ABSTRACT

of the thesis for the degree of Doctor of Philosophy (PhD)
on the specialty 6D071000 - Materials Science and Technology of New Materials

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THE FORMATION OF CALCIUM-PHOSPHATE COATINGS ON TITANIUM SUBSTRATE WITH HIGH FUNCTIONAL PROPERTIES BY THE METHOD OF HIGH-FREQUENCY MAGNETRON SPUTTERING

Relevance of the topic

In the last decade, the direction on creation of materials, ensuring the formation of a transition zone between the bone and the implant appeared in the development of biomaterials. Such a zone, along with a strong connection with the implant material, should have an acceptable macro- and microstructure for the organism, biocompatibility. Such structural materials as stainless steel, alloys based on cobalt, titanium are widely used for the manufacture of artificial implants due to their excellent mechanical properties, but in some cases they cause allergic reactions and, as a result, rejection. In addition, a violation of joining of the endoprosthesis surface with the bone tissue causes its gradual slacking, which requires repeated operations to replace or strengthen the implant. To increase the biocompatibility of these materials, additional coatings are applied to their surface. Recently, interest in calcium-phosphate (CaP) and hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ (HA) coatings, which significantly increase the adhesive strength of implants with bone tissue, has increased.

To date, a wide range of methods developed and tested to create CaP coatings on metal implants are used: plasma spraying process, microarc oxidation (MAO), methods based on crystallization of coatings from various solutions, method of detonation-gas spraying, electrochemical deposition, sol-gel coating, etc. Each of the listed methods has its own advantages and disadvantages. Among the shortcomings, the following can be noted: poor adhesion of the coatings to the substrate, the inability to regulate their elemental composition, and limited choice of the substrate material to form the coating.

Studies show that using the magnetron sputtering method provides high adhesive strength between the substrate and the coating. Under optimal spraying conditions, the stoichiometric composition of coatings is close to hydroxyapatite. The method of high-frequency magnetron sputtering (HFMS) is flexible, since it allows to vary elemental composition of the coating by changing either the composition of the initial sputtering target or the deposition parameters (discharge power, working gas, etc.).

HFMS is the most promising method, due to the availability of the possibility of uniform application of coating with high adhesion, as well as the ability to use substrates with a complex geometric shape. In addition, CaP coatings obtained by this method have good mechanical properties, osteoinductance and strong adhesion. However, the development of methods for the formation of thin

biocoatings, optimally combining bioactivity and mechanical strength, is an important task of medical materials science and new formation modes are currently under intensive search.

Solving the problem of increasing biocompatibility and osteointegration of implants in orthopedics and surgery have great social importance, since at present, there is a high probability of rejection, development of allergic reactions, loosening in the postoperative period, which requires repeated operations and can lead to long-term rehabilitation of the patient. The application of CaP layer close in composition to HA on the surface of the implant, allows not only to ensure high biocompatibility, but also to provide osteointegration. However, in case of insufficient adhesion of CaP layer to the implant surface, its loosening occurs, and its fragments can migrate to the friction unit, deteriorating the tribological properties and increasing the amount of wear products.

The method of HFMS is characterized by low productivity, which significantly increases the cost of modifying the surface of implants. Increasing the power of sputtering leads to a decrease in adhesion and an increase in ratio Ca/P, which is not acceptable. To improve the method of HFMS, it is important to study the effect of sputtering parameters of a hydroxyapatite target and subsequent heat treatment on the structure, phase and chemical composition, adhesion characteristics of the forming layer.

Novelty themes

The selected topic of the thesis has a novelty, since the work is focused on establishing patterns of structure and phase formation of calcium phosphate coatings on a titanium substrate when they are deposited using the method of HFMS a hydroxyapatite target, and determining changes in the properties of coatings obtained in various sputtering conditions and subsequent heat treatment, in order to improve such characteristics of biocompatible calcium-phosphate layers applied to the surface of implants made of titanium alloys, such as adhesion to the substrate and the wettability of the surface with water. This allows to improve the technology of producing biocomposite based on CaP coating and titanium by the method of HFMS.

The aim of the work is to study the formation of the structure and properties of calcium phosphate coatings on the surface of titanium, depending on the conditions of high-frequency magnetron sputtering of a hydroxyapatite target and subsequent heat treatment, and to identify the optimal conditions for obtaining biocompatible coatings.

