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EXPERIMENTAL RESEARCH OF MULTICOMPONENT MULTILAYER ION-PLASMA AVINIT COATINGS

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Metallographic examination of improved structures of **Avinit** C multilayer nitride-based coatings, particularly coatings of Ti-Al-N system and Mo-N system-based coating have been carried out. Use of effective methods of surface cleaning and three-level arc control system in the techniques under development for prevention of surface damaging, caused by micro arcs, allows to apply coatings of precision and high finish class surfaces up to 12 – 13 grade of finish without deterioration of surface finish class. The experimental findings confirm a possibility of low-temperature deposition of very hard **Avinit** C coatings based on nitrides of metals under the conditions providing good adhesion to the parent material (steel DIN 1.2379 (Х12Ф1) without decrease in strength properties of the steel (<200 °C) and without distortion of the coated surfaces.

Tribological examination of advanced constructions of multicomponent multilayer **Avinit** coatings under aviation fuel TS-1 for the purpose of selection of coating materials for friction parts of precision couples used in aggregate building. Deposition of coatings effectively raises durability of friction pairs to scoring. Advanced coatings have low friction coefficients (0.75 – 0.095) at loadings up to 2.0 kN and have shown high wear resistance.

The received results allow to develop software products for obtaining of multicomponent multilayer coatings of required composition using **Avinit** equipment and tryout stable techniques for deposition of functional coatings to be used in friction parts of precision couples of standard aircraft units.

Keywords: Plasma-vacuum deposited multicomponent multilayer, nanolayer coatings; tribology.

ЭКСПЕРИМЕНТАЛЬНОЕ ИССЛЕДОВАНИЕ МНОГОКОМПОНЕНТНЫХ МНОГОСЛОЙНЫХ ИОННО-ПЛАЗМЕННЫХ ПОКРЫТИЙ AVINIT

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Проведены металлографические исследования улучшенной структуры многослойных, на основе нитридов, покрытий **Avinit** С, в частности, покрытий систем Ti-Al-N и Mo-N. На стадии разработки методов использовались эффективные средства очистки поверхности и трехуровневая система управления дугой для предотвращения повреждения поверхности, вызванного микродугами. Методы позволяют наносить покрытия высокой точности с финишной чистотой поверхности 12 – 13 класса без снижения качества исходной поверхности. Экспериментальные данные подтверждают возможность низкотемпературного осаждения трудно осаждаемых покрытий **Avinit** С на основе нитридов металлов в условиях, обеспечивающих хорошую адгезию к основным материалам (сталь DIN 1.2379 (Х12Ф1)) без снижения прочностных свойств стали (< 200 °С) и без искажений покрытием. Трибологические качества предложенных конструкций многокомпонентных многослойных покрытий **Avinit** под авиационное топливо ТС-1 с целью выбора лакокрасочных материалов для точных трущихся пар деталей машин также рассматриваются в данной работе. Показано, что применение защитных покрытий эффективно повышает долговечность пар трения. Покрытия обладают низким коэффициентом трения (0.075 – 0.095) при нагрузках до 2,0 кН показали высокую износостойкость. Полученные результаты позволяют разрабатывать программные продукты для получения многокомпонентных многослойных покрытий необходимого состава с использованием **Avinit** оборудования и стабильных функциональных покрытий для использования в точных трущихся парах деталей стандартных модулей самолетов.

Ключевые слова: вакуумно-плазменное осаждение многокомпонентных, многослойных, нанослойных покрытий; трибология.

ЕКСПЕРИМЕНТАЛЬНЕ ДОСЛІДЖЕННЯ БАГАТОКОМПОНЕНТНИХ БАГАТОШАРОВИХ ІОННО-ПЛАЗМОВИХ ПОКРИТТІВ AVINIT

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Проведено металографічні дослідження поліпшеної структури багатошарових, на основі нітридів, покриттів **Avinit** С, зокрема, покриттів систем Ti-Al-N і Mo-N. На стадії розробки методів застосовувалися ефективні засоби очищення поверхні і трирівнева система управління дугою для запобігання пошкодження поверхні, викликаного мікродугами. Методи дозволяють наносити покриття високої точності з фінішною чистотою поверхні 12 – 13 класу без зниження якості вихідної поверхні. Експериментальні дані підтверджують можливість низькотемпературного осадження, покриттів **Avinit** С, які важко осаджуються, на основі нітридів металів в умовах, що забезпечують хорошу адгезію до основних матеріалів (сталь DIN 1.2379 (Х12Ф1)) без зниження міцнісних властивостей сталі (< 200 °С) і без спотворень покриттям. Трибологічні якості запропонованих конструкцій багатокомпонентних багатошарових покриттів **Avinit** під авіаційне паливо ТС-1 з метою вибору лакофарбових матеріалів для точних пар тертя деталей машин також розглядаються в даній роботі. Показано, що застосування захисних покриттів ефективно підвищує довговічність пар тертя. Покриття характеризуються низьким коефіцієнтом тертя (0.075 – 0.095) при навантаженнях до 2,0 кН і показали високу зносостійкість. Отримані результати дозволяють розробляти програмні продукти для отримання багатокомпонентних багатошарових покриттів необхідного складу з використанням **Avinit** обладнання і стабільних функціональних покриттів для застосування в точних парах тертя деталей стандартних модулів літаків.

Ключові слова: вакуумно-плазмове осадження багатокомпонентних, багатошарових, ношарових покриттів; трибологія.

INTRODUCTION

Up-to-date research in the field of creating new materials with record characteristics on wear resistance, surface roughness, and possibility to work in extreme conditions are related to the development of nanotechnology, which allows to create multicomponent compositions with structure elements ranging from several hundreds to a few nanometers. Compared with the materials of the same composition and conventional structure, these materials can have several times higher corresponding characteristics of their tribological and other properties. This also applies to coatings, which offer an effective way of increasing the scope of application of certain materials [1 – 7].

The carried out examinations [8, 9] of deposition of functional coatings based on titanium, molybdenum and their compositions with nitrogen using vacuum-plasma deposition methods have demonstrated that multicomponent multilayer coatings exhibit higher wear resistance and tribological characteristics compared to single-layer coatings based on one composition. The experimental & process equipment developed by the authors is presented in papers [10, 11], i.e. – **Avinit** installation intended for deposition of multilayer functional coatings allowing to implement complex methods of deposition of functional coatings (plasma chemical – CVD, plasma vacuum – PVD (vacuum-arc, magnetron), processes of ion saturation, implantation and treatment of surfaces by ions) are united in one technological cycle.

Substantial growth of the range of spectrum sources provided by the integrity of used methods allows obtaining coatings practically from any elements and alloys, refractory oxides, carbides, nitrides, metal-ceramic compositions based on refractory metals and oxides, which largely expands possibilities of making essentially new materials and coatings for assemblies and parts of different uses working in extreme conditions of temperature, exposure to corrosive environment, and high mechanical loads.

