ABSTRACT

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

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Effect of Au-ions implantation on the microstructure, mechanical and tribological properties of nanocomposite coatings (TiAlSiY)N/CrN

The dissertation is devoted to experimental and theoretical studies of nanocomposite coatings based on (TiAlSiY)N/CrN with a nanolayer architecture, obtained by vacuum arc deposition followed by implantation of Au^- ions with a dose of 1×10^{17} cm^{-2} with an energy of 60 keV. The paper presents the results of studies of the effect of ion implantation with Au^- ions on the structural-phase state, elemental composition, physical-mechanical, tribological, and antibacterial properties of coatings based on (TiAlSiY)N/CrN, as well as the results of theoretical calculations based on the molecular dynamics method.

Relevance. Multicomponent and multi-element nitride coatings are widely used to increase strength, abrasion and corrosion resistance, as well as to improve the tribotechnical characteristics of mechanisms operating under high contact loads. Recently, the triple nitride compound TiAlN has found wide application, which has thermal stability, high hardness and corrosion resistance. However, the requirements for this class of coatings are increasing. They must withstand high temperatures and loads, have a low coefficient of friction, and sufficient wear resistance. Thus, the relevance of creating new coatings with improved properties has increased significantly.

Recently, a multilayer composite architecture based on a modulated Ti1-xAlxSiN / MeN (Me-transition metal) combination has been able to demonstrate structural perfection with nanohardness up to 50 GPa, while effectively resisting plastic deformation and thermal stresses. In the process of relaxation, the coating on the substrate forms a dislocation structure, which determines the distribution and concentration of zonal stresses in accordance with the influence of the surface strain energy.

Along with this, the formation of multilayer interfaces in nanocomposite materials obtained by ion implantation makes it possible to modify the structure and also significantly change the mechanical, chemical, electrical, tribological, and other properties of solids. In addition, the use of accelerated ions helps to obtain the required concentration of the introduced alloying element and the nature of its distribution over depth at the surface region. Typically, such distributions of the alloying element cannot be realized in other ways.

Ion implantation is a versatile tool for modifying and alloying surface layers of solids. The undoubted advantages of the method are the small thickness of the alloyed layer, surface roughness, independence from adhesion and localization of the action (without residual stresses in the depth of the material), as well as good reproducibility of results. Implantation of heavy ions, such as Au-, makes it possible to obtain a high density of cascades and regions of formation of local defects as a result of interaction and penetration of ions, as well as subsequent radiation-accelerated diffusion. Consequently, irradiation with Au ions with a dose of 1 · 1017 cm-2 can lead to ionic "mixing" at the boundaries of the monolayer. On the other hand, nanocomposite coatings with a nano-sized layer structure provide good mechanical protection of substrates. Multi-element coatings formed from alternating nanolayers of two or three types of materials with different structures demonstrate increased hardness (30-50 GPa). They can form an epitaxial structure or even exhibit a superhardness effect, depending on their structure and modulation period.

Materials containing nanoparticles of gold, zinc or silver in their matrix are highly antibacterial and (at a certain concentration) biocompatible, making them ideal candidates as protective layers for prostheses and biological implants. Recent developments in antibacterial materials have experienced instant growth through the integration of advanced nanomaterials, accompanied by state-of-the-art biotechnological techniques.

At the same time, an analysis of the literature data shows that the study of the influence of interphase boundaries and lattice mismatch in multilayer systems based on CrN on the character of their decay has not yet been sufficiently studied. To clarify this issue, this thesis studied the interaction between phase stability under extreme conditions, such as intense ion implantation of heavy Au ions, which is important for understanding changes in physical and mechanical properties. In addition, to characterize the thermodynamics of mixing of deposited multilayer coatings, Ti1-xAlxN solid solutions and Ti1-xAlxN / CrN heterostructures were investigated in a comparative way within the molecular dynamics method.

The goal of the thesis is to study the effect of implantation of Au- ions on the phase-structural state and physical and mechanical properties of nanocomposite coatings with nanolayer architecture based on (TiAlSiY)N/CrN.

