New technology, properties and application of nanostructured antifriction electrochemical coatings

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Abstract. The presented paper describes a new technology of nanostructured electrochemical silver- diamond coatings. Results of a development of methods and engineering solution for an application and quality control of antifriction silver coatings are presented. Results of a study of mechanical and tribotechnical properties of coatings are discussed. Results of an implementation and effectiveness evaluation of the developed technology of antifriction silver-diamond coatings' application on frictional units are presented.
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Introduction

Quality of surfaces on a contemporary stage of scientific and technical development provides main properties of reliability, technical perfection and competitiveness of technology, energy and transport related machines during their design, production, and operation [1]. In the world practice required quality indicators of working faces of machines' parts are ensured more and more by an application of functional coatings [2]. The most critical parts high-quality machines and equipment, which are imported to Russia, are almost always have (antiwear, antifriction, protective and decorative, etc.) coatings and that becomes design-engineering routine, a sign technical literacy and a production standard, because special coatings provide an increase of operating characteristics without significant financial expenses [3]. An application technology of service life increasing coatings is especially important in a production of friction units' parts, which failures are the main cause of operating capacity loss of the majority of mechanical systems [4].

Among various types of functional coatings, the most widespread are antifriction and wearresistant coatings, which are designed for strengthening, durability improvement, friction reduction and rework of friction units' parts and mechanisms. To date, with a development of advanced technology, new, mainly physical methods became widely spread [5]. However, so far more than 80% of technologies, which allow to obtain surfaces of high class, are based on "classic" methods. The most promising among them is electroplating [6]. Its advantages are high quality of coatings, an opportunity to obtain platings of varying structure and thickness on metallic and non-metallic products, a deposition of coatings with a wide range of properties, an obtainment of metal alloys of varying composition and phase composition without use of high temperatures, a development of new types of coatings and so on.

Silver coatings remain the most widely used among antifriction and antiscuff coatings in modern industry [7]. In addition, chrome based coatings are used as strengthening coating for parts operating in abrasive environments with high loads.

Uniqueness of silver as antifriction material is related with its properties [8]. Silver is highly chemical resistant and dissolves only in concentrated nitric acid and hot sulfuric acid (with 85 % concentration). In a context of corrosion resistance, silver practically rated as noble metal, i.e., those metals that don't oxidize on air. At normal pressure with room and high temperatures oxygen does not affect silver and only in a case of pressure of 1.5 MPa and 300 ^{0}C temperature oxidization of metal occurs. Dry friction coefficient of silver coatings on steel is 0.14-0.19. Silver is a good antifriction material in atmosphere, vacuum, inert medias, oils, which do not contain significant quantities of sulfur, some aggressive medias [9].

In order to increase hardness, durability and resistance to fogging of silver coatings, electrical deposition of silver based alloys is used. Alloying of silver by other metals in the most cases does not result in an increase of tribotechnical, electrical and protective properties in complex [10]. For covering of silver alloys, generally, cyanic electrolytes are implemented, electrolytes, which are mixed and based on other complex silver compounds and alloying metals are used rarely, because of their instability.

One of promising ways of high-performance protective coatings' creation is a co-deposition ultradispersed diamonds (UDD) with metals during their chemical or electrochemical reduction from aqueous solutions. Used SDD are particles which shape is close to spherical or oblong. Nowadays, they are increasingly defined as "nanodiamonds". Each particle of nanodiamond is composed of a variety of individual diamond crystals with size of 5...7 nm (fig.1). Those particles may form stable, in contexts of sedimentation and coagulation, systems in electorlytes. At that, UDD possess properties, which combine properties of one of the hardest substances in nature with chemically active shell in a form of functional groups, that are capable to participate in chemical and electrochemical processes [11, 12].