When depositing **Avinit** coatings there is a possibility of transition to nanodimensional range for implementation of controllable formation processes of multicomponent nano- and microstructural coatings with the preset characteristics, which is attained due to the performed fundamental reorganization of operation control of all systems of the process equipment on the basis of technology of through operation synchronization of ion-stimulated deposition systems and nanodimensional coating diagnostics equipment due to integration into the equipment of new microprocessor systems for power supply, synchronization and control of synthesis and diagnostic processes, and development of a complex of methods for technological parameters monitoring during deposition of coatings for object-orientated process control.

There appears a possibility to create multilayer structures containing a large number of layers with different chemical composition (metal, nitride, carbide, oxide, etc.) with thickness ranging from a few to hundreds of nanometers. The structure of layers is provided by the programmed correlated operation modes of plasma sources (both PVD and CVD), working gases and high potential applied to the carrier material.

Correct selection of individual materials of layers, deposition methods and optimization of technological parameters create a background for synthesis of materials with a complex of unique properties, including exclusively high hardness, strength, chemical stability, low friction coefficient and improved wear resistance.

The performed renovation of the process equipment and the developed software products have permitted to move to a qualitatively new level of further modification and improvement of structures of functional **Avinit** coatings, stability of technologies and their quality control enhancement while depositing these coatings for the developed friction couples with possible use in parts of precision friction couples.

In the study, results of metallographic and tribological examinations of improved **Avinit** coatings based on Ti-Al-N and Mo-N systems are presented.

Examinations of deposition process of vacuum-arc coatings were carried out with the purpose of determination of optimum process parameters for getting high-quality coatings based on nitrides of metals in the conditions of specific **Avinit** process equipment. These data are necessary for working out of software products for deposition of functional composite multilayer hardsurfacing coatings in order to raise wear resistance of working areas of precision friction couples of parts of aircraft units.

RESEARCH TECHNIQUES

THE PROCEDURE OF MAKING COATINGS

The development of processes for deposition of new functional multilayer composite coatings was performed on **Avinit** vacuum plant [11] created for implementation of complex methods of deposition of coatings (plasma chemical CVD, plasma PVD (vacuum-arc, magnetron), processes of the ionic saturation and treatment of surfaces by ions).

Within the frameworks of paper [11] a number of hardware and technological developments (application of advanced separating devices, improved diagnostic of plasma and gas flows, improved IR measuring (in the infra-red spectrum) of temperature fields in products being coated, improvement of mechanical and electronic systems of protection against micro arcs and upgrading of the cathode assemblies and control system) have been executed, which has permitted to enhance essentially the possibilities of the process equipment and allow deposition of qualitative coatings on precision surfaces.

Avinit coatings are deposited on high finish precision surfaces up to 12 – 13 grades without decrease in surface finish class. It is attained due to the possibility to use in the technologies under developed effective methods of surface cleaning, and particularly, Ar glow-discharge cleaning, cleaning in a double-stage vacuum-arc reactive discharge and cleaning by metal ions at voltages above the zero-charge point of increase, as well as due to prevention of surface damaging by micro arcs; for this purpose the three-level arc control system providing high quality of surface cleaning from oxides and other impurities without causing electrical breakdowns is provided in the **Avinit** plant. Deposition takes place at low temperatures not exceeding the tempering temperature of the carrier material, providing retaining of mechanical characteristics and absence of distortion in coated products.

For implementation of processes of controlled formation of multicomponent nano and micro multilayer coatings with controlled composition using plasma and plasma-chemical processes, the authors have developed a method of through synchronization using the computer to control the process of coating deposition. The method provides possibilities to control the sources of deposition, puffing of reaction gas and other systems of the plant in the set program and record parameters of the equipment during the whole technological cycle.

To obtain multilayer coatings **Avinit** from hard compositions in Ti-Al-N system a technological two-cathode circuit design was used at simultaneous operation of two sources of deposition, which are placed towards each other, in the environment of reaction gas with the specimen revolving round its axis.

For deposition of multilayer coatings resting on a sequence of hard and soft layers (TiN-Ti, MoN-Mo systems), a one-cathode scheme was used with continuous operation of the deposition source and pulsed (periodic) supply of reaction gas; it has been implemented thereby in two versions, with the carrier rotating around its axis, when the whole surface of the specimen was coated, and without rotation, when one side of the specimen was coated only.

Before loading into a vacuum chamber, the carriers were cleaned from contaminations in a hypersonic bath using a washing solution with surface active agent additives, then flushed by running water and by distilled water and dried by warm air. After fixing of carriers in the vacuum chamber, their surfaces were additionally wiped using light ether. The vacuum chamber was rarefied to the pressure of $(1.3 – 2)\cdot 10^{-3}$ Pa, the vacuum-arc source was switched on and ionic-plasma surface cleaning of carriers with gradual magnification of bias potential from 50 – 100 V to 700 – 1000 V was started. The time of the cleaning cycle varied from 3 to 5 minutes, thus, the temperature of the carriers that was determined with the help of the IR pyrometer "Raytek", reached 200 – 250 °C. This mode of carriers cleaning provided obtaining of qualitative tightly interconnected coatings without chipping and local separation of layers.

The potential of vacuum-arc discharge current with molybdenum cathode made 140 – 150 A, and with titanium or aluminum cathode 100 – 110 A respectively. During deposition of coatings in the nitrogen environment its pressure was within $(1.3 – 3)\cdot 10^{-1}$ Pa.

The coatings are deposited on specimens of steel DIN 1.2379 (Х12Ф1) with hardness of 56 ÷ 61 HRC and surfaces precisions used for manufacturing of parts of various units. For this purpose the working planes of the specimens were machined under the production method to surface finish of 0.016 – 0.021 μm (12 – 13 grade of finish).

Photos of specimens with the coatings made of various compositions obtained using to above process flow sheets are presented in fig. 1, 2.

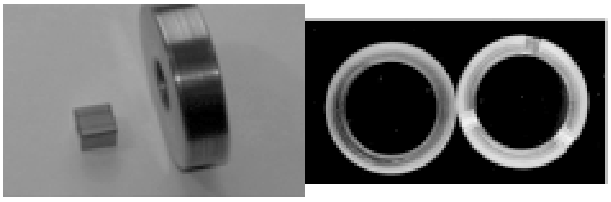

a) b)

Fig. 1. Multilayer coatings in Ti-Al-N system.

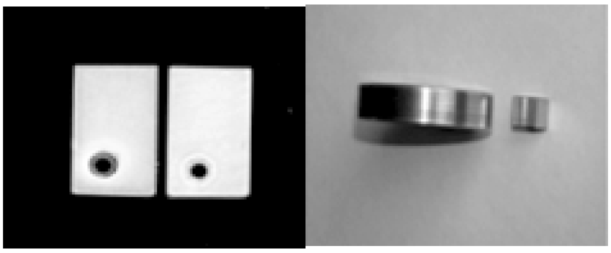

a) b)

Fig. 2. Multilayer coatings: a) TiN-Ti; b) MoN-Mo.

THE PROCEDURE OF METALLOGRAPHIC EXAMINATION

Metallographic examination and determination of materials' parameters (thickness of coatings, evenness, imperfection and structure of the material) were carried out using microscope MMR-4. Microhardness of coatings was tested with the help of microhardness gauge PMT-3 at the load of 50 g. Hardness of the material was measured using the hardness gauge by impressing a diamond point according to Rockwell method. Roughness of samples before and after deposition of coatings was measured by profilograph-profilometer.

