

Research of the Protective Characteristics of Decorative-Protective Ion-Plasma Vacuum Coatings

Aleksandrs Urbahs¹, Svetlana Bogdanova², Margarita Urbaha³, Konstantins Savkovs⁴, Gints Rijkuris⁵, ¹⁻⁵ Riga Technical University, Institute of Aeronautics

Abstract – Modern industry makes ever-growing demands towards decorative characteristics and protective properties of manufactured products, as well as requires increasing level of environmental friendliness. One of the most efficient technologies for improving durability of a product is applying different coatings on the effective area. Due to their flexibility ion-plasma methods of applying decorative and protective coatings are becoming more widely used in modern industry. Methods differ with high controllability of the process; capability of getting chemical compounds and alloys of given composition including films from refractory materials; better film adhesion to the surface, etc.

Keywords – adhesive sustainability coatings, ion-plasma method, sputtering.

I. INTRODUCTION

One of the most important characteristics of a coating for any purpose is adhesion.

Ion-plasma sputter were produced by the upgraded vacuum unit NNV-6, 6-II [1]. For the experimental research two sources of metallic plasma were used – the electric arc vaporizer and magnetron. During sputtering with the electric arc vaporizer electromagnetic movement stabilization, focus of the cathode spot on the face of the evaporated cathode and separation of the flow of the sputtered material from the droplet phase were provided.

The argon pressure in the chamber was $1\div4\cdot10^{-3}$, the nitrogen pressure - $2\div1\cdot10^{-4}$.

The microhardness of the coatings was measured by nanoindentation with help of the micro-durometer PMT-3M.

Hitachi S-3000N scanning electron microscope was used for researching chemical composition of the obtained compound [5].

Research was made around decorative and protective coatings on the basis of Ti-Al-N.

In the research process changes in the structure and microhardness of films depending on chemical composition of coatings were determined.

The experiment was carried out with six decorative protective coatings selected from 30 previously obtained coatings. The thickness of the coatings varies from 0.20 to 0.40 μm .

II. RESEARCH OF ADHESIVE SUSTAINABILITY OF VACUUM ION-PLASMA DECORATIVE-PROTECTIVE COATINGS

Conditions providing high adhesion are physical contact between the coating and substrate, chemical interaction at the boundary of two contacting phases.

Increased roughness of the workpiece surface may promote better adhesion of the coating to the substrate. In turn, the presence of the workpiece surface prior to the deposition of coarse defects: sinkholes, scratches, cracks, has a negative effect.

Chemical interaction at the border of the contacting environment can be obtained by activating the interacting atoms of materials on the phase border during heating, pulsed mechanical stress on the surface of the base in the process of coating.

Earlier a series of experiments designed to produce coatings imitating gold was conducted.

These coatings have a high degree of destruction in changing temperature conditions.

In order to determine the chemical composition of the created coatings an energy dispersive electron microprobe analysis was conducted. As a consequence of the large relative error analysis on the content of nitrogen N, spectral analysis was performed on two elements – Ti and Al [2].

The work analyses the properties of decorative, protective multi-component coatings on the basis of Ti-Al-N, which are obtained by vacuum ion-plasma sputtering. A series of experiments has been carried out aimed to obtain single-layer coatings according to a certain pattern of sputtering modes in argon and nitrogen environment. The obtained coatings have a wide variety of colors.

III. RESEARCH OF MICROHARDNESS OF DECORATIVE-PROTECTIVE COATINGS BY NANOINDENTATION

Microhardness was determined by the means of Vickers hardness test [6]. Diamond four-sided pyramid with an apex angle of 136° was used as an indenter. About 10-12 penetrations of each sample under a load 0,1 H were conducted. The number of Vickers hardness HV was determined by the formula:

$$HV = k \frac{P}{d^2}, \quad (1)$$

where $k=0,1891$ – constant;

P – load used for the measure, H ;

d – conditional lateral surface area of the print, mkm^2 .

To exclude the substrate from the measured hardness, coatings were made on glass plate substrates 64 X 88 mm in size. The microhardness was determined with the micro-durometer PMT-3M [7]. Table 1 presents the data on the chemical composition and micro-durability of the coatings.

TABLE I
INDICATORS OF MICROHARDNESS AND CHEMICAL COMPOSITION OF THE COATINGS

T%	Al%	Microhardness (MPa)
46.45	53.55	4043.94
55.07	44.93	3340.05
69.23	30.77	4127.71
74.33	25.67	4897.75
74.77	25.23	4016.21
78.88	21.12	3766.15

Figure 1 shows the graph of microhardness dependency on percentage content of Ti in the coating.

