded high quality HAp coatings. PLD has recently been used to direct the plume of material ablated from a biocompatibile ceramic target onto substrate materials that may be used in dental or orthopedic implants to produce thin-film biocompatible coatings on those substrate [9,10]. In the PLD technique, a pulsed laser beam is focused onto a target in order to evaporate its surface layers by ablation mode in vacuum or low-pressure process gas conditions [10,11]. The vaporized material, consisting of atoms, ions and atomic clusters, is then deposited onto the substrate. The outstanding advantage of this technique is its ability to deposit any thin films of various materials of high chemical purity and good adhesion onto different substrate materials at room temperature. Furthermore, a high rate of film growth can also be achieved on surface areas situated perpendicular to the targets surface plane by using a low pressure process gas. Applying a reactive process gases also makes it possible to vary the film stoichiometry over a wide range.

Calcium phosphate (CaP) ceramics form the major inorganic constituent of bone, and are therefore an obvious candidate to be used as a bone-bonding biomaterial. Indeed, CaP ceramics are known to form a strong and continuous interface with bone and exhibits bioactive properties [1, 2]. Even hydroxyapatite (HAp), the same as the main inorganic component of bone, has disadvantage. Hydroxyapatite $(Ca_{10}(PO_4)_6\ (OH)_2$, is generally

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accepted as the best biocompatible material. However, poor adhesion to the substrate of thick layers of order of 50–200μm as well as brittleness of the layers commonly produced using, namely, thermal sprying and subsequent heat treatment, have limited their application [3]. HAp characterizes a low mechanical properties, thus, the tendency is to diminish its thickness to few micrometers. However, to take profit of the HAp bioactive properties in spite of its brittleness as a bulk material, it can be applied as coating on the surface of metallic implants [4–7]. Thus pulsed laser deposition (PLD) seems to be a very perspective method in this case by producing good quality HAp thin layers of order of nanometers to few micrometers [10,11]. HAp is usually produced using chemical syntesis [3], however, it has been recently performed a method to extract natural HAp from the animal bone by their treatment with hot NaOH solution [12,13].

The aim of this work was to produce novel HAp coatings from natural HAp with titanium nitride interlayer beneath which could improve adhesion and biocompatibility as well as dimension tolerance and mechanical properties due to small thickness of high quality coatings. Contribution of laser wavelength and laser frequency applied, on crystallinity of the deposited layer as well as crystallographic texture and level of residual stress was studied in the work.

2. Experimental

Pallets for laser ablation of natural powder of HAp fabricated from animal bones [12,13] were prepared by compression at 70 MPa, for 3h at 850°C. They were used as targets in pulsed laser deposition systems working with a Nd:YAG (1064 nm) and ArF (193 nm) excimer laser.

A new layer composition was fabricated to reduce the influence of crack formation as much as possible. The initial material Ti6Al4V alloy, used subsequently as substrate, was subjected to glow discharge nitriding before the laser deposition [15]. Application of the diffusion method allows to achieve high but uniform roughness of the surface, thus extends the active area. Samples of titanium alloy Ti6Al4V after grinding and cleaning in acetone were subjected to glow discharge nitriding at 850°C, pressure 2hPa in nitrogen environment for 4h. This procedure led to formation of diffusive surface layer of whole thickness of 40μm comprising the following phases: TiN+Ti_2N+αTi(N) within the TiN was located in external zone of 4 μm thickness showing a nanostructure with crystallite sizes of order of 30 nm and roughness R_a = 0.9 μm. The prepared samples in this way were subsequently subjected to pulsed laser deposition process of HAp in two systems working with Nd:YAG and ArF excimer lasers. Moreover, the biocompatibile TiN layer beneath the biocompatibile HAp layer (Fig. 1) could decrease the risk of the methalosis. According to the literature the methalosis was ascertained in 10% patients whom the artificial bones without the surface modification were implanted [1,2].

