ABSTRACT

of dissertation for the Philosophy Doctor (PhD) degree in specialty
6D072300 - "Technical Physics"

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FORMATION PATTERNS, STRUCTURAL FEATURES AND PROPERTIES OF BIOMEDICAL COATINGS BASED ON TITANIUM OXYNITRIDE FILMS FORMED BY REACTIVE MAGNETRON SPUTTERING

General description of work. The thesis is devoted to experimental and theoretical studies of biomedical titanium oxynitride coatings obtained by reactive magnetron sputtering. The paper presents the results of a study of the influence of the ratio of nitrogen and oxygen on the structural-phase state, physical-mechanical, tribological and antibacterial properties of biocompatible coatings. The research of this work used advanced, proven experimental methods carried out in scientific centers of Kazakhstan, Tomsk, Ukraine.

The relevance of the topic. In recent years, scientific developments have increased the possibility of using very thin coatings of titanium dioxide and oxynitride obtained by ion plasma technology in medicine and many other fields. Due to the high bio- and hemocompatibility of these coatings with human tissues, hardness, anti-corrosion properties and biological indifference, the binary and three-layer combination of these coatings, i.e. heterostructure, highly suitable for use in cardiovascular implants.

Titanium oxide is cheap and chemically stable; this coating increases the corrosion resistance of implants and reduces the coagulation of fibrinogens, and the titanium oxynitride coating provides an increase in endothelial cells and antithrombogenic properties. In addition, due to its high photocatalytic self-purifying activity, titanium oxide is used for photo-induced purification of water and air from harmful organic compounds. As for the research results, we note that only titanium dioxide coatings with an anatase structure have high photoactivity. To prepare such coatings, the sol-gel method is used, which is a chemical method.

It is known that any method has its advantages and disadvantages. Likewise, this method also has its disadvantages. When the coating is heated to a temperature of more than 600°C, it harms the environment due to the release of harmful substances into the air.

Therefore, there are restrictions on the shape and area of coverage. And the advantages of the reactive magnetron sputtering method used in this research are very high compared to other methods, such as it does not harm the environment and the sputtering speed is very high. In addition, the amount of negative voltage offset and the control level of the amount of working and reactive gases are very high.

The characteristics of a magnetron sputtering system depend on the structure and properties of the resulting coatings, application mode, composition of the working gas, power and electrical displacement values in the gun. Because these issues are unique

to each mode of operation of a magnetron sputtering system, this study focuses on how these factors affect the structure, phase, and chemical properties of the deposited coating. One of the important properties of the surface coating layer is the electrical charge that regulates the contact of the surface coating layer with the surrounding tissue.

Currently, there are many problems of increasing the wear resistance of coating materials. To increase wear resistance, it is necessary to increase the hardness of the material.

Oxynitride and titanium dioxide coatings are widely studied due to their high hardness, high anti-corrosion properties, high biological indifference and high compatibility with human tissues.

When the layer is given a negative bias potential along with the deposition of the coating, the ions released from the substrate and the positive ions of the working gas, i.e. excess energy of the ions begin to move towards the substrate. The number of atoms adsorbed on the surface of the substrate begins to increase, which leads to an increase in their energy and migration time.

As a result of this, the surface layer of the coating is loosened, the atoms of the surface layer and the particles added to it are mixed, and the transition zone near the coating-substrate thickens. By controlling the negative shear stress applied to the substrate, the growth of the coating layer can be controlled. In this regard, it is necessary to conduct research in order to control the influence of spraying mode parameters on the physical and mechanical properties, phase and elemental composition and structure of the coating.

The aim of work. Study of the morphology and structural features of coatings based on titanium oxynitride, obtained by reactive magnetron sputtering, and the study of the physical, mechanical and tribological composition of the coatings.

Research objectives:

- production of coatings based on titanium oxynitride using magnetron sputtering applied to the surface of stainless steel used in medicine;
- study of the electrical potential and electrophysical structure of the surface of titanium oxynitride coatings;
- study of the physicomechanical and adhesion structure, elemental and phase composition, structure, morphology of dense thin coatings of titanium oxynitride deposited on steel substrates;
- study of the relationship between the structural and phase characteristics of oxynitride coatings and application conditions;
- study of the molecular product of dissolution and coating dynamics in a liquid stimulating the biological fluid of the body;
- study of the tribological characteristics of oxynitride coatings obtained by magnetron sputtering.

The object of the research. Changes in coating properties depending on the oxygen and nitrogen content in biomedical coatings based on titanium oxynitride.

The subject of the research. Changes in surface microstructure and tribomechanical properties of coatings depending on the ratio of active gases. In

addition, measuring the nanohardness and elastic modulus of coatings deposited by reactive magnetron sputtering and determining changes in these characteristics.

Research methods. The dissertation work is devoted to the optimization of coating technology based on titanium oxynitride, obtained by magnetron sputtering, for the bioengineering of blood vessels. The dependence of the structure and design of the resulting films on the deposition mode, including the composition of the working gas, power and the magnitude of the electrical displacement in the substrate, has been studied. Based on fundamental and experimental results, recommendations are given for determining the optimal coating spraying regime in the range of controlled bioinertness/biocompatibility using the feedback principle. The process of tribocorrosion of coatings based on titanium oxynitride in salt solutions and a chloride environment has been studied. In practice, the results obtained can be used in cardiovascular surgery to create the wall of coronary vessels. This comprehensive method, proposed by young scientists, is innovative and based on original fundamental methods focused on applied aspects.