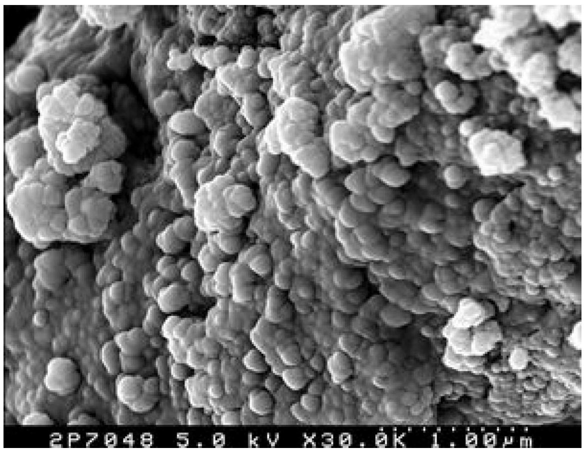
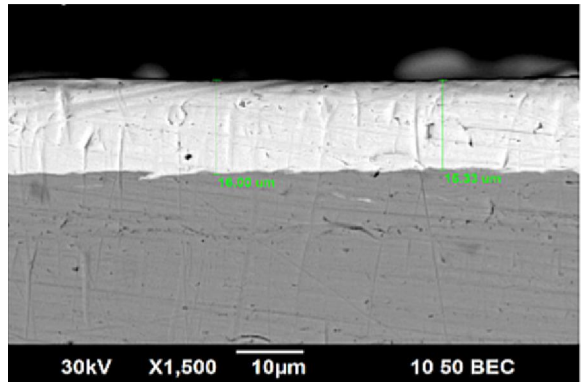


Fig.1. Ultradispersed diamonds in the water suspension

In a laboratory of nanostructured coatings of Samara State Technical University (SamSTU) a technology is developed for strengthening of silver antifriction coatings' on friction units' parts with an implementation of cluster materials in electrolytes, that doesn't contain cyanide.

Coating application technology is based on a method, which comprises a change of metal deposition mechanism, in particular, silver, through an introduction of colloid particles of cluster (ultradispersed) nanodiamond in electrolyte. Cluster materials (nanodiamonds) substantially alter a process of galvanic depostion of metals, which, in turn, modifies a structure of wear-resistant coating. As a consequence, adhesion of silver considerably improves and full reproduction of deposited surface microrelief is achieved, which seriously increases ultimate stresses of shearing and normal tear of galvanic surface from basis [13]. An obtainment of silver-diamond coatings is based on an ability of nanodiamonds with 4-6 nm size to codeposit with metals during their electrochemical and chemical reduction from aqueous solutions of their salts. That leads to a formation of biphasic composite electrochemical coating, consisting of a metal matrix and embedded dispersed particles of nanodiamonds.

Scanning electron microscopy of silver-diamond coatings demonstrated (fig.2), that obtained plating possesses uniform and continuous (nonporous) structure. Coating color is white semi glittering or matte. Matt of coating is related with an emerge of deposited silver crystals with 1 micron size on a surface. Obtained coating has uniform thickness. Average thickness of antifriction coatings is 10...20 micron [14].



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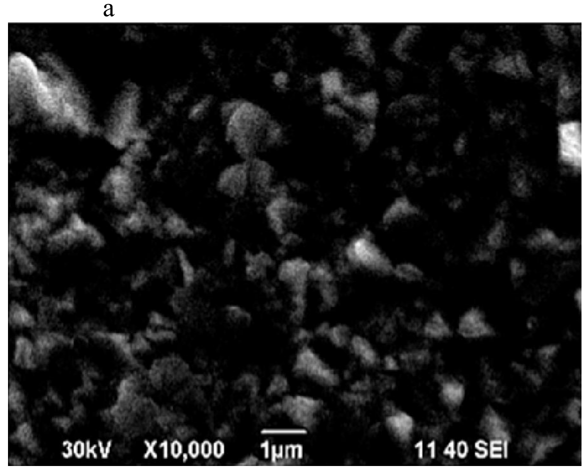

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Fig.2. Structure of silver-diamond coating: a) transverse section; (b) surface

For a formation of galvanic coatings non-standard modes of an application are widely used. The results of conducted studies shown that one of the most effective technological solutions is use of asymmetric alternating current. In the laboratory of nanostructured coatings of SamSTU automated galvanic device was developed, for an application of electrochemical coatings using asymmetric alternating current, which allows to produce coatings with a positive gradient of mechanical properties (fig.3).