Fig. 1. Scheme of multilayer with improved biocompatibility material comprising TiN interlayer obtained by glow discharge nitriding and HAp outer layer deposited by PLD

2.1. Deposition using Nd:YAG laser. HAp layers were deposited in use of Nd-YAG laser under the following conditions; 1064 nm wavelength, pulse energy 1100 mJ, frequency 10 Hz with 10 ns pulse duration. The substrate was heated up to 400°C. The atmosphere in the reactive chamber was chosen as one of the parameter under examination which influence on the HAp crystallinity of the deposited layers. The first group of the materials was deposited in argon atmosphere with the 30 sccm gas flow while the next one under the mixed gas conditions, i.e., 15 sccm Ar and 15 sccm O_2. The last part was deposited only under the 30 sccm oxygen flow. According to the literature, the most appropriate conditions which would give the best quality layers should be in the oxygen atmosphere or water vapour [3–11].

2.2. Deposition using ArF excimer laser. Hydroxyapatite (HAp) layers were deposited by means of the ArF laser ($\lambda = 193$ nm) on Ti6Al4V alloy used as a substrate heated up to 550°C±50°C (temperature was measured on the surface of heater). Three different laser frequency were applied for the hydroxyapatite deposition: 5 Hz; 20 Hz; 50 Hz (all samples were deposited with H_2O; pressure of water vapour $p = 2 \times 10^{-1}$ mbar).

The crystalline phases present in the deposited HAp coatings were studied by means of X-ray diffractometry (XRD), as well as measurements of crystallographic texture and residual stress were performed. Application pseudo-position sensitive detector allows to measure the pole figures of the macro residual stress distribution. Atomic force microscopy (AFM) was used to examine the surface morphology of the deposited HAp layers.

The thickness of the deposited HAp layers were obtained in use of the profile measurement gage and it revealed its value on the level of 600 nm. It is necessary to produce relatively thin layers for the biological application. The deposition time according to the laser parameters, needed thickness as well as the deposition model [10] was calculated to be of order of 30 minutes.

3. Results and discussion

3.1. Morphology. The images of the surface of the coatings made by atomic force microscopy (AFM) are shown in Fig. 2. The results are presented on the first derivation

of the colour on the 2D images as well. The characteristic conglomerates on the surface proves the amorphous character of the layer. It is well observed that the more oxygen in the reactive chamber the less amorphous conglomerates on the surface are observed. In the third case when the hydroxyapatite was deposited under the 30 sccm oxygen flow and the substrate was heated up to 400°C, no amorphous structure was observed.

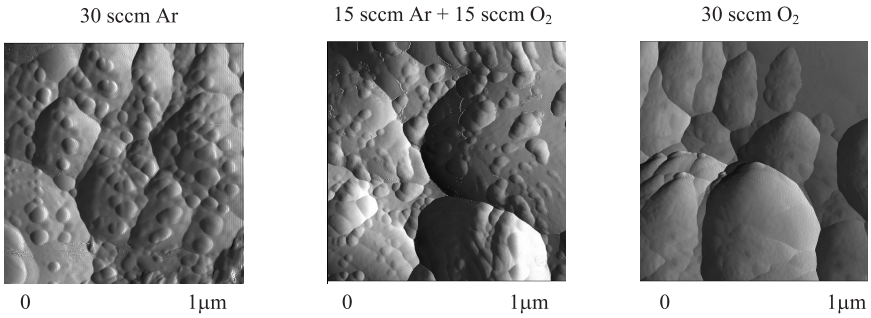

Fig. 2. AFM micrographs of HAp surface layer produced using Nd:YAG laser in various gas atmosphere in the reactive chamber

