

RIGA TECHNICAL UNIVERSITY

Margarita URBAHA

**CREATION OF NANOSTRUCTURED WEAR RESISTANT
ION-PLASMA COATINGS FOR RESTORATION AND
PROTECTION OF MACHINE PARTS**

Summary of Doctoral Thesis

Riga 2011

RIGA TECHNICAL UNIVERSITY
Faculty of Transport and Mechanical Engineering
Institute of Transport Vehicle Technologies

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CONFIRMATION

I confirm that I have developed this Doctoral Thesis submitted to Riga Technical University, to obtain the Scientific Degree of Doctor in Engineering. The Doctoral Thesis has not been submitted to any other University for obtaining a Scientific Degree.

Margarita Urbaha(signature)
Date:2011.

The Doctoral Thesis is written in Latvian, it consists of introduction, five chapters, resume, references and 22 appendixes. The bibliography includes 86 sources. Doctoral Thesis contains 65 figure, 15 tables. The total volume is 173 pages.

CONTENTS

1. TOPICALITY OF THE RESEARCH THEME.....	6
2. PURPOSE AND OBJECTIVES OF THE RESEARCH	6
3. RESEARCH METHODS.....	7
4. OBJECT OF THE RESEARCH	7
5. SCIENTIFIC NOVELTY AND MAIN RESULTS OF THE RESEARCH.....	8
6. PRACTICAL IMPORTANCE OF THE WORK	10
7. IN THIS PAPER AUTHOR DEFENDS.....	10
8. APPROBATION OF THE RESEARCH RESULTS.....	10
9. STRUCTURE OF DOCTORAL THESIS AND SUMMARY OF RESEARCH RESULTS .	12
1. ANALYSIS OF THE METHODS OF RESTORING THE SURFACES OF VEHICLE PARTS AND UNITS.....	13
1.1. Analysis of Causes and Basic Types of Failures in Machine Parts.....	13
1.2. Characteristics of Machine Part Surfaces being Restored.....	13
1.3. Characteristics of Methods for the Restoration of Machine Parts and Units	13
1.4. Election-ion Plasma Technologies and Nanotechnologies for Creating Coatings of Part Surfaces.....	14
2. MODELLING OF PROCESSES FOR CREATING NANOSTRUCTURED COATINGS AND ASSESSING THEIR QUALITY	15
2.1. Theoretical Modelling of the Process of Ion-plasma Sputtering of a Multicomponent Nanostructured Coating by the Combined Method.....	16
2.2. Theory of Decision Making by Assessing the Quality of Tribo-elements with Wear-resistant Coatings	17
3. METHODS AND FACILITIES FOR EXPERIMENTAL RESEARCH ON THE CREATION OF VACUUM ION-PLASMA COATINGS AND EVALUATION OF THEIR PHYSICO-MECHANICAL PROPERTIES	19
3.1. Equipment and Methods for Experimental Research on the Creation of Wear Resistant Nanostructured Multi-component Coatings	19
3.2. Modernization of Installation NNV-6.6-II for the Improvement of Engineering Process for Deposition of Vacuum Ion-plasma Coatings	20
3.3. Equipment and Methods for the Investigation of Microstructure and Chemical Composition of Materials and Coatings	21
3.4. Methods and Facilities for Measuring Microhardness of Materials and Coatings.....	22
3.5. Methods and Facilities for Measuring Roughness, Macrogeometric Deviations of Form and Geometric Characteristics of the Surface of Coated Parts	22
3.6. Equipment and Methods for the Experimental Investigation of Tribotechnical Properties of Coatings.....	24
3.7. Investigation of Hardness and Elastic Properties of Multilayer Coating Material by Nano-indentation.....	25
4. EXPERIMENTAL INVESTIGATION AND OPTIMIZATION OF TECHNOLOGICAL PROCESSES FOR DEPOSITION OF WEAR-RESISTANT VACUUM ION-PLASMA COATINGS	26
4.1. Investigation of Technological Process for Deposition of Ion-plasma Coatings on Samples and Products Made of Constructional Materials Using the Method of Condensation and Ion “bombardment”.....	26
4.2. Optimization of the Technological Process for Depositing Wear Resistant Nanostructured Multi-component Ion-plasma Coatings by the Combined Method.....	28
4.3. The technology of Creating Ion-plasma Wear-resistant Multi-component Coatings for the Protection and Restoration of Precision Pair Parts of Vehicle Power Units.....	30
5. EVALUATION OF PHYSICO-MECHANICAL PROPERTIES AND QUALITY CONTROL OF WEAR-RESISTANT NANOSTRUCTURED COATINGS.....	30
5.1. Ensuring the Uniformity of Measurements of Physico-mechanical and Tribological Properties of Nanostructured Surfaces.....	30
5.2. Experimental Evaluation of Adhesion Strength of Wear-resistant Nanostructured Ion-plasma Coatings.....	31
5.3. Results of Investigation of Hardness and Elastic Properties of Multilayer Coatings by Nano-indentation.....	33
5.4. Experimental Investigation of Tribotechnical Properties of Nanostructured Protective Coatings.....	35

1. TOPICALITY OF THE RESEARCH THEME

Most failures of vehicle power units including failures of hydraulic units occur as a result of damage of regulating and distributing devices as well as plunger and piston pairs of pumps and hydraulic motors. All types of failure and destruction of precision pair parts occur according to one of the performance criteria (wear, corrosion, etc.) and usually start from the surface of a part. All service properties of parts and their parameters are closely connected with geometrical and physico-mechanical properties of surface layers. The analysis of different methods of increasing wear resistance (constructive, technological or maintenance) shows that the most perspective method is related to the improvement of part surface properties by creating special protective coatings. Innovative nanostructured coatings, which are created on the basis of ion-plasma sputtering technologies, are of special interest. Coatings of this type differ by technological effectiveness and a wide range of physico-mechanical and service properties.

The main aim of the Latvian National Innovation Concept is to achieve the industrial engineering level of the developed countries. The development of transport engineering branch is closely related to nanostructuring of materials, which makes it possible not only to improve functional capabilities of technical objects but also to ensure more rational use of manufacturing, natural and energy resources. Moreover, in the European Commission's report titled "An Action Plan for Europe 2005-2009", the Commission emphasizes the potential of nanotechnologies in the context of fostering Europe's competitiveness.

Taking into consideration the objectives put forward in the dissertation as well as the fact that the thesis corresponds to the country's priority direction of science "Innovative Materials and Technologies", makes contribution to the development of the relevant branch of science and additionally promotes the integration of science and production, the theme of this thesis can be considered topical and necessary both in Latvia and abroad.

2. PURPOSE AND OBJECTIVES OF THE RESEARCH

The purpose of the Doctoral Thesis is to develop innovative technology for obtaining nanostructured multicomponent wear-resistant coatings by the combined ion-plasma method for restoration and protection of surfaces of machine parts.

The objectives of the the Doctoral Thesis are as follows:

1. To develop a theoretical model, which justifies the effectiveness of applying the combined method of depositing nanostructured multicomponent ion-plasma coatings in order to provide them with optimum service properties and to intensify the technological process of deposition;
2. To develop a theoretical model, which is based on the probabilistic approach and intended for assessing the quality of tribo-elements with wear-resistant coatings by using diagnostic data of acoustic emission testing method;
3. To carry out an experimental investigation of the technological processes for obtaining ion-plasma coatings by the method of condensation by ion bombardment and the method of magnetron sputtering;

4. To develop a new ion-plasma technology for obtaining nanostructured wear-resistant composite coatings (multilayer, multicomponent) by the combined method for restoration and protection of machine part surfaces in the process of manufacturing and repair;
5. To develop a prototype of protective nanostructured coating for restoration of industrial products;
6. To carry out an experimental investigation of the quality characteristics of created nanostructured coating (physico-mechanical properties, structure, chemical composition and geometry). Perform the assessment of coating adhesion strength by using the method of "scratching". To develop a quality assessment methodology for coatings of tribo-elements on the basis of the probabilistic approach and the carried out experimental investigation. On the basis of the results of nano-indentation, to assess the wear resistance of the created nanostructured coating.
7. To carry out an experimental investigation of the influence of the process-dependent parameters of coating sputtering process (correlation of working gases in sputtering chamber) and service properties (coating roughness) upon the tribotechnical properties of the coating.

3. RESEARCH METHODS

Methodology of the research parts and applied research methods:

Theoretical methods:

- mathematical modelling;
- solid body physics;
- mathematical statistics and correlation analysis;
- probability theory.

Experimental methods:

- methods of ion-plasma deposition of coatings in vacuum;
- experimental investigation of microstructure and chemical composition of materials and coatings;
- experimental assessment of adhesion strength of coating and basic material;
- investigation of hardness and elasticity properties of a coating material with the help of nano-indentation;
- experimental investigation of tribotechnical properties of coatings;
- experimental investigation of parameters of coating surface roughness and macrogeometrical deviation of form;
- statistical processing of results of experiments.

4. OBJECT OF THE RESEARCH

As a research object was used diesel engine high pressure pump hydro-fuel plunger precision pair parts (PP).

5. SCIENTIFIC NOVELTY AND MAIN RESULTS OF THE RESEARCH

Scientific novelty of the research carried out in the context of the dissertation:

As a result of the work the following innovative products were created:

- a new high-performance ion-plasma technology for obtaining nanostructured wear-resistant composite coatings by the combined method (the following patent was received: Method of obtaining multilayer wear-resistant coating for precision pair parts – Patent of the Republic of Latvia No. LV 14057 B, 20.03.2010)
- a new nanostructured ion-plasma composite coating (two-layer, three-component) on Ti–Al–N basis with increased wear-resistance.

These innovative products promote the integration of Mechanical Engineering branch and the integration of production as well as the introduction of research results in accordance with the country's priority directions of science: Innovative Materials and Technologies (nanostructured multifunctional materials and nanotechnologies).

