ABSTRACT

of the dissertation work on the topic:

"Studying the formation of structure and properties of wear-resistant coatings based on titanium carbonitride through their alloying with various elements", submitted for the degree of Doctor of Philosophy (PhD)

in the specialty 6D071000 - "Materials Science and Technology of New Materials"

BAKHYTULY NAURYZBEK

The purpose of this work is to study the influence of the regimes of reactive magnetron sputtering of Ti/(Cr; Zr; Al; Ta) composite targets on the formation of properties of titanium carbonitride coatings on AISI 304 steel and VT1-0 titanium substrates.

The main research objectives are:

– determination of optimal deposition conditions for coatings based on titanium carbonitride;

– study of the morphology, structure and composition of deposited coatings obtained by reactive magnetron sputtering;

– determination of the effect of alloying elements such as Cr, Zr, Al, Ta on the mechanical properties of titanium carbonitride coatings;

– assessment of the effect of alloying elements such as Cr, Zr, Al, Ta on the tribological properties of titanium carbonitride coatings;

– deposition of optimized coatings on the contact areas of the thrust bearing and carrying out full-scale tests.

The object of research is wear-resistant coatings based on titanium carbonitride alloyed with various elements.

Research methods. In the dissertation work, all obtained coverages were characterized by a combination of a number of advanced research and analysis methods:

– measurement of the coating thickness and surface images after tribological tests were carried out with Leica DM IRM metallographic optical microscopes (LEICA, Wetzlar, Germany);

– study of morphology and determination of elemental composition was performed using a JEOL JXA-8230 scanning electron microprobe analyzer (JEOL, Tokyo, Japan);

– analysis of the topography and surface roughness of the coating before and after tribo testing was carried out on a JSPM 5200 probe microscope (JEOL, Tokyo, Japan);

– measurement of the cross-sectional area of the wear track of coatings after tribological testing was carried out with a profilometer brand 130 (Proton, Zelenograd, Russian Federation);

– the phase composition of the deposited coatings was studied using diffraction patterns obtained using a BRUKER D8 ADVANCE X-ray diffractometer (BRUKER, Karlsruhe, Germany);

– wear testing of coatings according to the “ball-on-disk” scheme was performed using a tribometer TRB3 CSM Instruments (CSM Instruments, Pese, Switzerland);

– the results of coating hardness measurements were obtained on a Nanoscan-4D nanohardness tester (Nanoscan, Moscow, Russian Federation).

Main provisions (proven scientific hypotheses and other conclusions that are new knowledge) submitted for defense:

– The results of experimental determination of the optimal condition for the deposition of carbonitride coatings at flows of Ar 1.1, C_2H_2 0.28, N_2 0.1 l/h, by the method of reactive magnetron sputtering of Ti/(Cr; Zr; Al; Ta) composite metal targets;

– Data on the effect of alloying elements Cr, Zr, Al, Ta on the morphology and topography of the surface, structure, elemental and phase composition, nanohardness and friction coefficient, wear rate of coatings based on titanium carbonitride;

– Dependence of mechanical and tribological properties of wear-resistant coatings based on TiCN on alloying by means of magnetron sputtering of composite metal targets Ti/(Cr; Zr; Al; Ta).

Relevance of the topic. Parts, components, machine mechanisms, and cutting tools must provide a level of mechanical strength and chemical stability that ensures both durability and performance. To solve these problems, a wide range of hard coatings are used. In recent decades, a solid solution has been developed between TiC and TiN, namely TiCN. The TiCN coating exhibits excellent mechanical strength and thermal stability. Therefore, the development of efficient methods for the deposition of coatings from TiCN is of great technological importance.

Among the deposition methods, one of the most suitable for the production of superhard and wear-resistant coatings is DC magnetron sputtering, used in both reactive and non-reactive environments under high vacuum conditions. The possibility of varying such parameters and conditions of deposition as potential shift on the substrate, the flow rate of reaction and inert gases, plasma current, pulsed deposition mode, the use of a composite target, and others open up new possibilities for deposition of TiCN coatings with improved mechanical and tribological characteristics. Determining the relationship between the deposition conditions and the microscopic structure and properties of the deposited films is the key to determining the best process conditions for obtaining coatings with desired properties. Based on the above, the topic of this dissertation is relevant.

