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INVESTIGATIONS OF TITANIUM IMPLANTS COVERED WITH HYDROXYAPATITE LAYER

ABSTRACT

To reduce unfavorable phenomena occurring after introducing an implant into human body various modifications of the surface are suggested. Such modifications may have significant impact on biocompatibility of metallic materials. The titanium and it`s alloys are commonly used for joint and dental implants due to their high endurance, low plasticity modulus, good corrosion resistance as well as biocompatibility. Special attention should be given to titanium alloys containing zirconium, tantalum and niobium elements. These new generation alloys are used by worldwide engineering specialists. The experiments were performed with hydroxyapatite layer on titanium specimens with the use of electrophoresis method (different voltage and time).

Keywords: *electrochemical deposition method, biomaterials, hydroxyapatite, titanium*

INTRODUCTION

Among the metallic biomaterials, particular place considering useful properties should be given to titanium and its alloys. They are ones of most perspective implantation materials. Using titanium and its alloys is constantly increasing, which results in positive effectsof traumatic treatment. Titanium and its alloys are used to produce the endoprosthesis, implants and stabilizing elements. They also increase the convenience of surgical operations as they are used to make surgical tools, as well as surgical apparatus. Titanium and its alloys are relatively new materials used in medicine. But they are becoming increasingly popular due to their high corrosion resistance as well as the best biological indifference. They also possess good mechanical properties, while having low density, which is about twice less, than stainless steels used in medicine.

Inserting an implant into the body is followed by a chain of reactions between the material and the natural tissue, called an inflammation reaction. The inflammation may be caused by mechanical and thermic damage, the immunological reactions, toxic reactions and possible microorganisms infection [1].

The presence of aggressive ions in the alive tissues leads to the formation of chemical compounds, as well as protein and metal gatherings. Therefore it`s important to protect an implant surface from corrosion by means of passive oxide layers or other ceramic layers for eg. hydroxyapatite. On the other hand it`s advantageous for osteoblasts to stick, which can be achieved by increasing the amount of protein. According to numerous *in vitro* research the least advantageous is polishing the metal surface, which in the 1980`s was commonly used as the most efficient method to avoid corrosion [2,3].

Regardless of the place of an implantation, the body reacts to it as an alien item. The process of healing depends on its biocompatibility. On the other hand osseointegration means the ability of natural tissue to form the connection with an implant surface without penetrating the joining layer surrounding a foreign body [4,5].

The topography of the surface influences the variety of osteoblast and mineralization – on the roughness, texture, porous surface layers. The porous surface has an influence on the reaction occurring between the tissue and implant surface during the healing process, but also on the reaction of a tissue in the process of remodeling. For that reason the porous surfaces are created. They cause the growth of the tissue in the extent sufficient to implant mechanical stabilization [3].

Hydroxyapatite (Fig.1) is widely used for covering metal implants, as well as filling decrement in human bones. Bioceramics promotes the growth of bone on its surface, as its compounds are similar to natural bone. Besides, bioceramics increases adhesion of bone tissue to implants and insures mechanical stability on the implant - bone border. It enables proper interaction between body and tissue. The stability between, which is difficult to achieve is the main reason for bone implant damage [6].

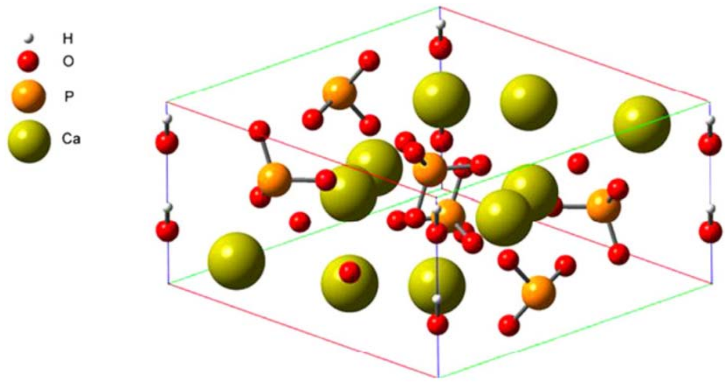

Fig. 1. The elementary cell of hydroxyapatite [6]

Different methods of HAp coverings on the metallic base have been carried out so far. They aimed at discovering most efficient method of covering. They were for ex.: plasma spraying, sol-gel method, biomimetic, as well as electrophoretic. It turned out, that the numerous limits, while generating coverings with the use of electricity: uneven formation of coverings on elements of variety of shapes, little degree of crystallization, as well as weak stickiness to the surface. All this considered the electrophoresis has some priority among other methods of hydroxyapatite adhesion. This method enables an accurate control of the process, high purity of the covering material rarely achieved by means of other methods as well as equal covering of surfaces of variety of shapes. Moreover, electrophoretic adhesion enables covering the porous metallic materials, which is use to produce scaffolds for bone regeneration. This method creates possibility to receive different thickness of coverings [7-11].

