ABSTRACT

of the dissertation submitted for the degree of Doctor of Philosophy (PhD) in the specialty **8D05301 – Technical Physics** on the topic **"Study of the microstructure and tribo-mechanical properties of multicomponent nitride coatings"** conducted by

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The dissertation research represents a comprehensive experimental work in the fields of condensed matter physics, surface physics, and plasma physics. The work was conducted within the specialty "8D05301 –Technical Physics" and is dedicated to establishing the physical principles and mechanisms governing the formation of the structure and functional properties of promising classes of nanomaterials – multicomponent, multilayer, and gradient nitride coatings, synthesized by ion-plasma deposition methods (cathodic-arc evaporation, reactive magnetron sputtering). The central focus is the investigation of the interrelationships between "physical vapor deposition parameters – growth kinetics – structure – properties."

Relevance of the Dissertation Topic

The relevance of the work is determined by fundamental challenges in surface physics related to controlling the structure and properties of solids at the nanoscale during their synthesis under non-equilibrium conditions. There is a significant lack of knowledge regarding the physical mechanisms governing phase formation, stress relaxation, interface formation, and texture development in complex multicomponent systems (WN/MeN, TiAl(Si)N) under the influence of intense ion fluxes with varying energy. Addressing these challenges is essential for creating the scientific foundation for novel plasma technologies aimed at the targeted synthesis of materials with extreme performance characteristics for operation under extreme conditions. This aligns with the development priorities of physical and technical sciences and the objectives of import substitution.

Research Objective

To identify and investigate the fundamental physical relationships between the parameters of physical vapor deposition (ion energy, reactive gas pressure, deposition geometry, substrate bias voltage) and the growth kinetics, structural-phase transformations, formation of internal stresses, and the complex of functional (mechanical, tribological) properties in multilayer WN/MeN (Me = Zr, Cr, Mo, Nb) systems and gradient TiAl(Si)N coatings.

Research Tasks

The following objectives were set within the scope of this work:

1. To synthesize multilayer WN/MeN (Me = Zr, Cr, Mo, Nb) coatings using the cathodic arc physical vapor deposition (CA-PVD) method, as well as gradient TiAl(Si)N coatings using magnetron sputtering;
2. To investigate the phase composition, structure, mechanical, and tribological properties of the deposited multilayer WN/MeN and gradient TiAl(Si)N coatings;
3. To analyze the microstructure of the films using transmission and scanning electron microscopy;
4. To establish the relationship between microstructure and tribomechanical properties of various multilayer systems;
5. To study the effect of negative substrate bias voltage on the properties of WN/NbN coatings deposited at room temperature;
6. To examine the influence of coating thickness on the microstructure and tribomechanical properties of the gradient TiAl(Si)N system.

Object of Research

Multilayer nanostructured WN/MeN (Me = Zr, Cr, Mo, Nb) coatings synthesized by cathodic-arc evaporation (CA-PVD), and gradient TiAl(Si)N coatings obtained by reactive magnetron sputtering.

Subject of Research

Physical phenomena and processes occurring during the synthesis and modification of coatings: growth kinetics under non-equilibrium plasma conditions, phase formation and polymorphic transformations, the formation, relaxation, and influence of internal stresses, and deformation behavior during nanoindentation and sliding friction.

Research Methods

Coatings were deposited using an advanced CA-PVD Bulat-6 system equipped with pure metal targets. Phase analysis was performed using grazing incidence X-ray diffraction (GIXRD). Morphology and elemental composition were studied using scanning electron microscopy (SEM) with wavelength-dispersive spectroscopy (WDS) and energy-dispersive spectroscopy (EDS) attachments. Additional characterization included Auger electron spectroscopy (AES), Raman spectroscopy, and confocal laser scanning microscopy (CLSM) of the coating surfaces. Thin cross-sectional lamellae of the coatings were prepared using a focused ion beam (FIB) and examined with a transmission electron microscope (TEM). First-principles calculations were performed using the Quantum ESPRESSO software package. Mechanical properties such as nanohardness and elastic modulus were evaluated using nanoindentation testing, while adhesion strength was assessed using a Rockwell indenter adapted for scratch testing. Wear rate and friction coefficient were analyzed using a ball-on-disk tribometer.

Main Findings and Results Presented for Defense

1. Multilayer WN/MeN (Me = Cr, Zr, Mo, Nb) coatings were synthesized using the CA-PVD method. It was established that the WN/NbN system demonstrates the lowest wear rate (1.7×10^{-6}) compared to WN/ZrN, WN/CrN, and WN/MoN systems, exceeding them by approximately 200, 6.5, and 5 times, respectively;

2. It was found that increasing the bias voltage to −200 V results in grain growth in β-W_2N, ε-NbN, and δ-NbN phases and reduces residual stresses in WN/NbN coatings;

3. It was determined that increasing the thickness of the gradient TiAl(Si)N coating to 600 nm affects its microstructure and increases hardness up to 38 GPa.