During the implementation of the work the following basic results were achieved:

1. The work offers a theoretical model that justifies the effectiveness of applying the combined method of depositing nanostructured multicomponent ion-plasma coatings in order to provide them with optimum service properties and to intensify the technological process of deposition. It was proved that the presence of different metal impurities during the deposition of multicomponent coatings by the combined method lead to the intensification of deposition process, i.e. to the increase of deposition velocity and creation of a more uniform coating structure and to the increase of hardness and adhesion strength.
2. The work offers a theoretical model, which is based on the probabilistic approach and intended for assessing the quality of tribo-elements with wear-resistant coatings by using diagnostic data of acoustic emission testing method. It theoretically justifies the methodology for determining an objectionable level as well as the risk value related to its choice in the process of testing tribo-elements with coatings.
3. The experimental investigation of the technological processes for obtaining ion-plasma coatings by using different methods of material sputtering (condensation by ion bombardment as well as magnetron) was carried out. The advantages and disadvantages of the methods of coating sputtering were demonstrated experimentally. The basic advantage of the CIB method is high velocity of coatings deposition (5...7 $\mu\text{m/h}$). However, coatings created by the CIB method have a very considerable "drop phase", while the average value of coating roughness parameter R_a reaches 0.688 μm . The average nanohardness of the coating is 26 GPa. When the method of magnetron sputtering is used, the coatings differ by low roughness ($R_a = 0.015 \mu\text{m}$) and increased nanohardness (41GPa) while the sputtering velocity is low (0.5...1 $\mu\text{m/h}$).
4. There was developed a new high-performance ion-plasma technology for obtaining a nanostructured wear-resistant composite coating by the combined method (KJONBOMU – condensation and ion bombardment + magnetron sputtering). The combined technology makes it possible to create nanostructured coatings, ensure high microhardness and wear-resistance of a coating, its adhesion and thickness uniformity on a large area; to vary the composition of a coating in a wide range within a single technological cycle; to obtain high smoothness of coating surface (the influence of "drop phase" and the parameters of coating roughness decrease considerably) and more uniform coatings from the point of view of

composition; as well as to ensure the ecological cleanliness of production cycle (the following patent was received: Method of obtaining multilayer wear-resistant coating for precision pair parts. – Patent of the Republic of Latvia No. LV 14057 B, 20.03.2010)

5. There was developed a prototype of nanostructured composite coating (two-layer, three-component) on Ti–Al–N basis with increased wear-resistance. The coating is intended for the protection and restoration of tribo-element surface, i.e. for the parts of valve and plunger precision pairs in the process of their manufacturing and repair. The developed multicomponent coating provides the opportunity to reduce the friction coefficient and the wear of contact surfaces by 2 times and, as a result, to increase the life of friction parts.
6. The experimental investigation of the quality characteristics of created nanostructured coating (physico-mechanical properties, structure, chemical composition and geometry (thickness, two-dimensional (2D) and three-dimensional (3D) parameters of surface roughness)) was carried out.
7. The experimental investigation of the failure mechanism of created wear-resistant nanostructured coating was carried out; and the assessment of its adhesion strength by the system "coating-sample" and "coating-part" was performed using scratch tester CSM Revetest Xpress. On the basis of measurement of different physical parameters (acoustic emission, friction coefficient, indenter penetration depth, normal load, friction force) performed during the tests, failure mechanisms and threshold values of certain critical load, which leads to coating destruction, were described. The value of coating adhesion strength exceeds the strength of the coatings obtained by traditional methods of ion-plasma sputtering 4...5 times. On the basis of the offered probabilistic approach and the carried out experimental investigation, there was developed a quality assessment methodology for the coatings of tribo-elements depending on the threshold values of critical load, which leads to the deterioration of coatings adhesion and can be determined with high sensitivity by the acoustic emission method.
8. On the basis of the results of nano-indentation, the assessment of the wear resistance of created nanostructured coating was performed. The average nanohardness of the coating increases considerably. The value of hardness for plungers with coatings created with the help of the combined method is 37...41 GPa with the modulus of elasticity of 440...475 GPa. The average value of correlation H/E is 0.085, while $H^3/Er^2 = 0.283$ GPa. The range of obtained values for parameters H/E and H^3/Er^2 indicates at the nanostructure of the coating and confirms its high wear-resistance and ability to resist plastic deformation.
9. On the basis of the results of experimental investigation of tribotechnical properties of nanostructured ion-plasma coatings, the assessment of influence of the process-dependent parameters of coating sputtering process (correlation of working gases in sputtering chamber) and service properties (coating roughness) upon the friction coefficient was performed. Thus, when creating a coating by the KJONBOMU method, it is possible to achieve more than two-fold decrease of surface roughness, i.e. from 0.35 to 0.13 μm , by increasing the concentration of nitrogen in gas mixture from 2 to 10. Coating roughness in its turn exerts a considerable influence on friction coefficient. Therefore, after reducing the average value of coating roughness (R_a) from 0.607 μm (for a coating obtained by the KJB method) to 0.097 μm (for a coating obtained by the KJONBOMU method), the friction coefficient considerably decreases (from 0.417 to 0.181).

6. PRACTICAL IMPORTANCE OF THE WORK

The results of the work have wide practical significance and application, because the work deals with the development and patenting ("Method of obtaining multilayer wear-resistant coating for mechanical engineering parts") of a new high-performance ion-plasma technology for obtaining nanostructured wear-resistant coatings by the combined method.

The results of the work can be used mainly in transport engineering for manufacturing and repair of precision pair parts of vehicle engines, hydraulic and fuel equipment, cargo handling equipment, multipliers, etc.

The developed technology for the creation of composite coatings by ion-plasma sputtering is a high-tech, environmentally friendly and resource-saving technology, i.e. it completely corresponds to requirements for modern manufacturing process.

The application of the new technology in industry for manufacturing of new products and repair of existing products will provide companies with the opportunity to increase their competitiveness and foster the development of Latvian national economy. The results of the work were experimentally approbate in Latvian company "Metalserviss" and used for creation of protective coatings for metal goods.

7. IN THIS PAPER AUTHOR DEFENDS

1. Developed theoretical model that justifies the effectiveness of applying the combined method of depositing nanostructured multicomponent ion-plasma coatings.
2. Developed methodology for determining an objectionable level as well as the risk value related to its choice in the process of testing tribo-elements with coatings.
3. Developed new high-performance ion-plasma technology for obtaining a nanostructured wear-resistant composite coating by the combined method (KJONBOMU – condensation and ion bombardment + magnetron sputtering).
4. Developed prototype of nanostructured composite coating (two-layer, three-component) on Ti–Al–N basis with increased wear-resistance.
5. Developed quality assessment methodology for the coatings of tribo-elements depending on the the threshold values of critical load, which leads to the deterioration of coatings adhesion.
6. Assessment of influence of the process-dependent parameters of coating sputtering process (correlation of working gases in sputtering chamber) and service properties (coating roughness) upon the friction coefficient.

8. APPROBATION OF THE RESEARCH RESULTS

Results of this Doctoral Thesis have been reported at the 16 international scientific conferences:

1. International Conferences "Maritime Transport and Infrastructure" (IC MTI), LJA, Riga, Latvia: 9. IC MTI, April 19-20, 2007; 12. IC MTI, April 29-30, 2010; 13. IC MTI, April 28-29, 2011.
2. 2nd International Nanotechnology Conference Nanolsrael 2010, November 8-9, 2010, Tel Aviv, Israel.

3. International Convention AES-ATEMA'2010: Advances and Trends in Engineering Materials and their Applications, June 19-23, 2010, Brixen, Italy.
4. 5th International Conference on Surfaces, Coatings and Nanostructured Materials - NANOSMAT 5, October 19-21, 2010, Reims, France.
5. 2nd International Specialized Symposium "Space & Global Security of Humanity" (SGS 2010), July 5-9, 2010, Riga, Latvia.
6. International Scientific Conferences of Riga Technical University (ISC), Riga, Latvia: 47. ISC, October 12-14, 2006; 48. ISC, October 11-13, 2007; 49. ISC, October 13 -15, 2008; 50. ISC, October 12 -16, 2009.
7. 1st International EJC-PISE Workshop "Plasma Surface Engineering – Protective and Decorative Coatings", June 9-10, 2009, Riga, Latvia.
8. 7th International Nanotechnology Symposium: New Ideas for Industry "Nanofair' 2009" May 26-27, 2009, Dresden, Germany.
9. 3rd International Conference on Nanotechnology and Nanoscience „NanoAfrica 2009", February 1-4, 2009, Pretoria, South Africa.
10. Nanotech Northern Europe 2008, September 23-25, 2008, Copenhagen, Denmark.
11. XV International scientific-technical conference, trans&MOTAUTO'08, September 18-20, 2008, Sozopol, Bulgarn.
12. 2nd international conference on Advanced Nano Materials, Advanced Nano Materials, June 22-25, 2008, Aveiro, Portugal.
13. International conference MCM 2008, Mechanics of Composite Materials - 2008, May 26-30, 2008, Riga, Latvia.
14. 5th International Conference "Metals, Welding&Powder Metallurgy: MET-2007", September 13-14, 2007, Riga, Latvia.
15. International Conference on Composites/Nano Engineering ICCE-15, July 15-21, 2007, Haikou, Hainan island, China.
16. 9th International Conference „Transport Means' 2005", October 20-21, 2005, Kaunas University of Technology, Kaunas, Lithuania.

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1. Urbaha M., Savkovs K., Kumermanis M., Martinovs J. Nanotehnoloģijas transportlīdzekļu spēka iekārtu detaļu virsmu inženierijā // Proceedings of International Conference "Maritime Transport and Infrastructure-2011", ISSN 1691-3817, Latvija, Rīga, 2011. - 162.-169. lpp.
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5. Urbaha M. Nanokristāliskie nodilumizturīgie pārklājumi kuģu dzinēju detaļu aizsargāšanai un atjaunošanai // Proceedings of 12th International Conference "Maritime Transport and Infrastructure-2010", ISSN 1691-3817, Latvija, Rīga, 2010. - 99.-105. lpp.

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7. Urbaha M., Savkovs K., Urbach A. Development of protective coating for advanced aero engines// Book of abstracts of the 2nd International Symposium “Space & Global Security of Humanity”, Latvia, Riga, 2010. – p. 95.
8. Urbahs A., Savkovs K., Urbaha M. Multifunctional protective technological coverings// Abstracts of the 1st International EJC-PISE Workshop “Plasma Surface Engineering – Protective and Decorative Coatings”, Riga, Latvia, 2009.
9. Urbahs A., Savkovs K., Urbaha M. Nanostructured composite coatings for the protection and restoration of precision friction pair parts // International Journal Machines, Technologies, Materials. - ISSN 1313-0226, 2008. – pp. 58.-59.
10. Urbahs A., Savkovs K., Nesterovskis V., Urbaha M. Synthesis of nanostructured composite coatings for the protection and restoration of precision friction pair parts // Book of abstracts of International conference MCM 2008, Mechanics of Composite Materials - 2008, Latvija, Rīga, 2008. – pp.267-268.
11. Urbahs A., Savkovs K., Urbaha M. Technology for the Design of Nanostructured Composite Coatings // Book of abstracts of 3rd International Conference on Nanotechnology and Nanoscience „NanoAfrica 2009”, Dienvidāfrikas Republika, Pretoria, 2009.-58.-59.pp

Scientific projects:

1. IZM “Zinātniskās darbības attīstība augstskolā” finansētais projekts Nr. R7073 „Rūpniecisko izstrādājumu funkcionālo kompozīto pārklājumu izveide ar jonu – plazmas uzputināšanu”, 2006.g.;
2. RTU zinātniskais projekts Nr. ZP/2005 – 06 „Jonu - plazmas pārklājumu izstrāde transportlīdzekļu spēku iekārtu detaļu aizsardzībai un atjaunošanai”, 2005.-2006.g.;
3. LZP zinātniskais projekts Nr. 09.1088 “Daudzkomponentu jonu - plazmas pārklājumu izveide mašīnbūves izstrādājumu aizsardzībai un atjaunošanai”, 2009.
4. LZP zinātniskais projekts Nr. 09.1612 Materiālu virsmu un makrostruktūras īpašību izpēte, 2009.-2010.g.
5. LZP cooperations project Nr. 10.0009 “Development of technology for the creation of multicomponent nanostructured protective coatings for industrial products”, from 2010.g.
6. ERAF project “ Development of industrial technology prototype for multi-component nanostructured ion-plasma wear-resistant coatings”, from 2010.g
7. Nanopārklājumu raupjumu raksturojošo telpisku nestandarta parametru pētījumi (FLPP-2010/1), from 2010.g.

