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INVESTIGATIONS OF MICROSTRUCTURE AND PROPERTIES IN BIOCERAMIC COATINGS USED IN MEDICINE

BADANIA MIKROSTRUKTURY I WŁASNOŚCI POWŁOK BIOCERAMICZNYCH STOSOWANYCH W MEDYCYNIE

Metallic materials such as titanium and titanium alloy generally show good mechanical properties but their biocompatibility is limited. Hydroxyapatite is a well-know bioceramics that is extensively used in medicine. Due to its reasonable mechanical behaviour under low-load conditions and excellent biocompatibility, combined with slow replacement by the host bone after implantation, this compound is commonly used as a coating for hip prostheses and implants. In order to manufacture implants which combine improved mechanical properties of metallic material with biotolerance of ceramics, hydroxyapatite coatings are applied.

Principal object this paper were the plasma sprayed coatings (deposited on titanium Ti6Al4VELI alloy) treated by laser remelting. The morphology, topography, element analysis, phases and mechanical properties of both sprayed and alloyed coating were analyzed.

Keywords: biomaterials, hydroxyapatite, coatings

Materiały metaliczne, takie jak tytan i jego stopy, posiadają zazwyczaj dobre własności wytrzymałościowe, natomiast ich biotolerancja jest ograniczona. Hydroksyapatyt jest dobrze znanym materiałem bioceramicznym, który ze względu na swoje zalety (bioaktywność) znajduje szerokie zastosowanie w medycynie. Z powodu stosunkowo dobrych własności mechanicznych w warunkach niższych obciążeń oraz doskonałej biozgodności wraz z powolnym obrastaniem tkanką kostną po przeszczepie, związek ten jest powszechnie stosowany na powłoki protez i implantów kości biodrowych.

Mając na celu wytworzenie implantów łączących wysokie własności wytrzymałościowe materiału metalicznego z biotolerancją materiałów ceramicznych, na powierzchni stopów tytanu nakłada się powłoki hydroksyapatytowe.

Celem poniższego opracowania jest analiza własności powłok natryskiwanych plazmowo (na stop tytanu Ti6Al4VELI) oraz określenie wpływu przetopienia powłok wraz z podłożem na własności użytkowe. Analizowane własności obejmowały morfologię i topografię materiału, skład chemiczny i fazowy oraz własności mechaniczne uzyskiwane w powłokach natryskiwanych i przetapianych.

1. Introduction

Modifications of chemical composition of metallic implants have not provided fully satisfying clinical results so far [1].

Materials used inside human body include titanium alloys, used not only for manufacturing of bone implants but also in prostheses for dentistry (Fig. 1). The range of applications for titanium alloys is very wide, from skeleton prostheses or dentures, comprehensive studies on telescope crowns and bolts through fixed structures such as crowns and bridges to precision solutions for implant structures supported on pillars – implants [2-5].

Fig. 1. Implant in bone structure

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Nowadays, with more frequent allergies to a variety of external conditions, a discussion has arisen concerning oversensitivity to titanium used in oral cavity in the form of dental implants and dentures. Development of manufacturing technologies and use of protective surface layers aim to minimize oversensitivity to titanium.

The solutions commonly used during process of titanium implant manufacturing include modification of its surface by means of deposition of bioceramics or combined composite and bioceramic coatings. Issues connected with suitability of bioceramics to bone surgeries are the subject of a number of scientific studies [2-7].

One of the types of coatings used for titanium implants is hydroxyapatite. Hydroxyapatite ceramics (HAp, HA), based on calcium phosphates, i.e. chemical substances being a natural bone component, are found to be one of the best implantation materials for bone surgery and dentistry. HAp is a material which is poorly soluble and slowly resorbed in tissues. Insufficient strength of HAp coatings, however, makes it impossible to use it for elements which bear high load.

The most popular method for deposition of hydroxyapatite on titanium implant coating is plasma spraying.