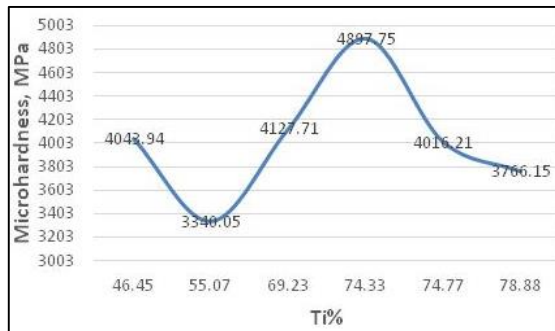


Fig. 1. Effect of chemical structure on the value of microhardness in coatings

All six coatings are characterized with high index value of micro-durability. The consequence of this is cracking and delamination of coatings. Degradation of coatings occurred almost immediately after they cooled down.

With the help of software package Statistika10, a linear regression analysis was carried out to determine the influence of coating chemical composition and a number of technological parameters on the microhardness. The assessed parameters are: correlation of main components in the coating composition – Ti/Al; strength of arc evaporator current ($I_{arc\ evap.}$), strength of magnetron current (I_m), magnetron voltage (U_m), argon reactive gas pressure (P_{Ar}). Table 2 presents the values of the above-listed parameter correlation coefficients for the coating microhardness.

TABLE 2
THE INFLUENCE OF PARAMETERS ON MICROHARDNESS OF THE COATING

Variables	microhardness
Ti% content	0.34
$I_{arc\ evap.}$	0.69
I_m	-0.64
U_m	0.19
P_{Ar}	0.02

In the table, significant coefficients are marked in grey.

Influence of chemical composition on microhardness of the coating is insignificant. Increasing current of the electric arc evaporator and decreasing current of magnetron lead to higher index value of microhardness.

IV. DEVELOPMENT OF TECHNOLOGY FOR THE COATING WITH THE SPECIFIED COLOR PARAMETERS AND IMPROVED ADHESION CHARACTERISTICS

One of the six coatings was selected for further study. The coating had the closest match to the shade of gold. Figure 2 shows microfractography of the coating (index value of micro-durability - 3766,15 MPa, Ti content – 78,88%) [10].

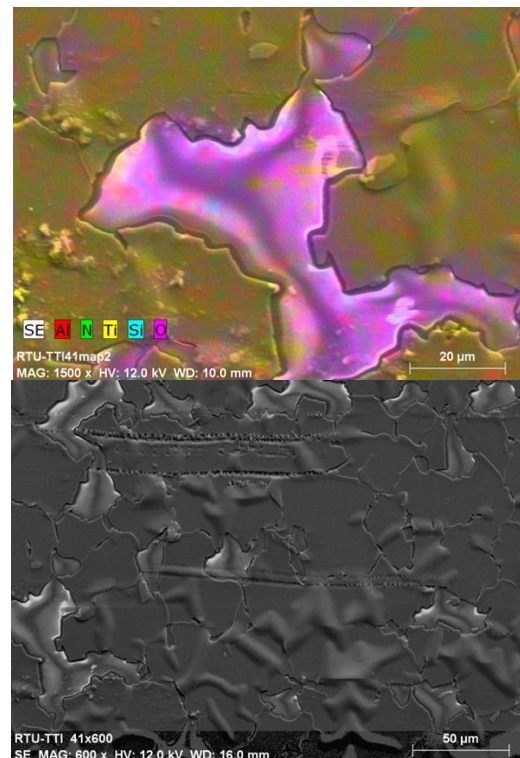


Fig.2. The surface morphology of the golden coating on a scale 20 and 50 µm

As a result of a series of experiments the coating with good adhesion characteristics was obtained.

Figure 3 shows the improved microfractography of the golden coating. The given coating has micro-durability index value of 3930, 50 MPa and Ti content 67,54%.