9. STRUCTURE OF DOCTORAL THESIS AND SUMMARY OF RESEARCH RESULTS

The Doctoral Thesis consists of introduction, five chapters, resume, references and 22 appendixes.

1. ANALYSIS OF THE METHODS OF RESTORING THE SURFACES OF VEHICLE PARTS AND UNITS

The given chapter includes five subchapters, which consider the issues that have the basic significance for further theoretical investigation and practical application of research results. The work represents the results of a comparative analysis of the methods of coatings deposition in vacuum and considers the ways and schemes of implementing these methods. It also formulates the goal and objectives of the research.

1.1. Analysis of Causes and Basic Types of Failures in Machine Parts

Machine failures occur as a result of permanent or sudden deterioration of physico-mechanical properties of the material of parts, their wear, deformation, crushing, corrosion, aging, redistribution of residual stresses and other reasons causing destruction of parts. In most cases, changes in couplings, i.e. change of specified clearances in movable joints or interferences in fixed joints, occur. Practically any failure is caused by a change in the composition, structure or mechanical properties of the material, structural dimensions of parts and condition of their surfaces.

The occurrence of failures is conditioned by structural, technological and operational factors.

Failures of machine parts can be divided into three groups: wear, mechanical damages and chemical-thermal damages.

The prevalent type of failures is *wear of parts*. The intensity of parts wear increase and the change of clearances in movable connections occur with a definite regularity, depending on the operating period.

1.2. Characteristics of Machine Part Surfaces being Restored

Among the surfaces being restored, there are external and internal cylindrical surfaces (53.3%), thread surfaces (12.7%), spline surfaces (10.4%), jagged surfaces (10.2%), flat surfaces (6.5%), all other surfaces (6.9%). In modern interpretation, the study of part surface engineering implies the development of a theory of scientifically substantiated definition of operating surface form, geometrical parameters (macro deviations, waviness, roughness) and physicochemical properties that ensure reliability and required durability of parts, it also implies the development of technologies for creating such surfaces, their inspection, testing, change during operation, repair, restoration and utilization.

The investigation and improvement of the surface layer of machine parts should be carried out in complex, on all stages of its life cycle.

1.3. Characteristics of Methods for the Restoration of Machine Parts and Units

In the process of parts restoration, the main task is to provide worn surfaces with initial parameters. The basic techniques are building-up and sputtering of metal coatings, metal deposition, forming, diffusion, structural changes, deposition of polymer metals, etc.

Tens of different parts restoration methods have been developed and applied in manufacturing environment. The choice of the most acceptable method includes the technical, economic and organizational analysis of requirements for restoration parts with account of conditions of their operation in couplings, production program, equipment of plants, provision with materials, energy, labour force and other arrangements.

Coatings made of metals, alloys, pseudoalloys and plastic are deposited on the surface of parts for their protection from destruction during operation, increase of their service life,

restoration of dimensions, obtaining antifrictional as well as heat-, wear- and corrosion-resistant parts. Plasma methods for machine parts restoration are based on the use of thermalphysic properties of ionized gas (plasma). As it is very difficult to separate plasma per se, an arc discharge enriched with plasma is used for technical purposes, i.e. neutral particles are contained in the arc discharge along with charged particles (ions and electrons). Such condition of gas is called low-temperature plasma (temperature at the exit of plasmatron nozzle is 5000...7000K).

During the plasma sputtering, powders, wires and rods are used as sputtering materials.

A considerable drawback of sputtered coatings is their porosity, which can be explained by small contact area both among the particles and among the particles and the substrate. When comparatively small loads act upon such a layer the possibility of its detachment is high. In order to improve the quality of sputtered coatings, they are subjected to subsequent melting.

The method of plasma sputtering gives the opportunity to obtain several millimetres thick coatings, however, along with the increase of layer thickness $> 1...1.3$ mm the strength of its adhesion with the substrate decreases, therefore it is most expedient to use it for the restoration of parts, the wear of which does not exceed $0.4...0.6$ mm. This method obviously does not give the opportunity to restore and create coatings on nano- and microlevel.

1.4. Election-ion Plasma Technologies and Nanotechnologies for Creating Coatings of Part Surfaces

The method of chemical deposition of thin coating is implemented by injecting into a working chamber (reactor) a mixture of gases, which contains the components of the obtained coating and is divided into the deposition of atoms and molecules directly from the gas phase and plasma chemical deposition of electrically neutral atoms, molecules and radicals. There exist CVD methods (CVD – Chemical Vapor Deposition), vapor-phase epitaxy, thermal oxidation, methods of plasma chemical deposition.

The main advantage of the method of chemical deposition is a wide range of deposition velocities v_0 and the possibility of obtaining the desired crystal structure of a coating (right up to monocrystals), while the basic drawback lies in the use of toxic, ecologically dangerous gas mixtures.

The term PVD (Physical Vapor Deposition) often appears in literature and means the deposition of thin coatings, which includes all the above-mentioned methods except CVD.

In the last years, electronic technologies and nanotechnologies are more and more becoming the object of interest for mechanical engineers. Part surface engineering is of especial interest because it provides the opportunity to form the functional properties of parts on the level of separate atoms and molecules.

Gas-discharge plasma, which consists of electrons, ions and electrically neutral atoms, molecules and radicals, and generates different types of radiation, can also be used as a tool for materials treatment.

Plasma treatment is carried out under pressure, which is lower than the atmospheric pressure and therefore compatible with other vacuum processes.

One of the most typical examples of using gas-discharge plasma in mechanical engineering is cleaning and etching of the surface of the product being treated and deposition of thin coatings.

If plasma is ignited in a separate vacuum chamber (autonomous source of ions) and ions are extracted from it as a beam directed to the sample, this process is called ion-beam treatment. Ion implantation is an instance of this kind of treatment.

Among the virtues of *the method of thin coatings deposition by thermal evaporation* there are: high frequency of the material being deposited (the process is carried out in high and ultrahigh vacuum conditions), universality (coatings of metals, alloys, semiconductors, dielectrics are deposited) and relative simplicity of implementation. The method has such limitations as uncontrolled deposition rate v_0 , low, changeable and uncontrolled energy of particles being deposited E .

Deposition of thin coatings by arc discharge in vacuum occurs as a result of substance erosion in high-current arc discharges (with cold and hot cathodes), formation of ionized vapor phase (20...100% ions), its transfer with higher velocity (energy of particles E up to 10eV) and condensation on the substrate surface.

Among the advantages of the method of thin coatings deposition by arc discharge in vacuum there are: practically unlimited electric power; high ionization coefficient of the evaporated particles k_i ; possibility of obtaining coatings of alloys, oxides, nitrides, carbides, etc., both by using targets from these materials and by the reactive method; unnecessary of additional gas for ionization. Among the drawbacks there are the presence of a drop phase in the flow of the substance being deposited, uncontrolled energy of particles E and relative structural complexity of arc sources.

The method of ion deposition of thin coatings is based on the combination of two processes:

- 1) generation of parent substance plasma with the help of one of the types of electric discharge or high frequency (HF) inductor;
- 2) acceleration of ions or all quasi-neutral plasma with subsequent condensation on the surface of a substrate (part).

Parent substance is obtained with the help of one of the methods of thermal evaporation (thermoionic method); from gas mixture containing the components of the coating being deposited (ion-plasma and ion-beam methods); by the use of arc discharge, which is used as the first stage of plasma accelerator (plasmatron method).

The above specified method is implemented in one of the following ways:

- *Ion-plasma* (diode on direct current, diode HF, three-electrode, magnetron on direct current, reactive);
- *Ion-beam* (with hot cathode, with cold cathode, reactive).

When the mixture of Ar and reactive gas (O_2 , N_2 , etc.) is used as working gas, the reactive method of deposition of oxides, nitrides, etc. is implemented.

Among the advantages of the method of thin coatings deposition by ion sputtering there are universality (possibility of depositing metals, alloys, dielectrics, magnetic compositions), adjustable deposition rate v_0 and relatively simple construction of installations. Among the drawbacks there are low purity of the coating being deposited (due to the presence of working gas), low and uncontrolled energy of the particles being deposited E .

2. MODELLING OF PROCESSES FOR CREATING NANOSTRUCTURED COATINGS AND ASSESSING THEIR QUALITY

The chapter contains 2 subchapters devoted to theoretical modelling of the processes of coatings sputtering and subsequent assessment of their quality. It offers a theoretical justification of the influence of different metal impurities on the efficiency of the engineering process of deposition during the deposition of multicomponent coatings by the combined method. It is suggested to assess the quality of created coatings on the basis of diagnostic data obtained by acoustic emission testing with account of the probabilistic approach.

2.1. Theoretical Modelling of the Process of Ion-plasma Sputtering of a Multicomponent Nanostructured Coating by the Combined Method

The work offers a theoretical justification of the influence of different metal impurities on the efficiency of the engineering process of deposition and the quality of the created coatings during the deposition of multicomponent coatings by using the combined method taking into consideration the physics of the processes, which are inherent in both electric arc and magnetron methods.

The density of ion current on the cathode, which is equal to the number of ions falling to the unit of the cathode surface during a unit of time, can be determined from the following expression:

$$i = \frac{\rho \mathcal{G}_T}{4}, \quad (2.1)$$

where \mathcal{G}_T is the thermal velocity of ions, ρ is plasma density.

At the same time the velocity of motion of cathode material surface due to erosion is equal to: $\mathcal{G}_p = \frac{\gamma i}{n}$,

where γ is sputtering ratio, n is the number of atoms in the unit of material volume.

