ABSTRACT

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

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DIFFUSION AND MICROSEGREGATION PROCESSES IN NANOSTRUCTURED CrN/ZrN/Cr/Zr COATING IMPLANTED WITH SILICON IONS

The dissertation is devoted to experimental and theoretical studies of multilayer nanosized nitride coatings based on CrN/ZrN/Cr/Zr before and after implantation of silicon ions (60 keV) with a dose of 1×10^{17} cm^{-2}. The paper presents studies of the microstructure, structural-phase state, elemental composition, radiation-induced microsegregation, atomic diffusion, the results of theoretical calculations using the methods of molecular dynamics of atomic configuration processes. The influence of metal atoms on the process of segregation during implantation of Si ions, as well as on the process of formation of microstructure and redistribution of atoms and their effect on wear during friction, coefficient of friction, and microhardness is shown.

Relevanc. In modern devices, mechanisms and apparatus for operation in space, aviation and nuclear reactors, high radiation resistance of structural materials to flows of particles, plasma and radiation is required, along with high performance properties, such as wear resistance, coefficient of friction, hardness, corrosion resistance, and others. It is well known that surface modification is one of the most effective and cost-effective solutions for extending the life of tools and products. This can be easily achieved with hard coatings. Most approaches to increasing the hardness of coatings are based on the Hall-Petch effect of hardening materials by modifying the grain size. However, hard coatings are usually brittle and it is important to maintain adequate elasticity and toughness to resist damage. Multilayer design of coatings can help prevent crack propagation through the interlayer boundaries to the substrate, which has been experimentally confirmed by many published works. In addition to the usual alternation of nitride layers, a multilayer approach can be implemented through the Me/MeN architecture, where Me and MeN are metal and metal nitride layers, respectively. Periodic deposition of layers of hard nitride and soft metal phases and a significant difference in shear moduli make it possible to improve the functional properties of Me/MeN coatings. In particular, the work proved that the combination of hard but brittle metal nitrides and hard but relatively soft metal phases in a multilayer architecture improves the wear resistance of each constituent material in accordance with the Keller model and leads to high adhesion, strength and excellent wear resistance characteristics of experimental films.

At the same time, it is known that ion implantation is a good tool for surface modification, which, in comparison with other surface treatment methods, has a number of advantages, such as, for example, stability of properties in the base material, small dimensions of surface roughness, good adhesion and high reproducibility of results, and others. One of the successful approaches was the production of nitride-based film mixtures, which, in single-layer and multilayer form, provided a significant increase in the hardness and ductility of the coated surface. The

growing need for low-friction, wear-resistant coatings requires a specific structural process based on the lubricating properties of loosely bound nanoparticles and phases. In combination with the above concept, a significant increase in the service life and productivity of parts can be achieved. However, the addition of an amorphous phase drastically reduces the material's ability to withstand plastic deformation. Therefore, there is currently a need for new methods of creating a nanocomposite architecture and self-lubricating structure while maintaining mechanical stability. One such method is ion implantation, in particular Si implantation, which has become popular in integrated circuit processing to create p junctions near the surface. Threshold voltage control and good implantation depth accuracy serve as an advantageous adaptation to the required impurity distribution and concentration. Recently, ion implantation was introduced into the design of heterostructures, which made it possible to create new phases and structures in nanometer layers. The literature on metal-based nitrides indicates their superior mechanical and tribological properties and expands the range of applications for these coatings. So, chromium nitride coatings are actively used to reduce the coefficient of friction of some types of cutting tools. At the same time, zirconium nitride coatings have high hardness, thermal stability, at least up to 600° C in air. The combination of these properties in a multilayer nanocomposite coating provides those necessary characteristics that are superior to the separately taken listed coatings.

The goal of the thesis is investigation of the processes of radiation-accelerated diffusion and microsegregation in a multilayer nanocomposite coating CrN/ZrN/Cr/Zr and their relationship with the microstructure, elemental composition and physical and mechanical properties.

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

– To develop a method for obtaining multilayer nitride coatings CrN/ZrN/Cr/Zr based on vacuum-arc, ion-plasma deposition.

– To investigate the elemental and phase composition of coatings, substructure and interfaces in a multilayer nanostructured coating before and after irradiation with Si ions with an energy of 60 keV, a dose of 1×10^{17} cm^{-2}.

– Evaluate the effect of Si ion implantation on the processes of "ionic mixing of interfaces", redistribution of elements, formation of profiles and compare the obtained experimental results with SRIM calculations of both displaced atoms and vacancies.

– Using the molecular dynamics method, make calculations to assess the influence of the microstructure and internal stresses at the interfaces (interfaces) on the process of microsegregation and diffusion of silicon as a result of implantation and mechanical characteristics.

– To study the mechanical characteristics, wear resistance, coefficient of friction, hardness of nanostructured multilayer coatings before and after implantation.

Object of research – formation of microstructure, composition and properties of coatings based on CrN/ZrN/Cr/Zr as a result of implantation of Si ions (60 keV).

Subject of research – phase composition, elemental composition, microsegregation, diffusion, stoichiometry, thermodynamic and mechanical

properties of CrN / ZrN / Cr / Zr coatings before and after implantation of Si ions with a dose of 1 × 1017 cm-2, with an energy of 60 keV.

Research methods.