2. Material and methodology

In order to improve functional properties in titanium, creation of a layer based on HAp was suggested to be made within the following stages:

- application of HAp coating on Ti-6Al-4VELI base by means of plasma spraying
- “remelting” of the coating (using laser technology) with different current and voltage parameters in order to melt the coating and alloy it with base material.

This method of obtaining of composite layer was adopted in order to solve the problem concerning poor mechanical properties of the coating/base material coupling.

Ti6Al4V ELI titanium alloy was employed for the investigations. The samples of 25mm and 5mm were cut out from this material. The surfaces of titanium tablets were then sandblasted and plasma-sprayed. In order to produce the layer, hydroxyapatite powder (HAp) with mean grain size of 50 micrometers, characterized by high degree of purity (Pb = 0.8ppm, As<1.0 ppm, Cd, Hg<0.1 ppm) and Ca/P ratio = 1.67 was used.

In order to spray the layers, plasmotron with internal arc, fed with direct current was used. The parameters of the process of spraying were as following: $U = 45 \div 60V$, current intensity: $I = 350 \div 550$ A, gas flow rate: argon – 3 m3/h, H_2 – 0,5 m3/h, distance of the nozzle from the sample surface: 15-35 cm.

The surfaces of the samples were remelted using Nd:YAG laser (1064 nm wavelength) with continuous beam and scanning rate of 10mm/s.

Sample surface testing was carried out by means of confocal microscope and Jeol JSM-5400 scanning microscope.

Analysis of phase composition in the coatings obtained after spraying and after remelting was conducted using Seifert 3003 T-T X-ray diffractometer with cobalt lamp.

Microhardness testing was carried out using Future – Tech FM-7 hardness tester.

3. Results and analysis

MICROSTRUCTURAL INVESTIGATIONS

Microstructures in the coating after spraying, obtained with confocal microscope, are presented in Fig. 2-3. Geometrical surface in hydroxyapatite coating is shown in Fig. 4.