Measurements of nanohardness and Young modulus in multilayer and nanolayer **Avinit** coatings of 1÷ 3 μm thick were made using the nanohardness measuring device manufactured by CSM firm (Switzerland) (loading rate 20.00 mH/min, max depth 100.00 nm at the load 0.6 g, processing of results according to Oliver – Pharr model).

Examination of chemical identity of surface area of functional coatings was carried out using the method of the secondary ion mass spectrometry (SIMS), electron X-ray microanalysis (EXRM), and raster electron microscopy (REM). Taking chemical identity readings of nanolayers of functional coatings was made with the help of the secondary ion mass spectrometry (SIMS) method using secondary-emission mass-spectrometer MS 7201M. The maximum profiling depth is 5 μm. Ar^+ ion beam with the energy of 5 – 7 keV was used for spraying. Examination of functional sections of specimens' surface was made using raster electron microscopy (REM). Taking readings of spatial distributions of chemical elements was done using electron X-ray microanalysis (EXRM).

Metallophysics measurements of the coatings were taken on a raster-type electron microscope JSM T-300.

PROCEDURE OF FRICTION AND WEAR BEHAVIOR EXAMINATION

Tribological tests of antifriction and wear properties and seizure of samples with coatings were carried out with friction and wear machine 2070 SMT-1 under the "cube"-"roller" test pattern at an incremental loading in 1 – 20 MPa loading range according to the procedures presented in [12]. Tests were carried out under aviation fuel TS-1. To define seizure of surface layers of materials of friction pairs there applied loading ranged from P_{min} to critical value P_{cr} at which seizure takes place.

During tribological tests values of frictional force $F_{тр}$, normal loading N, contact pressure P by which value mechanical losses in tribological systems have been estimated were registered. Friction coefficients were defined as $f = F_{тр}/N$.

To research tribological behavior of friction pairs with nanocoatings at friction and wear tests under the "cube-roller" test pattern, following samples have been made.

Multilayer coatings (Ti-Al-N system-based) **Avinit** C/P 310, **Avinit** C/P 300, **Avinit** C/P 100, **Avinit** C/P 320, **Avinit** C/P 350 were deposited on basic samples-cubes made of steel DIN 1.2379 (X12Ф1) with hardness 56 ÷ 61 HRC and working planes polished by diamond paste to reach required geometrical parameters (nonflatness – ≤ 0.001 mm, surface roughness – R_a 0.08 μm).

Multilayer coatings (Mo-N system-based) **Avinit** C/P 210 and **Avinit** C/P 220 were deposited on an effective area of rollers (as counterbodies) made of steel DIN 1.2379 (X12Ф1) with hardness 56 ÷ 61 HRC polished with paste КТ10/7.

EXPERIMENTAL RESULTS

Influence of key parameters on changing properties of formed coatings based on nitrides of molybdenum, titanium, and aluminum has been studied.

An important parameter is the temperature of coating formation. In many cases it is necessary to retain mechanical properties of the carrier material while depositing coatings, this can be attained using corresponding modes of heat treatment, at this tempering temperature does not exceed 180 – 240 °C. It imposes certain restrictions on the temperature of deposition of coatings on such materials. Achievement of sufficient adhesion of coatings at such temperatures even for vacuum-arc methods, which are among the best in comparison with other methods, is not always an easy problem and demands careful preparation and selection of modes of plasma processing of surfaces, especially for processing of precision surfaces, and the subsequent deposition of coatings. This moment is chosen as a fundamental one for development of modes of deposition of coatings.

The performed examinations proved that during deposition of coatings in various technological modes the extent of uniformity of coating distribution is very sensitive to the parameters of coating deposition. Choosing optimum process parameters, it is possible to form coatings on acute edges and on a spherical surface. At the same time, sensitivity of uniformity of coating distribution to process conditions calls forth expediency of optimization of the latter during optimization at a stage of process development for deposition of coating on prototype and real products.

The carried out examinations are taken as a basis for selection temperature and time parameters for obtaining hardsurfacing coatings to increase wear resistance of working areas of precision friction couples, which provides obtaining of coatings with the specified composition.

One of the parameters of the multilayer coatings, which determine their properties to a large extent, is, certainly, the thickness of a separate layer. During coating formation the necessary thickness of the layer is set by the time of operating a relevant source that implies the knowledge of the growth rate. The coating growth rate generally depends on the deposition source power, the distance from the source to the carrier material, its orientation and position in relation to the axis of the direction diagram of the atomic stream of the deposition source, the shape of the direction diagram and the bias potential applied to the carrier. The carrier can be fixed, rotate around the fixed axis or make orbiting motion.

When depositing coatings a mask was placed on the carrier material surface that partially covered the surface. The thickness of the mask made 0.1mm, and the mask was held tightly to the carrier material surface. Due to this a step was formed on the carrier material surface, the height of which matched the thickness of the coating. Using the profilogram taken on the transitional boundary from the carrier material surface to the coating surface allowed not only to determine its thickness (and growth rate using this value), but to avoid possible discrepancies when comparing values of coating roughness due to noncoincidence of places of their determination on the carrier plane.

Tabl. 1 shows the results of the experiments for determining growth rates of various coatings obtained both on the fixed carriers and on the carriers having planetary motion.

Table 1

Coatings growth rate of various compositions

Coating	Growth rate, *V*, мм/hour	Remarks
Ti	0.25	Planetary motion
Mo	0.2	– ″ –
TiN	0.16	– ″ –
MoN	0.14	– ″ –
TiAlN	0.7	
TiN	0.9	Fixed position
MoN	0.7	– ″ –

The obtained results coincide with the estimates that can be made by comparison of the value of the full ionic current making nearly $0.1\,I_d$, where I_d – the arc current magnitude, and the magnitude of the ionic current at the separator output making nearly $0.01\,I_d$, i.e. approximately 10 times less. It is exactly the relation between the values of coatings growth rates obtained without separating devices.

To determine radial distribution of coatings growth rate with respect to the axis of the deposition source in the perpendicular plane, the possibility of determining the thickness of optically transparent coatings by the quantity of the interference maximums on the sections with variable thickness [13] was used.

Coatings based on aluminum nitride, which were formed on the carriers during deposition of coatings of metal targets in the reaction gas medium (nitrogen), were used as optically transparent coatings. Strips made of iron plate 20 mm wide and 400 mm long were used as carriers. The carriers were placed perpendicularly to the axis of the vacuum-arc source, with a separator placed at the distance of 160 mm and 370 mm from the end part of the separator which the diameter of 190 mm at its outlet. Coatings were deposited at vacuum arc current 120 A. At the initial stage the bias potential 400 V was applied to the carrier material, and its surface was cleaned within 30 minutes in glow-discharge plasma at Ar pressure equal to 5 Pa. Then Ar supply to the chamber was terminated, the bias potential was read and the chamber was refilled with nitrogen to the pressure of $3\cdot10^{-1}$ Pa with simultaneous switching of vacuum-arc discharge. The process of deposition of coating lasted 30 – 45 minutes. During deposition the floating potential was applied to the carrier material. Distribution curves of coating growth rate depending on the distance to the axis of the source for various conditions of deposition are presented in fig. 3.

