# BONE-LIKE COATINGS DEPOSITION BY USING OF MODERN PULSED ION-PLASMA TECHNOLOGY

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The technology of synthesis of multilayer coatings on the basis of alumina oxide and structures, like tricalcium phosphate and hydroxylapatite, was suggested by Reactive Ion-Beam Synthesis (RIBS) method in a same vacuum cycle. The substance of the method consists in a physical sputtering of target of compound composition on the specimens with its simultaneous bombardment by intensive ion beams of chemically active gases. The concurrent using of pulsed ion-plasma technology offer the ability to beneficially modify a wide array of surface properties at low temperature; to increase adhesion, density, deposition rate and quality of oxide coatings, to deposit complex multilayer dielectric coatings with ultra disperse structure. The analysis of results obtained in the work, allows to make a conclusion about the advantages of combining of pulsed ion-plasma technology with RIBS method using for the purpose of strong attachment of metal prosthesis in bone tissue and the activation of osseogenesis and osseointegration processes.
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## 1. INTRODUCTION

At present the metal artificial prosthesis with coatings deposited by various physical and chemical methods are widely used in medical practice. The most perspective are coatings with bioactive properties having the tendency to a gradual diffusion in organism and replacement by bone tissue. However series of significant deficiencies, in particular, weak strength properties of coatings, high porosity, boosted diffusion of substrate metal ions, may lead to undesirable clinical consequences. The principal problems, which limit wide application of coatings in medicine, are weak strength coating properties and insufficient adhesion between a film and a metal substrate. Other important problem is the structure of deposited bioactive coatings. The basic distinctive feature of hydroxyapatite crystal of human bone is its ultra disperse structure with more than 25% of atoms at the crystal surface. These atoms are especially suitable for a chemical exchange and bone ingrowth activation processes. The application of multilayer coatings combining the protective functions through the stop-layer formation (preventing a diffusion of substrate metal ions in organism, electrochemical processes etc.) and activation functions - through the deposition of bioactive calcium-phosphate layer which dissolves and is substituted by bone tissue - is of great interest.

## 2. MATERIALS AND METHODS

The modern technologies of functional coatings deposition on products of microelectronics, mechanical engineering, tool industry, offer a wide spectrum of methods of influence on a surface, including chemical, electrochemical, gas-phase, thermal, plasma-chemical, ion-plasma ones, etc. Each of methods has certain advantages and disadvantages. The choice of optimal technological modes assumes realization of complex investigations of the basic characteristics of the substrate material and coating (structure, surface morphology, stoichiometric and impure composition, thermal expansion coefficients, mechanical properties, etc.).

The technologies of oxygen passivation of titanium surface by thermal or electrochemical ways and obtaining of rather thick (about 100 micron) film $TiO_2$. have received the greatest distribution [1]. Such methods allow to obtain hard and anticorrosive oxide coatings, which can be easily and cost-effectively fabricated. However these coatings by long use in organism have a number of restrictions: insufficiently dense connection implant with bone, formation of a fibrous tissue in the zone of contact, biochemical changes in structure of a saliva and blood as a result of electrochemical reactions, excess concentration titanium in lungs and lymphatic glands of patients.

Many techniques have been investigated for deposition of ceramic bioactive coatings onto metallic surfaces, including flame, plasma and HVOF spraying, ion beam sputtering, chemical vapor deposition, dip coating, electrophoresis and electrochemical deposition. For application of such coatings made of calcium-phosphate ceramics (hydroxyapatite (HA)) the most popular in modern medical practice is the Plasma Spray method [2]. The basic advantage of this method is its high productivity. The basic disadvantages are: low adhesion and strength characteristics, problems with the control of stoichiometric composition, phase and structural properties of received films.

One of the modern plasma methods of HA coatings deposition is the method of Magnetron Sputtering. The films received in this case have higher density and uniformity. In comparison with the Plasma Spray method, there is the opportunity of improvement of adhesive characteristics and coatings structural properties. Further advancing of the method allows to combine sputtering of a target with simultaneous activation of a sample surface before deposition (methods Reactive Ion-Beam Synthesis (RIBS) [3] and Ion-Beam Assisted Deposition (IBAD) [4]. These methods improve coating properties and make process of deposition more controllable

During the recent years the technology of synthesis of ductile, dense ceramic coatings with good adhesion based on alumina oxide and zirconium oxide was developed. Such materials are widely used in the world medical practice. Oxide coatings allow to protect the organism from the substrate metal corrosion, to avoid the electrochemical reactions on the metal surface and inflammatory processes in the surrounding tissues.