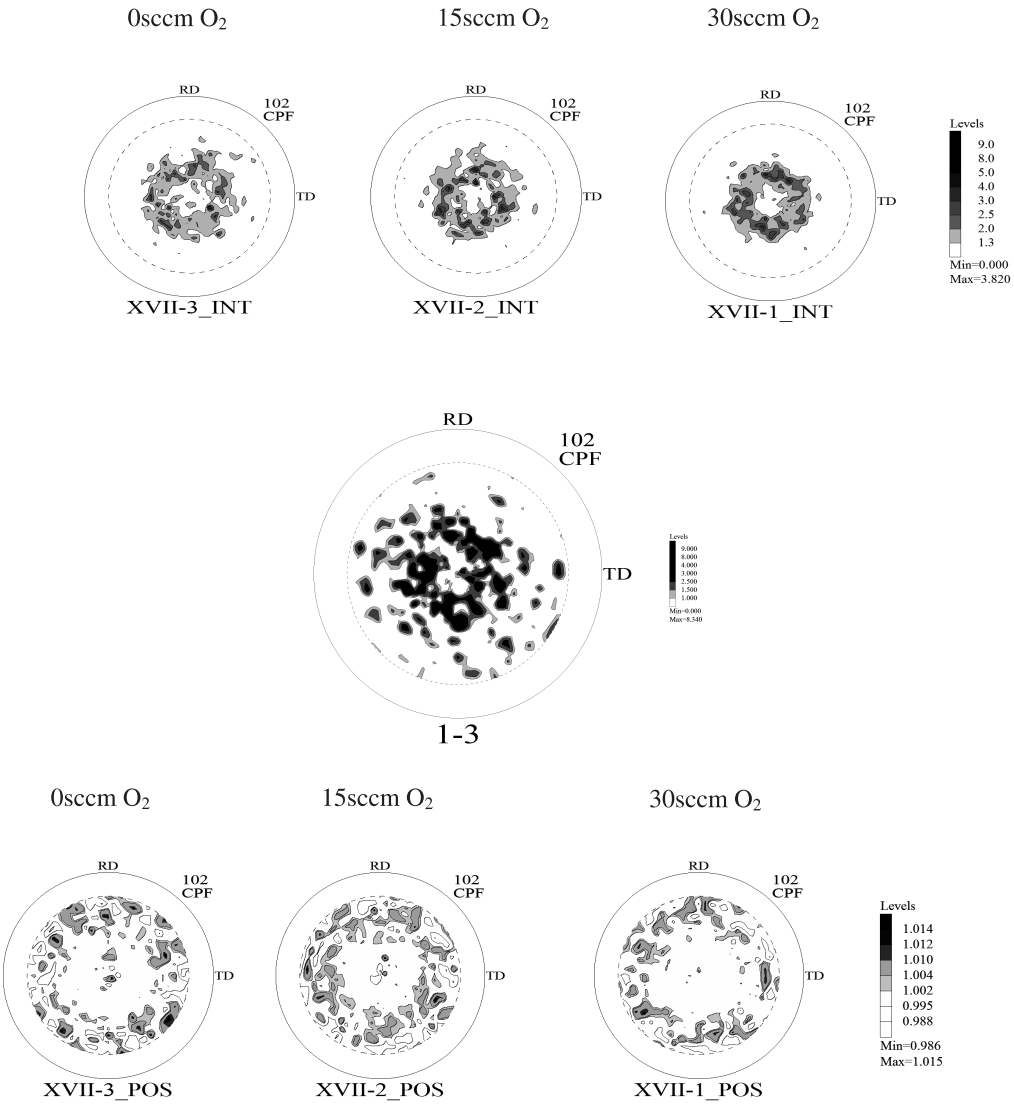

Fig. 3. (102) pole figures of crystallographic texture of HAp surface layer produced using Nd:YAG laser at various gas atmosphere in the reactive chamber (top): 0 sccm O_2/30 sccm Ar (a); 15 sccm O_2/15 sccm Ar (b); 30 sccm O_2/0 sccm Ar (c) and differential pole figure of texture calculated by subtraction of pole figure (a) and (b) and pole figure of residual stress distribution in the same materials (bottom)

3.2. Crystallographic texture and residual stress distribution. On basis of the XRD phase analysis the 2 theta angle frames were chosen. Texture examination was performed for the (102) planes. In all cases axial character of the texture of the deposited layers was observed Fig. 3. The axis was close to (102) plane. The strongest orientation occurred in the layers deposited in the 30 sccm oxygen atmosphere. The weakening of the orientation is directed towards the lowering of the oxygen flow in the reactive chamber.

