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TEXTURE AND MICROSTRUCTURE OF HAp THIN LAYERS ON Ti6A14V

TEKSTURA I MIKROSTRUKTURA CIENKICH WARSTW HAp NA PODŁOŻU Ti6A14V

A new biocompatybile HAp/TiN multilayer coatings were developed by a multiplex technology comprising glow discharge nitriding and pulsed laser deposition. Glow discharge method was used to fabricate TiN interlayer on the Ti6Al4V substrate. Alternately depositing TiN and HAp layers on Ti6Al4V substrates applied to prevent direct contact of the human tissue with metallic substrates. Coatings bioinert implants with bioactive hydroxyapatite ceramics offers a potential for biological interaction between the bone and the coated implant, which enables positive biological/chemical material connections. With the objective of producing a new generation of biomaterials, titanium alloys submitted to glow discharge nitriding were used as a substrate for hydroxyapatite coating, deposited by the pulsed laser deposition method. Hydroxyapatite (HAp) layers were deposited at 250°C by means of the Nd-YAG laser (λ = 1064nm) working at the repetition of 10Hz. Stoichiometry of the HAp target was generally transferred to the Ti6Al4V/TiN substrate. However, a respectively high volume fraction of amorphous phase was formed due to not high enough temperature for full crystallization (250°C) which was stated on the basis of XRD examinations. Contribution of the gas flow in the reactive chamber was stated in relation to the observed crystallographic texture. The performed AFM studies revealed that the high level of crystallization has been obtained when oxygen was introduced into the reactive chamber.

Nowe wielowarstwowe powłoki HAp/TiN uzyskano multipleksową technologią azotowania jarzeniowego i osadzania laserem impulsowym. Azotowanie jarzeniowe zastosowano w celu wytworzenia warstwy TiN na stopie Ti6Al4V celem zabezpieczenia bezpośredniego kontaktu tkanki z metalowym podłożem. Powłoka biobojętnego implantu z bioaktywną hydroksyapatytową ceramiką swarza potencjalną możliwość biologicznego oddziaływnia pomiędzy kością a powłoką implantu. Nowa generacja biomateriału na bazie stopu tytanu uzyskana została osadzając hydroksyapatyt metodą PLD na uprzednio poddany azotowaniu

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jarzeniowemu podłoże metaliczne. HAp osadzano w temperaturze 250°C laserem Nd:YAG przy repetycji 10 Hz. Uzyskano bliskie stechiometrii fazy HAp na podłożu Ti6Al4V/TiN. Metodą XRD stwierdzono obecność pewnego udziału fazy amorficznej ze względu na niewystarczająco wysoką temperaturę do pełnej krystalizacji. Stwierdzono wpływ wielkości przepływu gazu w komorze reakcyjnej na teksturę krystalograficzną. Badania mikroskopią sił atomowych (AFM) ujawniły wysoki stopień krystaliczności przy maksymalnym przepływie tlenu.

1. Introduction

Many people enjoy a lifetime of appropriate skeletal function, but for many others bones and joints become damaged or diseased and require replacement [1]. Arthritis of skeletal joints- particularly hip and knees is a major health issue and produces pain and loss of mobility.

Biomaterials are either modified natural or synthetic materials, which find application in a 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. The report of the Institute of Materials Strategy Commission [1, 2], claims that: *biomaterials saves lives, relives suffering and improves the quality of life for a large number of patients every year*. For this purpose, the synthetic materials have to be used which possess suitable mechanical and wear properties, and show optimal tissue response. 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. Currently, the materials demand is satisfied mainly by using real bone, either the patient‘s own living bone from other sides (autografts) or dead bone from cadaver or other sources (allografts). However, the load bearing implants cannot be entirely made of HAp because it is a brittle ceramic material [3, 4]. HAp is used in mixing with metals in this case. 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. [3, 5]. Among the different HAp deposition methods, the pulsed laser deposition (PLD) technique, firstly demonstrated in 1992, yielded high quality HAp coatings. 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 [6]. 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 very high chemical purity and 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 target's 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. Contribution of reactive atmosphere by deposition of the HAp layers to the surface morphology, texture and residual stress distribution was under examination.