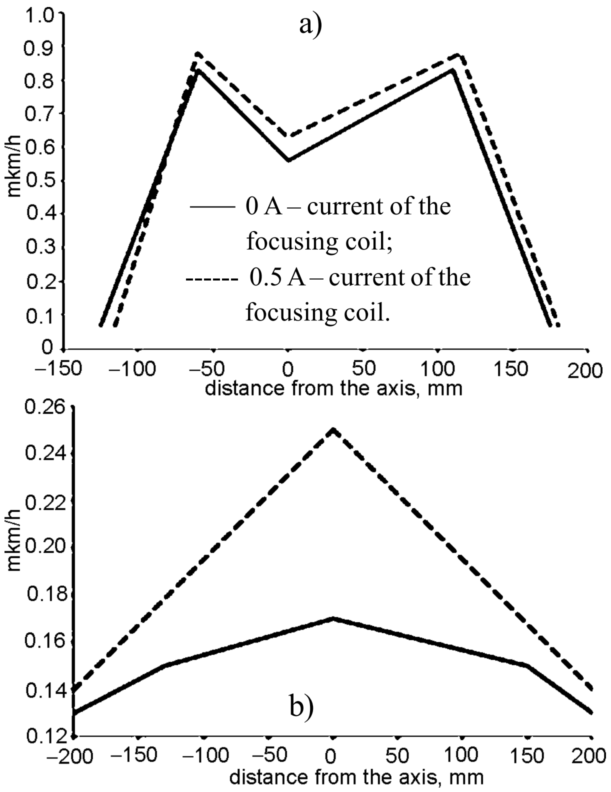


Fig. 3. Dependence of growth rate distribution on the distance to the axis of the source for the carriers which are located at the distance of: a) 160 mm and b) 370 mm from the separator, at different current values of the focusing coil.

It is clear from the rate distribution curves that there is a shift of their centre of symmetry with regard to the source geometrical axis. In relation to the centre of the vacuum chamber, deviation of a plasma stream is observed towards the attachment flange of the pumping-out system of the installation. Such an asymmetry of radial distribution of velocity also occurred in examinations of unseparated plasma stream of the vacuum-arc source [14], i.e. in the present examinations asymmetry of the separated stream is not related to the separator as a structural element of the installation, but is characteristic for this particular structure of the installation.

Increasing of focusing coil current up to 0.5 A, preset as optimal for such a separator, not only led to acceleration of coating growth rate at the center approximately by 20%, but slightly reduced inhomogeneity of its distribution. Thus, coatings growth rate with the use of the separator, depending on the material of the coating and the requirements of its formation can range within several tenths to several micrometers per hour.

Basing on the coatings growth rate figures, the data were entered into the program to control **Avinit** installation for several variants of nanosized layer coatings, and particularly for:

– Ti-TiN coatings with the recurrence interval 10 nanometers and thickness of individual nanolayers 2 and 8 nanometers, respectively;

– Mo-MoN coatings with the recurrence interval 20 nanometers and equal thickness of separate nanolayers;

– TiN-AlN coatings with the recurrence interval 12 nanometers and thickness of separate nanolayers equal to 4 and 8 nanometers.

The process of formation of the coating starts with the moment of diminution of the bias potential to the value when condensation rate of the coating exceeds the rate of its deposition by the faster ions. The process of Ti-TiN coating deposition lasted 1.5 hours, and Mo-MoN and TiN-AlN coatings – three hours.

The **Avinit** control system provided stable formation of nanolayers of the preset composition and thickness during the entire process. At this, the formation scheme for both monocomponent nanosized layer constructions from two sources and nanosized layer coatings of Me, Me-MeN, Me_1N-Me_2N type with the use of plasma chemical reactions of generation of metal nitrides (jet deposition) was implemented.

During the vacuum-arc discharge, along with highly ionized atomic particle flux, a part of the cathode material is transferred towards the coating growth surface in the form of drops. Presence of the drop component in the coating structure is one of the characteristic features of vacuum-arc coatings. During formation of nanosized layer coatings and studying the dependence of their characteristics from composition and periodicity of the structure, presence of macro particles generated by the cathode spot of the vacuum arc, will considerably reduce characteristics of the formed coatings, especially, during deposition of coatings on precision surfaces. Drops size, flow density and angle distribution depend on the operating mode of the source of vacuum-arc deposition and on the cathode material. It offers an opportunity to influence to a certain extent the value of this component in the general stream of the substance being condensed on the carrier material in the form of the coating.

The authors used and improved, with reference to the task of deposition of nanosized layer coatings on precision surfaces, a rectilinear separator of insular type as a simple in implementation and, at the same time, effective enough structure [15]. It has a choke and a system of catcher rings made of a hard to melt material that provides reliable protection of the anode against burn-through by the arc spot.

The efficiency of the vacuum-arc source with separation of the plasma stream depends on the construction of a separation device, configuration of the magnetic field and its intensity. Therefore experiments for optimization of parameters of the separating device installed on the basis of use of the focusing coil of a standard vacuum-arc deposition source were carried out.

Position and size of the separator element nontransparent to drops were selected taking into account the requirement of maximum possible cut off of the drops while retaining the sufficient value of the total ionic current at the separator outlet, which was assumed to be a ∅ 250 mm collector. The value of the magnetic field intensity in the plasma distributor depended on the solenoid current, which was selected so that the ionic current at the separator outlet was maximal. Examination of dependence of ionic current value on the bias potential applied to the collector showed that the curve of the ionic current reaches saturation when voltage is about 60 V, and in the subsequent experiments it was constant.

In the optimal mode selection of optimum current strength of the focusing coil (about 0.5 A), depending on the size and position of the separating is let, maximum value of the full ionic current at the separator outlet, which made 1.2 A at the arc current 120 A was obtained.

As the experimental findings showed, use of such a rectilinear separator ensures formation of plasma streams that are essentially cleaned of cathode material micro particles, which permits to deposit coatings on the surface of V 11 – 13 grade of finish practically without changing the surface finish class. All subsequent experimental and technological developments were made using a rectilinear separating device.

Composition and some characteristics on hardness, microhardness and surface roughness of the investigated coatings obtained at various process flow sheets, are presented in tabl. 2.

All coatings were deposited on samples made of steel DIN 1.2379 (Х12Ф1) with hardness 56 ÷ 61 HRC (H_v = 770 – 800 MPa) and a surface roughness – R_a 0,025 μm.