The differential pole figure was calculated by subtraction the weakest orientation of the layer deposited under the argon atmosphere from the strongest orientation of the layer deposited under the oxygen atmosphere. The area presented on the differential pole figure shows the area of the loss of axiality Fig. 3 (top right).

Application the pseudo-positive sensitive detector allowed to draw pole figures of the residual stress distribution. Position pole figures represent the macro residual stress, Fig. 3 (bottom).

The axial symmetry of the position pole figures was observed in all layers. The stress distribution in the amorphous layer, deposited in argon and crystallized one deposited in oxide, is approximately equal. The differences were observed in the layer deposited in mixed atmosphere. It is probably caused by the substrate influence on the layer. It is associated with the fact that the line shifting in that layer was observed closer to the centre of the figure than it is the layers deposited under the boundary conditions.

3.3. Crystalline structure of HAp. The XRD diffractograms of HAp coatings obtained using Nd:YAG and ArF eximer lasers are presented in Fig. 4. It was impossible to identify any phases in the layers deposited using Nd:YAG laser in the 30 sccm argon atmosphere and mixed 15 sccm argon with 15 sccm oxygen atmosphere as well. In both cases the typical waves, in the x-ray diffraction pattern, for the amorphous structure occurred. 30 sccm oxygen flow allowed to achieve crystalline hydoxyapatite coatings. X-ray diffraction diagrams presents picks of the HAp phase. They are slight and difficult for the analysis, because of the very low thickness. Deposition of HAp using ArF excimer laser led to formation of crystalline HAp phase.

Influence of deposition process parameter like reactive atmosphere and repetition on the HAp crystalline phase formation revealed that at 550°C of substrate, the most pronounced diffraction line of HAp were stated for type of process with H_2O atmosphere. Despite the fact that an increase of the repetition should shift the process from the diffusion controlled to the kinetic type, great changes have not been observed.

Morphology of the deposited surface layer showed uniform fine structure. It could be seen that beside the basic matrix of grains, fine subgrains ten magnitude smaller are visible. They could be formed by contribution of kinetic process (Fig. 5).

The ring shape of the pole figures proves the axial character of the crystallographic texture. The ideal, central axial orientation type (002) was calculated and it was revealed that with the lowering of the laser frequency, the orientation was more pronounced (Fig. 6). To observe the area of the changes in orientation, the differential pole figures gained by subtracted intensities of pole figures type 002 and 211 (Fig. 7) were performed for 5 Hz and 50 Hz laser frequency. Presented results show the area which are responsible for the texture orientation weakening.

The texture character as well as residual stress distribution (Fig. 8) could inform about the crystallite packing and its homogeneity in the layer which strongly influence on biocompatibility.