2. Experimental

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

HAp is also possible to be deposited on three dimensional shape substrate. Xenon lamps are used to heat the substrate to increase the probability of the layer crystalisation. The kinetic energy of the particles in the case of Nd:YAG laser is higher than in use of excimer laser, thus more energy is transformed into heat. It seems that it is no need to apply so high temperature as in excimer laser application. The authors revealed the possibility to decrease the temperature of the substrate with application of Nd:YAG laser. Additionally a new layer composition was proposed to reduce the influence of the crack formation as much as possible. The initial material, before the laser deposition, consisted of the substrate material Ti6Al4V with the 1μm TiN layer formed by glow discharge nitriding. Application of the diffusion method allows to achieve uniform roughness of the surface and its extension (Fig. 1). Moreover, the

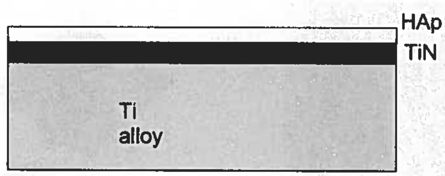

Fig. 1. Composition of the multicomponent HAp layer deposited by PLD on the TiN produced by glow discharge nitriding

biocompatibile TiN layer beneath the biocompatibile HAp layer decreases 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 [7].

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 250°C. The atmosphere in the reactive chamber was the parameter which changed and its influence on the quality of the deposited layer was under investigation. The layers were deposited in argon atmosphere with the 30 sccm (standard cubic cm per minute) gas flow the next under the mixed gas conditions e.i., 15 sccm Ar and 15 sccm O_2 and the last under the 30 sccm oxygen flow. According to the literature, the most appropate conditions which would give the best quality layers should be in the oxygen atmosphere or evaporated water [8].

The crystalline phases present in the coatings were studied by means of X-ray diffractometry (XRD), as well as measurement of crystallographic texture examination. Application of pseudo- position sensitive detector allows to measure simultaneously with texture 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 and the contribution of to the crystallisation process as well.

3. Results and discussion

The contribution of the laser frequency to the quality of the deposited layer were taken under the investigation in the layers obtained by excimer laser. The quality of the layers deposited in use of Nd:YAG laser firmly depended on the oxygen flow in the reactive chamber, thus this parameter was taken under the investigation.

3.1. Morphology by ArF excimer deposition

Morphology of the surface of the deposited layer showed uniform fine structure (Fig. 2). Atomic force microscopy investigation revealed the formation the typical for amorphous, agglomerates on the layer deposited under the highest laser frequency. It could be seen that beside the basic matrix of grains, fine subgrains of ten magni-

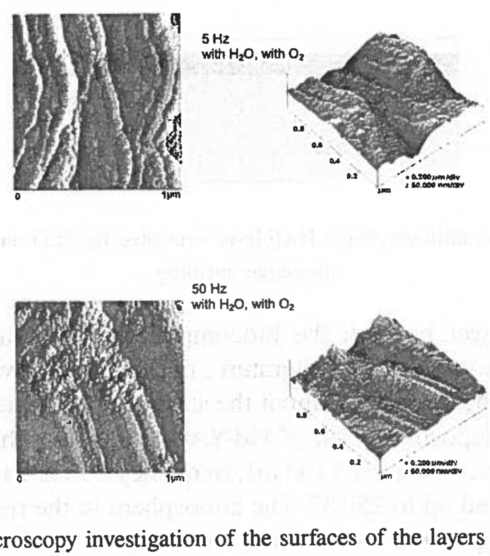

Fig. 2. Atomic force microscopy investigation of the surfaces of the layers deposited by ArF excimer laser with 50 and 5Hz laser frequency

tude smaller, are visible. They could be formed by contribution of kinetic process in formation of the layer.