The main objectives of the research include:

- to establish the influence of modes of high-frequency magnetron sputtering of hydroxyapatite target on the structure, phase and elemental composition, water wetting parameters and adhesive properties of CaP coatings formed on titanium substrate VT1-0;

- experimentally identify the optimal conditions for high-frequency magnetron sputtering to obtain biocompatible CaP coatings on titanium VT1-0;

- to establish the influence of heat treatment conditions on the structure, morphology, topography and adhesion properties of the obtained coatings;

- to investigate CaP coatings obtained by the method of microarc oxidation and compare their characteristics with the coatings formed by HFMS.

The object of research is CaP coatings on titanium substrate VT1-0 obtained by the method of HFMS.

The subject of the research is the structure and properties of calcium phosphate coatings formed on a titanium substrate, with different parameters of magnetron sputtering and subsequent heat treatment.

Methodological base of research

The main methods of research and analysis used in the implementation of the thesis are:

- electron scanning microscopy using microscope JEOL JXA-8230 (Japan) at accelerating voltage of 20 kV and electron beam current of up to 7 nA at various magnifications;

- studies by the method of infrared spectroscopy using spectrometer Avatar-370 CsI FT-IR from Termo Nicolet (USA);

- study of the structure and composition of CaP coatings by X-ray phase analysis using diffractometer D8 Advance (Bruker, Germany). X-ray patterns of the samples were obtained using copper radiation ($\lambda = 1.5406$ Å) in digital form;

- study of the concentration profiles of the main elements in the depth of the obtained CaP films by the method of Auger spectroscopy on instrument Schooner-2 (Russia);

- research by atomic force microscopy using microscope AFM PSIA XE-100 (Korea). Pictures were taken in contact mode;

- analysis of samples by the method of sclerometry (scratch test) for the determination of adhesive properties on device CSEM Micro Scratch Tester (Switzerland).

New scientific results

The following new scientific results were obtained in the course of carrying out dissertation. It was established that:

- during magnetron sputtering of target from HA, the growth of coatings of calcium phosphate compounds on the substrate develops by layer-island mechanism. At the first stage, layer-by-layer growth of crystals occurs, and further growth on the island principle. The reason for this is the formation of single protrusions with an increased growth rate at the stage of layer-by-layer growth, which is associated with the presence of defects on the substrate surface. Subsequently, the deposition of matter in these areas becomes predominant and islands are formed.

- obtaining CaP coatings by the method of HFMS with a plasma discharge power of 200, 250 leads to the successful formation of CaP coatings similar in structure, elemental and phase composition to hydroxyapatite.

- sputtering of HA in the range of power 200-250 W leads to the deposition of CaP coatings with the ratio of Ca/P 1.67 ± 0.7, with an increase in power to 300-350 W this ratio increases to 1.9.

- adhesive properties of the titanium surface improve in the range of thickness of CaP coatings l = 0.45-1.6 μm. Films formed at a power of 200, 250,

300 W and having layer thicknesses from 0.45 to 1.6 microns have strong adhesion of up to 20-25 N during scratch test and a low coefficient of friction of 0.4.

- crystallization of CaP coatings on the surface of titanium begins to develop when heated to 700 °C.

The practical significance of the work - results of research play an important role in the development of deposition modes of CaP coatings during HFMS for the formation of biocoatings on the surface of endoprostheses from titanium alloys.

The results of the study presented in the work allow to develop scientific recommendations for the development of an effective, reliable technology for the production of CaP and HA coatings with high functional properties. The influence of the parameters of obtaining biocoatings on the structure, morphology and adhesive properties will allow to approach the use of a biocompatible coating that meets the medical and technical requirements.

Provisions for defense

The following provisions are submitted to the defense of the thesis:

- the influence of high-frequency magnetron sputtering regimes on the growth rate of calcium phosphate coatings on the surface of titanium substrates, on their structure, phase and chemical composition;

- the dependence of the adhesion properties and water wetting parameters on the thickness of the calcium phosphate coating and modes of formation by the method of high-frequency magnetron sputtering.

- the effect of heat treatment on the structure and phase composition of calcium phosphate coatings on titanium substrate.