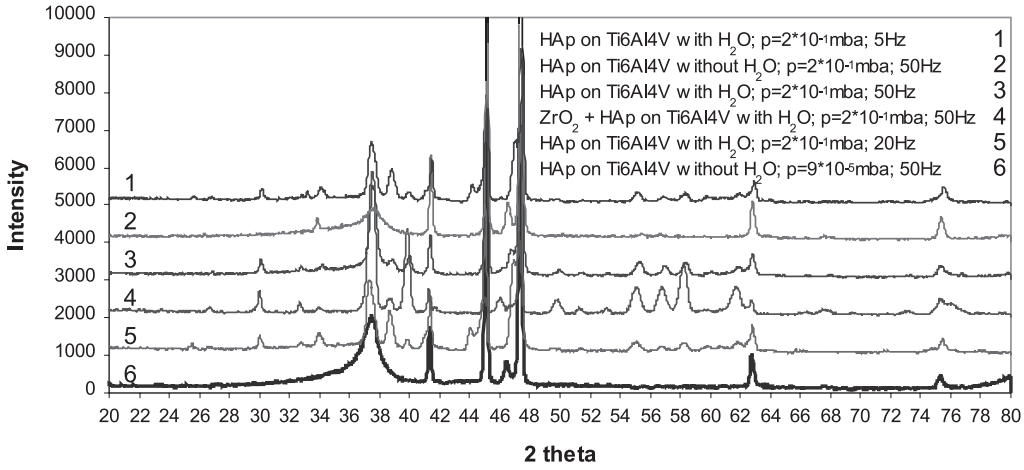

Fig. 4. Set of XRD patterns (CoKα radiation) of HAp surface layer produced using ArF excimer laser with application of different deposition conditions at 550°C temperature of substrate

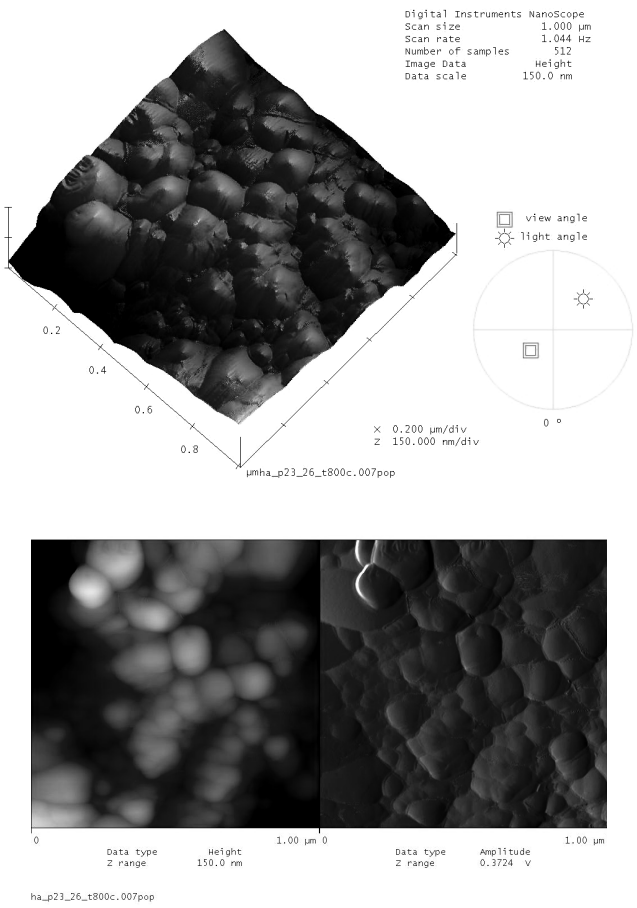

Fig. 5. AFM micrographs of HAp surface layer produced using ArF excimer laser at 550°C and repetition of 5Hz in H_2O atmosphere

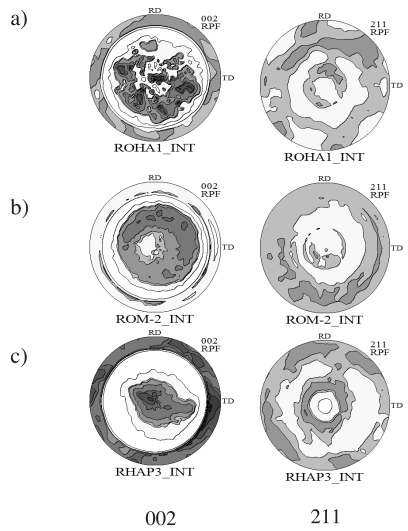

Fig. 6. (002) and (211) pole figures of crystallographic texture of HAp surface layer produced using ArF excimer laser in H2O atmosphere at 550°C temperature of substrate with repetition variation: a) 50Hz; b) 20Hz; c) 5Hz