3.2. Crystalline structure of HAp by ArF excimer deposition

The XRD diffraction patterns of HAp coatings obtained using an ArF eximer laser at different deposition conditions are presented in Fig. 3. Due to the fact that penetration of X-ray was deeper then the thickness of the deposited layer, diffraction lines of substrate were additionally seen on the diffraction patterns. A sequence of lines located in the 2 theta range from 54 to 62° and belonging to the hydroxyapatite have been considered in examination. The most appropriate conditions for HAp crystalline phase formation revealed that deposition on 550°C substrate heating and evaporated H_2O in the reactive chamber caused the most pronounced diffraction lines of hydroxyapatite.

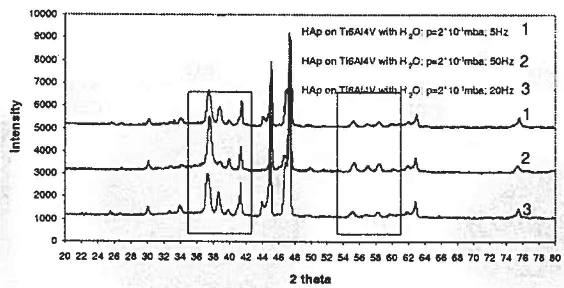

Fig. 3. Phase analysis of the hydroxyapatite layers deposited in different laser frequency

3.3. Crystallographic texture and residual stress distribution by ArF excimer deposition

Contribution of laser frequency (repetition), at the constant other deposition parameters, to the crystallographic texture developed in the deposited HAp layer was studied on the basis of the pole figure measurement from the (002) and (211) planes. 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. 4). The differential pole figures gained by subtraction the intensities from the pole figures type 002 and 211 (Fig. 5) the lowest intensity 50Hz and from the highest intensity 5Hz laser frequency. Presented results in Fig. 5 shows the area which were responsible for the texture orientation weakening. The texture character could inform about the crystallite packing and its homogeneity in the layer which could strongly influence on biocompatibility. Deviation from the symmetrical circle shape of the pole figures could inform about non-symmetrical planar residual stress distribution in the deposited layer.

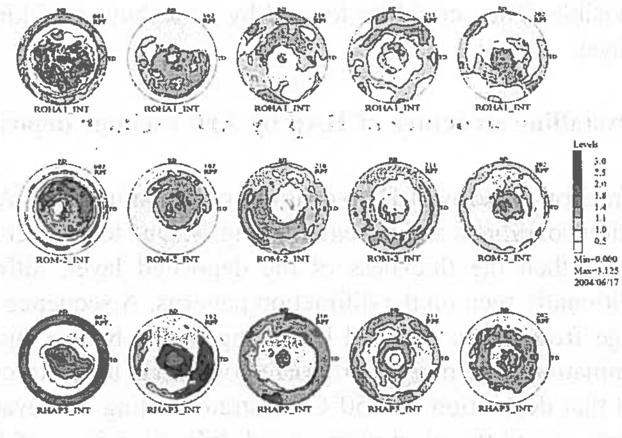

Fig. 4. Texture examination of the hydroxyapatite layers deposited by excimer laser

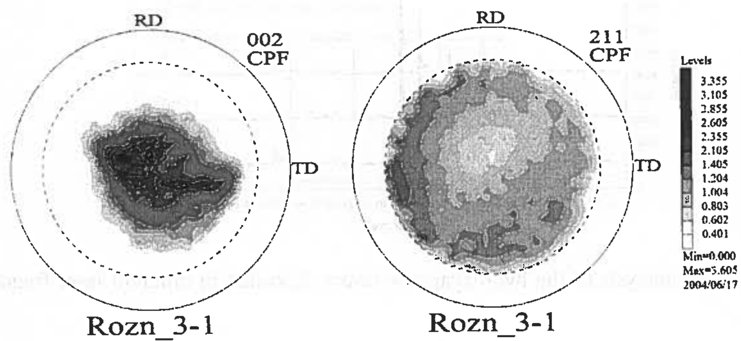

Fig. 5. Differential pole figure calculated by subtraction the weakest intensity from the strongest

3.4. Residual stress in ArF excimer deposited coatings

First type of residual stress is called macro residual stress and its influences on the lattice parameter change from a0 to a1 leading to the diffraction line shifting. Moreover, X-ray investigations allow to establish the micro- residual stress so called second and third type and in this case the diffraction line broadening was studied. On the 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 highest frequency (Fig. 6). To examine the values of the residual stress, $\sin^2\psi$ method was used. It was found that the laser frequency could strongly influence even on the character of the residual stress. The results are shown on (Fig. 7).