Wei and all [12] obtained layers nanoparticles hydroxyapatite from the ethanol substance. Heating at the temperature of 1000-1300^{0}C allowed to obtain layers with adhesion crackings of several MPa [12,13].

The improvement of stickiness and decreasing crackings was obtained according to Xiao and all [14] by lowering the temperature of heating to about 850^{0}C, as well as by increasing the stability of the substance.

Stojanovic and all [15] suggested using the EPD method for producing the gradient glass-apatite layers by the usage of apatite nanoparticles. The obtained layers possessed little porosity, partly sintered. Another attempt to increase the quality and the adhesion of hydroxyapatite layer obtained by EPD method is oxygen layer produced by sol-gel method. It has been found that effectiveness of this method depends on thickness of the layer between others (the increase in density makes it more difficult for hydroxyapatite to adhesion), as well as on the temperature of heating (the best result was obtained at 750 ^{0}C) [16].

The research concern the electrophoretic method and hydroxyapatite coverings.

MATERIALS AND METHODS

The samples were made of Ti6Al4V (Fig.2) and Ti13Zr13Nb (Fig.3) alloys. Afterwards small cuttings were done on the side surface of each sample to introduce copper wire to place the sample into special container for conducting the electrophoretic process (Fig. 4).

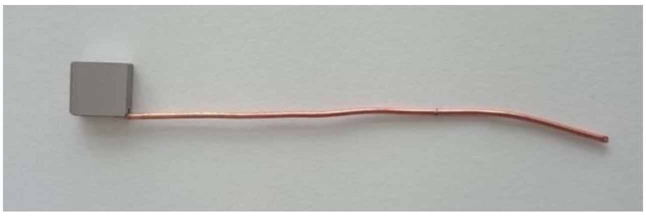

Fig. 2. The Ti6Al4V alloy sample

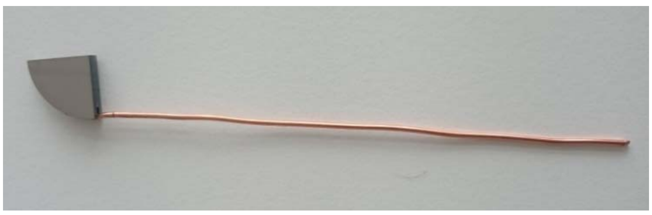

Fig. 3. The Ti13Zr13Nb alloy sample

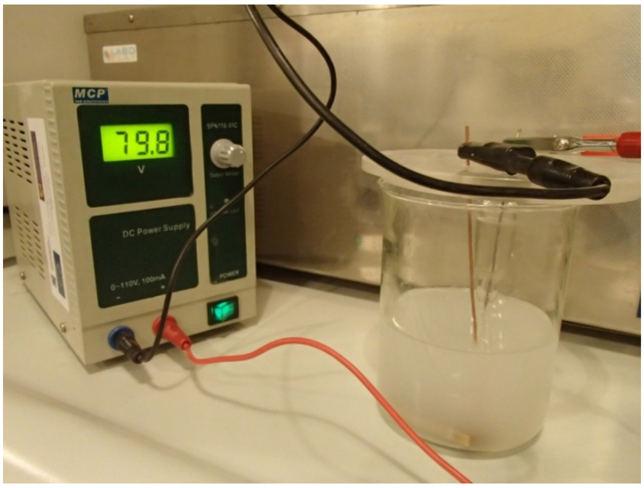

Fig. 4. The electrophoretic equipment

Further preparation of samples was to grinding them on polishing wheel from 1500 to 2400 gradation. Then the samples were polished by the use of polishing paste diamond. The solution for electrophoretic research consisted of: 200 ml of ethyl alcohol 99,8% and 0,4 g of hydroxyapatite (acc. to literature) [17]. Afterwards the samples with hydroxyapatite covering were put into vacuum stove at 500 ^{0}C for 20 min. The time and tension of the electricity was: 7 min. and 60V. Further research dealt with sample observation on the Scanning Electron Microscope Philips XL-30.