The device, which is developed on a basis of programmable controller with a built-in microprocessor, allows to automatically control electrolysis using specified program with a feature, that allow to freely select type of current (direct, alternating, impulse, asymmetric, etc.), provide a selection of value and duration of pulses direct and reverse currents, a pause between them, positive or negative offset of permanent part of current, stabilization of current and voltage. A distinctive feature of the equipment is an ability to generate pulses with varying steepness of pulse edge and varying frequency of asymmetric AC with adjustable asymmetry coefficient. Main technical characteristics are preseneted in table 1 [15].

Table 1. Main technical characteristics of galvanic device

Maximum load current, A	50
Accuracy of specified load current, A	0.1
Duration of current pulse, s	1-0.005
Duration of a single cycle of the program	Not limited
Number of possible cycles in the program	10
Power from network 50 Hz with voltage, V	220
Dimensions, mm	200×500×250

Programming of galvanic device is possible both from a control console and directly from a computer. The program keeps a record of generated diagrams of current parameters of electrolysis (current and voltage at output of a source, voltage on electrodes in a galvanic bath, electrolyte temperature, specific conductivity of electrolyte) throughout a process of coating application.

In a process of coating application a pre-programed sequence of technological regimes of coatings' deposition is conducted, in which each subsequent regime generates coating with less hardness. That allows to obtain a favorable positive gradient of mechanical properties in coatings, which are designed to improve service life of friction units of machines. The device allows to produce high-quality coatings on parts of machines with a possibility for an optimization and saving of selected sequences of technological regimes for an application of coatings on sets of parts of various configurations.

A study of a formation of nanostructured silver-diamond coatings demonstrated, that use of asymmetric AC provides an ability to control properties of coatings in a wide range by selecting a ratio of anode and cathode currents (from 1/1.2 to 1/10) and current density (up to 1.5 A/dm^2). A disperse phase's content in deposited metal is from 0.03 up to 1.0 mass %. Nanodiamond particles have a negative surface charge, and because they possess a strong adsorption capacity, they partially bound silver ions, which improves cathode polarization.

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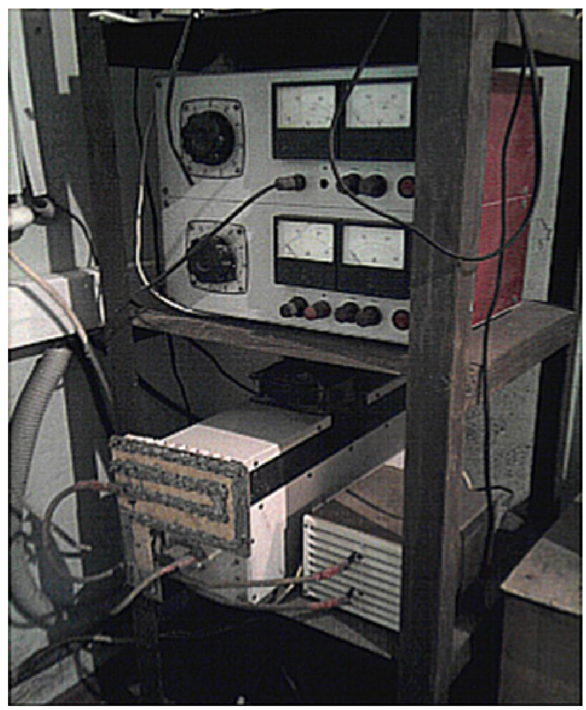

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Fig.3. Automated galvanic device for an application of electrochemical coatings with use of asymmetric alternating current: a) control unit b) current source.

Studies of an influence of parameters of asymmetric FC (density, frequency and current asymmetry coefficient) on quality of coatings shown, that with an increase in current density a proportional increase in speed of coatings deposition takes place and a certain increase in size of grains and a decrease of deposited coating's hardness. A possibility of qualitative silver plating with use of cianide free electrolyte with asymmetric alternating current and speed of deposition up to 1 micron/min with an increase of current density to 11 A/dm^2 is demonstrated.