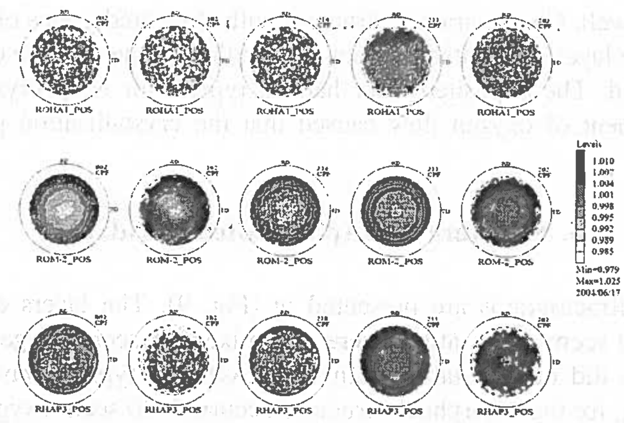

Fig. 6. Pole figures of macro residual stress distribution

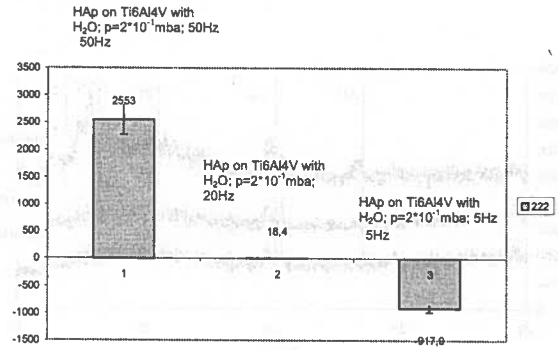

Fig. 7. Results of macro residual stress examination gained by $\sin^2\psi$ method

3.5. Morphology of HAp deposited by Nd:YAG

The images of the surface of the coatings made by atomic force microscopy (AFM) are shown in (Fig. 8). The results are presented on the first derivation of the colour on

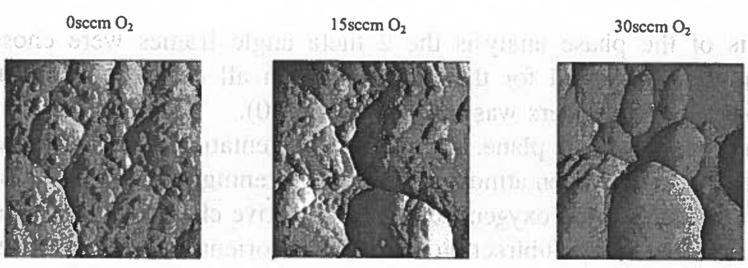

Fig. 8. Influence of the gas flow in the reactive chamber on thestructure on the structure and amorphous phase content

the 2D images as well. Coarse grained structure with elongated grains of the $1.0 \div 1.5 \mu m$ size on the surface layers deposited without oxygen flow in the reactive chamber (0sccm O_2) were observed. The deposited layer had no typical for HAp crystallite structure [9]. The increasment of oxygen flow caused that the crystallisation process of HAp was observed.

3.6. Structure of HAp deposited by Nd:YAG

The XRD diffractograms are presented in (Fig. 9). The layers deposited in the 0 sccm oxigen 30 sccm argon atmosphere and mixed 15 sccm oxygen with 15 sccm argon atmosphere did not crystallized. In both cases the typical waves, in the x-ray diffraction pattern, for the amorphous structure occurred. 30 sccm oxygen flow allowed to achieve crystallised hydoxyapatite coatings. X-ray diffraction diagrams presents picks of the HAp phase. Very low thickness of the layers strongly influenced on the detected intensity.