The further improvement of the technology and equipment are the deposition on implants the double protective bioactive films based on alumina ($Al_2O_3$) and calcium-phosphate ($Ca_3(PO_4)_2$) ceramics and also hydroxylapatite ($Ca_{10}(PO_4)_6(OH_2)$) which are able to improve biochemical and biomechanical properties of implants and so, to achieve their reliable fixation in bones and the stimulation of osseogenesis and osseointegration mechanisms.

## 3. EXPERIMENTAL DETAILS

This study represents the technology of two-layer bioactive-bioinert coatings synthesis on the basis of alumina oxide and structures, like tricalcium phosphate and hydroxylapatite (Fig. 1), suggested by Reactive Ion-Beam Synthesis (RIBS) method in a same vacuum cycle [5]. The substance of the method consists in a physical sputtering of target of compound stoichiometrical composition on the specimens with its simultaneous bombardment by intensive ion beams of chemically active gases. To realize the method the vacuum system (Fig. 2) with two sources of intensive ion beams based on RF inductively coupled discharge (ICD) was used; the high energy ion source ($E_i$ ~2-5 KeV) for the sputtering of the target of compound composition and the pulsed source of low energy ions ($E_i$ ~ 50-300 eV) of chemically active gases for the substrate surface clearing and activation before deposition [6-8], which allowed to correct the stoichiometry and structure of condensed films. The concurrent using of pulsed ion-plasma technology offer the ability to beneficially modify a wide array of surface properties at low temperature, to increase adhesion, density, deposition rate and quality of oxide coatings, to deposit complex multilayer dielectric coatings with ultra disperse structure.

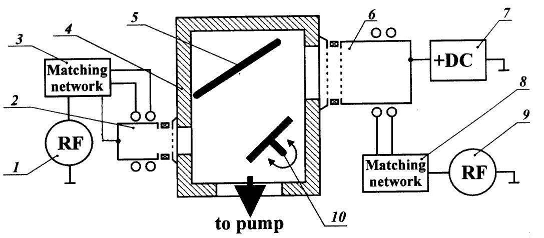


*Fig. 1. Working scheme of installation for Reactive Ion-beam Synthesis Method*

*1,9 – RF power*

*2 – high energy ion source of intensive ion beams, based on RF inductively coupled discharge (ICD)*

*3,8 – matching network system*

*4 – chamber*

*5 – rotative target system*

*6 – pulsed source of low energy ion of chemically active gases*

*7 – DC power*

*10 – substrate-holder rotative system*

Samples from Ti, stainless steel by a diameter of 30 mm and thickness of 10 mm were exposed to pretreatment ultrasonically clearing in alcohol and washing by water. The process of a vacuum work cycle consists of three stages: ionic clearing and preparations of a surface; formation of the underlayer of alumina oxide; synthesis of hydroxyapatite coatings.

The deposition rate of alumina oxide depending on various conditions was 300-2500 Å/min. For calcium - phosphate layer formation. Al target was exchanged on the compound composition target containing 70 % hydroxyapatite and 30 % tricalcium phosphate. The thickness of alumina oxide coatings is varied in the range 3-5 μm and hydroxyapatite layers 1-3 μm depending on deposition conditions. In the further amorphous calcium - phosphate layer was exposed to heat treatment at temperature $600^0$ C [9] during several hours and subsequent immersion in a water solution up to it recrystallization in a dense and homogeneous hydroxyapatite layer.

## 4. RESULTS AND DISCUSSION

The analysis of structure and composition of the layer were carried out by the methods of a X-ray diffraction (XRD), SEM (scanning electron microscopy). The crystal structure of coating layer was investigated by XDR. The coatings show the amorphous structure before the annealing. After heat treatment at temperature $600^0$C amorphous structure is transformed to crystalline. The crystalline phase started to become visible (Fig. 3) with peaks corresponding to the (200), (002), (102), (210), (211), (300), (202) and (310) reflections within the angle interval 20<2□<40 (degrees). Annealing process led to crystalline phase formation and is very effective in

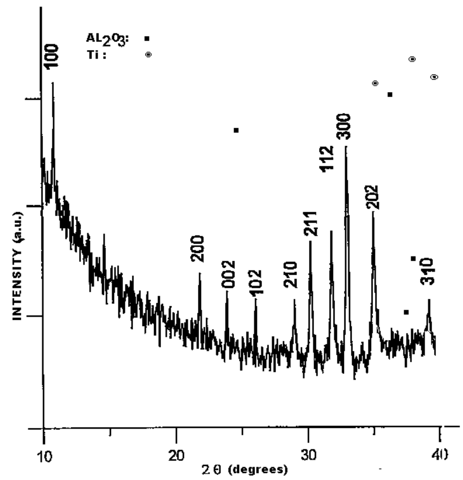


*Fig. 2. XDR analysis of coatings crystalline phase*

coating transforming. SEM observations indicated that the surface of coating layer was homogeneous and dense. There were no cracks in coatings before and after annealing process. The surface morphology was the same in the both case.