Main Research Findings

1. Establishment of the Superiority of the WN/NbN Multilayer System and Identification of the Physical Reasons for its Record Wear Resistance

A comparative study of four multilayer systems - WN/ZrN, WN/CrN, WN/MoN, and WN/NbN - synthesized under identical conditions by CA-PVD, was conducted.

It was experimentally proven that the WN/NbN system possesses the best combination of properties: high hardness (35.7 GPa) is coupled with a low elastic modulus (383.9 GPa) and a maximum plasticity index of H/E = 0.093.

It was found that the WN/NbN system has a record-low specific wear rate of 1.7×10^{-6} $mm^3/N \cdot m$, which is an order of magnitude lower than the other studied systems (e.g., 3.8×10^{-4} $mm^3/N \cdot m$ for WN/ZrN).

Using XRD and TEM methods, it was determined that the high wear resistance of WN/NbN is due to the nanocomposite structure of the NbN layer, consisting of two nanocrystalline phases - hexagonal (ε-NbN) and cubic (δ-NbN). The hexagonal phase provides increased hardness, while the cubic phase provides plasticity; their combination creates a synergistic effect.

A Systematic Study of the Influence of Thickness on the Structure and Properties of TiAl(Si)N Gradient Coatings was Conducted for the First Time, Revealing Non-Monotonic Dependencies.

2. Three samples of TiAl(Si)N gradient coatings with thicknesses of ~400 nm, ~600 nm, and ~800 nm were synthesized.

Using SEM and XRD methods, a clear evolution of the microstructure was established: from fine-grained with the formation of microcracks (400 nm) to a large columnar structure with pyramidal grains (800 nm) as the thickness increases.

Nanoindentation revealed that maximum hardness (~38 GPa) and elastic modulus (~550 GPa) are achieved at an intermediate thickness of 600 nm (Sample 2-600). This is explained by an optimal balance between solid solution strengthening and the formation of a nanocomposite structure.

3. The Influence of Substrate Bias Voltage (U_s) on the Structural Evolution and Tribological Mechanisms of WN/NbN Multilayer Coatings was Established and Studied in Detail.

It was shown that an increase in the substrate bias potential from -50 V to -200 V leads to significant structural changes: a decrease in the bilayer period (Λ) from ~15 nm to ~10 nm, enhanced interlayer mixing, and the formation of a gradient texture.

Using GIXRD, the evolution of the crystallographic texture from a mixed (200)+(111) to a sharply defined (111) orientation with increasing coating thickness was recorded for the first time, being especially pronounced at high substrate bias potentials. This is explained by the minimization of the total system energy (surface and deformation) during the growth process.

It was discovered that as the substrate bias potential increases, the proportion of the brittle hexagonal ε-NbN phase in the surface layer decreases, which has a positive effect on the properties.

Scientific Novelty of the Obtained Results

1. For the first time, the physical mechanism of synergistic strengthening and enhanced wear resistance in the WN/NbN multilayer system, based on the formation of a nanocomposite structure in the NbN layer and an anomalously high plasticity index, has been identified and described.
2. For the first time, the physical relationship governing the influence of coating thickness on the optimal balance between hardness and elastic properties in TiAl(Si)N gradient coatings, determined by growth kinetics, has been established.
3. For the first time, the evolution of the crystallographic texture in WN/NbN multilayer coatings depending on the bias voltage and thickness, which has a determining influence on their wear mechanisms, has been discovered and studied in detail.
4. For the first time, WN/MoN multilayer coatings have been synthesized and characterized using the vacuum cathodic-arc deposition method, expanding the class of promising materials for tribological applications.

Practical Significance

The results of the work are of practical importance for the development of the physical and technical foundations of ion-plasma technologies. The obtained data allow for the targeted control of synthesis processes to create coatings with predetermined properties.

The significance of the research results lies in the possibility of their use for the development of new protective coatings with improved characteristics for application in various technical fields, such as:

Production of tools and mechanisms with increased requirements for wear resistance and heat resistance, such as cutting and abrasive tools, especially under high temperatures and aggressive environments.

Creation of protective coatings for components in the aviation and automotive industries, where a high degree of protection against abrasive wear, corrosion, and high temperatures is required.

Application in the energy industry for protection against abrasive and corrosive wear of equipment components operating under high temperatures and aggressive environments, for example, in nuclear reactors.

Use in the medical industry for creating tools and devices with increased wear resistance, such as surgical instruments and implants.

Reliability and Validity of the Obtained Results

The reliability of the results is ensured by:

The application of a complex of complementary physical research methods (XRD, SEM, TEM, nanoindentation, tribological testing).