In the magnetron with a balanced magnetic field, the magnetic field near the cathode surface is parallel to its surface. Plasma density ρ decreases in the direction of the cathode because magnetized electrons of plasma can deviate from its limits by the amount of radius:

$$r_\lambda = \frac{m \mathcal{G}_e c}{e B}, \quad (2.2)$$

where m is electron mass, \mathcal{G}_e is electron velocity, e is electron charge, c is light speed, B is magnetic field.

Ions, in their turn, can "tear away" from electrons only by the volume:

$$r_d = \left(\frac{T}{4\pi \rho e^2} \right)^{1/2}, \quad (2.3)$$

where T is plasma temperature.

As a result the characteristic distance of plasma decrease can be determined as:

$$r_0 = r_\lambda + r_d.$$

The work analyses the mechanism of enhanced diffusion, which is observed when the concentration of different metal impurities is high, with due account of interaction among impurities. During the interaction of impurity atoms, there occurs the "knock out" of separate impurity atoms from the surface layer of the part into the depth of the material.

Interaction of impurities leads to the change of chemical potential by the value:

$$\Delta\mu = \varepsilon C, \quad (2.4)$$

where C is the concentration of impurities, fractures of atoms; ε is a constant characterizing the interaction of impurity atoms. In particular, during the repulsion of impurity atoms from one another, $\varepsilon > 0$.

The gradient of chemical potential causes the action of force on an impurity atom:

$$F = -\frac{d(\Delta\mu)}{dx}.$$

The diffusion equation of impurity atoms can be presented as follows:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} + K \frac{\partial}{\partial x} \left(C \frac{\partial C}{\partial x} \right), \quad (2.5)$$

where D is a diffusion coefficient; $K = D\varepsilon/T$.

In case of the three time increase of impurities concentration ($C > 1...3$ atomic fractions, %) the second summand of the equation (2.5) will exceed the first one, which is related to the marked amplification of impurities transfer.

In this case, the equation (2.5) can be reduced to a linear diffusion equation:

$$\frac{\partial C}{\partial t} = K \frac{\partial}{\partial x} \left(C \frac{\partial C}{\partial x} \right). \quad (2.6)$$

With the specified impurity flux to the surface, the equation (2.6)

$$KC \frac{\partial C}{\partial x} \Big|_{x=0} = -\theta$$

has the following solution:

$$C = \left(\frac{\theta^2 t}{K} \right)^{1/3} f \left(\frac{x}{x_e} \right), \quad (2.7)$$

where $X_e = \varepsilon \left(\frac{\varepsilon \theta^2 t}{T} \right)^{1/3}$ is the depth of impurity atoms penetration, which increases

along with the growth of impurity flux to the surface θ .

The depth of impurities penetration can by an order exceed the depth during normal diffusion. Thus, the presence of different metal impurities during the deposition of multicomponent coatings by the combined method should lead to the intensification of deposition process, i.e. to the increase of deposition velocity, creation of more uniform structure of a coating as well as to the increase of its hardness and adhesion strength. The latter circumstance is related to the increase of depth of impurities penetration into the material of a part being treated. In this case, the coatings obtained by the combined method should be purer (decreased influence of the "drop phase") due to the use of additional magnetron sputtering.

2.2. Theory of Decision Making by Assessing the Quality of Tribo-elements with Wear-resistant Coatings

The decision about the operational suitability of tribo-elements with wear-resistant coatings can be made, for instance, on the basis of the analysis of informative parameters recorded during the testing of parts by one of the well-known acoustic methods of non-destructive testing (ultrasonic or acoustic emission (AE)).

It is also necessary to note that the process of making a decision about the quality of tribo-element coating is not a simple action reduced to a usual comparison of some diagnostic parameters. In addition to the knowledge of the physics of structural changes in the material and the nature of defects as well as of the mechanics of their propagation, it is necessary to use the laws of mathematical statistics and probability theory in full.

In case of AE testing of products, devices record some values of the informative parameter of signals $x = \{x_1, x_2, \dots, x_n\}$. Let us designate the totality of possible values of vector components x by X . On the set X , it is possible to define functions $W(x/H_0)$ and $W(x/H_1)$ describing the conditional probabilities (or probability densities) of values distributions x for defect-free and defective products of the inspection lot respectively. These

laws are established either theoretically or experimentally by testing two sufficiently representative consignments, each of which consists of defect-free and defective products respectively. On the basis of the totality x , which is recorded in the process of testing, it is possible to accept two hypotheses:

1) hypothesis H_0 : the totality x is obtained from the sample, which is subject to the distribution law $W(x|H_0)$, and, consequently, the product being tested is defect-free;

2) hypothesis H_1 : the totality x is obtained from the sample, which is subject to the distribution $W(x|H_1)$, and the product being tested is defective.

In accordance with the task of defects detection the set X should be split into two subsets X_0 and X_1 . A product is blocked if x refers to the range X_1 , and it is considered acceptable if x belongs to X_0 . Thus, the rule of making a decision about the quality of the object being tested (rejection rule) is reduced to defining a limit between sets X_0 and X_1 . The splitting of the range X into X_0 and X_1 is carried out in accordance with different rules (criteria) of decision making. The use of one or another criterion is determined by the presence of a priori information about products being tested.

In a general case, the rule of blocking can be presented as the following relation:

$$\lambda(x) = W(x|H_1)/W(x|H_0) \underset{H_1}{\overset{H_0}{<}} \lambda_c, \quad (2.8)$$

where $\lambda(x)$ is a universal characteristic describing the probability of a defect and called a *likelihood ratio*; λ_c is its threshold (critical) value determined by the used decision making criterion. The likelihood ratio contains all information about the presence of a defect, which becomes available as a result of diagnostic measurements.

If the $\lambda(x)$ is known, it is possible to find the probability of presence or absence of a defect. When $\lambda(x) > \lambda_c$ the decision (hypothesis) H_1 about the rejection of a product is made, when $\lambda(x) < \lambda_c$ the hypothesis H_0 about its fitness is accepted.

If the decision about the defectiveness of a product is made, the errors of two types are possible. Error of the first type (excessive rejection) is the rejection of a fit product, i.e. the acceptance of the hypothesis H_1 , when the hypothesis H_0 is true. Error of the second type (insufficient rejection) is the acceptance of a product with an inadmissible defect, i.e. the acceptance of the hypothesis H_0 when the hypothesis H_1 is true.

Let us assume that with fixed discrimination level D the level of recorded acoustic signals was Δk . It is necessary to make a decision about the faultiness of a coated tribo-element. It is known that the probability density Δk for defect-free products is governed by the one-sided normal distribution law with an average $\overline{\Delta k}_0$ and dispersion S_0^2 ; while in the case of defective products, it is governed by the one-sided normal law with an average $\overline{\Delta k}_1$ and dispersion S_1^2 .

Making a decision about the fitness of a product is reduced to the testing of a hypothesis H_0 saying that the value Δk is obtained from the distribution:

$$W(\Delta k | H_0) = \frac{1}{\sqrt{2\pi}S} \exp\left(-\frac{[\Delta k - \overline{\Delta k}_0]^2}{2S^2}\right), \quad \Delta k > 0,$$

and a product being tested is defect-free, against the alternative that Δk is obtained from the distribution:

$$W(\Delta k | H_1) = \frac{1}{\sqrt{2\pi}S} \exp\left(-\frac{[\Delta k - \overline{\Delta k}_1]^2}{2S^2}\right), \quad \Delta k > 0,$$

and, consequently, a product being tested is defective. In this case, the hypothesis H_1 about the defectiveness of a product is accepted if the following inequality is true for the recorded level of signals Δk :

$$\lambda(\Delta k) = W(\Delta k | H_1)/W(\Delta k | H_0) \geq \lambda_c. \quad (2.9)$$

The probability of excessive rejection is related to the threshold value of the level of recorded signals Δk , relation:

$$P_p = \int_{\Delta k_c}^{\infty} W(\Delta k | H_0) d\Delta k = 1 - \Phi\left(-\frac{\Delta k_0 - \overline{\Delta k}_0}{S}\right),$$

in which $\Phi(\Delta k) = \left(1/\sqrt{2\pi}\right) \int_{-\infty}^{\Delta k} \exp\left(-\frac{t^2}{2}\right) dt$ - is error integral.

With the value P_p assigned, the threshold of defects detection can be determined from (2.9):

$$\Delta k_0 = \overline{\Delta k}_0 + \delta S_0, \quad (2.10)$$

where δ is a one-sided tolerance coefficient, which depends on the number of measurements, accepted level of significance q of event $\Delta k < \Delta k_0$ and confidence probability of Δk falling into the specified range; S_0 is a sample standard deviation; $\overline{\Delta k}_0$ is a sample mean of the parameter.

Thus, if the signal of level $\Delta k \geq \Delta k_0$ has been recorded with the fixed level of AE equipment discrimination in the process of non-destructive testing of a coated tribo-element, the inequality (2.12) is true and a product is rejected; in other cases, a product should be considered acceptable. The probability of accepting a faulty product is:

$$P_n = \int_0^{\Delta k_0} W(\Delta k | H_1) d\Delta k = \Phi\left(\delta - \frac{\overline{\Delta k}_1 - \overline{\Delta k}_0}{S_0}\right) + \Phi\left(\frac{\overline{\Delta k}_1}{S_0}\right) - 1. \quad (2.11)$$

3. METHODS AND FACILITIES FOR EXPERIMENTAL RESEARCH ON THE CREATION OF VACUUM ION-PLASMA COATINGS AND EVALUATION OF THEIR PHYSICO-MECHANICAL PROPERTIES

The chapter contains 6 subchapters devoted to the development of methods for experimental research on the creation of vacuum ion-plasma coatings and evaluation of their physico-mechanical properties. They provide a characteristic and offer solutions for modernization of experimental equipment to increase the effectiveness of research and improve the engineering processes for creation of protective nanostructured coatings.

3.1. Equipment and Methods for Experimental Research on the Creation of Wear Resistant Nanostructured Multi-component Coatings

The process of creating coatings in vacuum consists of three stages: generation of atoms, molecules or ions, their transfer to the surface of a product and creation of a coating with the required parameters on the surface of the product. Composition and structure of

coatings depend on basic material as well as on the method and mode of deposition, which ensure the required energy-mass transfer of the material.

A *process installation*, which makes it possible to apply the method of ion-plasma sputtering of coatings, represents a vacuum installation that includes a working chamber with a built-in plasma evaporator and an arc initiation system, a power supply source, a gas station for feeding working gas into the chamber as well as measuring and control equipment (Fig.3.1).