Rationale for the need for research work. Extending the service life of machine parts or tools in industry, mechanical engineering and other industries is an important task. The solution of this problem involves the improvement of the technology for obtaining wear-resistant hard coatings. Through the development of the composition, structure and properties of such coatings, it is possible to achieve high rates of increasing the service life and functionality of machine parts or tools. Based on this, the rationale for the need for research work is associated with solving the problem of increasing the wear resistance of machine parts or tools, increasing their surface hardness.

Description of the main results of the study. The optimal conditions for the deposition of titanium carbonitride coatings by titanium reactive magnetron sputtering are determined by testing the deposition parameters (vacuum pressure in the working chamber, reaction gas flow, coating deposition rate, potential shift on the substrate, etc.), which affect the physical and mechanical properties of the coatings. Based on the results of tribological and mechanical tests, it was determined that the imposition of a substrate potential bias of -70 V and an increase in the acetylene flow rate to 0.28 l/h during the deposition process leads to a decrease in the wear rate, friction coefficient and an increase in the nanohardness of TiCN coatings. From the results of the study of the composition and structures, wear parameters, the most optimal mode called TiCN-2 was established. Based on this mode, further alloying of Cr coatings is proposed; Zr; Al; Ta.

The features of the influence of alloying elements, such as Cr; Zr; Al; Ta on the surface morphology and topography, structure, elemental and phase composition of deposited coatings based on titanium carbonitride on AISI 304 steel and VT1-0 titanium substrates. TiCN, TiCrCN, TiZrCN, TiAlCN, and TiTaCN coatings with thicknesses of 1.302, 1.55, 1.74, 1.40, and 2.23 μm with a fcc crystal structure have been obtained. According to the results of morphological and topographic studies of the surface, alloying the TiCN coating does not give significant changes. Due to the difference in the sputtering coefficients of alloying metals, their concentration in the deposited coatings varies from 5.5 to 17.5 at. % under the same spraying conditions. Doping leads to a change in the concentration of carbon and nitrogen in the elemental composition of the coatings, which led to the fluctuation of the ratio (C+N)/(sum of metals) from 0.94 to 2.33. Magnetron sputtering of Ti/(Cr; Zr; Al; Ta) composite targets forms a coating of two or more phases with a preferred orientation mainly in the (111) and (200) directions, except for the TiTaCN coating, where (111) and (200).

The effect of alloying elements such as Cr, Zr, Al, Ta on the structure, mechanical and tribological properties of titanium carbonitride coatings has been established. Introduction of Cr elements; Zr; Al; Ta into the crystal structure of TiCN coatings contributes to an increase in the nanohardness of coatings from 18.7 to 26 GPa. In terms of the ratio of nanohardness to Young's modulus H/E, the highest value among the deposited coatings are TiCN and TiZrCN coatings, which have H/E>0.1, indicating good fracture resistance. Tribological tests have shown that coatings with a high carbon content and amorphous phase show low coefficients of friction and wear rates. It was found that coatings with high ratios (C+N)/(sum of metals) can have high wear resistance under friction conditions. An assessment of the influence of alloying elements on the coefficient of friction of the coatings showed a slight increase to 0.2, except for Ta, which exceeded the substrate mark of 0.33. Alloying TiCN coatings with Cr and Zr in the established optimal mode of magnetron sputtering leads to a decrease in the wear rate to 10-7 mm3/m × N due to an increase in nanohardness and a decrease in the friction coefficient.

The effectiveness of the application of optimized coatings on the contact surface of the thrust bearing during full-scale tests in the developed stand was evaluated. The results of a field test with a load of 100 kg at a speed of 750 rpm of

thrust bearings with TiCN, TiCrCN, TiZrCN, TiAlCN and TiTaCN coatings deposited on the raceway showed correlated wear results, where according to the results of optical microscopy, the bearing with TiZrCN coating had the best wear resistance. This allows us to recommend this coating on the friction surfaces of machine parts and mechanisms to increase their functional characteristics, which helps to increase the service life of parts.