The reproducibility of results across sample series and their statistical processing.

The consistency of data obtained from independent experiments and by different methods (e.g., XRD and TEM).

Connection of the Research Topic with National Research Programs

The experimental results of this dissertation were obtained with financial support from the Committee of Science of the Ministry of Science and Higher Education of the Republic of Kazakhstan, under Contract No. 128ZhG 5 dated June 20, 2024, for the project *"New Superhard, Corrosion- and Wear-Resistant Multilayer TiAlN/Si Coatings"* (No. AP22684071). Additional support was provided by the targeted funding program *"Development and Implementation of Competitive, Scientifically Grounded Technologies to Ensure the Sustainable Development of the Mining and Metallurgical Industry of the East Kazakhstan Region"* (No. BR24992854).

The reliability and validity of the results obtained in this work are ensured by the correctness and systematic approach of the theoretical and experimental studies, which included detailed investigations of the chemical and phase composition, the application of effective analytical methods, and strict adherence to international standards. The main results of the dissertation have been published in journals recommended by the Committee for Quality Assurance in the Field of Science and Higher Education of the Ministry of Science and Higher Education of the Republic of Kazakhstan for disseminating scientific findings, as well as in a peer-reviewed international journal indexed in Scopus and Web of Science databases.

Personal Contribution of the Doctoral Candidate to Each Publication

Kassymbaev A., Myakinin A., Uazyrkhanova G. et al. Influence of Thickness on the Structure and Properties of TiAl(Si)N Gradient Coatings // Coatings. 2025.

Contribution: Direct participation in conducting the coating synthesis experiment, performing measurements of mechanical and tribological properties, analysis and interpretation of data, contribution to the preparation of the text and visualization of the results.

Smyrnova K., Sahul M., Harsáni M. et al. Microstructure, Mechanical and Tribological Properties of Advanced Layered WN/MeN (Me = Zr, Cr, Mo, Nb) Nanocomposite Coatings // Nanomaterials. 2022.

Contribution: Participation in planning the experiments, conducting tribological tests and data analysis, as well as obtaining grazing-incidence X-ray diffraction (GIXRD) spectra and interpreting the results from the perspective of friction and wear physics, contribution to writing and editing the article text.

Smyrnova K., Sahul M., Harsáni M. et al. Composite Materials with Nanoscale Multilayer Architecture Based on Cathodic-Arc Evaporated WN/NbN Coatings // ACS Omega. 2024.

Contribution: Participation in obtaining GIXRD spectra, discussion and analysis of the results, contribution to the interpretation of data on the influence of bias voltage on coating properties, preparation of graphical materials, and text editing.

Kasymbayev A., Plotnikov S., Turlybekuly A., Pogrebnyak A. Investigation of the Structural Properties of Multicomponent, Multilayer, Hard Nanocomposite Coatings // Bulletin of Shakarim University. Technical Sciences. 2024. No. 1(13).

Contribution: Conducting experimental work on the synthesis and ion implantation of coatings, participation in the analysis of XRD data and mechanical tests, discussion of the results, preparation of the manuscript text.

Kasymbaev A., Smirnova K., Pogrebnyak A. Physical Principles of Obtaining WN/ZrN Composite Coatings by Vacuum Arc Deposition // Bulletin of Shakarim University. Technical Sciences. 2024. No. 2(14).

Contribution: Participation in planning the experiments, conducting tribological tests and data analysis, interpretation of the results, writing and editing the article text.

Publications

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Layered WN/MeN (Me = Zr, Cr, Mo, Nb) Nanocomposite Coatings // Nanomaterials. – 2022. – Vol. 12, Iss. 3. – P. 395. Q2 (Physics, applied), IF: 4.4. DOI: 10.3390/nano12030395

2. Smyrnova K., Sahul M., Harsáni M., Beresnev V., Truchly M., Čaplovic L., Čaplovicǒ M., Kusy M., Kozak A., Flock D., Kassymbaev A., Pogrebnjak A. Composite Materials with Nanoscale Multilayer Architecture Based on Cathodic-Arc Evaporated WN/NbN Coatings // ACS Omega. – 2024. – Vol. 9. – P. 17247-17265. Q2 (Multidisciplinary Chemistry), IF: 3.7. DOI: 10.1021/acsomega.3c10242

3. Kassymbaev A., Myakinin A., Uazyrkhanova G., Belisarova F., Sagidugumar A., Kimossov R. Influence of Thickness on the Structure and Properties of TiAl(Si)N Gradient Coatings // Coatings. – 2025. – Vol. 15, Iss. 6. – P. 710. Q2 (Materials Science, Coatings & Films), IF: 2.8. DOI: 10.3390/coatings15060710

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