According to the tasks set, the following methods of analysis were used: scanning electron microscopy (SEM); energy dispersive X-ray microanalysis (EDS); Rutherford backscattering of ions (RBS); X-ray structural analysis (XRD); transmission electron microscopy with electron diffraction (TEM); scanning and transmission electron microscopy (STEM); high-resolution transmission electron microscopy (HRTEM); secondary ion mass spectrometry (SIMS); molecular dynamics methods; measurements of nanohardness, microhardness, and wear and friction tests; computer modeling of multilayer coatings SRIM-2008.

Scientific novelty of the work:

For the first time, a method for producing multilayer nitride coatings CrN/ZrN/Cr/Zr based on vacuum-arc, ion-plasma deposition has been developed.

For the first time, the features of the distribution of Si ions in a multilayer nanostructured coating during ion implantation with a maximum concentration of 10 at.% And a minimum of 6 at.% At a depth of travel of ions of ≈ 150 nm were discovered.

As a result of the processes of atomic collisions during the implantation of Si ions in a multilayer coating, the thickness of the ZrN layer increases (blurring) from (25–26) nm to 36 nm and competing processes of diffusion and microsegregation at the interfaces in the first three layers of the CrN/ZrN/CrN coating form a two-humped silicon distribution.

It is shown that as a result of the implantation of Si ions into the first three layers of a multilayer coating and the formation of small siliconitrides in them closer to the interfaces, the friction coefficient decreases from 0.40 to 0.18.

Key points for defense:

1 Results of studying the microstructure and elemental composition of multilayer nanostructured coatings with nanoscale layer thicknesses based on CrN/ZrN/Cr/Zr compositions obtained on the basis of the developed method.

2 Regularities of the formation of Si-enriched interfaces with a two-hump shape of the depth distribution of the first 3 layers of CrN/ZrN/CrN multilayer nanostructured coatings, where a maximum concentration of Si (10 at.%) is observed near the interface, and only 6 at.% is observed in the middle of the CrN layer.

3 As a result of the implantation of Si ions with an energy of 60 keV, a dose of 1×10^{17} cm^{-2}, the friction coefficient decreases from 0.4 to 0.18 due to the formation of CrSi and SiNx and the use of these particles as a "lubricant" in the process of friction.

Scientific and practical significance.

The dissertation is devoted to fundamental problems of technical physics and materials science, namely, studies of the problem of interaction of ions with a multilayer structure, microsegregation of silicon at the interfaces near chromium nitride layers, as well as the competition between two processes of segregation and diffusion of silicon atoms, changes in the microstructure and, accordingly, changes in the mechanical characteristics of multilayer nanostructural coatings.

Patent №34722 for the invention "Method of vacuum-arc ion-plasma deposition of a hard coating" was received, RSE "National Institute of Intellectual Property" of the Ministry of Defense of the Republic of Kazakhstan, bulletin dated 20.11.2020. 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.

The association of the thesis' topic with the research projects.

The dissertation work was carried out at NJSC "VKTU im. D. Serikbayev", NJSC "VKU im. S. Amanzholov" (Ust-Kamenogorsk, Kazakhstan) and Sumy State University (Sumy, Ukraine) within the framework of the following state budget projects of grant financing:

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

2. on the topic: "Multicomponent and multilayer nanoscale coatings with variable architecture to protect 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 No. 104 dated March 5, 2018.

Personal contribution of the author.

The author analyzed the literature data on the research topic, conducted the bulk of the experiments, carried out the processing and analysis of the experimental data obtained, participated in writing publications, discussing the results at conferences and exhibitions. Together with scientific consultants, the goals and objectives of the study were determined. Assistance was provided in carrying out and interpreting studies based on the results of X-ray microanalysis with energy dispersion, scanning and transmission electron microscopy, and in carrying out work on measuring the nano and microhardness of coatings.

The degree of validity and reliability of the results obtained in the work is provided by: using modern methods of analysis SEM, HRTEM, STEM, RBS and ion irradiation, SIMS, TEM, XRD, EDS and unique equipment of a high-current implanter with negatively charged ions, conducting research in leading scientific centers in Kazakhstan and Ukraine, as well as confirming some fragments by literature data, obtained in foreign laboratories. In addition, we used calculations using the molecular dynamics method and their application to interpret the results. 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:

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

2. 8th International Conference on Nanomaterials: Applications and Properties (NAP-2018), Zatoka, Ukraine, 2018;

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

4. VI International scientific and technical conference of students, undergraduates and young scientists, VKTU named after D. Serikbayev, Ust-Kamenogorsk, 2020;

5. International Scientific and Practical Online Conference "Energy and Resource Saving Technologies: Experiences and Prospects", KSU named after Korkyt Ata, 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, 2021.

The main results were also reported and discussed at scientific seminars of the Department of Physics, joint scientific seminars of the Faculty of Basic Engineering Training VKTU im. D. Serikbayev and at a meeting of the department "Nanoelectronics" of Sumy State University, Sumy, Ukraine (May, 2018).

Publications. Just on the topic of the dissertation published 14 publications in collaboration, 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, and 2 articles were published in foreign scientific journals included in the international information resources Web of Science Core Collection and Scopus, journals have quartiles - Q2 and Q1, impact factors - 4.65 and 8.758, 6 articles in collections of materials of international conferences, including 2 articles in materials of foreign conferences and 1 patent for an invention.

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 129 pages, contains 48 figures, 8 tables and a list of used sources of 165 titles.