The following modern physicochemical methods were used in the dissertation: IR spectroscopy, scanning electron microscope, atomic force microscope, X-ray diffraction analysis, X-ray photoelectron spectroscopy.

The main provisions for the defense.

1. Large grains are formed in the microstructure of the substrate surface when applying TiO_2 coatings using reactive magnetron sputtering. The introduction of nitrogen leads to the formation of a fine-grained compacted structure. This is due to the fact that in the coating structure, nitrogen is localized on low-index planes, forming a two-dimensional layer of nitrogen oxide, which limits the epitaxial growth of TiO_2 nanocrystals.

2. The surface of oxynitride coatings with a $2N_2/O_2$ ratio obtained by reactive magnetron sputtering is uniform, smooth and the particle size is significantly smaller (28.3 nm) compared to coatings prepared in a ratio of 1 and 1.5, which means an increase in the volume fraction of rutile phase.

3. The hardness and elastic recovery of films increases with increasing nitrogen content during deposition, this prevents the formation of cracks on the coating surface. Coatings with a $2N_2/O_2$ ratio form a homogeneous layer without cell nuclei during 5 days of huMSC cell growth, which inhibits thrombus formation and restenosis in vascular stents.

Scientific novelty of the research:

- the influence of the amount of working and reactive gases and the negative value of shear stress on the elemental and structural properties of the titanium oxide coating was studied;
- the morphology of coatings based on titanium oxynitride obtained by reactive magnetron sputtering, related to the content of chemically active gases and the negative shear potential in the substrate, depending on the deposition mode, was studied;
- the structural and phase characteristics of coatings based on titanium oxynitride and the patterns between application conditions were determined;
- the influence of the structural-phase state of the coating on its physical and mechanical properties was studied.

Theoretical and practical significance of the work. There are many works describing the corrosion rate, mechanics (hardness, elastic modulus, roughness), microstructure and morphology of oxynitride coatings obtained by magnetron sputtering. Unfortunately, it can be said that there is no information describing friction and wear of the coating.

Therefore, one of the objectives of this project is to study the tribological characteristics of an oxynitride coating obtained by magnetron sputtering. The results obtained in the thesis can be used for tribological studies of cardiovascular devices in the field of medical materials science in a model human biological state.

In Kazakhstan, the formation of bio-coatings by magnetron sputtering has not become widespread, and the works of foreign scientists do not pay much attention to the processes at the coating-substrate interface, growth mechanisms and properties of multi-component coatings in biological use, the conditions of influence on the surface layer of the substrate are not taken into account, the molecular structure on the surface of magnetron coatings made of titanium oxynitride is not taken into account, and there is no information about the reaction mechanisms. There is practically no theoretical information about the processes occurring on the coating surface and in the magnetron discharge plasma that would allow predicting the chemical composition and properties of thin biocompatible coatings. The information obtained during the implementation of the project contributes to the development of technologies used in cardiovascular surgery (prosthetics of heart valves and blood vessels).

Author's personal contribution. The author's personal contribution lies in the search and analysis of literary publications on the topic of dissertation research, in particular, biocompatible coatings. Together with scientific supervisors, she determined the goals and objectives of the research, selected methods for applying and researching biocompatible coatings. The author of the dissertation was directly involved in the preparation of samples, studied the phase composition, surface morphology of these samples, measured microhardness and nanohardness in depth and surface, and also directly participated in the analysis of the results and the preparation of articles on the topic in collaboration with scientific consultants and laboratory specialists.

The reliability and validity of the results. Accuracy and clarity of problem setting, as well as the selection and use of experimental methods of well-tested research, comparison of the volume of data and statistics with the results obtained by famous scientists of the CIS and non-CIS countries.

Approbation of the research. Based on the results of the dissertation work, 12 works were published.

Articles with a high impact factor in publications included in the Thomson Reuters database or the international scientific database Scopus:

1. Buranych V.V., Pogrebnjak A.D., Pogorielov M., Diedkova K., **Aubakirova D.**, Savitskaya I., Kupchishin A.I., Kulenova N. Characterization, mechanical and biomedical properties of titanium oxynitride coating // Ceramics International, Vol. 49, Issue 17. – 2023. – P. 28167-28174 https://doi.org/10.1016/j.ceramint.2023.06.070

2. Pustovalova A., Boytsova E., **Aubakirova D.**, Bruns M., Tverdokhlebov S., Pichugin V. Formation and structural features of nitrogen-doped titanium dioxide thin

films grown by reactive magnetron sputtering // Applied Surface Science. – 2020. - Vol. 534. – P. 147572. https://doi.org/10.1016/j.apsusc.2020.147572

4 articles were published in journals recommended by the Science Committee of the Ministry of Science and Higher Education of the Republic of Kazakhstan and other publications, 1 monograph, 5 abstracts of reports were published at international conferences.

Relationship between the dissertation topic and plans for scientific work. The dissertation work was carried out within the framework of a scientific grant on the topic "Multicomponent and multilayer nanometer-scale coatings with variable architecture for protection against friction and wear" (2018-2020, state registration number AR05130362), funded by the Committee for Quality Assurance in the Field of Science and Higher Education of the Ministry science and higher education of the Republic of Kazakhstan.

The structure and scope of the dissertation. The dissertation consists of an introduction, three sections, a conclusion, a bibliography and contains four appendices. The work is presented on 100 pages of typewritten text, illustrated with 36 figures, 6 tables, the list of references contains 160 items.