The final stage was the biological research. The samples were inserted into bacteria liquid (the content as in Table 1. – Patent no. P 409082 from 4.08.2015) for the duration of 1, 3 and 6 months.

***Table 1.** Chemical composition of the bacteria liquid*

Component	Content (g/dm^3)
Caseine peptone	17
Pepton S	3
NaCl	5
Na_2HPO_4	2.5
Glucose	2.5

than added:

- Staphylococcus aureus 20% of the liquid;
- Staphylococcus epidermidis 20% of the liquid;
- Enterococcus faecalis 15% of the liquid;
- Enterobacter cloacae 10% of the liquid;
- Pseudomonas aeruginosa 35% of the liquid**.**

Afterwards the samples were observed by means of biological microscope to define the adhesion of bacteria to the surface.

RESULTS

Fig.5 show sample of the Ti6Al4V alloy covered with hydroxyapatite.

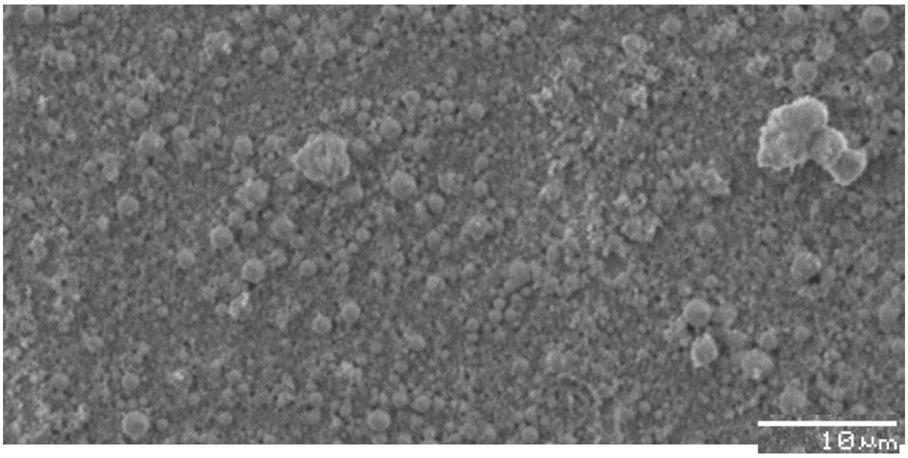

Fig. 5. Sample of the Ti6Al4V alloy covered with hydroxyapatite, SEM

Fig.6 show sample of the Ti13Zr13Nb alloy covered with hydroxyapatite.

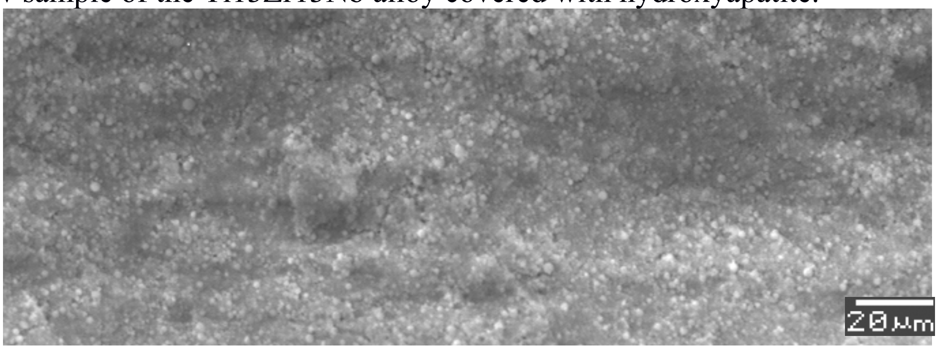

Fig. 6. Sample of the Ti13Zr13Nb alloy covered with hydroxyapatite, SEM

The final research concerned the adhesion of bacteria to the sample surface (Fig. 7-9).

