ABSTRACT

of the dissertation submitted for the degree of Doctor of Philosophy (PhD) in the field of study 8D071 - "Engineering and Engineering Science", within the educational programme 8D07102 - "Mechanical Engineering".

MARATULY BAUYRZHAN

JUSTIFICATION OF PARAMETERS AND DEVELOPMENT OF AN INNOVATIVE TECHNOLOGY FOR THE DEPOSITION OF PROTECTIVE METAL COATINGS USING MAGNETRON SPUTTERING

Relevance of the dissertation work. Modern mechanical engineering is characterized by the intensive use of metalworking equipment and precision CNC machine tools, the reliability and durability of which directly depend on the quality of the cutting fluids (CFs) used. Water-miscible CFs provide a favorable environment for the growth of microorganisms. Research shows that the bacterial contamination of recirculation systems rapidly reaches high levels, leading to the breakdown of the emulsion.

The formation of stable biofilms on the surfaces of equipment and parts poses a particular danger. Biofilms dominated by Pseudomonas aeruginosa strains exhibit high resistance to standard biocidal additives in CFs. The vital activity of bacteria not only degrades machining quality and leads to the clogging of CF supply channels, but also creates conditions for the occurrence of corrosion. Furthermore, biofouling clogs the narrow channels of CF supply systems, which disrupts the thermal cutting regime and reduces the machining accuracy of parts.

Traditional control methods, based on the periodic introduction of biocides into the bulk of the CF, provide only a temporary effect and are incapable of preventing biofouling directly on contact surfaces. Moreover, they are associated with environmental risks and potential harm to personnel health, as the bioaerosols generated during machining cause occupational respiratory diseases.

In this regard, a fundamentally new approach is required, which consists of imparting bactericidal properties directly to the surfaces of machine parts and equipment. A promising solution is the application of functional coatings that ensure continuous bacterial suppression directly within the contact zone.

Solving the problem of microbiological damage to the surfaces of machine parts and equipment requires not only the selection of an effective coating material, but also a well-founded approach to its deposition technology. Among the existing methods of physical and chemical vapor deposition of coatings, the magnetron sputtering (MS) method stands out as the most technologically advanced and industrially adapted for solving mechanical engineering problems. Unlike chemical vapor deposition methods that require high temperatures, MS is a low-temperature process. Additionally, the method is environmentally friendly, eliminating the generation of toxic wastewater typical of galvanic processes.

The tantalum–copper (Ta–Cu) system is of particular interest, where tantalum acts as a chemically resistant and refractory matrix providing mechanical strength and corrosion resistance, while copper, possessing a proven bactericidal effect, functions as the active component. The ability to independently regulate the power on the tantalum and copper magnetrons allows for purposeful control over the composition, microstructure, and, consequently, the functional properties of the coating. At the same time, according to global statistics, overcoming the consequences of wear and friction consumes about 23% of global energy consumption, and total losses in industrialized nations reach 1.5–4% of GDP, making the development of wear-resistant bactericidal coatings an economically significant task. Therefore, the substantiation of parameters and the development of an innovative technology for depositing Ta–Cu bactericidal metal coatings using the magnetron sputtering method is a relevant scientific and technical direction aimed at improving the operational reliability of machines and equipment.

The idea of the dissertation boils down to replacing the traditional strategy of periodically introducing biocidal additives into the bulk of the cutting fluid with a fundamentally different approach—imparting permanent bactericidal, wear-resistant, and anti-corrosion properties directly to the surfaces of machine parts and equipment by applying a coating based on the tantalum–copper system.

The problem solved in the dissertation work is the lack of scientifically grounded technological solutions for the surfaces of machine parts and equipment operating in contact with microbiologically contaminated cutting fluids.

The main hypothesis of the dissertation is that the use of MS for the formation of tantalum–copper coatings allows for the creation of a wear-resistant, corrosion-resistant, and bactericidal layer on the surfaces of machine parts. It is assumed that through the independent regulation of power on the tantalum and copper targets, it is possible to control the chemical composition of the coating, its microstructure, and, consequently, its operational properties.