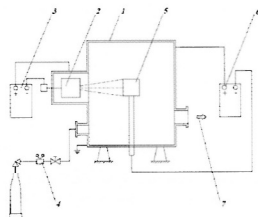


Fig.3.1. Circuit of a vacuum installation for creation of ion-plasma coatings:

1 – vacuum chamber, 2 – cathode of the evaporator, 3 – low-voltage power supply, 4 – doping gas feeding system, 5 – product being processed, 6 – high-voltage power supply, 7 – doping gas exhaust

The basic element of the installation is a vacuum chamber for sputtering with the sources of material being sputtered and a turntable with the parts being sputtered fixed on it. The installation is supplied with a vacuum pumping system, a working gas feed system, a cooling system and a power-supply system.

Deposition of evaporator material on the surface of parts occurs under the effect of constant electric and magnetic fields, which intensify the process of sputtering and enhance the density of the coating and its adhesion to the base.

Vacuum installation “NNV-6.6-II” has three evaporators making it possible to create multilayer coatings of different types and combinations. For example, an alloy can be used as one of the evaporated cathodes, while different materials can be used as the other two. Depending on the purpose, the required result can be achieved by changing cathode materials as well as the order, intensity and duration of their evaporation.

3.2. Modernization of Installation NNV-6.6-II for the Improvement of Engineering Process for Deposition of Vacuum Ion-plasma Coatings

The vacuum installation has been modified in order to improve its performance. A planar magnetron sputtering device “Magnetron 2” has been installed instead of one of the arc sources (Fig. 3.2.). The operating principle of the magnetron sprayer is based on the effect of spraying magnetron cathode surface by working gas ions, which are located in crossed electric and magnetic fields.

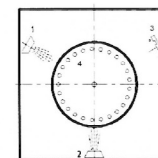


Fig. 3.2. Location of evaporators on the modified vacuum installation:
1, 2 – electric arc evaporators; 3 – magnetron; 4 – turntable

Magnetron sputtering has such advantages as absence of a drop phase, possibility of sputtering a wide spectrum of materials, high utilization of material, good adjustment characteristics, high density and uniformity even of thin coatings.

The possibility of combining the methods of electric arc and magnetron sputtering, which arose as a result of the modification of the installation, makes it possible to partially reduce the drawbacks of both methods by simultaneously using their basic advantages. This technique, in particular, gave the opportunity to reduce the drop phase without reducing the efficiency of ion bombardment. In addition, the spectrum of materials being sputtered has been widened and their quality has been improved.

3.3. Equipment and Methods for the Investigation of Microstructure and Chemical Composition of Materials and Coatings

3.3.1. Equipment and Methods for the Investigation of Microstructure of Materials and Coatings

In order to carry out the investigation of microstructure of the created coatings on a nano-level, a scanning electron microscope SEM HITACHI-S3000N was used.

The microscope is intended for investigation of solid surfaces with the help of an electron probe. The maximum resolution of the microscope is 3.5 nm; magnification is 15...300000. The electron microscope was used not only for the investigation of microstructure but also for the analysis of surface topography of the created coatings. The microscope also gives the opportunity to define with high precision the thickness of a multilayer nanostructured coating.

Microsections were made with the help of special equipment, i.e. “Grinding and polishing machine Beta/2”, providing the opportunity to carry out high precision grinding of surface in the section of samples and parts for the subsequent investigation of microstructure of materials and coatings.

3.3.2. Equipment and Methods for the Investigation of Chemical Composition of Materials and Coatings

The *Chemical analysis of composition of the created nanostructured coatings* was carried out by the method of micro X-ray spectrum analysis, which is one of the most sensitive analytical methods. For this purpose, a micro X-ray energy dispersive analysis system (EDS) BRUKER-QUANTAX 200 was used.

The QUANTAX set includes an X-ray detector, a signal processing module with an integrated scanning system and a computer.

The system gives the opportunity to obtain information about elemental composition with spatial resolution of 1 μm and the limits of detection of mass percent tenths order.

BRUKER-QUANTAX 200 system is supplied with ESPRIT software with intuitive interface, which includes a quantitative analysis, an expanded library of lines for the range of low energies, mapping, etc.

3.4. Methods and Facilities for Measuring Microhardness of Materials and Coatings

Microhardness (hardness of separate structural components of an alloy or material as well as a surface layers) is determined by the resistance to penetration of a diamond pyramid under the influence of small loads. Microhardness was measured with the help of devices of PMT-3 type (range of loads – 0.0196 ...4.9 N) and MTI-3M type (range of loads – 0.05 ...10.0 N).

Interferential microhardness testing machine PMT-3 makes it possible to measure microhardness of different materials depending on the depth of diamond pyramid impression (Vickers pyramid).

3.5. Methods and Facilities for Measuring Roughness, Macrogeometric Deviations of Form and Geometric Characteristics of the Surface of Coated Parts

3.5.1. General Characteristic of Roughness Parameters and Macrogeometric Deviations of Parts Surface Form

The work analyses the basic terms and designations in relation to 2D and 3D geometrical parameters of roughness and macrogeometric deviations of parts surface form in accordance with ISO standards.

It considers 4 basic categories of 3D parameters related to the analysis of surface:

- *Amplitude parameters* (Height)
- *Spatial parameters* (Spacing)
- *Functional parameters* (Function – Bearing Area)
- *Hybrid parameters* (Height & Spatial).

The work presents the results of a comparative analysis of how 3D parameters affect the properties of materials and technical characteristics of machine structural elements.

3.5.2. Measurement of the Roughness of Samples and Parts Surface with the Help of a Contact Testing Instrument

The roughness of the surface of samples and parts material was measured with the help of a contact testing device SURFACE ROUGHNESS TESTER TR100.

The testing device makes it possible to measure the basic parameters of roughness Ra and Rz within the following range: Ra: 0.05 – 15.0 μm ; Rz: 0.1 – 50 μm with the error of measurement $\pm 6\%$. The transformation of surface geometrical parameters into an electric signal is carried out with the help of a piezoelectric converter with a diamond needle with radius of $5 \pm 1 \mu\text{m}$. The length of the scanning track is 6 mm, the length of the working area for the evaluation of roughness parameters value is 1.25 mm/4.0 mm/5.0 mm. The scanning speed is 1 mm/sec. In accordance with the requirements of ISO and DIN standards the device makes it possible to carry out measurements on flat surfaces, external surfaces of cylinders and angled surfaces. It is equipped with an external calibration function.

3.5.3. Methods for Measuring Roughness and Macrogeometric Deviations of Form of the Surface of Coated Samples and Parts by using contact profilograph- profilometer

The measurement of geometric parameters and roughness of coated and non coated sample surface was carried out with the help of a contact profilograph- profilometer “Form Talysurf Intra 50” manufactured by Taylor Hobson company.¹

The device gives the opportunity to simultaneously measure the size, form and texture of a sample surface.

Device resolution is 16 nm in 1 mm range. The measurements were carried out in accordance with the requirements of ISO 3274 standard.

The device Form Talysurf Intra makes it possible to make measurements of both 2D parameters of surface profile and 3D areas of a surface with high resolution (up to 3.2 nm). The error of measurement of altitude parameters, for instance, is 2% ± 6 nm (Fig. 3.3.).

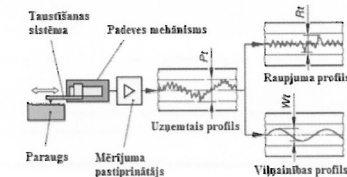


Fig.3.3. Schematic diagram of contact profilograph- profilometer operation

At first, in order to determine the rough value of surface roughness parameter, for example, Ra or Rz, it is necessary to obtain a profilogram for an arbitrarily chosen area. In this case, the error of intention R_a does not exceed 5... 10 % for the majority of technical surfaces. The value of sampling length is defined on the basis of the obtained parameter value in accordance with operating standards.

The measurements in the context of this work were carried out with the following parameters: the sampling length was 0.25 mm, the size of surface working area to be measured was 5x5 mm. The total number of measurement points for each sample was 140625.

3.5.4. Equipment for Measuring Coating Thickness

Nondestructive express measurement of surface thickness was carried out with the help of such devices as “Coating thickness measurement eXacto®” and “Coating thickness measurement MiniTest™ 600FN”.

The operating principle of “eXacto®” and “MiniTest™ 600FN” devices is based on magnetic induction (F-model) or vortex-current (N-model) principles of operation. In FN-models both operation principles are used.

“eXacto®” device gives the opportunity to measure the thickness of coatings within the following range: F-probe: 0 ...3000 μm ; N-probe: 0...2000 μm ; FN-probe: 0 ...2000 μm with precision $\pm (2 \mu\text{m} + 3\%$ of the readings).

For the precise measurement of coating thickness on micro- and nano-level (with 3.5 nm resolution) (Fig. 3.4.) a scanning electron microscope was used.

¹ The research was conducted on the basis of the Institute of Mechanical Engineering Technologies of the Faculty of Transport and Mechanical Engineering in the framework of joint projects with the Institute of Transport Vehicle Technologies titled “Development of industrial technology prototype for multi-component nanostructured ion-plasma wear-resistant coatings” and “Development of technology for the creation of multicomponent nanostructured protective coatings for industrial products”.

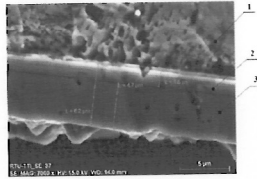


Fig. 3.4. The results of determining the thickness of a multilayer nanostructured coating:
1 - basic material; 2 – first layer of the coating; 3– second layer of the coating

3.6. Equipment and Methods for the Experimental Investigation of Tribotechnical Properties of Coatings

3.6.1. Determining the Friction Coefficient of a Coating

The friction coefficient of the coating was determined with the help of a special installation, the circuit of which is presented in Fig. 3.5.

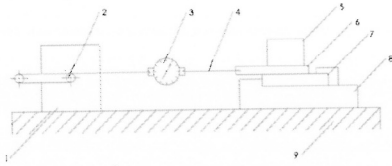


Fig.3.5. Circuit of the experimental installation for investigating tribotechnical properties of coatings:
1 – bridling equipment, 2 – shaft, 3 – dynamometer, 4 – cable, 5 – load, 6 – coated sample, 7 – counter sample, 8 – holder, 9 – base.

Steel plates 100x30x1.5 mm in size were used as experimental samples.