Table 2

Properties of samples

Item No.	Coating composition	Process flow-sheet*	Technological parameters			Properties of coatings		
			The programmed composition	T,°C	Pressure of nitrogen, P, Pa	Thickness of a coating, мм	Microhardness of coating, H_{v}, (MPa)	Surface roughness R_{a}, мм
I	Ti-N system-based coatings							
1	**Avinit** C/P 100 (TiN)	1 (without separator)	monolayer	250	$1.5\cdot10^{-1}$	12.0	15000 – 18000	0.70 (7c)
2	**Avinit** C/P 100 (TiN)	1	monolayer	250	$1.5\cdot10^{-1}$	1.0	15000 – 19000	0.040 (11c)
3	**Avinit** C/P 110 (TiN)	2	monolayer (A recurrence interval – 10 nm and thickness of separate nanolayers – 2 nm and 8 nm)	250	$1.5\cdot10^{-1}$	1.0	13000 – 18000	0.036 (12a)
II	Mo-N system-based coatings							
1	**Avinit** C/P 200 (MoN)	1 (without the separator)	monolayer	250	$1.5\cdot10^{-1}$	10.0	20000 – 22000	0.60 (8a)
2	**Avinit** C/P 200 (MoN)	1	monolayer	250	$1.5\cdot10^{-1}$	1.0	20000 – 23000	0.040 (11c)
3	**Avinit** C/P 210 (Mo-MoN)	2	monolayer (A recurrence interval – 10 nm and thickness of separate nanolayers – 2 nm and 8 nm)	250	$1.5\cdot10^{-1}$	1.0	17000 – 19000	0.036 (12a)
4	**Avinit** C/P 220 (Mo-MoN)	2	monolayer (A recurrence interval of 20 nm and equal thickness of separate nanolayers)	250	$1.5\cdot10^{-1}$	1.0	18000 – 20000	0.036 (12a)
III	System-based coatings Ti-Al-N (TiN-AlN)							
1	**Avinit** C/P 300	3 (without the separator)	multilayer	200	$3\cdot10^{-1}$	10.0	26000 – 30000	0.040 (11b)
2	**Avinit** C/P 310	3	nanolayer (A recurrence interval – 12 nm and thickness of separate nanolayers – 4 nm and 8 nm)	200	$3\cdot10^{-1}$	–	26000 – 35000	0.036 (12a)
3	**Avinit** C/P 320	3	nanolayer (A recurrence interval – 12 nm and thickness of separate nanolayers – 8 nm and 4 nm)	200	$3\cdot10^{-1}$	–	26000 – 35000	0.036 (12a)
4	**Avinit** C/P 350	3	nanolayer (A recurrence interval – 20 nm and equal thickness of separate nanolayers)	200	$3\cdot10^{-1}$	–	26000 – 35000	0.036 (12a)

*) 1 – one-cathode operation scheme with continuous operation of the deposition source in the reaction gas medium with carriers rotating around their axes; 2 – one-cathode operation scheme with continuous operation of the deposition source in the reaction gas medium and without the gas, with carriers rotating around their axes; 3 – two-cathode operation scheme during simultaneous operation of two sources of deposition placed towards each other, in the reaction gas medium with carriers rotating around their axes.

Comparison of carrier material surface roughness and coating by their profile diagrams (fig. 4, tabl. 2) shows that after deposition of coatings on samples with surface finish of 12 – 3 grade, the surface roughness practically does not change or exhibits a slight increase in surface roughness, which

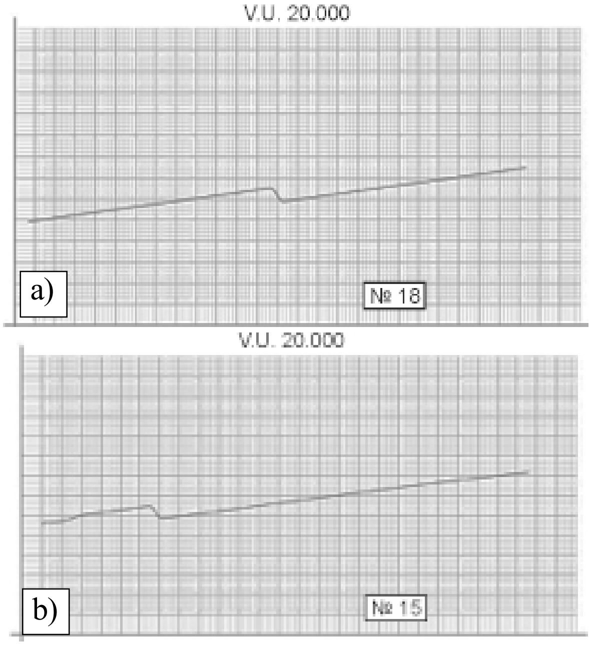


Fig. 4. Profile diagram of the carrier with a) Ti-TiN, b) Mo-MoN. coatings.

practically does not place it in another grade in accordance with the classification by grade surface roughness.

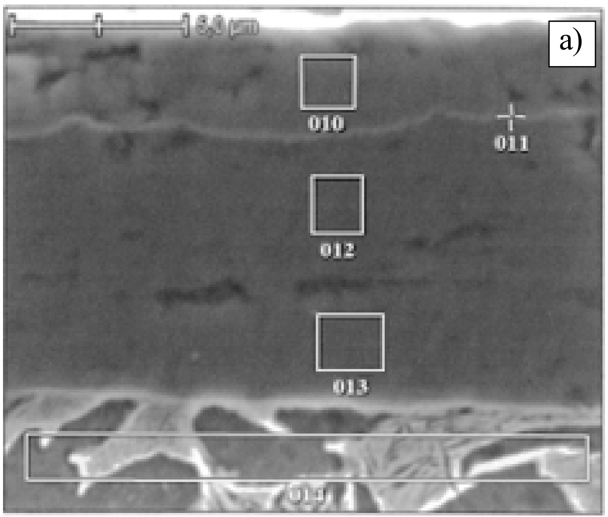
As the results of examination of the profile diagram show, the quality of the coating surface essentially deteriorates without application of a rectilinear separator. A considerable quantity of macro particles (mainly, metal drops) characteristic for condensation from unseparated streams of plasma, occurs on the surface of coatings. Roughness of the original surface (grade 12b) when depositing such coatings decreases very strongly (grade 7c, tabl. 2).

When depositing coatings based on molybdenum without application of separating devices the coatings' surface roughness corresponds to *V*7 – 8 grade, if deposited on steel DIN 1.2379 (Х12Ф1) surface polished to surface finish class *V*12.

As one would expect, titanium-based coatings have a somewhat higher roughness when compared to coatings based on molybdenum, which is accounted for by higher drop component and larger sizes of drops in comparison with the plasma generated by the arc with molybdenum cathode [14].

The carried out X-ray examinations of **Avinit** coatings C/P 320 revealed that coatings comprise ~45 at.% of aluminum. Their crystal structure matched TiN structure, with lattice parameter close to values of this composition. According to the X-ray examination, the size of the coherent-scattering region (CSR) in the coating made 32 nm. This value is well consistent with the sizes of separate TiN and AlN nanolayers taking into account the nanolayer growth rate per revolution, which made ~35 nm, that, as a whole, confirms availability of nanolayer structure in accordance with the process flowsheet of coating formation.

To determine coating thickness and for visual estimation of quality of Ti-Al-N coating adhesion with the material of the test parts, a metallophysics measurement of **Avinit** coatings was made at a raster-type electronic microscope JSM T-300 (fig. 5, 6).