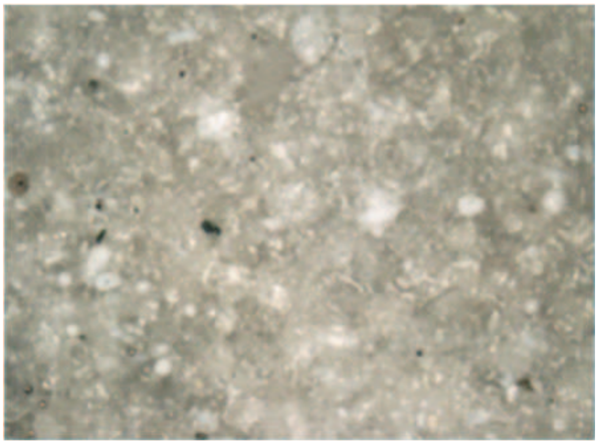


Fig. 2. Microstructure of HAp coating after spraying

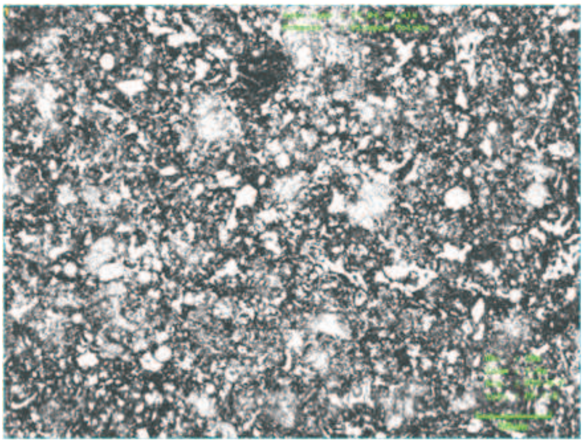


Fig. 3. Binary view of the coating after spraying

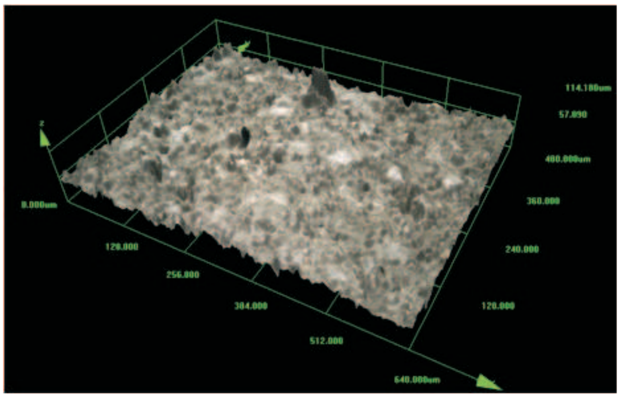


Fig. 4. Surface of hydroxyapatite coating after plasma spraying

As a result of the applied plasma spraying, a hydroxyapatite layer was obtained with thickness of ca. 150 μm (Fig. 5) and roughness of R_a = 5μm. The obtained coatings show elements of structure typical of this method of deposition – porosity, layers, heterogeneity. They have typical, porous lamellar structure with cracks and non-melted particles.

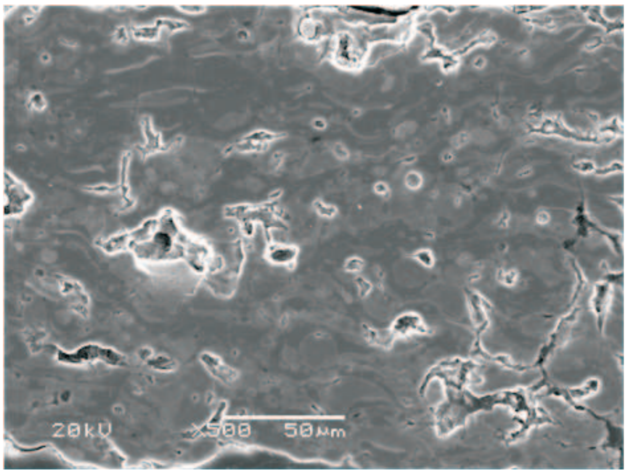


Fig. 5. Microstructure in cross section in hydroxyapatite layer

Microstructure in the surface of the samples after laser remelting closely depend on the applied parameters of surface treatment (Fig. 6). Increase in density of laser beam causes rise in the width of remelting path and change in its microstructure (more cracks, bigger homogeneity and smoothness (R_a: od 2,3 do 1,82μm).