Four steel plates identical in size to the samples being investigated were used as counter samples. During the experiments, two counter samples with titanium nitride (TiN) coating were used; the surface of one of the counter samples was polished after coating deposition (its average roughness parameter value was $Ra = 0.15 \mu\text{m}$). Roughness of counter samples with unpolished surface corresponded to average value $Ra = 0.62 \mu\text{m}$. During the experiments, uncoated counter samples (2 pieces) were used as well; for one of them the average value of roughness parameter Ra after polishing was $0.11 \mu\text{m}$, while for the other one (without polishing) it was $Ra = 0.45 \mu\text{m}$.

Friction coefficient was determined for the case of dry friction (without lubrication).

3.6.2. Experimental Evaluation of Coating Adhesion Strength with Basic Material

One of the most reliable ways of determining adhesion of a coating with basic material is scratching of coating surface with Rockwell type diamond indenter under continuously increasing load.

The investigation of coating adhesion properties on a micro-level and nano-level was carried out with the help of a scratch tester CSM Revetest (CSM Instruments) (normal force range - 0.5...200 N; maximum friction force - 200 N; maximum scratch length - 70 mm; resolution by depth - 1.5 nm) through the testing of samples and products by scratching. The

installation is intended for determining adhesion strength, scratch resistance and coating destruction mechanism.

The indenter (diamond or tungsten carbide) (see fig. 3.6) in automatic mode is moved along the surface of a sample by applying constant, stepwise increasing or progressive normal load F_N . In order to determine the adhesion strength of a coating, the load is increased linearly, in a specified range.

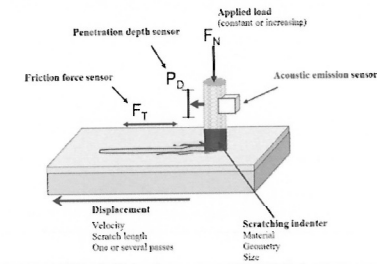


Fig. 3.6. Schematic diagram of operation of CSM Revetest Xpress installation intended for testing adhesion strength of coatings

During the tests, the recording of different physical parameters depending on the applied load and scratch length is carried out. The moment of coating adhesion or cohesion destruction is fixed after the tests, either visually with the help of an optical microscope equipped with a digital camera or on the basis of a change of one of the five parameters:

- acoustic emission,
- friction force F_T ,
- friction coefficient,
- indenter penetration depth.

A coating will start to destroy under certain critical load. The moment when the critical load is reached is very precisely fixed on the basis of results of recording acoustic emission signals (AE). AE signals were recorded with the help of a portable acoustic emission device (Vallen Systeme GmbH) built in the scratch tester, which makes it possible to record acoustic emission parameters. The range of AE channel frequencies is from 100 KHz to 1 MHz. For the multiplication of initial signal a preamplifier with constant amplification of 26 dB in frequency range from 100 KHz to 1 MHz was used. AE sensor SE 150-M (Dunegan Engineering Company) is structurally built in the loading device. During the experiments, the amplitude of AE signals was recorded.

As a result of tests, minimum (critical) load (F_{Nc}) leading to the destruction of a coating can be determined. The given method complies with the international standard ISO 20502.

3.7. Investigation of Hardness and Elastic Properties of Multilayer Coating Material by Nano-indentation

The method of nano-indentation (NI) makes it possible to evaluate different physico-mechanical properties of materials and coatings on a nano-level: hardness H , modulus of material elasticity E (Young's modulus), etc.

Nano-hardness testers use a method for measuring hardness of thin coatings, which is based on continuous recording of load and hardness indentation depth.

The investigation of hardness and elasticity modulus of multilayer coating material was carried out with the help of a Nano-hardness Tester (NHT) or nano-indenter (CSM Instruments) (normal force range - 0.1...500 mN; resolution by load - 0.04 μ N; maximum depth - 200 μ m; resolution by depth - 0.04 nm) in accordance with the standard ISO14577 and ASTM E 2546-07.

The device operates according to the following principle: the indenter, which is perpendicular to the surface of a sample, is embedded into the sample by applying increasing load up to the prespecified value. Then the load is gradually decreased up to the complete or partial relaxation of the material.

The nano-hardness tester NHT is equipped with a modified Berkovich indenter in the shape of a regular triangular pyramid with a base in the form of an equilateral triangle.

The measurements were carried out in the mode of continuous indentation, while hardness calculation was carried out by the Oliver-Pharr method.

The force of indenter loading was measured in the range 0.5...20 mN, while the loading-unloading velocity was respectively measured in the range 1...40 mN/min.

4. EXPERIMENTAL INVESTIGATION AND OPTIMIZATION OF TECHNOLOGICAL PROCESSES FOR DEPOSITION OF WEAR-RESISTANT VACUUM ION-PLASMA COATINGS

4.1. Investigation of Technological Process for Deposition of Ion-plasma Coatings on Samples and Products Made of Constructional Materials Using the Method of Condensation and Ion "bombardment"

One of the most prospective methods of creating nanostructured ion-plasma coatings in vacuum is the *method of condensation of a substance with ion "bombardment"* (KJB), which relates to the category of methods of Physical Vapor Deposition (PVD).

The KJB process can be represented as two sequentially occurring processes:

- ion "bombardment" of the surface of a part being processed;
- sedimentation of a coating.

In order to sputter fine metals and their alloys, argon is fed into the chamber for obtaining, for example, nitrides, carbides – a reaction gas (nitrogen, methane, etc.). Thus, fine titanium in the form of atoms and liquid drops deposits on parts in argon environment with titanium evaporator. When nitrogen gets into the chamber, a plasma chemical reaction occurs. It results in the formation of titanium nitride compounds that form a coating.

Experimental samples, i.e. steel plates (100x30x1.5 mm) and a precision pair (PP) of hydro fuel plunger, which is a part of high-pressure pump of a diesel engine, were used as an object of research. The precision pair consists of an internal element called plunger and an external element called sleeve (Fig. 4.1.).

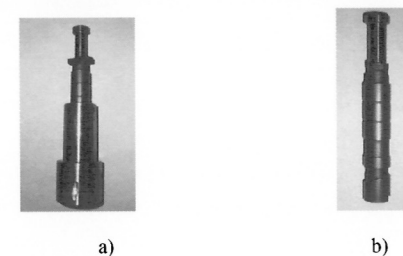


Fig. 4.1. Precision pair (a) of hydro fuel plunger, which is a part of high-pressure pump of a diesel engine, and plunger (b)

Firstly, the samples being tested were deposited multicomponent protective coatings using the following sputtering modes:

- *reference voltage* – $U_{\text{pam}} = 120 \text{ V}$,
- *current strength* on cathode-evaporator – $I_{\text{iziv}} = 110 \text{ A}$
- *vacuum level* in the sputtering chamber was not less than $1.33 \times 10^{-1} \text{ Pa}$

The relation of working gases from the point of view of volume (nitrogen N_2 to argon Ar) was varied for separate groups of samples and included the following variants: 1:1, 2:1, 3:1 etc. up to 12:1.

One of the most essential drawbacks of the method is the presence of a "drop phase".

As it can be seen from Fig. 4.2., the coating contains "drop phase" particles of different sizes as well as some craters.

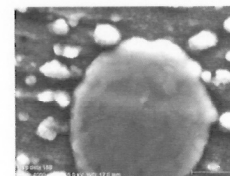


Fig. 4.2. Surface microtopography of the coating obtained by the KJB method

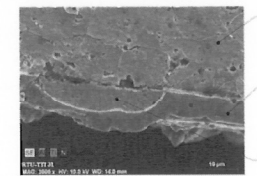


Fig. 4.3. Structure of the material of coated sample and results of microx-ray-spectral analysis of its chemical composition: 1 – basic material; 2 – coating; 3 – coating defect (formation of "drop phase")

In some cases large-size particles of "drop phase" appeared to be "imprinted" through the whole thickness of the coating (see Fig. 4.3).

The comparative analysis of "drop phase" sizes showed that generally (25%) the sizes of drops (reduced diameter) are within the range of 1...1.5 μ m, for a substantial part of drops (17%) they are within the range of 1.5...2.5 μ m. The maximum size of drops detected in the coating was 16...18 μ m. Their relative number did not exceed 2%.

It was determined that the height of separate "drop phase" peaks in the coatings obtained by the KJB method reached 15.4 μ m (see Fig. 4.4.) with mean value of roughness

parameters $S_a=0.778 \mu\text{m}$ and $R_a=0.688 \mu\text{m}$. In addition, the average thickness of the coatings was equal to $15.0 \mu\text{m}$.

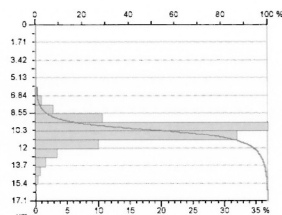


Fig. 4.4. Coating surface support curve and a histogram of peaks distribution (KJB method)

4.2. Optimization of the Technological Process for Depositing Wear Resistant Nanostructured Multi-component Ion-plasma Coatings by the Combined Method

In order to eliminate the drawbacks of the KJB method, the magnetron ion sputtering (MS) method was additionally applied in experimental research.

Magnetron sputtering helps to create practically any kind of coating for metals and alloys. Depending on the composition of working environment, it is possible to create coatings of oxides, nitrides, carbides and sulfides of different materials including coatings that cannot be obtained by using thermal evaporation method.

In the case of combined sputtering, device “NNV-6.6-11” was equipped with two end arc evaporators with cone-shaped cathodes 2 (Ti un Al) and a magnetron sputtering cathode (Al).

One of the multicomponent nanostructured two-layer coatings obtained by the combined method is presented in Fig. 4.5.

It is seen from the figures that the influence of drop phase on the process of coating formation was substantially reduced (sporadic drops of much smaller size were observed), and the coating structure is homogeneous.

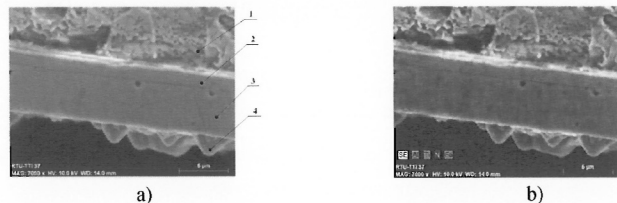


Fig. 4.5. Structure of two-layer coating material of the product (a) and results of microxentgen-spectral analysis of the chemical composition of material (b): 1 – basic material; 2 – internal layer of the coating; 3 – external layer of the coating; 4 – “drop phase”

The total thickness of the coating obtained by the KJONMOBU method changed within the range of $5...15 \mu\text{m}$. The application of the combined method resulted in a substantial (4 times) decrease of coating roughness.

It was stated that in coatings obtained by the combined method, the height of separate “drop phase” peaks reached only $2.25 \mu\text{m}$ with the average value of roughness parameters $S_a=0.154 \mu\text{m}$ and $R_a=0.062 \mu\text{m}$ (see Fig. 4.6.- 4.7.).