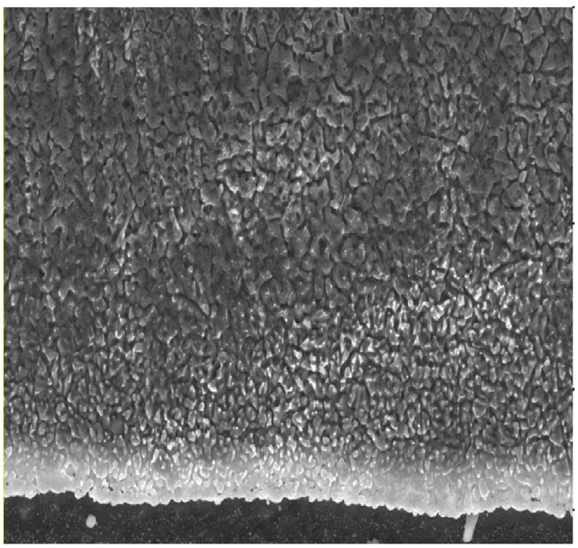


Fig.4. Structure of gradient silver-diamond coating on angled thin section (×5000)

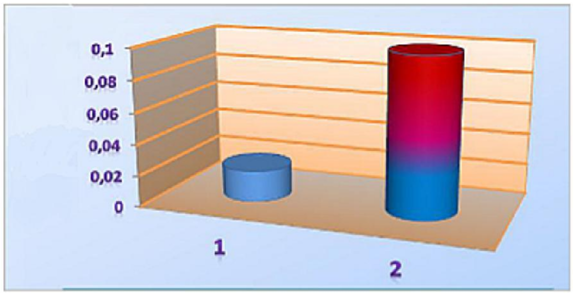
Such an influence on properties of silver coating is provided by current asymmetry coefficient. That allows to apply coatings with higher current density and with a possibility to control hardness through a change of asymmetry coefficient in a range k =(1.2...8). That allowed to create coating with a positive gradient of mechanical properties (fig.4), which provides, according with studies of I.V. Cragelski [16], increased antiscuff resistance. An improvement of strength characteristics of coatings, which are applied with asymmetric alternating current, is, that after half wave of cathode current (deposition) there is half wave of anode current (dissolution), but, since anode current density is less than cathode current density, only sites with a small energy of adhesion with a basis are becoming dissolved. Thus, hard plating is formed on a surface. An influence of asymmetry coefficient on properties alkali of deposited coating is presented in table 2.

Table 2. An influence of grain size of electrochemical silver-diamond plating on wear resistant properties of coating

Asymmetry coefficient	1.1	1.5	2	8
Grain Size, µm	5…7	7…9	10…12	18…21
Microhardness, kgf/mm^2	115…120	110…115	100…110	100…85
Wear rate, µm/hour	1.7	4.2	6.3	9.88

In order to improve effect related with an influence of asymmetric AC use, it is suggested to specify rational frequency of AC, in which in one half wave of cathode current one atomic layer of coating is applied. In order to assess rational frequency f of asymmetric sinusoidal AC voltage, speed s of coating's deposition is determined with use of direct current with specified current density (micron/min), then frequency is calculated using the equation $f = \frac{s}{d60}$ Hz, where d – distance between two closest atomic layers of deposited material. If frequency speed is be less than rational, defective areas of coating with low energy of adhesion with a basis can become covered with an additional layer of deposited atoms and become protected from dilution during halfwave of anode current, which will lead to an increase of coating's deficiency and a reduction of its strength characteristics. If frequency exceeds rational, during cathode current halfwave time monatomic layer of coating will not be able to form and, consequently, during anodic current halfway time dissolution of defect-free zones is possible, which is unpractical. Studies of microstructure of silver coatings on various frequencies (from 1 to 200 Hz) showed that, in an area of rational frequencies coating has the least defective structure (fig.4). An influence of porosity on properties of deposited coating is presented in table 2.