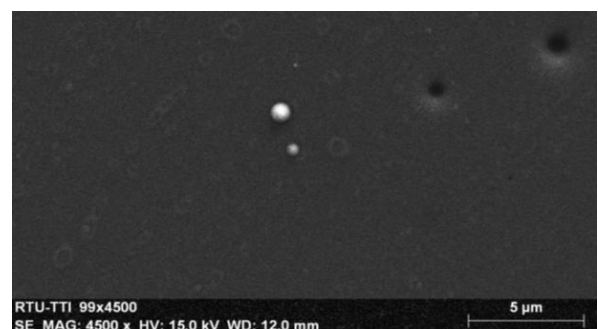


Fig.3. The surface morphology of the improved golden coating on a scale 5 µm

V. THE STUDY OF CORROSION RESISTANCE OF PROTECTIVE DECORATIVE COATING

The destruction of the surface of the decorative and protective coatings proceeds through the mechanism of chemical corrosion. By the nature of damage, corrosion can be divided into:

- General corrosion, when the corrosion process is distributed evenly over the entire surface;
- Local corrosion, when certain parts of the metal corrode.

During the research the corrosion resistance of the previously developed decorative and protective coatings was evaluated in atmospheric conditions, in water, and immersed in 35% solution of NaCl.

There are three categories of atmosphere corrosive activity. According to the International Standard ISO 9223:1992 Corrosion of metals and alloys they are:

- Unheated rooms where condensation can form - lowest category (C2);
- Production areas with high humidity and high air pollution - the average category (C3);
- Marine areas with high salinity - a very high category (C5 M)

To determine the corrosion resistance the following parameters of corrosion damage progress were used:

- Changes in the mass of coating - can be negative or positive;
- Loss of brilliance of coating in service.

Further to determine the loss of brilliance the reflectance coefficient at the angle of incidence of 60 degrees is considered.

To determine the reflectivity of the coatings, it was necessary to assess the value of reflection coefficients at the angles of incidence of 20, 60 and 85°C. The measurements were carried out with the help of glossmeter PICOGLOSS 503.

Measurements of the reflection coefficient at an angle of 60° are carried out for all coatings. For high-gloss coatings measurement should be carried out at an angle of 20° (if the reflection coefficient, measured at an angle of 60° is more than 70 units), for frosted coatings measurements are carried out at an angle of 85° (when the reflection coefficient, measured at an angle of 60° is less than 10 units).

Changing brilliance of coatings is an indication of the initial stage of surface destruction.

Loss of brilliance during the operation was calculated by the formula:

$$X = F^{-1} \cdot (F - F_1) \cdot 100\%, \quad (2)$$

where X - loss of brilliance;

F - original brilliance of the coating;

F₁ – brilliance of the coating after the operation.

Using software package Statistical 10 linear regression analysis was carried out to determine the effect of titanium percentage on the brilliance loss value using the results of studies [9]. Table 3 shows the values of the correlation coefficients.

TABLE 3

EFFECT OF TI CONTENT ON THE LOSS OF BRILLIANCE

	Atmosphere	H ₂ O	NaCl
Ti %	0.36	-0.31	-0.78

The most resistant to decay in the marine environment were decorative-protective coatings titanium content of 55-65%. Those are the coatings of light blue and golden shades. Further increase of titanium leads to higher fragility of decorative-protective coatings (increase of microhardness index value) [3].

VI. INVESTIGATING THE HEAT RESISTANCE OF PROTECTIVE DECORATIVE COATING

The experiment included step-by-step heating of the samples of protective decorative coatings in a furnace within the temperature range of 100 – 550°C. One step is equal to 50°C. The hold-up time under each temperature was 15 minutes. After each heating stage, reflection coefficients were measured at the angles of incidence of 20, 60 and 85°C (see Fig.4).

Heat resistance was determined with the help of the following characteristics:

- 1) gradual change of coating reflection coefficients measured after each hold-up under the predetermined temperature;
- 2) final loss of coating gloss after the experiment calculated by the formula (1) [4].

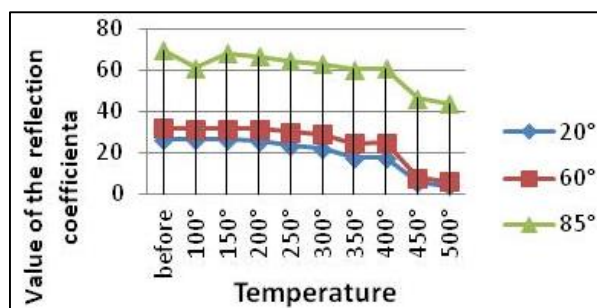


Fig.4. Change of the reflection coefficient of coatings at the angle of incidence of 20, 60 and 85° (Ti=67,54%)

Coatings with reflection coefficient values not exceeding 10.00 units were included into the category of frost coatings – these coatings were exposed to considerable destruction.