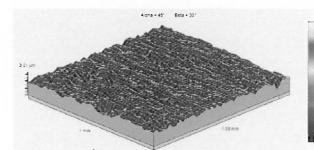


Fig. 4.6. Coating surface roughness (KJONBOMU method)

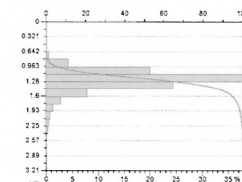


Fig. 4.7. Coating surface support curve and a histogram of peaks distribution

Alloying of a coating with aluminium (up to 4...5% of the composition) leads to the formation of nanocomposite structure with crystalline phase TiN base grain sizes $15...20 \text{ nm}$.

Table 4.1, as well as Figure 4.8, present the results of microxentgen-spectral analysis of the chemical composition of two-layer coating material.

Chemical composition of the coating surface

Table 4.1

El	AN	Series	unn. [wt.-%]	norm. [wt.-%]	Atom. [at.-%]	Error [%]
N	7	K-series	35.15	35.66	65.29	2.3
Al	13	K-series	0.69	0.59	0.56	0.1
Ti	22	K-series	64.16	63.76	34.15	2.8
Total:			100.00	100.00	100.00	

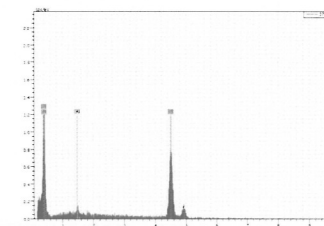


Fig. 4.8. Chemical composition spectrum of the coating surface

4.3. The technology of Creating Ion-plasma Wear-resistant Multi-component Coatings for the Protection and Restoration of Precision Pair Parts of Vehicle Power Units

The technology is intended for creating coatings that help to restore the required size and protect the surface; the coatings are deposited by the method of ion-plasma sputtering and differ by improved service properties (high hardness, increased wear resistance, reduced friction coefficient).

The investigated PP was used in rather complex operating conditions. The permissible radial coupling joint of the PP does not exceed $2 \mu m$.

The proposed technology for creating multilayer wear-resistant coatings for precision pair parts made of stainless steel virtually imply the creation of protective coatings with the help of the combined sputtering method (KJONBOMU).

The peculiarity of the technology lies in the fact that in the process of repair a two-layer coating on the basis of nitrides, oxides, metal carbides and other elements or conglomerates is sputtered on the internal construct of a precision pair. The internal coating layer of variable thickness with the microhardness of up to 10000 MPa is deposited to restore the size of a part. The external protective layer with microhardness above 10000 MPa possesses increased wear resistance.

This technology provides higher quality coatings with considerably higher nanohardness, microhardness and adhesion as well as lower roughness and friction coefficient.

In accordance with the proposed method the technological cycle of precision pair repair includes the following *basic stages*:

1. Measurement of a part, which is going to be restored;
2. Determining the required size of surface layer to be sputtered;
3. Ion-plasma sputtering of the first "size restoring" layer;
4. Ion-plasma sputtering of the second (external) layer with increased wear resistance;
5. Processing of the part after sputtering;
6. Plunger pair lapping;
7. Check measurements of the restored part.

In order to check the thickness and hardness of the layer sputtered on the restored part, there was made a microsection, the microstructure of which is shown in Fig. 4.11.

Thus, as a result of implementation of the technological process, which forms the basis of the proposed technology, it is possible to ensure the accuracy of the required joint and improve the operating parameters. Moreover, there is no need to perform a selective matching of associated parts.

The developed technology is peculiar due to its novelty, which is confirmed by the awarded patent. It provides the opportunity to obtain coatings of low thickness with unique anti-friction properties and high adhesion with the base.

5. EVALUATION OF PHYSICO-MECHANICAL PROPERTIES AND QUALITY CONTROL OF WEAR-RESISTANT NANOSTRUCTURED COATINGS

5.1. Ensuring the Uniformity of Measurements of Physico-mechanical and Tribological Properties of Nanostructured Surfaces

The considered experimental methods of evaluating physico-mechanical and tribological properties of nanostructured coatings are based on the analytical solution of so-

called Hertz problem regarding the mutual deformation of two solid balls during their compression.

The use of Hertz model for the description of interaction between an indenter and a sample is considered correct only in the case when surface forces are negligible in comparison with total forces of interaction and the radius of contact area is considerably less than the radius of indenter.

5.2. Experimental Evaluation of Adhesion Strength of Wear-resistant Nanostructured Ion-plasma Coatings

Evaluation of adhesion strength, resistance to scratching as well as investigation of failure mechanism of wear-resistant coatings was carried out with the help of a scratch tester CSM Revetest Xpress. Scratches on the coating surface were made with a diamond spherical indenter of "Rockwell S" type with the rounding radius of $200 \mu m$ under a continuously increasing load. During the tests, the recording of such physical parameters as acoustic emission, friction coefficient, indenter penetration depth, normal load rate F_N , and friction force F_f was carried out.

Experimental samples and finished products, i.e. plungers of precision pairs with coatings deposited on them, were used as research objects.

The test mode for coated plungers complied with the following conditions: load on indenter F_N was increased linearly in the range from 0.3 to 80 N, loading rate was 3.0 N/s, rate of indenter moving was 6 mm/min, scratch length was 3 mm.

The results of coating deformation with a diamond indenter were additionally investigated with the help of a built-in optical microscope and a scanning electron microscope SEM HITACHI – S3000N equipped with Bruker Quantax integrated system for microanalysis.

The obtained results (see Fig. 5.1. and 5.2.) gave the opportunity to analyse the failure mechanism and evaluate the adhesion strength of coatings created by the KJONBOMU method.

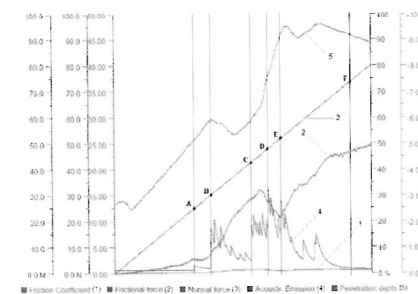


Fig. 5.1. Results of adhesion tests of the system «coating (TiAlN) - plunger (stainless steel)»: 1 – friction coefficient μv ; 2 – friction forces F_f ; 3 – normal load F_N ; 4 – amplitude of acoustic emission signals AAE ; 5 – indenter penetration depth h

The comparative analysis of experimental investigation data showed that the most informative parameter for the evaluation of failure mechanism and adhesion strength of

coatings is the parameter of AE signals amplitude A_{AE} (see Fig. 5.1.). At the same time the behaviour of friction coefficient μ_v and friction force F_f is comparable with changes of parameter A_{AE} .

The values of loads that correspond to certain stages of coatings damage were determined on the basis of results of AE measurements. For the considered example, the minimum (critical) load F_{Nc1} equal to 25.02 N corresponds to the first peak of AE amplitude and is the evidence of first damages on the microlevel in the system "coating-plunger" (point A Fig. 5.1., 5.2.). Along with the substantial increase of parameter A_{AE} when reaching F_{Nc1} the increase of parameters μ_v and F_f is observed as well (see Fig. 5.1.), which increases the reliability of conclusions about the appearance of first damages in coating material. The comparative analysis of structural peculiarities of the scratch gives the opportunity to conclude that on the initial stage of loading (load less than 25.02 N) the indenter practically does not leave any marks on the coating (see Fig. 5.2a.). The diamond indenter slides across the coating with a very low coefficient of friction (less than 0.1).

Further increase of load leads to the formation of multiple chips on the coating, which is reflected in AE amplitude curve (with the load of $F_{Nc2} = 30.05$ N) (point B Fig. 5.1., Fig. 5.2b.). Load $F_{Nc3} = 42.63$ N corresponds to the point when multiple flaking of some areas of the coating begins (point C Fig 5.1., Fig. 5.2c.), which then is followed by the process of mass flaking with the load of $F_{Nc4} = 47.32$ N (point D Fig. 5.1., Fig. 5.2.d.). The formation of this type of damage entails the growth of AE signal amplitude as well as the monotonous increase of parameters μ_v (up to 0.2) and F_f . The appearance of multiple chips on the coating is followed by sharp bursts of curve μ_v and F_f upwards, while curve h goes downwards (see Fig. 5.1.).

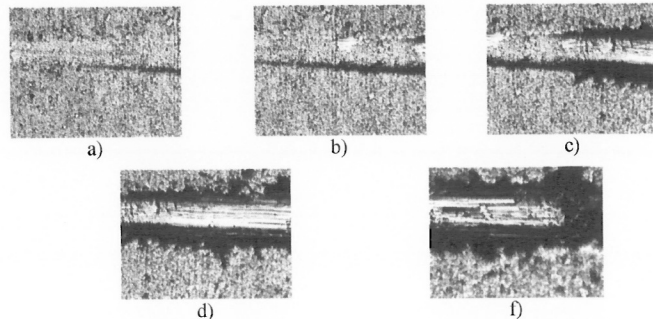


Fig. 5.2. Photos of plunger coating scratches during observation through the optical microscope for the following indenter loads: a) 25.02 N; b) 30.05 N; c) 42.63 N; d) 47.32 N; e) 73.68 N

The appearance of substrate material on the bottom of the scratch under high loads $F_N = 40...50$ N indicates in its turn at the high adhesion strength of the coating.

The following stage (point E Fig. 2.) with the load of $F_{Nc4} = 52.51$ N corresponds to the transition of the coating destruction process to the subsequent plastic deformation (wear) of substrate material (plunger). On the last stage of indenter travel across the surface of the object being tested with the load of $F_{Nc5} = 73.68$ N a mass concentration of destruction fragments that represent a conglomerate of coating and substrate materials is observed (point F Fig. 5.1., Fig. 5.2.f.). This circumstance is an indicative of the fact that during scratching

coatings wear off and separate together with the basic material of a product, i.e. the destruction occurs by a cohesive mechanism, which is related to plastic deformation and formation of cracks in coating material.

Thus, the coating adhesion strength for the considered example is $F_{Nc1} = 25.02$ N.

On the basis of the obtained experimental data for a rather large sampling (59 measurements for 7 samples and 40 measurements for 5 products), the mean value of critical load F_{Nc1} is 25.15N. The received value of adhesion strength of the created nanostructured wear-resistant coatings considerably (4...5 times) exceeds the known data for coatings of such type.