×9500

Point No.	N	Al	Ti	Mo	Total %
010	9.10	27.93	62.96	–	100
011	6.89	16.73	76.38	–	100
012	10.7	45.87	43.44	–	100
013	10.71	47.22	42.07	–	100
014	–	3.64	88.94	7.41	100

b)

Fig. 5. Appearance of **Avinit** coating C/P 320 (a traversal metallographic sample): a) with marked areas for analysis; b) an approximate chemical composition of the analyzed areas.

For thickness gauging a traversal static fracture of test parts having coatings was made. The thickness of the coating makes ~9 µm. No peeling of the coating from the carrier was revealed at the examined sections.

Thickness of thick unfiltered multilayer **Avinit** coatings C/P 100 and **Avinit** C/P 220 made 10 ÷ 15 µm, microhardness of coatings – 2000 – 2500 kg/mm^2. Thickness of thin multilayers and nanolayers of **Avinit** coatings C/P 320 and Avinit C/P 210 – 1 ÷ 2 µm. The measured values of hardness of **Avinit** coatings C/P 320 made not less than

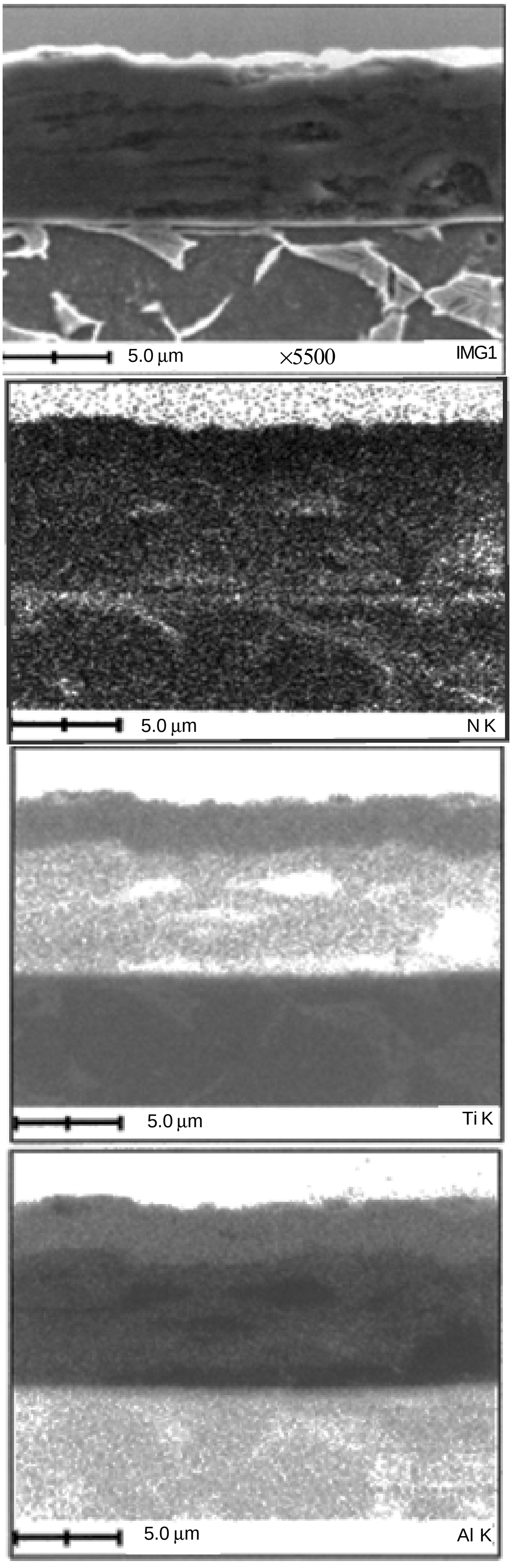
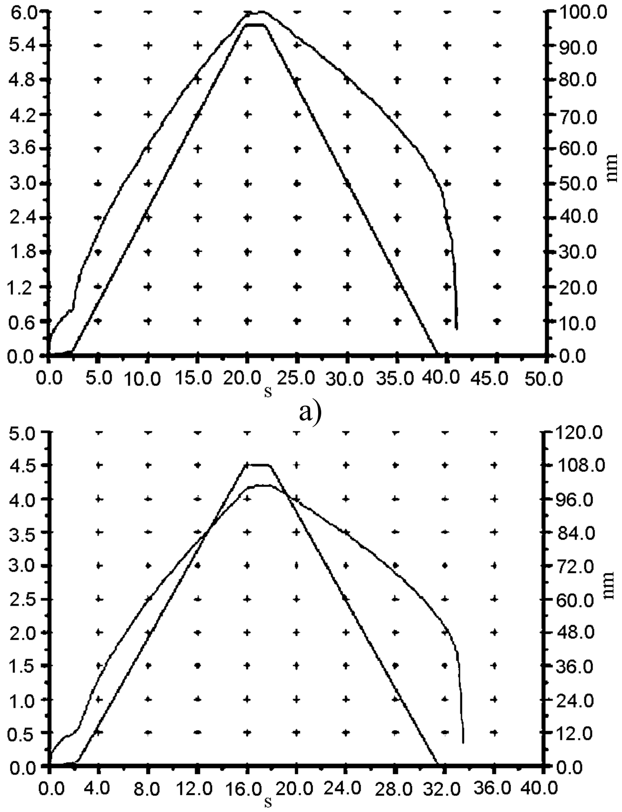


Fig. 6. Appearance of **Avinit** coating C/P 320 (a traversal metallographic section) in the mode of mapping of the coated section. The higher element content, the more intensive coloring.

$HV = 3500$ kg/mm^2, **Avinit** coatings C/P 210 – not less than $HV = 2000\ \ 2500$ kg/mm^2.

The taken measurements of nanohardness and Young modulus in 1.4 мм thick **Avinit** coatings C/P 320 gave the values of $HV = 1600 – 2300$ kg/mm^2, $E = 250 – 300$ GPa, a Poisson's ratio $K = 0.30$ (diagrams of loading and the obtained nanohardness, Young modulus and Poisson's ratios values are presented in fig. 7a).

Similar measurements for **Avinit** coatings C/P 210 with the thickness 1.0 µm yielded the following results – $HV = 1500 – 1800$ kg/mm^2, $E = 200 – 260$ GPa, a Poisson's ratio $K = 0.30$ (fig. 7b).



a)

b)

Fig. 7. Measurement results of nanohardness and Young modulus: a) – **Avinit** coating C/P 320; b) – **Avinit** coating C/P 210.

It should be noted that in Oliver-Pharr model Young moduli of the coating and the carrier are assumed to be equal, and thus the computed values can be a little underrated.

The performed measurements of nanohardness show that in thin layers of hard and superhard coatings, where application of usual methods of testing microhardness by means of microhardness gauge PMT-3 is impossible (coating thickness for obtaining of reliable information should be not less than 5 µm), as high values of hardness, as in thick layers are attainable. This permits to state that many technological developments made by the authors for thick coatings, can be successfully applied to thin coatings of precision surfaces.

Metallographic examination of **Avinit** coatings using methods of secondary ion mass spectrometry (SIMS), electron X-ray micro analyzing (EXRM), raster electron microscopy (REM) were carried out.