A substantial decrease of reflection coefficient values under the heating temperature of 400°C is observed with decorative protective coating.

With the help of software package Statistika10, a linear regression analysis was carried out to determine the influence of coating chemical composition and a number of technological parameters on the loss of coating gloss in the process of heating up to 550°C. The assessed parameters are: correlation of main components in the coating composition – Ti/Al; strength of arc evaporator current (I_{arc evap.}), strength of magnetron current (I_m), magnetron voltage (U_m), argon reactive gas pressure (P_{Ar}), nitrogen reactive gas pressure

(PN), coating microhardness (M.hard.). Table 4 presents the values of the above-listed parameter correlation coefficients for the loss of gloss at the angles of incidence of 20, 60 and 85 degrees.

TABLE 4
DEPENDENCE OF GLOSS LOSS VALUE ON TI CONTENT

Variables	Gloss loss value		
	20°	60°	85°
Ti% content	0.30	0.07	0.30
I _{arc.evap.}	0.30	0.58	0.82
I _m	0.13	-0.13	-0.61
U _m	-0.15	-0.49	-0.45
P _{Ar}	-0.11	0.13	-0.11
P _N	-0.54	-0.63	-0.59
M.hard.	0.07	0.11	0.59

In the table, significant coefficients are marked in grey.

The task of Statistika10 software is to assess the influence of the considered parameters on the increase of coating gloss loss, which does not serve our purposes (the higher is the index of gloss loss the more considerable is coating destruction).

It can be concluded that the increase of eddy-current evaporator current (Ti) and the decrease of nitrogen pressure in the vacuum chamber results in obtaining coatings that have low heat resistance.

Ti-Al-N protective decorative coating were tested for heat resistance within the range of 100-550°C.

The protective decorative coatings with the content of titanium of more than 65 percent are not resistant to temperatures above 400°C.

Figure 5 shows the surface morphology of the coating after sustaining 500°C temperature in the oven.

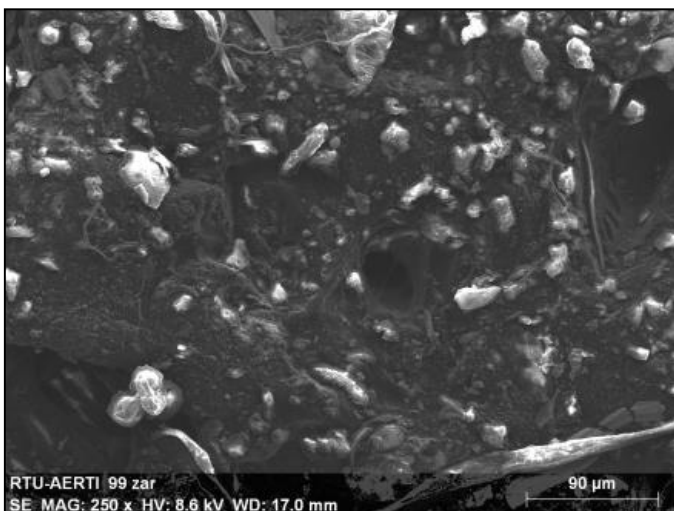


Fig.5. Morphology of the surface of coating (Ti%=67.54) after heating under the temperature of 550°C

The characteristics of microhardness of decorative-protective coating are shown in Table 5.

TABLE 5
QUALITATIVE CHARACTERISTICS OF PROTECTIVE DECORATIVE COATING

T% content	Reflection coefficient value (20/60/80°)	Colour indices Red/Green/Blue	Tone description
67.54	28.5/33.26/67.76	122/104/89	goldish

To study protective characteristics of the given coating it was sputtered over a stainless steel plate. Figure 6 is the graph of microhardness index values of the given coating on the surface of glass and stainless steel, as well as stainless steel without coating.

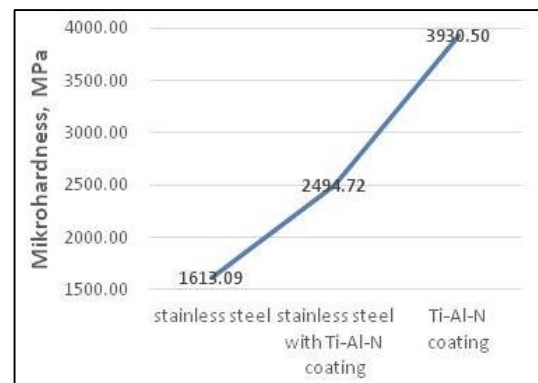


Fig.6. The graph of microhardness (MPa) index changes

The microhardness index value of a stainless steel plate has increased by 1.53 due to protective properties of vacuum ion-plasma decorative coating on Ti-Al-N basis.