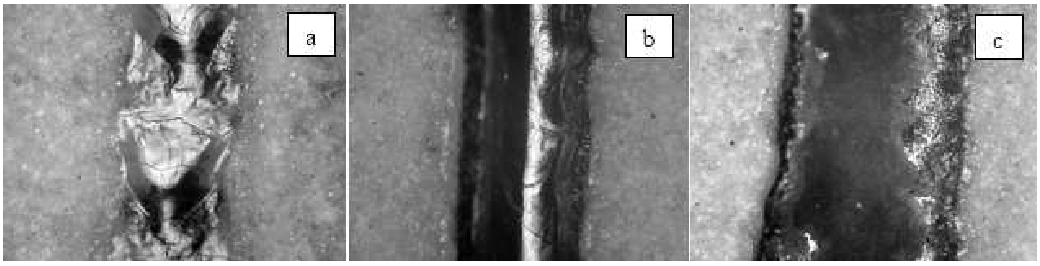
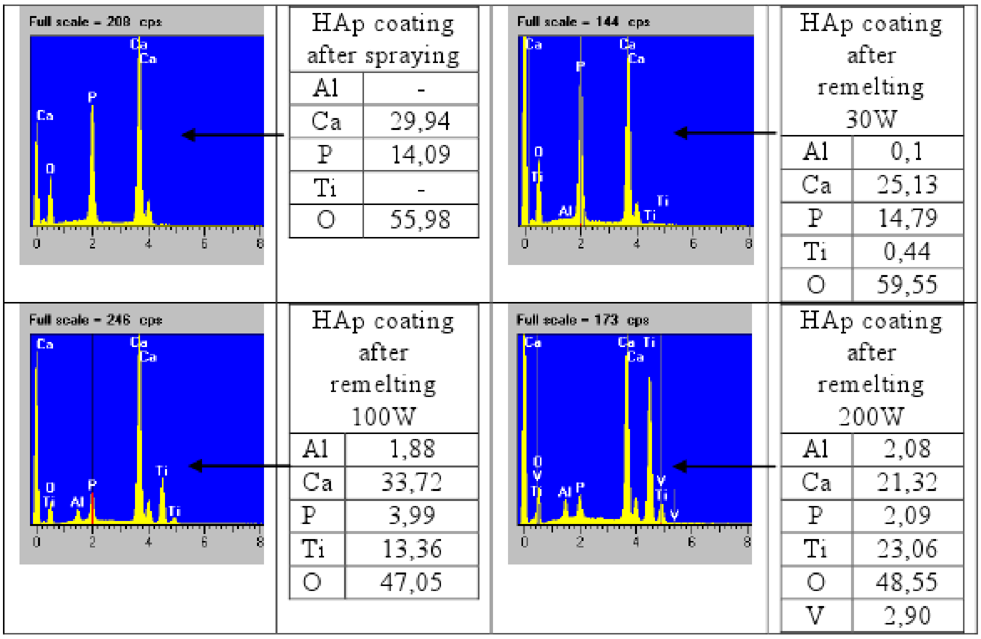


Fig. 6. Microstructure of the remelted paths: a) 30W, b) 100W, c) 200W



HAp coating after spraying	
Al	-
Ca	29,94
P	14,09
Ti	-
O	55,98

HAp coating after remelting 30W	
Al	0,1
Ca	25,13
P	14,79
Ti	0,44
O	59,55

HAp coating after remelting 100W	
Al	1,88
Ca	33,72
P	3,99
Ti	13,36
O	47,05

HAp coating after remelting 200W	
Al	2,08
Ca	21,32
P	2,09
Ti	23,06
O	48,55
V	2,90

Fig. 7. X-ray spectra and chemical composition of the coating after spraying and the layers remelted with laser

CHEMICAL COMPOSITON TESTING

Chemical composition testing was carried out in order to determine the degree of mixing of coating and base material elements.

The results are presented in the form of X-ray spectra with numerical data (Fig. 7).

The conducted testing revealed that increase in beam power caused rise in the degree of HAp coating remelting, manifested in the drop in content of such elements as Ca and P and rise in content of the elements from base material: Ti, Al, V.

X-RAY TESTING

X-ray quantitative analysis revealed that in the coatings obtained from 100% powder of HAp, the amount of crystalline phase was at the level of ca. 85%. X-ray structural analysis (Fig. 8) revealed presence of the following phases: HAp, small content of CaO, amorphous phase and presence of TCP$_\alpha$.

As a result of remelting, phase compositions are not subject to considerable changes (Fig. 9). Presence of HAp, TCP$_\alpha$ phases was revealed as well as CaTiO$_3$ phase which was probably strongly textured. Peaks from CaO were not observed.

X-ray beam width used for investigations of phase composition in surface layers after remelting encompassed at least two of the investigated pathways with different parameters of remelting (limited technical conditions of the used diffractometer). Due to this fact, it was impossible to precisely determine percentage of individual phases in each remelting pathway.