Substantiation of the novelty and importance of the results obtained

A technology has been developed for the deposition of wear-resistant TiCN coatings with improved mechanical and tribological characteristics by reactive magnetron sputtering of titanium in an argon-acetylene-nitrogen gas mixture.

For the first time in the deposition of hard coatings based on TiCN by the method of reactive magnetron sputtering, composite targets with deposited alloying metal Cr were used; Zr; Al and Ta to increase the hardness and wear resistance of the coating.

The influence of alloying elements Cr has been determined; Zr; Al and Ta on the structure, composition and mechanical, tribological properties of TiCN coatings. The TiCrCN and TiZrCN coatings obtained under the established conditions are characterized by an order of magnitude increased wear resistance up to 10^{-7} $mm^3/m*N$ compared to similar coatings obtained earlier.

For the first time, the structure and properties of TiCrCN and TiTaCN coatings deposited by magnetron sputtering have been obtained and studied.

Compliance with the directions of development of science or government programs.

The dissertation work was carried out in the laboratory "Metallurgy" of JSC "IMOB". The main provisions were developed within the framework of grant projects of applied research on the topic: “Development of wear-resistant, multifunctional, composite coatings based on titanium carbonitride” (No. AP08857049, 2020-2022), funded by the Ministry of Education and Science of the Republic of Kazakhstan under the priority “Rational use of natural resources, including water resources, geology, processing, new materials and technology, safe products and structures”.

Author's personal contribution

The author of the dissertation substantiated the problem, took part in setting up and conducting experiments, obtained and analyzed all the experimental results, formulated a conclusion, and wrote articles and reports.

Approbation of work

The main provisions of the dissertation work were reported and discussed at the domestic international conference entitled "Innovative development of the industry of Kazakhstan: problems and solutions" Materials of the international scientific and practical conference dedicated to the 85th anniversary of the birth of Nariman Kalybekuly Davilbekov, academician of the International Academy of Sciences of Higher School, Doctor of Technical sciences, professors, Almaty, - 2022

Publications

1. Mamaeva A.A., Kenzhegulov A.K., Panichkin A.V., Kshibekova B.B., Bakhytuly N. Deposition of carbonitride titanium coatings by magnetron sputtering

and its effect on tribo-mechanical properties //Kompleksnoe Ispol’zovanie Mineral’nogo Syr’a = Complex Use of Mineral Resources. – 2022. – V. 321. – №. 2. – C. 65-78. https://doi.org/10.31643/2022/6445.19

2. Kenzhegulov A., Mamaeva A., Panichkin A., Alibekov Z., Kshibekova B., Bakhytuly N., Wieleba W. Comparative Study of Tribological and Corrosion Characteristics of TiCN, TiCrCN, and TiZrCN Coatings //Coatings. – 2022. – V. 12. – P. 564. https://doi.org/10.3390/coatings12050564

3. Бахытулы Н., Мамаева А.А., Кенжегулов А.К., Паничкин А.В. Effect of magnetron sputtering modes on the formation and composition of TiCN coatings //Интернаука: электрон. научн. журн. – 2022. – Т. 37. – №. 260. https://doi.org/10.32743/26870142.2022.37.260.345662

4. Bakhytuly N., Kenzhegulov A.K., Nurtanto M., Aliev A.E., Kuldeev E.I. Microstructure and tribological study of TiAlCN and TiTaCN coatings //Kompleksnoe Ispol’zovanie Mineral’nogo Syr’a = Complex Use of Mineral Resources. – 2023. – V. 327. – №. 4. – P. 99-110. https://doi.org/10.31643/2023/6445.45

5. Mamaeva A.A., Kenzhegulov A.K., Panichkin A.V., Alibekov Zh.Zh., Kshibekova B.B., Wieleba W., Leśniewski T., Bakhytuly N. The study of the tribological properties under high contact pressure conditions of TiN, TiC and TiCN coatings deposited by the magnetron sputtering method on the AISI 304 stainless steel substrate //Materials Science-Poland. – 2023. – T. 41. – №. 1. – C. 1-14.**The structure and scope of the dissertation**

The dissertation work includes the following elements: "Regulatory references", "Introduction", a literature review devoted to the formation of hard wear-resistant coatings, an experimental part of 4 sections, "Conclusion", "List of references" and "Appendices".