VII. CONCLUSIONS

The paper discusses the features of the technology of application of single layer decorative-protective coatings on the basis of Ti-Al-N. A series of experiments was conducted to create multicomponent single layer ion-plasma coatings by vacuum deposition in argon and nitrogen.

The quality of the adhesive coatings was researched. Using nanoindentation method microhardness index values of decorative-protective coatings were obtained. Energy dispersive electron microprobe analysis was used to study the structure of the surface of coatings and their chemical composition.

The application of vacuum ion-plasma decorative-protective coating allowed increasing the strength characteristics of the surface of sputtered materials.

The results of the research can be used in practice for manufacturing and repair of vehicles, particularly sea-going vessels.

REFERENCE

1. **Urbaha, M.** *Nodilumizturīgo nanostrukturēto jonu-plazmas pārklājumu fizikāli-mehānisko īpašību eksperimentālā pētīšana* // RTU zinātniskie raksti. 6. sēr., Mašīnzinātne un transports. - 10. sēj. (2010), 80.-88. lpp.
2. **Urbahs, A., Savkovs, K., Bogdanova, S.** *Transporta mašīnbūves izstrādājumu jonu-plazmas aizsargpārklājumu dekoratīvo īpašību novērtējums.* - In the Book: Proceedings of the 13th International Conference "Maritime Transport and Infrastructure", ISSN 1691-3817, Rīga, 2011, 174. – 179. lpp.
3. **Urbaha, M., Bogdanova, S., Savkovs, K., Rijkuris, G.** *Research on Corrosion Resistance of Decorative and Protective Ion Plasma Coating on Ti-Al-N Base* // Transport Means 2012: Proceedings of the 16th International Conference, Lithuania, Kaunas, 23.-26. October, 2012. - pp 58-61. SCOPUS Database.
4. **Urbahs, A., Bogdanova, S., Urbaha, M., Savkovs, K., Rijkuris, G.** *Investigation of the heat resistance of protective decorative ion-plasma coatings.* In: Proceedings of International Congress on Engineering and Technology, ISSN 1338-2330, Dubrovnik, Croatia: 2013, pp. 267.-270.
5. **Urbahs, A., Urbaha, M., Savkovs, K., Bogdanova, S.** *Wear resistant nanostructured multi-component coatings* (2012) NATO Science for Peace and Security Series B: Physics and Biophysics, pp. 161-170. Scopus EXPORT DATE: 25 January 2013.
6. **Golovin, Y.I.** *Nanoindentirovanije i jego vozmožnosti.* M. Mashinostrojenije, 2009 – 312s.
7. **Geller, Y.A., Rahshtad, A.G.** *Materialovedenije.* M. Metallurgija, 1989 – 454 s.
8. **Williams, S.R.** *Hardness and Hardness Measurements* / Williams S.R. – Cleaveland: ASM, 1942.
9. <http://bourabai.kz/tpoi/statistica/>
10. **A.C. Dürr, F. Schreiber, M. Kelsch, H.D. Carstanjen, H. Dosch.** *Morphology and Thermal Stability of Metal Contacts on Crystalline Organic Thin Films.* Max-Planck-Institut für Metallforschung, Heisenbergstraße 1, 70569 Stuttgart, Germany and Institut für Theoretische und Angewandte Physik, Universität Stuttgart, Pfaffenwaldring 57, 70550 Stuttgart, Germany (Thursday, 11 April 2002)

Aleksandrs Urbahs graduated from the Faculty of Mechanical Engineering, Riga Civil Aviation Engineering Institute, in 1981, and was awarded the degree of Dr.sc.ing. by the same faculty in 1986. In 1997 he was awarded the degree of Dr.habil.sc.ing. by Riga Aviation University. In 1989-1999 he was a Vice Dean and the Dean of the Faculty of Mechanical Engineering of Riga Aviation University. Since 1999 he is a full time professor of Riga Technical University. In 1999-2012 he was the Director at the Institute of Transport

Vehicles Technologies of Riga Technical University. Since 2012 he is the Director of the Institute of Aeronautics of Riga Technical University. Publications: 297scientific papers and 19 patents. Fields of research: aeronautics; transport and mechanical engineering.