The objective of the study is to substantiate and experimentally determine the optimal parameters of the MS technological process for forming Ta-Cu bactericidal coatings possessing a specified set of tribological and protective properties.

The research tasks are:

- Optimize the parameters of the tantalum-copper coating deposition process.
- Study the influence of deposition modes on the microstructure, morphology, and elemental composition of the formed coatings.
- Evaluate the mechanical and tribological characteristics of the formed surfaces.
- Conduct tests to evaluate the corrosion resistance of the coatings.
- Develop a modernized design for the working head of the magnetron unit.
- Develop a technological process for applying coatings with protective properties.

The object of research - the technological process of forming thin-film protective metal coatings on parts of engineering equipment using the magnetron sputtering method.

The subject of research - regularities and interrelationships between the technological parameters of magnetron sputtering and the tribomechanical, corrosion, and protective properties of the formed tantalum-copper coatings.

The scientific novelty includes:

- For the first time, the concept of combining the high corrosion resistance of tantalum and the antibacterial properties of copper in a composite tantalum-copper coating system formed by magnetron sputtering has been scientifically substantiated for the protection of parts in contact with cutting fluids.
- New quantitative regularities regarding the influence of magnetron sputtering process parameters on the chemical composition and mechanical properties of the formed coating have been established.
- The "technological window" of the magnetron sputtering process has been mathematically determined and described at a working gas pressure of 0.18–0.28 Pa and a target power density of 8–15 W/cm^2, which ensures the formation of a dense, pore-free tantalum-copper structure dominated by the tantalum phase.

The practical significance of the research lies in:

- the development and scientific substantiation of the technological regulations for the DC magnetron sputtering process to form bactericidal coatings;
- the determination of optimal technological parameters and the reproducibility of results under industrial production conditions;
- the creation of an engineering methodology for calculating the kinetic parameters of the process for the EPOS-PVD-440 unit, which allows for predicting the productivity and cost of processing parts;
- the development and manufacture of the design of the magnetron unit's working head, including a sealing assembly to ensure high vacuum.

The following scientific statements are submitted for defense:

- DC magnetron sputtering technological modes that ensure the formation of a composite structure of tantalum-copper coatings with a uniform distribution of elements and minimize layer porosity.
- Quantitative relationships and a regression model linking changes in the copper target current in the range of 0.6–1.4 A with the final copper content in the coating from 3.2% to 19.6%.
- Scientific and technical substantiation of the technological process for applying protective tantalum-copper coatings, which includes preparation and deposition at a rate of 1.46 nm/rev on the EPOS-PVD-440 unit.

Summary. In the first chapter of the dissertation, an analysis of the current state of the problem regarding the microbiological contamination of cutting fluids and the mechanisms of stable biofilm formation on the surfaces of metalworking equipment is carried out. It has been established that traditional control methods have only a temporary effect and do not prevent the re-infection of recirculation systems. A comparative analysis of coating deposition methods was performed, on the basis of which the choice of DC magnetron sputtering was substantiated as the most productive, scalable, low-temperature, and environmentally safe method. The objective and tasks of the research are formulated.

In the second chapter, the theoretical foundations of ion-plasma sputtering, the mechanisms of coating nucleation and growth, the formation of adhesion properties, as well as the principles of operation and magnetic field configuration of magnetrons are considered. Thornton's structural zone model is presented, which allows for predicting the microstructure of coatings depending on the homologous temperature and working gas pressure. The advisability of forming a dense, pore-free structure of the "Zone T" type to ensure mechanical integrity, corrosion resistance, and controlled diffusion of bactericidal copper ions is substantiated.

In the third chapter, the methodologies for conducting research and evaluating coating properties are provided. The equipment and methodology for tribological testing, scanning electron microscopy with energy-dispersive X-ray spectroscopy (EDS), electrochemical testing, adhesion evaluation, as well as methods for evaluating bactericidal activity are described. The methodology for substrate surface preparation is outlined.

In the fourth chapter, experimental studies on the development of the coating deposition technological process are presented. The experimental setup on the EPOS-PVD-440 unit is described, involving the variation of the current on the copper target at a fixed power of the tantalum magnetron and a working pressure of 0.18 Pa.