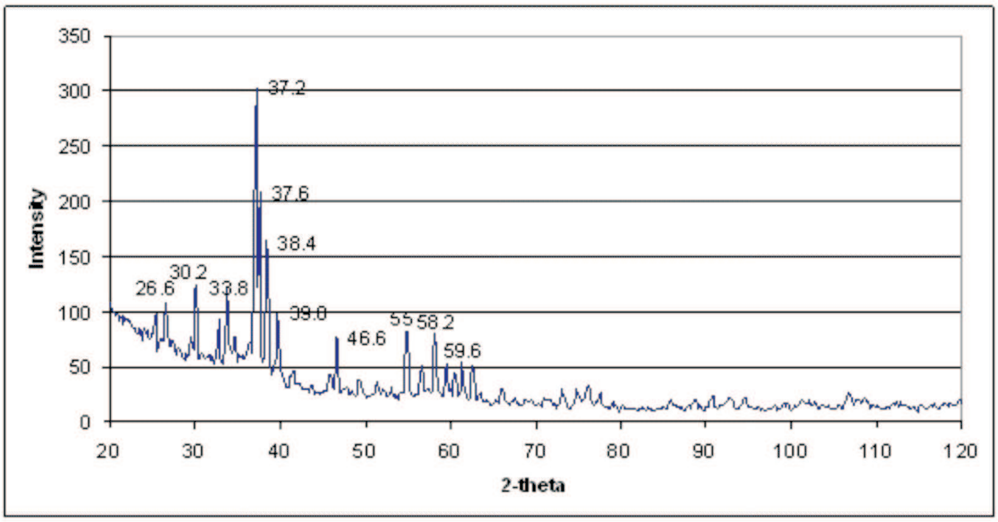


Fig. 8. X-ray phase pattern in HAp coating after spraying

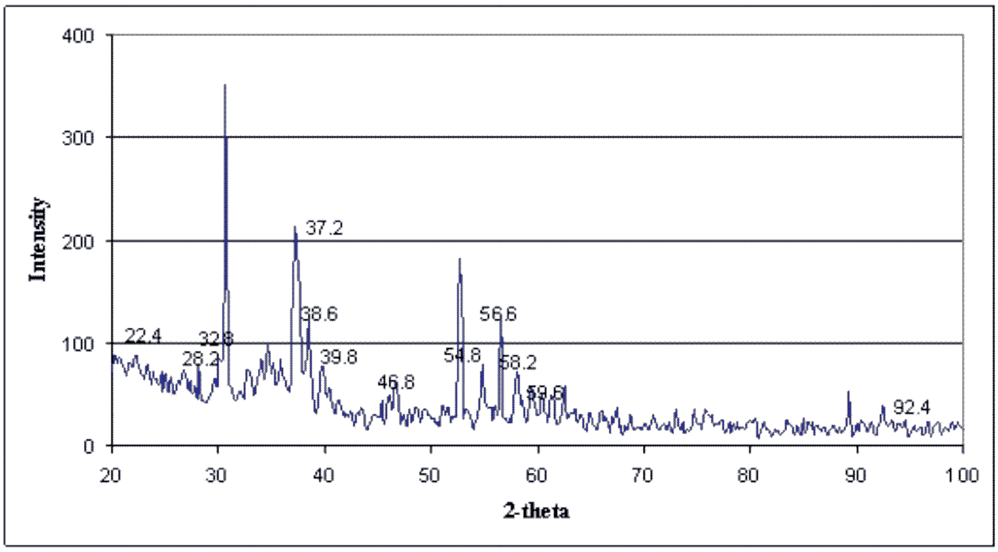


Fig. 9. X-ray phase pattern in HAp coating after remelting

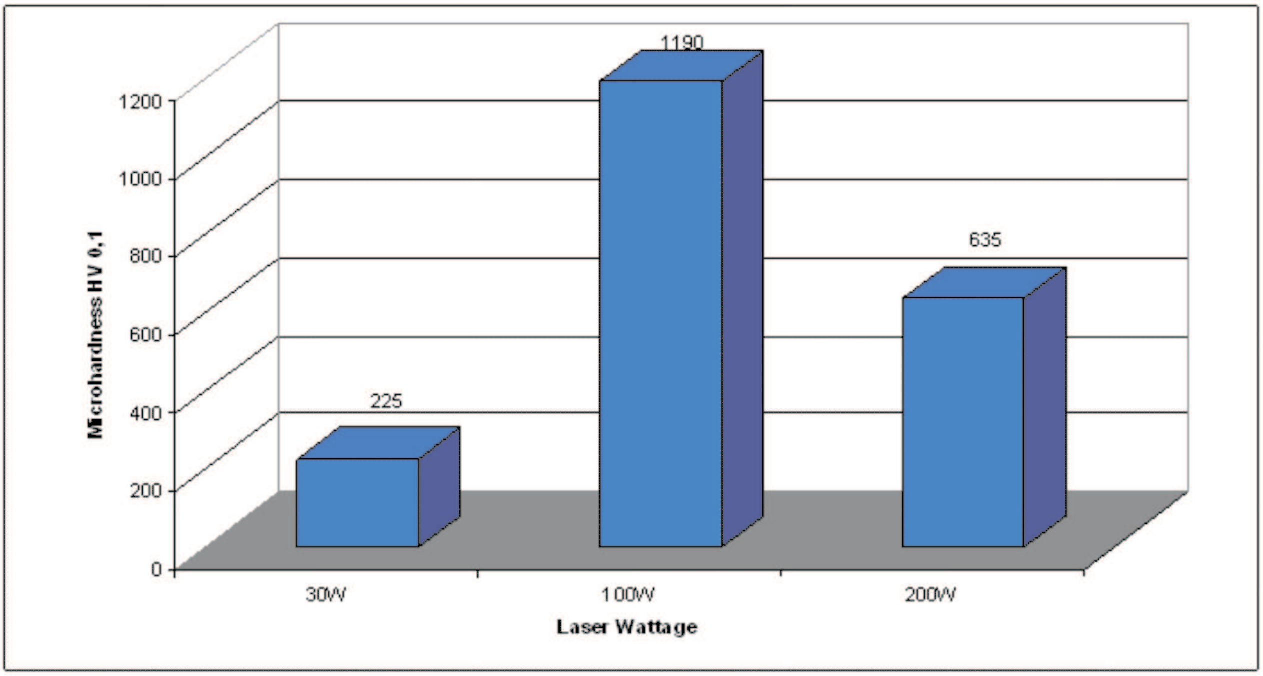


Fig. 10. Microhardness in the alloyed surface layers

Potentiodynamic investigations carried out in Ringer's solution in the paper [8] confirm beneficial effect of addition of zirconium dioxide on corrosion properties in coatings after spraying. Remelting of bioceramic coatings with laser beam shifts corrosion potential towards the negative range, which can be attributed to the obtained phase composition [8-9].

MICROHARDNESS TESTING

Microhardness testing was carried out by means of Vickers hardness tester with the load of 100g. The obtained results are presented in Fig. 10.

4. Conclusions

Low mechanical properties in hydroxyapatite coatings are mainly connected with low adhesion to titanium base material. The methods to improve these properties include remelting of the coating and alloying it with base material, which allows for obtaining metallurgical bond.

X-ray testing proved efficiency of the conducted alloying treatment. As a result of remelting of hydroxyapatite coating using Nd-YAG laser, a surface layer rich in base material elements (Ti, Al, V) and coating elements (Ca, P, O) was obtained. Contents of each element depends on the degree of remelting, closely related to the applied beam parameters. Presence of new $CaTiO_3$ phase was also revealed in the remelted layer.

Laser treatment is accompanied by extreme heating and cooling rates ($\sim 10^{4-5 K/s}$), which, however, did not impact on hydroxyapatite distribution. HAp particles do not have time to reach high temperature before they cool down.

The results of microhardness testing in the alloyed layers also seem to be interesting. They differ depending on the parameters of remelting treatment, however, value of 1190HV0.1 (100W), is most optimal in terms of the goal of enhanced mechanical properties.

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