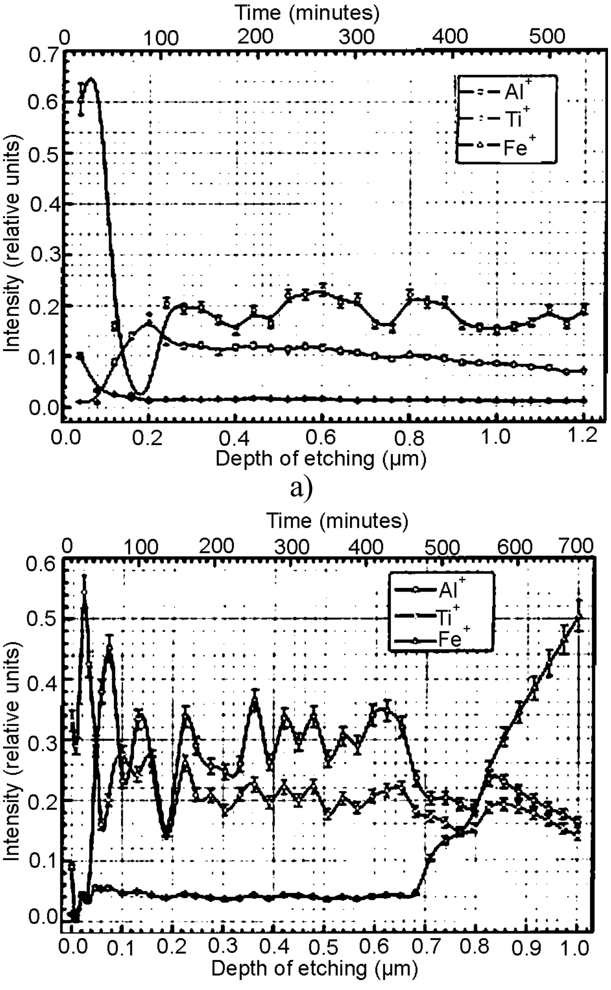
Functional relationship of currents of secondary ions Al^+, Ti^+ on the time of deposition and depths of components' distribution profile for **Avinit** coating C/P 310 are presented in fig. 8a.

Changing of secondary ions current in both experiments characterizes change of concentration of respective elements deep into the sample in course of deposition on the near-to-surface area by a beam of primary ions Ar^+. It follows from the obtained dependencies that the top surface of the coating has a higher concentration of aluminum, which decreases with the depth. Further changes of current intensity for Al^+ and Ti^+ reflect, in fact, the processes which occur during coating deposition and lead to change of concentration of respective components due to the deposition mode. It is also possible that the behavior of these relations can characterize the change of chemical identity of aluminum and titanum compounds in course of formation of coating thickness.

Similar relations for profiles of aluminum and titanum distribution in the near-to-surface area of the sample with the deposited functional coating Avinit C/P 320 are presented in fig. 8b. Synchronous changes of Al^+ and Ti^+ current intensities from ~1.8 μm depth are related to the technology of coating formation.

The carried out examination permitted to optimize technological parameters of process of nanosized layer coatings deposition with higher (or lower) concentration of aluminum in the near-to-surface layers.

Metallographic examination of samples after deposition of coatings of various composition show that the developed modes have provided formation of qualitative coatings. Hardness and microhardness of the carrier material in the selected modes of coatings deposition practically do not decrease in comparison with the original state. Coatings had good adherence with the parent material. Pilling of coatings during application of a net of scratches was not observed.



a)

b)

Fig. 8. Functional relationship of currents of secondary ions Al^+, Ti^+ on deposition time: a) **Avinit** coating C/P 310, b) **Avinit** coating C/P 320.

Thus, the experimental findings confirm a possibility of low-temperature deposition of very hard **Avinit** C coatings based on nitrides of metals in the modes providing good adhesion to the parent material ((steel DIN 1.2379 (Х12Ф1) without reducing strength properties of the steel (< 200 °C) and without decreasing surface finish class of the original surface.

RESULTS OF TRIBOLOGICAL TESTS

Tribological tests (coating over coating) (under the test pattern "cube-roller") of multilayer and nanolayer **Avinit** C/P 320 and **Avinit** C/P 510c coatings using counterbodies with multilayer **Avinit** C/P 220 and **Avinit** C/P 100 coatings (TiN-Ti based) of 10 – 15 μm thickness which are deposited from unfiltered plasma flows with the subsequent additional polishing. Results are presented in fig. 9.

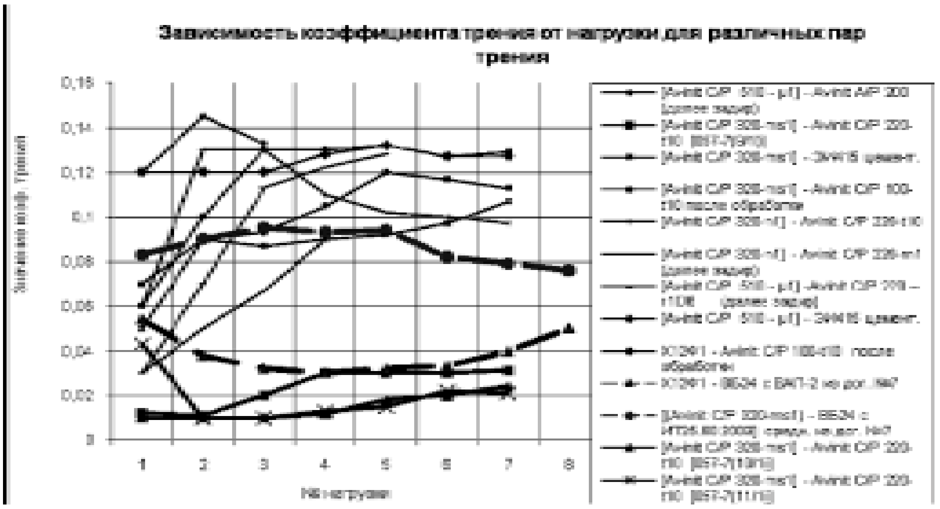


Fig. 9. Dependence of friction coefficient on loading.

More detailed examination of samples during tribological tests was carried out with application of methods on examination of chemical identity of near-to-surface areas of the functional coatings.

Fig. 10 represents results of electron X-ray microanalysis (EXRM) for three elements: aluminium, iron and titanum for **Avinit** C/P 320 sample at its scanning by an electronic beam along width of a ring from its external surface to the internal one.