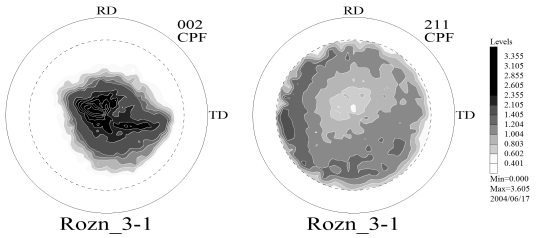

Fig. 7. (002) and (211) differential pole figures of texture calculated on the basis of pole figures presented in Fig.6 by subtraction of pole figures for 5Hz (c) and 50Hz (a)

Residual stress is generated in all physico-chemical processes. First type is called macro residual stress and it influence on the lattice parameter change from a_0 to a_1. X-ray investigations allow to estimate micro- residual stress so called second and third type. They play a main role in the a_1 level fluctuation. On basis of the pole figures examination, correlation between laser frequency and texture as well as macro type of the residual stress was observed, especially in the layer deposited with the lowest laser frequency. The stress decreased with the laser frequency increase. Position pole figures which inform about the macro stress distribution revealed the axial character and weakening towards the high frequency. To examine the values of the residual stress, $\sin^2\psi$ method was used. The examination was performed for the 20 and 5 Hz deposition conditions. The results showed (Fig. 9) that the change of the stress character could even be observed in respect to the frequency of deposition. Deposition of the HAp at room temperature should lead to domination of kinetic processes and formation of the amorphous phase. The presented in Fig. 10 cross-section of the deposited layer revealed two regions. One area very close to substrate where the cellular structure could be seen and the subsequent columnar region formed at the condition of kinetic processes. It was proved that the former layer was adhered to the substrate while the columnar one could be easy removed. It could be suggested that surface diffusion controlled processes occurred at the onset of deposition leading to the semi-equilibrium growth while an increase of deposition rate made possible the Krastianov-Stransky model to occure [10].

A role of the TiN interlayer could be studied in Fig. 11. Even cracking of the deposited HAp layer makes possible to keep good biocompatibile conditions because of the TiN beneath the brittle surface. Such architecture of the coating leads to improvement of coating in respect to metalosis.