A clear interface boundary between the coating and substrate wasn't recognized. The adhesive strength of coatings was measured by a scratch test method. The adhesion upper critical loads in the case of alumina oxide coating and hydroxyapatite with alumina oxide coatings were 8 and 10 N and increases with layer thickness. The corrosion tests show corrosion resistance of deposited coatings in 3.5%NaCl solution. The uncoated Ti specimens gave the lowest corrosion potential and the highest corrosion current. The highest corrosion potential possessed alumina oxide coating. The investigations have shown that in aggressive environment chemically stabilized intermediate dense layer acts as natural barrier against corrosion of metal-basis ions and prevents electrochemical reactions in human body and thus avoids deleterious effects [10].

## 5. CONCLUSIONS

The technology of synthesis of multilayer coatings on the basis of alumina oxide and structures, like tricalcium phosphate and hydroxylapatite, was suggested by Reactive Ion-Beam Synthesis (RIBS) method in a same vacuum cycle. The substance of the method consists in a physical sputtering of target of compound composition on the specimens with its simultaneous bombardment by intensive ion beams of chemically active gases. The concurrent using of pulsed ion-plasma technology offer the ability to beneficially modify a wide array of surface properties at low temperature; to increase adhesion, density, deposition rate and quality of oxide coatings, to deposit complex multilayer dielectric coatings with ultra disperse structure. The analysis of results obtained in the work, allows to make a conclusion about the advantages of combining of pulsed ion-plasma technology with RIBS method using for the purpose of strong attachment of metal prosthesis in bone tissue and the activation of osseogenesis and osseointegration processes.

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## НАНЕСЕННЯ КІСТКОПОДІБНИХ ПОКРИТТІВ З ВИКОРИСТАННЯМ СУЧАСНОЇ ІОНО-ПЛАЗМОВОЇ ТЕХНОЛОГІЇ


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Технологія нанесення багатошарових покриттів на основі оксиду алюмінію та структур, типу трикальційфосфат та гідроксилапатит запропонована методом реактивного іонно-плазмового синтезу (РІПС) в єдиному вакуумному циклі. Сутність методу полягає у фізичному розпиленні мішені складного стехіометричного складу на підкладенку з її одночасним бомбардуванням інтенсивними іонними пучками хімічно активних газів. Сумісне використання імпульсної іонно-плазмової технології дозволяє успішно змінювати в широкому діапазоні поверхневі властивості отриманих покриттів: підвищити адгезію, щільність, швидкість нанесення та якість оксидних покриттів, а також отримати багатошарові діелектричні покриття з ультрадисперсною структурою. Аналіз отриманих результатів дозволяє зробити висновок відносно значних переваг сумісного використання імпульсної іонно-плазмової технології та методу РІПС з метою забезпечення надійної фіксації металевого протезу у кістковій тканині та активації процесів остеосинтезу та остеоінтеграції.


## НАНЕСЕНИЕ КОСТЕПОДОБНЫХ ПОКРЫТИЙ С ИСПОЛЬЗОВАНИЕМ СОВРЕМЕННОЙ ИОННО-ПЛАЗМЕННОЙ ТЕХНОЛОГИИ


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Технология нанесения многослойных покрытий на основе оксида алюминия и структур, типа трикальцийфосфат и гидроксилапатит предлагается методом реактивного ионно-пучкового синтеза (РИПС) в едином вакуумном цикле. Сущность метода состоит в физическом распылении мишени сложного стехиометрического состава на образец с его одновременной бомбардировкой интенсивными ионными пучками химически активных газов. Совместное применение импульсной ионно-плазменной технологии позволяет успешно варьировать в широком диапазоне поверхностные свойства получаемых покрытий: повышать адгезию, плотность, скорость нанесения и качество оксидных покрытий, а также наносить многослойные диэлектрические покрытия с ультрадисперсной структурой. Анализ результатов, полученных в работе, позволяет сделать вывод о преимуществах комбинированного

использования импульсной ионно-плазменной технологии и метода РИПС для обеспечения надежной фиксации металлического протеза в костной ткани и активации процессов остеосинтеза и остеоинтеграции.