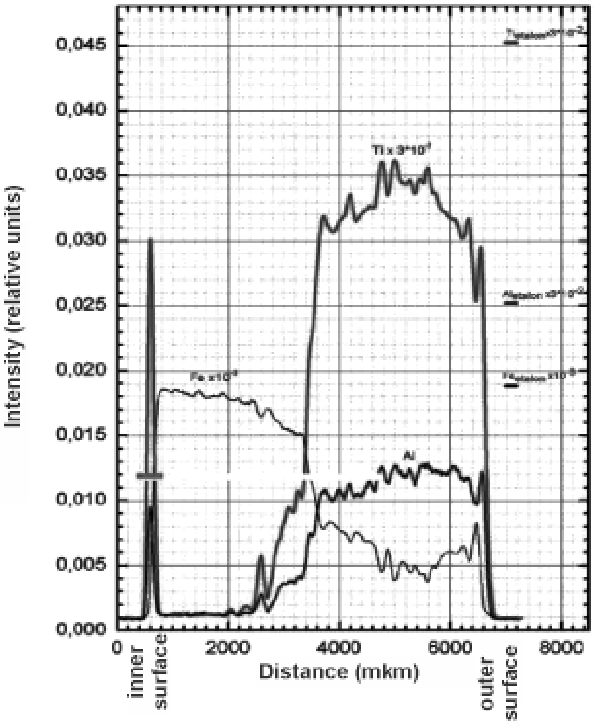


Fig. 10. Distribution of elements in coating **Avinit** C/P 320.

Results are represented in the form of dependences of a characteristic X-radiation of atoms of those metals from the electron microprobe location on a surface of the sample (diameter of electron microprobe ∅ = 30 nm, characteristic radiation was registered from a near-to-surface layer of the sample at 1 μm depth).

When scanning from larger to smaller diameter, curves begin with peaks of the titanium and the aluminium intensities caused by characteristic radiation of these metals deposited on an external cylindrical part of the sample. Peak values of Al and Ti characteristic radiation with the same order intensities are also observed on interfaces of side, internal and external cylindrical surfaces of the ring. Al and Ti distributions over all analyzed surface are qualitatively close to each other.

No matter the fact that unaffected functional coating exists, surfaces with such coating already exhibit Fe characteristic radiation which intensity is much less, than from Al and Ti. The form of dependence of a signal on Fe is contrary to form of dependence for Al and Ti. Observable regularity of distribution of metals over a surface of the sample along an analyzing line is illustratory. Minimums on distribution curve Fe there match to all maximums on distribution curves for Al and Ti, and vice versa. At the same time, Fe intensity is basic for a surface put to tribological tests. At that, rather wide transitive area (200 – 360 μm) is observed.

Sections of a surface of **Avinit** C/P 320 sample put to tribological tests were examined by means of a secondary ion mass spectrometry (SIMS).

Metallophysics measurements carried out provide fuller appreciation of dynamics of wearing process over a thickness of a coating and more reasonable approach to selection of technological parameters for deposition of nanolayer coatings with various thickness.

Analysis of results of tribological examinations carried out shows, that presence of the developed coatings essentially improves scoring resistance of tribological pairs raising values P_{cr} of scoring and practically preventing scoring.

Coatings on the basis of **Avinit** C/P 220 which have the highest P_{cr} values and the lowest values of coefficient of friction are especially effective. This is evidenced by not only increase in load at tests to maximum load, but also variation of dependence of friction coefficients on a load which after some raise with increase in load to 0,6 – 0,8 kN was downgraded to the maximum load of 2 kN.

Application of multilayer coatings (for example, **Avinit** C/P 110 of TiN-Ti type) leads to magnification of P_{cr} in comparison with monolayer coatings (for example, **Avinit** C/P 100 of TiN type).

For all types of coatings, friction coefficients have close enough values, and at loadings more than 1.0 kN they are within the range of 0.06 – 0.1.

Table 4

Values of wear of samples in the course of wearing tests for 8 hours

Friction pair	**Avinit** C/P 220/**Avinit** C/P 320		
Wear, g Test time 480 min	**Avinit** C/P 220	**Avinit** C/P 320	Σ
	static	movable	0.00091
	0.00091	0	
	movable	static	0.00101
	0.00087	0.00014	

The least friction coefficient is for the pair "coating **Avinit** C320 – coating **Avinit** C220". Value of friction coefficient of the pairs did not exceed 0,095 within all range of loadings, and at the maximum loading it made 0,065, that matches to the minimum value obtained in the study for friction pairs a with the examined coatings.

All coatings in tests have shown high wear resistance.

The friction pairs which working faces have micro- and nanolayer **Avinit** C/P 320, **Avinit** C/P 350, **Avinit** C/P 220 coatings, were tested in the conditions of a boundary lubrication, are characterized by:

– High scoring resistance;

– Absence of secondary abradability;

– High enough stability over time of friction coefficient in case of operation on an invariable loading.

All tested friction pairs with nanocoatings have pronounced running-in period of ≈ 60 min. after which values of friction coefficients are stabilized and, at an invariable loading 1600 N, are within limits 0,09 ÷ 0,132.

The friction pair **Avinit** C/P 220/**Avinit** C/P 320 has exhibited the most long runningin period before stabilization of friction coefficients values at a steady load in the study. This pair has exhibited the full coincidence of friction coefficients values of "direct" and "reverse" pairs at the long-term operation under an invariable loading. The mass wear revealed after 8 hours of wear tests is less than for "base" pair bronze/nitrided steel DIN 1.2379 (Х12Ф1) (chosen as one of the best actual alternatives for operation of friction pairs in an aviation fuel): 2.7 times less for "direct" pair and 8.1 times less for "reverse" pair.

CONCLUSIONS

1. Metallographic examination of improved structures of multilayer **Avinit** C type nitride coatings based on Ti-Al-N system – Avinit C/P 310, **Avinit** C/P 300, **Avinit** C/P 100, **Avinit** C/P 320, **Avinit** C/P 350 and coatings based on system Mo-N – **Avinit** C/P 210 and **Avinit** C/P 220 were made. **Avinit** coatings are deposited on precision surfaces of high finish class up to 12 – 13 grades without decrease in surface finish class, which is attained by use of effective methods of surface cleaning in the production engineering being developed, and by prevention of surface deterioration by micro arcs. For this purpose **Avinit** installation is equipped with a three-level arc control system providing high quality of surface cleaning from oxides and other fouling without occurrence of electrical breakdowns.
2. The experimental findings confirm a possibility of low-temperature deposition of very hard **Avinit** coatings C based on nitrides of metals in the modes providing good adhesion to parent material (steel DIN 1.2379 (Х12Ф1) without decrease in strength properties of the steel (< 200 °C) and without distortion of coated surfaces.
3. As tribological tests have shown, deposition of coatings very effectively improves scoring resistance leading to raise of value P_{cr} for scoring. Examined pairs with coatings had low friction coefficients at loadings up to 2.0 kN. Pair **Avinit**

C/P 320/**Avinit** C/P 220 had the least friction coefficient. Its value did not exceed 0.095 within all range of loadings, and at the maximum loading it made 0.075. During tests, all advanced coatings have shown high wear resistance which value did not exceed 0.8 μm. The pair **Avinit** C/P 320/A**vinit** C/P 220 has shown the best combination of wear hardness and tribological properties. It had the least friction coefficient and practically zero wear for 8 hour tests.

4. The carried out examination permitted to choose temperature/time parameters of production of hard surfacing **Avinit** C coatings to raise wear resistance of working areas of precision friction couples, which is necessary for development of software products for production of such coatings with preset composition using **Avinit** equipment and trying out of stable production engineering for deposition of functional multicomponent multilayer coatings for potential use in real parts of precision friction couples of serial aircraft apparatuses.

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