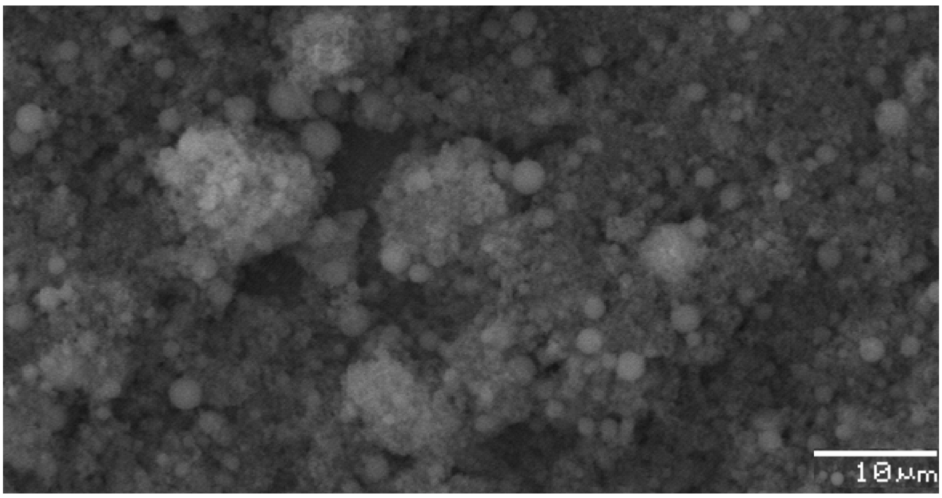

Fig. 7. The view of surface of the Ti13Zr13Nb alloy after 6 months being in bacteria liquid

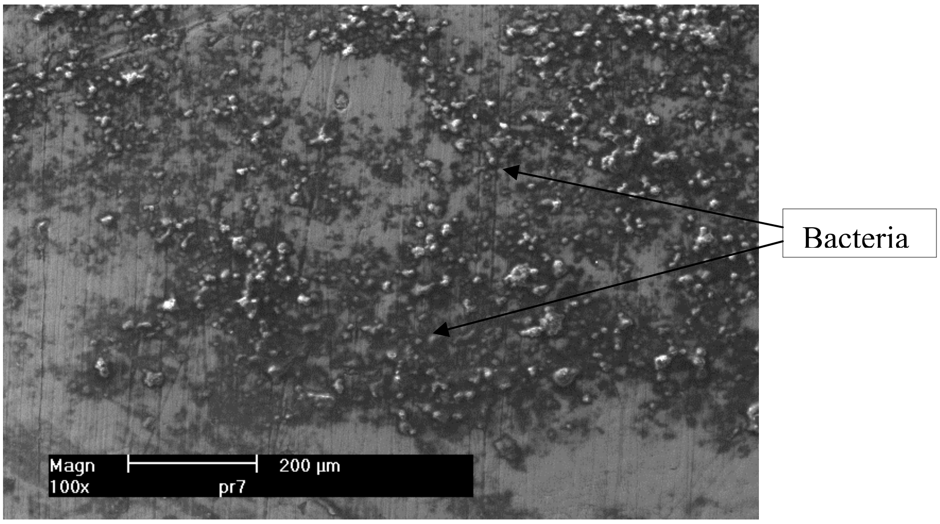

Fig.8 The view of surface of the Ti6Al4V alloy after 3 months being in the bacteria liquid

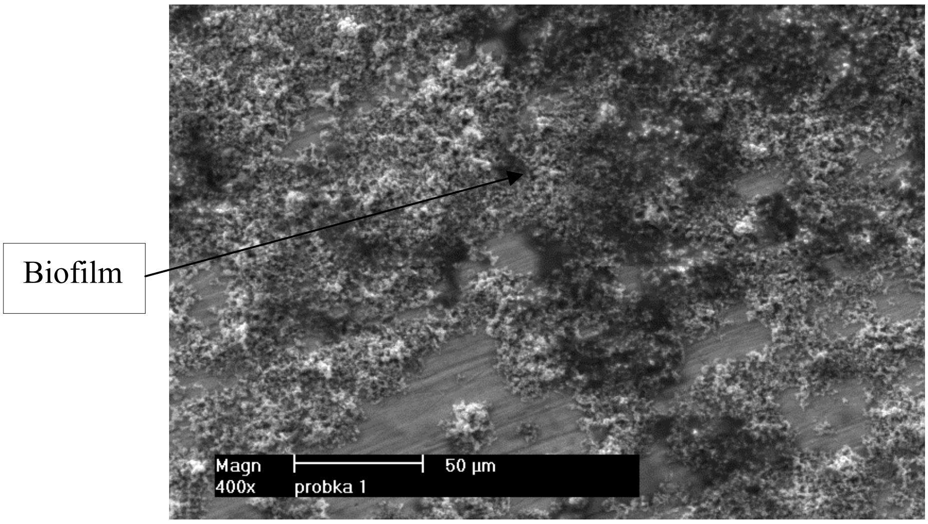

Fig. 9. The view of surface of the Ti6Al4V alloy after 6 months being in the bacteria liquid

DISCUSSION

Attention should be paid to the fact, that current experience in inserting metal implant into human body indicate, that biotolerance level has been reached. It was achieved by proper selection of chemical compounds the improvement of the structure and creating passive layers. One of the most serious inconveniences of using metal implants in dentistry is big complication risk, both in early post-operation and later stage infections. The complications may be aseptic and anti-aseptic, as well as releasing hydrogen in reactions and absorption of oxygen from tissues surrounding an implant. The local lowering of pH and oxygen density destroys surrounding cells and weakens the immunity of bacteria. Therefore the surfaces of implant should have different physical and mechanical features. Because of that, the techniques of surface engineering are more and more frequently used in forming them.