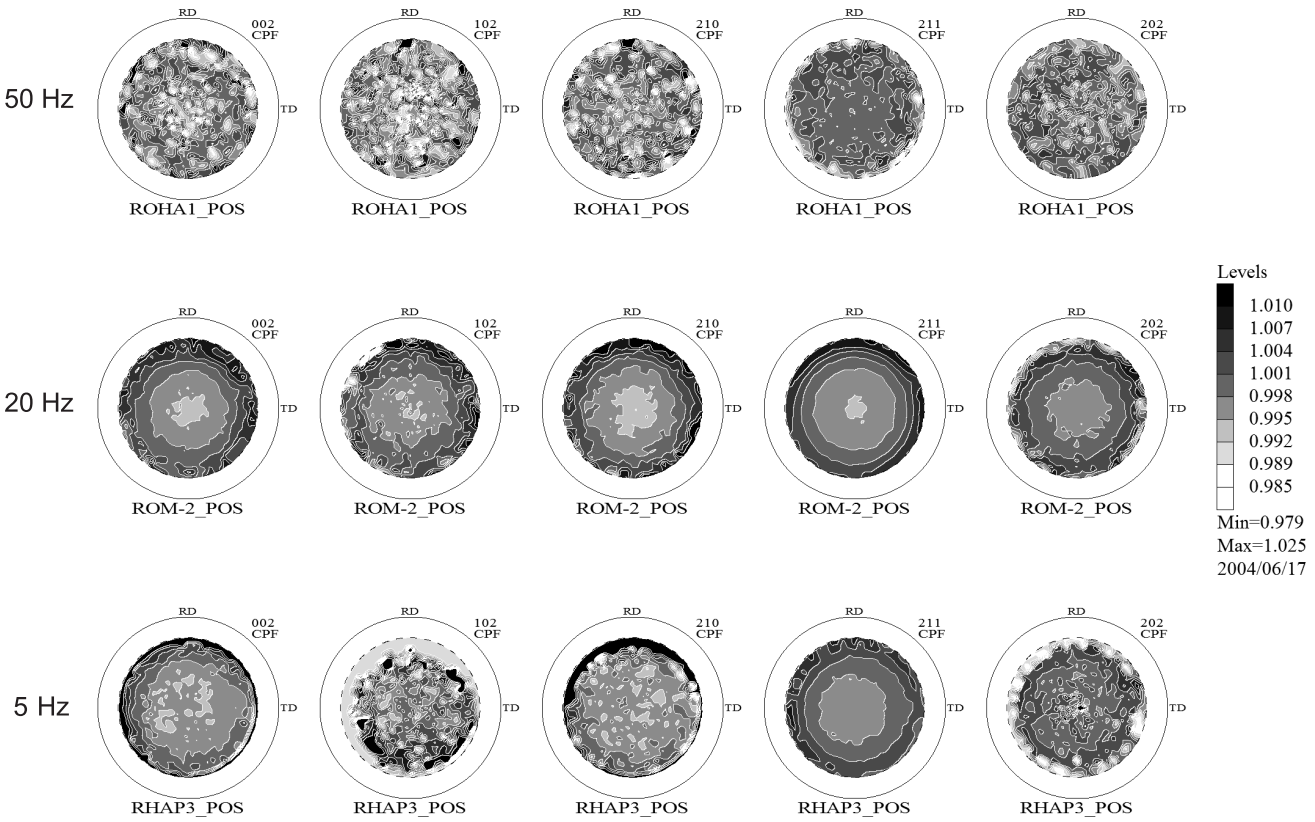

Fig. 8. (002); (102); (210) and (202) pole figures of residual stress distribution in HAp surface layer produced using ArF excimer laser in H_2O atmosphere at 550°C temperature of substrate with repetitions: 50 Hz; 20Hz and 5Hz

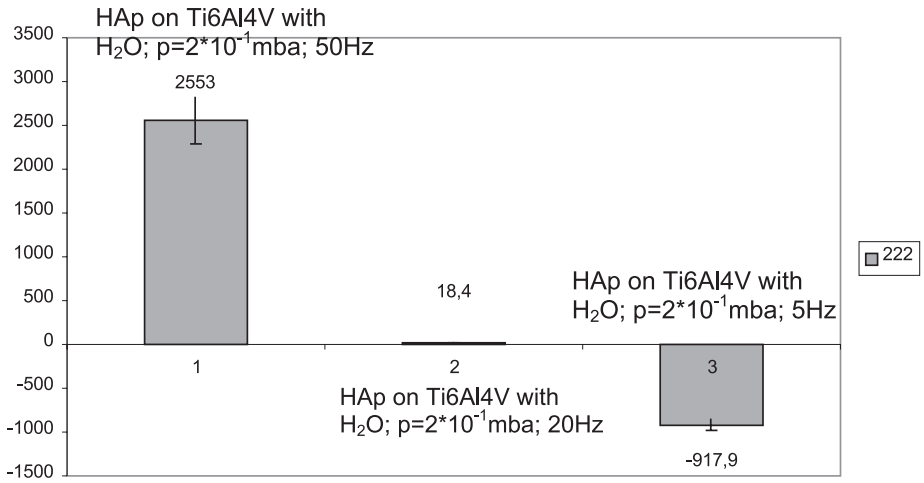

Fig. 9. residual stresses measured on the basis of 222 and 311 reflexions in HAp surface layer produced using ArF excimer laser in H_2O atmosphere at 550°C temperature of substrate with repetitions: 20 Hz and 5 Hz