To achieve this goal, the following **tasks** were solved:

- Obtain nanocomposite coatings based on (TiAlSiY)N/CrN with nanolayer architecture by vacuum arc vapor deposition onto a steel substrate and implant them with Au^- ions.
- Conduct studies of the structure, phase and elemental composition of coatings based on (TiAlSiY)N/CrN with nanoscale layers using X-ray diffraction analysis, SIMS, RBS analyzes and HR-TEM with microanalysis. Estimate the transfer of Au-ions in a multilayer coating.
- To study the effect of ion implantation on the mechanical, tribological and antibacterial characteristics (TiAlSiY)N/CrN coatings.
- Carry out calculations based on the molecular dynamics of $Ti_{1-x}Al_xN$/CrN (111) heterostructures, simulating the structure of deposited coatings to assess the thermodynamics of their mixing.

The object of research is a nanocomposite coating with a nanolayer architecture based on (TiAlSiY)N/CrN, the process of implantation of Au ions with a dose of 1×10^{17} cm^{-2}, the properties of the nanocomposite coating before and after implantation, as well as the results of calculations by the molecular dynamics method.

The subject of research is the change in the microstructure of the surface layer and the tribomechanical properties of coatings based on (TiAlSiY)N/CrN before and after implantation with gold ions. Determination using molecular dynamics of the mixing energy for solid solutions $Ti_{1-x}Al_xN$ and heterostructure $Ti_{1-x}Al_xN/CrN$ (111), energies of formation of heterostructures and lattice parameters of $Ti_{1-x}Al_xN$ alloys depending on the composition. Determination of adhesion / cohesive strength of coatings and determination of the mechanism of destruction during friction and cutting, as well as measurement of nanohardness and elastic modulus of coatings deposited by the vacuum arc method, and the effect of ion implantation on the change in these characteristics.

Research methods.

When performing this dissertation work, the following experimental methods were used: phase composition, microstructure and lattice parameters were analyzed using X-ray diffraction analysis (XRD) and high-resolution transmission electron microscopy (HR-TEM) with diffraction at selected areas and microanalysis; the elemental composition was studied using energy dispersive spectroscopy (EDS), secondary ion mass spectrometry (SIMS) and Rutherford backscattering spectroscopy (RBS); chemical bonds in the coatings were studied using X-ray photoelectron spectroscopy (XPS); the study of the surface and the near-surface layer was carried out using atomic force microscopy (AFM); measurements of nanohardness and elastic modulus were carried out on a nanoindentor; computer modeling of multilayer coatings B1-Ti1-xAlxN / B1-CrN with a preferred orientation of crystallites (111) was carried out using calculations using the pseudopotential method.

Scientific novelty of the work:

The effect of ion implantation of Au- on the phase-structural state of nanocomposite coatings with nanosized layers of (TiAlSiY) N and CrN, obtained by the developed method of deposition of multilayer protective coatings, has been studied for the first time.

Experimental methods HRTEM and XRD show for the first time the phase composition of the obtained heterostructure. It was found that the influence of the interface with a high formation energy determines the coherent growth of $Ti_{1-x}Al_xN/CrN$ bilayers with a columnar structure (111) and nanograins about 10 nm in size. The results of nanoindentation indicate a high "protective" ability of the coatings, despite the rather high radiation dose.

It is shown that protective layers based on a nanocomposite coating (TiAlSiY)N/CrN with a nanolayer architecture have high tribological properties.

Key points for defense:

1. Regularities of the influence of Au^- ions on the structural-phase state of coatings based on nanoscale layers consisting of (TiAlSiY)N/CrN, obtained by the developed method of deposition of multilayer protective coatings using a vacuum arc discharge.

2. Changes in tribomechanical properties with an improvement in the protective ability of the coating and antibacterial properties with a decrease in the activity of bacteria in the coatings (TiAlSiY)N/CrN as a result of implantation of Au^- ions.

3. Results of calculations of the energies of thermodynamics of mixing of nanocomposite coatings (TiAlSiY)N/CrN based on the method of molecular dynamics of $Ti_{1-x}Al_xN/CrN$ (111) heterostructures, simulating the structure of deposited coatings.

Scientific and practical significance of the work.

The results obtained provide a deeper understanding of the processes occurring at the interfaces of nanoscale layers, as well as in the interaction of heavy Au– ions with the nanolayer architecture of coatings.