5.3. Results of Investigation of Hardness and Elastic Properties of Multilayer Coatings by Nano-indentation

The characteristics obtained during nano-indentation are used for the evaluation of wear resistance of ion-plasma coatings. During nano-indentation, one of the basic characteristics of material is the relation of its hardness H to the modulus of elasticity (Young's modulus) $E - H/E$. Value H/E characterizes the ability of material to change its size and form in the process of deformation and can become a characteristic of its resistance to deformation during mechanical loading, i.e. this value reflects its structural condition. Value H/E is also used to characterize the ability of material to wear during friction.

Another quantitative comparative characteristic of resistance to plastic deformation is relation H^3/Er^2 where is E_r a modified (effective) modulus of elasticity in the contact "indenter - product coating". Usually this relation is 0.15 ... 1.52 GPa. In order to increase the deformation resistance, it is necessary to tend to the minimum possible Young's modulus provided that the hardness is high.

Investigation of hardness and elastic properties of coatings with the help of nano-indenter Nanoindentation - Hardness Tester.

In order to perform nano-indentation, this work involved the use of a trapezoidal profile of normal force change (Fig. 5.3.) consisting of segments of linear growth of the load with a desired constant velocity dP/dt , exposure with the maximum value of force P_{max} and subsequent unloading.

The investigation of two types of nanostructured coatings was carried out. Coatings of the first type were deposited on steel samples 3 by the KJB method; coatings of the second type were deposited on plungers made of stainless steel 12H18 by using the combined method (KJONBOMU).

The tests were carried out under the following loading conditions (Fig. 5.3.): maximum force of indentation $P_{max} = 20$ mN; exposure with maximum value of force $P_{max} - 10$ s; loading/unloading rate - 40 mN/min; total duration of the loading cycle - not more than 100 s. In the process of loading, loading and unloading diagrams were recorded in coordinates " $P-h$ ". A series of five measurements with the desired loading conditions was carried out for each sample. The results of nano-indentation on the example of the two-layer coating of one of the plungers are presented in Fig. 5.3. and 5.4.

The accuracy of determining load P was ± 1 mN, the depth of indentation was ± 2.5 nm.

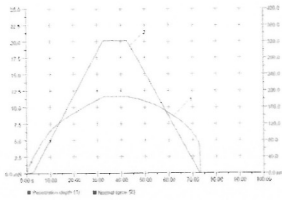


Fig. 5.3. The results of nano-indentation of the plunger coating: 1 – time curve of indentation depth h ; 2 – time curve of normal force P

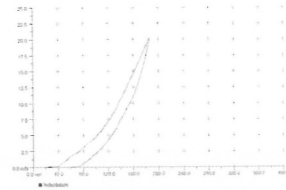


Fig. 5.4 Experimental diagram of nano-indentation (connection between normal force P , mN and indentation depth h , nm) of the plunger coating

Hardness H of the coatings was determined as the relation of currently applied force P to unrecovered indentation area A_c

$$H = P / A_c \quad (5.1)$$

Value A_c was calculated on the basis of the data on contact depth h_c of unrecovered indentation.

Parameter h_c was determined according to the Oliver-Pharr method (OPM) from the relation:

$$h_c = h_{\max} - \varepsilon_c P_{\max} / S \quad (5.2)$$

where $S = dP/dh$ - contact rigidity in system «indenter - sample» on the initial section of unloading branch (see Fig.5.5.); ε_c - a coefficient that depends on indenter geometry. In accordance with ISO14577, for Berkovich indenter, it is recommended to accept $\varepsilon_c = 0.75$.

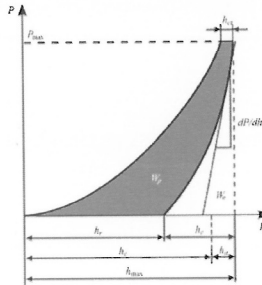


Fig. 5.5. Diagram of loading according to the Oliver-Pharr method: h_r – depth of residual indentation; h_e – elastic restitution; h_c – contact depth of unrecovered indentation; h_a – elastic deflection of sample surface; h_{\max} – maximum indentation depth under maximum load P_{\max} ; h_{cr} – creep with $P = \text{const}$; W_e – elastic work of deformation, W_p – plastic work of deformation with indentation deformation

Young's modulus E of the material being tested can be found from the following expression:

$$S = \beta \frac{2}{\sqrt{\pi}} E_r \sqrt{A_c} \quad (5.3)$$

where coefficient β is recommended to be used as $\beta = 1.05$ if there is no preliminary information.

Thus, in order to determine the modified (effective) modulus of elasticity in the contact «indenter – product coating» E_r , it is necessary to preliminarily determine the experimental values of S and A_c .

The modified modulus of elasticity E_r is related to the elastic constants of the investigated material and the indenter by the following expression:

$$\frac{1}{E_r} = \frac{1-\nu^2}{E} + \frac{1-\nu_i^2}{E_i} \quad (5.4)$$

where E and E_i are Young's modules, ν and ν_i are Poisson's ratios of the investigated material and the indenter respectively. For diamond indenter $E_i = 1141 \text{ GPa}$, $\nu_i = 0.07$.

From the expression (5.4) on the basis of the known values E_r and E_i , it is possible to determine the modulus of elasticity E of coating material.

The values of characteristics h_{\max} , h_c , h_r , S , A_c , H , E , E_r were determined in accordance with the above described methodology and calculated automatically.

For the coatings obtained by the KJB method, the values of the investigated parameters were as follows: nano-hardness $H = 25 \dots 27 \text{ GPa}$ with modulus of elasticity $E = 320 \dots 328 \text{ GPa}$. The average value of relation H/E was 0.08, while H^3/Er^2 was 0.167 GPa.

For the plungers with coatings created by the combined method, the values of hardness were 37... 41 GPa with modulus of elasticity 440...475 GPa. The average value of the relation H/E was 0.085, while H^3/Er^2 was 0.283 GPa. The range of received values of parameters H/E and H^3/Er^2 confirms the presence of nanostructure of the coating and is an indicative of its high wear resistance and ability to resist plastic deformation.

The application of the combined method of depositing ion-plasma coatings provided the opportunity to substantially increase their hardness from 27 to 41 GPa, while modified modulus of elasticity changed from 328 to 475 GPa, and thus the relation H^3/Er^2 increased from 0.167 to 0.283. This is the evidence of a significant increase in wear resistance.

5.4. Experimental Investigation of Tribotechnical Properties of Nanostructured Protective Coatings

During the experimental investigation of tribotechnical properties of coatings, the assessment of influence of such parameters as coating roughness and correlation of working gases in a sputtering chamber on the friction coefficient was performed.

On the basis of the received experimental data, it was possible to build friction coefficient curves from the value of roughness of a wear-resistant coating and from the correlation of gases N_2/Ar in a vacuum chamber for sputtering. For a series of experiments, the sample volume (number of tested samples) in each lot was 8...10 samples.

In Fig. 5.6., the results of experimental data received for different variants of friction pairs are presented: 1 – for friction pair «coated sample – coated counter sample» without preliminary polishing; 2 – for friction pair «coated sample – counter sample without coating» without preliminary polishing; 3 – for friction pair «coated sample – coated counter sample» with preliminary polishing. All listed dependences characterize the properties of coatings obtained by the KJB method. The dependence 4 (see Fig. 5.6 b.) characterizes the properties of coatings obtained by the combined method (KJONBOMU) for the friction pair «coated sample – coated counter sample» without preliminary polishing.

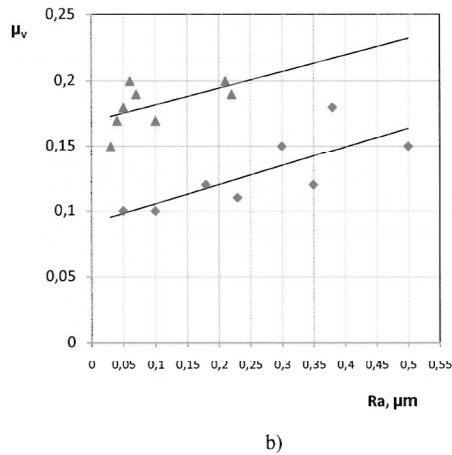
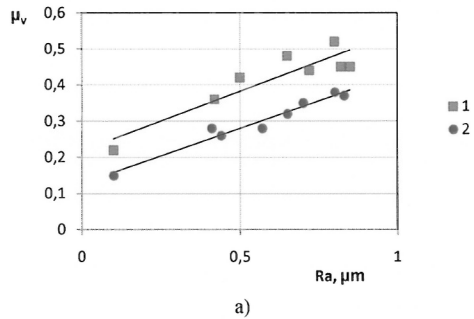


Fig. 5.6. Dependence of the coefficient of static friction on the roughness of a nanostructured coating

The obtained experimental dependences make it possible to conclude that coating roughness has substantial influence on friction coefficient.

Thus, along with the reduction of the mean value of coating roughness (R_a) from 0.607 μm (the coating obtained by the KJB method) to 0.097 μm (the coating obtained by the KJONBOMU method), friction coefficient substantially decreased (from 0.417 to 0.181).

The work also includes an investigation of the influence of composition of reaction gases (N_2 and Ar) on the quality of coatings, in particular, on the degree of their roughness. The results of experimental data are presented in Fig. 5.7. It is obvious that an increase in nitrogen concentration in a gas mixture leads to a substantial reduction of roughness. Thus, more than two-fold reduction in coating roughness, i.e. from 0.35 to 0.13 μm can be achieved by increasing the concentration of nitrogen in a gas mixture from 2 to 10.

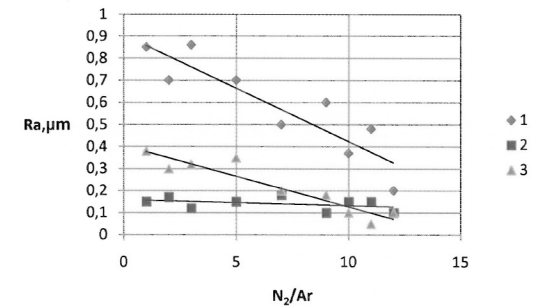


Fig. 5.7. Dependence of coating roughness on the correlation of gases in a vacuum chamber

Subsequent mechanical polishing of the surface of coated part leads to the achievement of optimum roughness. At the same time the influence of gas mixture composition is not observed in the whole range of parameter change (dependence 2, Fig. 5.7.). The mean value of roughness parameter R_a is 0.15 μm .

The obtained regularities of changes in tribotechnical properties of wear-resistant protective coatings have practical importance. Adjustment of technological parameters gives the opportunity to obtain wear-resistant nanostructured coatings with high anti-friction properties that can be used for restoration and strengthening of parts.

Margarita URBALLA

**CREATION OF NANOSTRUCTURED WEAR RESISTANT ION-PLASMA
COATINGS FOR RESTORATION AND PROTECTION OF MACHINE PARTS**

Summary of Doctoral Thesis