In the fifth chapter, the technological process for applying coatings in relation to the industrial EPOS-PVD-440 unit is developed. A detailed engineering calculation of kinematic parameters was performed: the linear speed of substrate movement, technological feed, mass deposition intensity, consumption of target materials, specific power consumption, and direct electricity costs. A modernized design of the magnetron unit's working head is presented.

Personal contribution of the PhD candidate. The dissertation work was performed by the author personally. The author carried out the following main stages of the research:

- independent analysis of scientific and technical literature on the problem of microbiological damage to cutting fluids, methods for applying functional coatings, and the physical foundations of magnetron sputtering;
- direct execution of experiments on the EPOS-PVD-440 magnetron sputtering unit as an operator: preparation of the vacuum system, management of deposition modes, and monitoring of the glow discharge stability;
- preparation of substrates for coating deposition;
- participation in the modernization of the magnetron unit's working head: assembly and sealing of the component;
- preparation of the obtained coating samples for physical-mechanical and structural analyses;
- processing and interpretation of the obtained experimental data, statistical analysis, regression modeling, and formulation of regularities;
- development of the technological regulations and an engineering methodology for calculating the parameters of the Ta–Cu coating deposition process.

Structure and volume of the dissertation. The dissertation work is presented on 171 pages of typeset text, consists of definitions and abbreviations, an introduction, 5 sections, and a conclusion, includes 39 figures, 11 tables, a list of cited sources containing 140 titles, and 4 appendices.

Research results and main conclusions. In the dissertation work, a relevant scientific and technical problem that is of great importance for modern mechanical engineering has been solved. The conducted theoretical and experimental studies allow for the formulation of the following results and conclusions:

1. An analysis of the current state of the problem regarding the microbiological damage to cutting fluids and the surfaces of metalworking equipment has been carried out. It has been established that traditional methods of combating biofouling have only a temporary effect. Based on a comparative technical and economic analysis of coating deposition methods, the choice of DC magnetron sputtering has been substantiated as the most productive, scalable, and environmentally safe method.
2. The technological process of applying Ta–Cu coatings includes three main stages: surface preparation, the magnetron deposition process itself, and subsequent quality control. A technological window for stable process operation has been experimentally determined, ensuring the reproducibility of the required properties. The power of the tantalum magnetron was 2.0–2.1 kW, the power of the copper magnetron varied at 0.33 kW, 0.46 kW, and 0.80 kW, and the working pressure was 0.18 Pa.
3. Regularities regarding the influence of technological parameters on the operational characteristics of the coatings have been established. Energy-dispersive X-ray spectroscopy confirmed the formation of a coating dominated by the tantalum phase with a uniform distribution of copper. The copper content in the coating linearly correlates with the current on the copper magnetron in the range of 0.6–1.4 A. Tribological tests demonstrated that the friction coefficient of the coatings stabilizes in the range of 0.6–0.7 over a distance of 100 m. The coating with the minimum copper content possesses the best anti-friction properties, whereas the introduction of copper, which is necessary for the bactericidal effect, naturally increases the friction coefficient.
4. A detailed engineering calculation of technological parameters was performed in relation to the industrial EPOS-PVD-440 unit. At a linear substrate movement speed of 10.05 m/min, the technological feed was 1.46 nm/rev. The consumption of target material amounted to 21–35 g, and the specific energy consumption was 13.95 kWh/m^2. An assessment of direct electricity costs was carried out, which for the optimal TaCu-2 mode amounts to 215 tenge/m^2.
5. Using the regression analysis method, quantitative relationships between the technological parameters of the process and the properties of the Ta–Cu coatings were established. The specific power consumption increases linearly with an increase in the power of the copper magnetron. An increase in copper content does not lead to a strictly linear change in the friction coefficient. The bactericidal activity of the coatings is threshold-based.

6. The developed technology for depositing the Ta–Cu bactericidal coating using the magnetron sputtering method underwent industrial trials on the intake screens of submersible pumps in the CF circulation system under the conditions of LLP "VK PROMENERGOREMONT".

7. A modernized design of the working head for the EPOS-PVD-440 magnetron unit has been developed and manufactured, providing the capability to mount a magnetron with a target diameter of 40 mm.