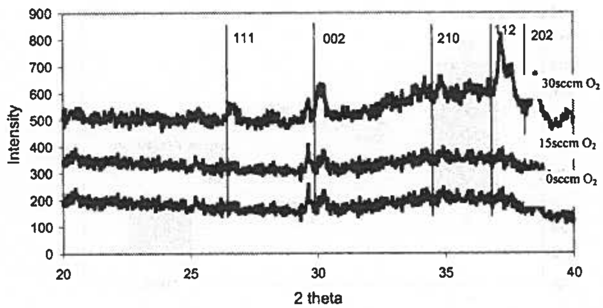

Fig. 9. Phase analysis of the HAp layer deposited under the different conditions

3.7. Crystallographic texture and residual stress distribution by Nd:YAG deposition

On basis of the 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. 10).

The axis is 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 figures 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. 11).

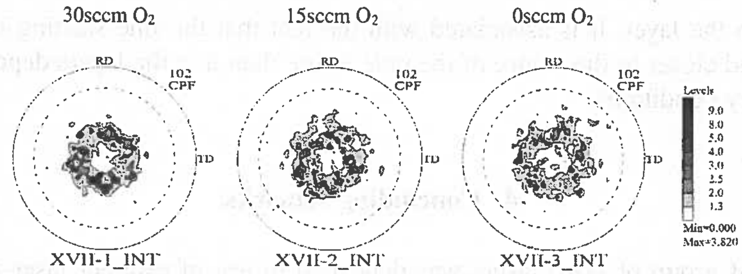

Fig. 10. Pole figures of the crystallite orientation depended on the oxygen flow in the reactive chamber

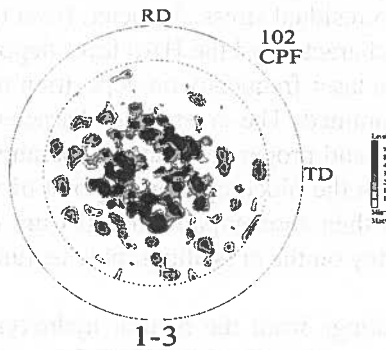

Fig. 11. Differential pole figure, calculated by subtraction the intensity of the weakest crystallite orientation from the strongest orientation

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. 12).

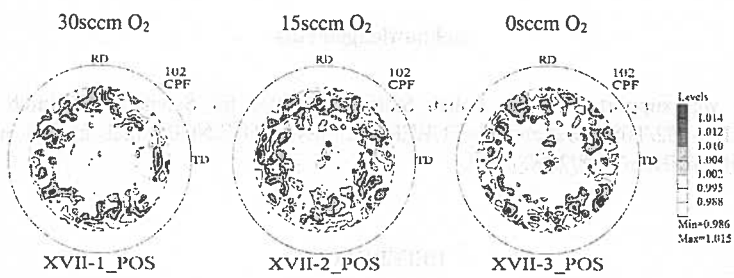

Fig. 12. Pole figures of the residual stress distribution for the 0sccm oxygen flow, 15sccm oxygen flow and 30sccm oxygen flow

The axial symmetry of the position pole figures was observed for all layers. The stress distribution in the amorphous layer, deposited in argon and crystallized one deposited in oxygen environment as approximately equal. The differences were observed in the layer deposited in mixed atmosphere. It could be 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 pole figure than it is the layers deposited under the boundary conditions.

4. Concluding remarks

The first group of HAp layers was deposited in use of excimer laser with evaporated water and 550°C of the substrate heating. It was found that the lower the laser frequency, the stronger the crystallographic orientation. Laser frequency influenced also on the character of the macro residual stress character, from tensile to the compressive. Compressive residual stress characterised the HAp layer deposited with the lowest laser frequency. The influence of a laser frequency on deposition of HAp layers produced in use of excimer laser 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.

The second type of 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. It was found that the most appropriate conditions to achieve crystallised 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.

Acknowledgements

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