Laboratory studies of nanostructured silver-diamond coatings shown a possibility of an achievement of hardness of 240 kgf/mm^2 (3 times higher than that of regular coating); durability of new coating exceeds to 2.5 times durability of silver coating, which is obtained with cyanide electrolyte with regular technology. Frictional torque, sell-heating temperature, wear rate for specimens with coatings, deposited using the developed technology are studied (see fig. 5, 6).



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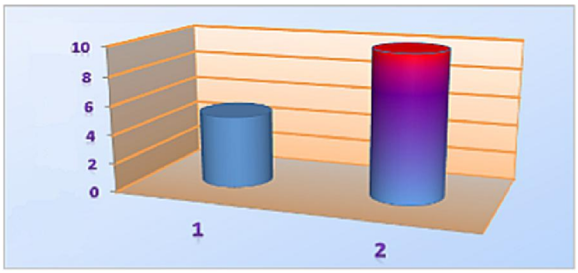

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Fig.5. Results of comparative evaluation of silver coatings: a) friction torque; b) wear rate.

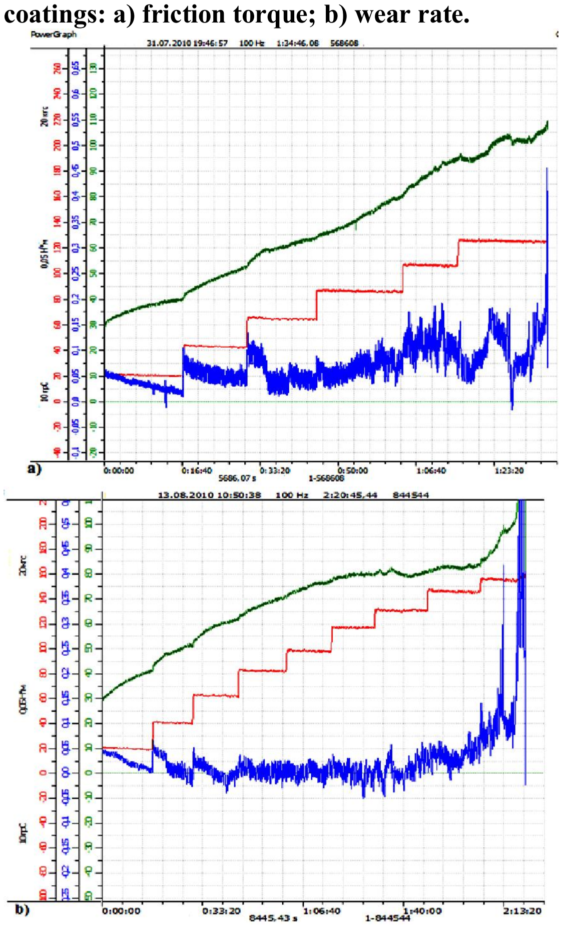

Fig.6. Diagram of comparative tests: a) regular silver coating made with cyanide electrolytes (seizure load 110 kgf); b) nanostructured silver-diamond coating (seizure load 160 kgf).

a

b

Fig.7. Area of application of silver coatings

A comparative analysis of silver coatings properties, which are produced with a new technology, with coatings from alloys "silver-antimony (2%)" and "silver-nickel (5%)", shown that silver-diamond coating with less hardness (60…80 kgf/mm^2) is 1.5...2 times exceeds durability of traditional silver coatings with antimony and has a smaller coefficient of friction. Sclerometric tests shown that developed coatings have higher plasticity reserve – accumulated energy in a case fracture exceeds that for regualr coatings for 53 %. That fact indicates that functional properties of antiscuff antifriction coatings are determined by plasticity, rather than hardness.

The new technology of silver coatings found a wide range of applications: current-carrying parts of electronics and electrotechnical equipment (fig.7a), including microwave equipment, protection of chemical equipment and devices, coatings for rubbing surfaces of slide bearings and rolling bearing in machine-building industry (fig.7b), for decorative purposes in jewelry and light industry.

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