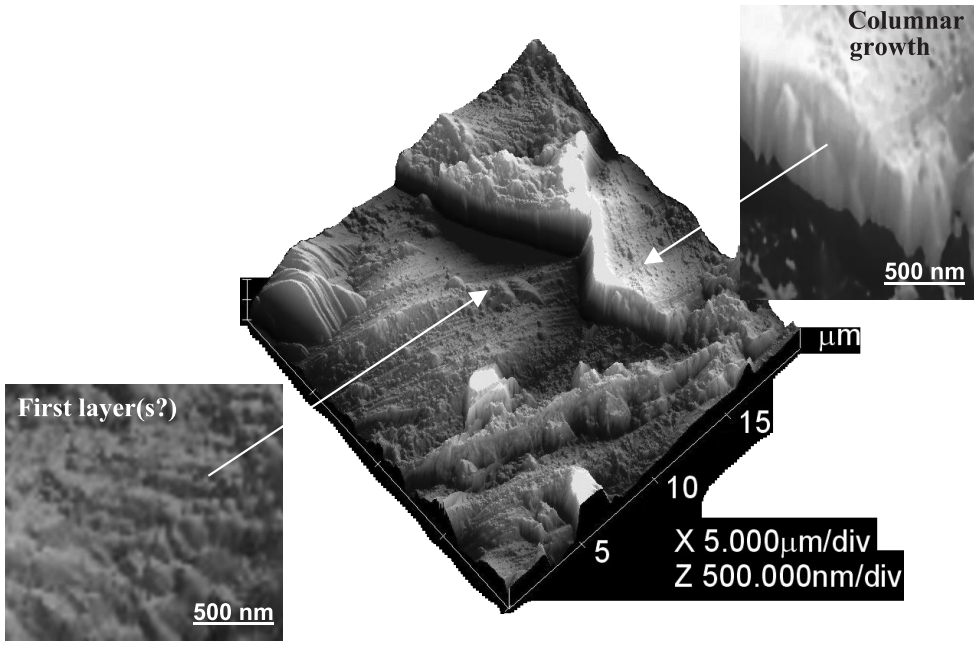

Fig. 10. AFM micrographs of HAp surface layer produced using ArF excimer laser at room temperature at 50 Hz repetition after scratch of the surface

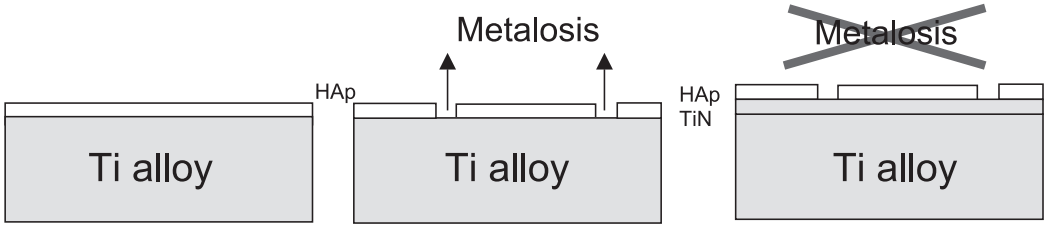

Fig. 11. Schemes presenting the role of the TiN interlayer in improvement of metallic implant preservation against metalosis

4. Concluding remarks

The coatings from the natural hydroxyapatite were deposited by the ablation with 1064 nm wavelength of Nd:YAG laser. The layers were produced on the heated substrate. The atmosphere in the reactive chamber was the parameter which influence on the quality of the layers was investigated. It was found that the most appropriate conditions to achieve crystallized coatings appeared under the 30 sccm oxygen flow in the reactive chamber. In the other two layers the amorphous structure was identified. The amount of the amorphous structure decreases with the amount of the oxygen. The influence of a laser frequency on deposition of HAp layers was examined. The crystalline character of HAp structure due to water atmosphere application and proper substrate temperature was stated. Crystallized layers are very important from the biocompatibility point of view. The more the layers are crystallized the better is their biocompatibility. Texture examination showed high influence of the laser frequency on the crystallographic texture as well as residual stress distribution. Increase of repetition caused shifting the deposition process to the kinetic controlled mode. Application of the proposed TiN interlayer improved the mechanical properties of resistance to cracking and in this way control the bio-compatibility of the deposited coatings.

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