It enables forming surface layers of good biotolerance and big endurance resistance [18,19].

Titanium and its alloys are increasingly frequently applied in biomedicine to replace the damaged hard tissue for ex. in the hip and knee joints as well as heart valve. As compared with other metallic biomaterials the titanium alloys show the following features: the lowest Young modulus, little thickness, high biotolerance, good resistance to corrosion, paramagnetic properties, high endurance and high tendency to self-passivation. One of the titanium alloys is Ti6Al4V. It used to be the most frequently applied titanium alloy for endoprosthesis. However, there was high possibility of releasing the toxic elements (in long term), which settle in the brain and result in cancer reactions, therefore other elements were introduced into the alloy. In this way a new alloy free from above mentioned toxic elements was created. This alloy is popular in medicine due to its high biocompatibility. Its plastic modulus is significantly lower than other metallic biomaterials. However it still remains higher, than bone plastic modulus. It means, that such an implant is more resistant to loads and enables proper regeneration of bone tissue [18,20].

The electrophoretic deposition (EPD) method is used to produced ceramic layers. It is an electrochemical process occurring in colloid environment, in which loaded powder particles scattered or being a suspension in liquid are attracted and placed on transmitting base with opposite mark as a result of provided tension of constant current. To produce ceramics layers they used electrophoresis (the base is cathode). The advantages of the EPD are: the speed of forming the layer, simplicity of the equipment, insignificant limits of the base shape, forming the layers environmentally friendly, as well as easy control of the thickness and morphology of the forming layer by the use of proper choice of time and process potential [21-23].

The interest in EPD is based not only on its high versatility to be used with different materials and combinations of materials, but also because EPD is a cost-effective technique usually requiring simple processing equipment and infrastructure. Moreover, EPD has a high potential for scaling up to large product sizes, ranging from micrometers to meters, and it can be adapted to a variety of device and component shapes [21].

The hydroxyapatite surface is porous and contains grains of different sizes. There is a close correlation between the pore size and entering the bone tissue. It was discovered, that if the size of pores doesn't reach 95 μm, the tissue doesn`t enter into the ceramic. In that case only fibrous tissue is formed. Optimal entering give pores sized 100 μm – 150 μm, while the quickest entering is in case of 500 μm – 1000 μm. Entering the bone into pores surfaces is also in close correlation with canting joint endurance, which according to the thickness of area changes from 2 to 20 MPa [18].

The EPD technique gained popularity owing to its possibility to form coverings on a wide range of materials, including composites. Moreover, it can be used as a base for powder coverings. In addition to that its advantage is ability to create different thickness coverings, whose range is between 0,1 μm to 100 μm. Besides EPD method is profitable from economical point of view, due to the simplicity of equipment necessary to create the covering and additionally it gives possibility to apply coverings on elements of different shapes and sizes. All this leads to increased interest in electrophoretic method, particularly in medical industry [21].

As compared with other methods of implant covering, electrophoresis is a better way of obtaining covering layers. Owing to it there is possibility to achieve big structural variety, which results in creation of equal coverings in all the surface. In addition to that this method enables controlling the density of the thickness of the layer, coverings on variety of shapes and porous structures.

CONCLUSIONS

1. The advantages of the EPD are: the speed of forming the layer, simplicity of the equipment, insignificant limits of the base shape, forming the layers environmentally friendly, as well as easy control of the thickness and morphology of the forming layer by the use of proper choice of time and process potential.
2. The HAp covers improve the resistance to abrasion of metallic implant materials, as well as they prevent undesirable compounds from entering the biological environment.
3. Biological research proved, that in case of Ti13Zr13Nb alloy after 6 months of being kept in bacteria liquid, the adhesion of bacteria and biofilm to the surface weren't found.
4. In case of Ti6Al4V alloy after 3 months of staying in bacteria liquid, separate bacteria appeared on the surface. While after 6 months the surface was totally covered with the biofilm.

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