An act of introduction into the educational process and an act of introduction without economic effect of the results of dissertation work into production for use in promising projects of «Mashzavod» LLP were received.

Patent №5824 for a utility model "Multilayer protective coating" was received, RSE "National Institute of Intellectual Property" of the Ministry of Justice of the Republic of Kazakhstan, bulletin dated 05.02.2021.

The association of the thesis' topic with the research projects. The work was carried out in NJSC "VKTU im. D. Serikbayev ", NJSC" VKU im. S. Amanzholov "(Ust-Kamenogorsk, Kazakhstan) and Sumy State University (Sumy, Ukraine) in the framework of the following state budget projects of grant financing:

1. on the topic: "Multicomponent and multilayer nanoscale coatings with variable architecture for protection against friction and wear", state reg. No. AP05130362, financed by the Science Committee of the Ministry of Education and Science of the Republic of Kazakhstan under Contract №104 dated March 5, 2018;

2. on the topic "Research and development of innovative technologies for producing wear-resistant materials for mechanical engineering products", state reg. No. 0118RK00989, funded by the Science Committee of the Ministry of Education and Science of the Republic of Kazakhstan under Contract № 197 dated March 16, 2018.

Personal contribution of the author. The personal contribution of the author consists in the search and analysis of literary periodicals devoted to the topic of dissertation research, namely, multicomponent nitride coatings based on refractory metals and ion implantation. Together with scientific consultants, the goals and objectives of the study were determined, methods of deposition and research of nanocrystalline nitride coatings were selected. The author of the thesis was directly involved in the preparation of samples, carried out a study of the phase composition, surface morphology, measured the microhardness and nanohardness of the surface and the depth of the obtained multicomponent coatings, as well as in the discussion of the results and writing of publications.

The degree of validity and reliability of the results obtained in the work is ensured by: the originality and clarity of the formulation of tasks and the choice and use of well-tested experimental research methods, the volume and statistics of experimental data and their comparison with the previously obtained experimental results of well-known scientists from the CIS and far abroad.

The research results were publicly tested: published in scientific journals, reported and presented by the author at republican and international conferences.

Testing the results of the thesis research. The materials of the dissertation work were reported and discussed at international scientific conferences:

1. 7^{th} International Conference on Nanomaterials: Applications & Properties (NAP 2017) (Odessa, Ukraine, 2017);

2. The International scientific-technical conference in honor of the 60^{th} anniversary of the D. Serikbayev EKSTU, «The role of universities in creating an innovative economy» (Ust-Kamenogorsk, 2018);

3. International Scientific and Practical Conference "Uvaliev Readings-2018": "Trends in the development of modern science and education", S. Amanzholov EKSU, (Ust-Kamenogorsk, 2018);

4. VI International Scientific and Technical Conference of Students, Undergraduates and Young Scientists, D. Serikbayev EKSTU (Ust-Kamenogorsk, 2020);

5. International scientific and practical online Conference on "Energy - and resource-saving technologies: Experiences and prospects", Korkyt Ata KSU, (Kyzylorda, 2020);

6. Advanced materials manufacturing and research: new technologies and techniques (AMM&R2021) international conference to be hosted virtually by D.Serikbayev East Kazakhstan technical university, (Ust-Kamenogorsk, 2021).

In addition, the main results were reported and discussed at scientific seminars of the Department of Physics, joint scientific seminars of the Faculty of Basic Engineering Training of D. Serikbayev EKTU and at the meeting of the Department of "Nanoelectronics" of Sumy State University, Sumy, Ukraine (May 2018).

Publications. In total, 14 co-authored publications on the topic of the dissertation were published, 6 of which were published in scientific journals recommended by the Committee for Control in Education and Science of the Ministry of Education and Science of the Republic of Kazakhstan, as well as 2 articles published in foreign scientific journals included in the international information resources Web of Science Core Collection and Scopus, journals have quartiles - Q1 and Q2, 6 articles in collections of materials of international conferences, including 1 articles in materials of foreign conferences and 1 patent for a useful model.

The structure and scope of the thesis. The work consists of an introduction, four sections, a conclusion and a list of sources used. It is presented on 125 pages, contains 49 figures, 6 tables and a list of used sources of 202 titles.