- comparison of the morphology, phase and elemental composition of CaP coatings obtained by the methods of high-frequency magnetron sputtering and microarc oxidation.

The work was carried out in the Laboratory of Metalworking of the Institute of Metallurgy and Enrichment, at the Department of Mechanical Engineering of the Wroclaw Technological University (Wroclaw, Poland) and at the Department of Theoretical and Experimental Physics of the Tomsk Polytechnic University (Tomsk, Russian Federation).

Communication of work with government programs and scientific-research works

The thesis work was carried out in the Kazakh National Research Technical University named after K.I. Satpayev, the main provisions were developed in the framework of grant projects of applied research funded by MES of RK on the priority "Rational use of natural resources, processing of raw materials and products" on the topic: "Development of technology for manufacturing metal-ceramic products based on titanium with oxide and calcium phosphate coatings" (2015-2017 y.) and on the topic: "Improving the technology of obtaining endoprostheses by casting titanium alloys with subsequent applying biocomposites on their surface" (2018-2020 y.).

Personal contribution of the author

The author of the thesis substantiated the problem, took part in the formulation and solution of problems, obtained and analyzed all the experimental work results. Also, the author's personal contribution was in planning experiments, formulating conclusions and statements, writing articles on the topic of the dissertation.

Approbation of work

The main provisions of the thesis were reported and discussed at domestic and foreign international conferences: international conference “Resource-saving technologies in ore beneficiation and nonferrous metallurgy”, Almaty, 2015 y.; the international conference INDUSTRY 4.0, Bulgaria, Sofia, 2016 y.; IX International Symposium "Combustion and Plasmochemistry", Almaty, 2017 y.; International Scientific Conference "Modern Problems of Condensed Matter Physics, Nanotechnologies and Nanomaterials" (Sarsembinov Readings), Almaty, 2018 y.

Publications

According to the results of the dissertation, 11 scientific papers were published, 4 articles of which in editions recommended by ESMC MES RK for publication of the main results of research in technical sciences, 1 article in the journal included in the RSCI database, 2 articles in the journal included in the Web of Science and Scopus database, 4 publications in materials of international and republican conferences, and there is a conclusion on issuing a patent for a utility model.

The structure and scope of the dissertation

The structure of the dissertation includes the following elements: "Normative references", "Designations and abbreviations", "Introduction", a literature review on the problems of formation of CaP coatings, the experimental part of 4 sections, "Conclusion", "List of references" and "Appendices ".

In his thesis, investigated the influence of the conditions of sputtering and subsequent heat treatment on the structure, phase and chemical composition, adhesion and cohesive properties of the forming calcium phosphate layer. The possibility of obtaining CaP coatings that are close in structure, elemental and phase composition to hydroxyapatite by the method of high-frequency magnetron sputtering has been established.

The first section of paper presents an extensive analysis of current literature data on the problems of formation of calcium phosphate coatings on the titanium substrate and its alloys. During the analysis of the literature, it was established that that one of the most promising methods for the formation of calcium phosphate coatings is high-frequency magnetron sputtering. Further, the optimal range of modes for obtaining calcium phosphate coatings by the method of high-frequency magnetron sputtering, at which the coatings were formed, is selected.

The second section presents the materials and methods for the study of calcium phosphate coatings. The choice of the target (hydroxyapatite) and substrate material (titanium VT1-0) has been substantiated. The equipment and experimental modes for obtaining calcium phosphate coatings are given.

The third section describes the results of study of calcium phosphate coatings formed by the method of HFMS. The elemental, phase composition and adhesive properties of CaP coatings were investigated by the methods of scanning electron microscopy, atomic force microscopy, X-ray phase analysis, IR and Auger spectroscopy, sclerometry (scratch test), also effect of heat treatment on the morphology and phase composition of coatings was analyzed.

In the fourth section, the results of study of calcium phosphate coatings obtained by high-frequency magnetron sputtering and microarc oxidation methods are compared. The technique of deposition of calcium-phosphate coatings on titanium substrate VT1-0 by microarc oxidation was described. The selection of optimal modes for the production of coatings by the method of MAO of titanium in phosphate electrolytes is performed. The advantages of CaP coatings formed by the method of HFMS, based on the results of study of the elemental and phase composition and adhesive properties are shown.