Svetlana Bogdanova, 2007-2009 - Professional Master Degree in Transport System Engineering. Since 2010 - Riga Technical University, Faculty of Transport and Mechanics, Institute of Aeronautics, PhD study program „Transports”, 4th year. Scientific publications: Urbaha, M., Savkovs, K., Bogdanova, S. Decorative properties of protective ion-plasma coatings for machine-building products (2011) *AES-ATEMA International Conference Series - Advances and Trends in Engineering Materials and their Applications*, pp. 59-63. *SCOPUS*; Urbahs, A., Urbaha, M., Savkovs, K., Bogdanova, S. Wear resistant nanostructured multi-component coatings (2012) *NATO Science for Peace and Security Series B: Physics and Biophysics*, pp. 161-170. *SCOPUS*; M.Urbaha, S.Bogdanova, K.Savkovs, G.Rijkuris (2012). Research on Corrosion Resistance of Decorative and Protective Ion Plasma Coatings on TI-AL-N Base– In the Book: Proceedings of the 16th international conference „Transport Means 2012”, ISSN 1822-296 X, 2012, 58-61 *SCOPUS*.

Margarita Urbach (Dr.sc.ing.) graduated from Riga Technical University, Faculty of Transport and Mechanical Engineering with PhD in Engineering in September 2011. She is a vice researcher at the Institute of Aeronautics of Riga Technical University. Her fields of scientific interests include: aeronautics, nanomaterials, surface protection technologies, nanocomposite coatings, structural materials, transport systems and logistics.

Konstantin Savkov graduated from the Faculty of Mechanical Engineering, Riga Civil Aviation Engineering Institute, in 1983. Since1983 he worked as an engineer, researcher at Riga Civil Aviation Engineering Institute, Riga Aviation University. Since 1999 he is an engineer, researcher at the Institute of Transport Vehicles Technologies of Riga Technical University. His fields of scientific interest include: mechanical engineering; transport; unmanned land/sea/air vehicles; science of aviation materials; aircraft construction mechanics; structural materials processing – surface protection technologies; diagnostics of machinery, scanning electron microscopy.

Gints Rijkuris (M.Sc.ing.) graduated from Latvian Maritime Academy as engineer-ship's navigator. From 2003-2008 he gained experience as merchant vessel navigator. From 2008 onwards – the Captain of ASD tugboat in Riga Free Port . In 2010 he graduated from Masters course. From 2011 onwards - a full time doctoral student at the Institute of Aeronautics. From August 2011 he is researcher at the Institute of Aeronautics of Riga Technical University. His fields of scientific interests include: aeronautics, nanomaterials, nanocoatings, structural materials, unmanned vehicles, transport systems and logistics.

Aleksandrs Urbahs, Svetlana Bogdanova, Margarita Urbaha, Konstantīns Savkovs, Gints Rijkuris. Dekoratīvo jonu plazmas vakuuma aizsargpārklājumu aizsargīpašību izpēte

Viens no efektīvākajiem tehnoloģiskajiem izstrādājumu stiprības īpašību paaugstināšanas veidiem ir dažādu pārklājumu uznešana uz pārklājumu darba virsmas. Darbā ir apskatīti vienslāņa dekoratīvo aizsargpārklājumu uz Ti-Al-N bāzes uznešanas tehnoloģijas īpašības. Tika veikti vairāki eksperimenti par vienslāņa daudzkomponentu jonu plazmas pārklājumu uznešanu, izmantojot vakuuma uznešanas metodi argona un slāpekļa vidē. Eksperimentālos pētījumos tika izmantoti divi metāliskās plazmas avoti – elektriskā loka iztvaikoņājs un magnetrons. Tika iegūti dekoratīvie aizsargpārklājumi, kas imitē zelta krāsu. Pētījuma objekts bija sekojošas raksturīpašības – struktūras izmaiņas un plēvītes mikrociētības atkarībā no pārklājumu ķīmiskā sastāva noteikšana. Ar nanoindentēšanas metodi tika iegūtas dekoratīvo aizsargpārklājumu mikrociētības vērtības. Izmantojot energodispersijas mikrorentģenospektrālo analīzi, tika izpētīta pārklājumu virsmas struktūra un tās ķīmiskais sastāvs. Eksperimentālā ceļā tika iegūti pārklājumi ar noturīgām adhēzijas raksturīpašībām.

Александр Урбах, Светлана Богданова, Маргарита Урбах, Константин Савков, Гинтс Рийкурис. Исследования защитных характеристик декоративных ионноплазменных защитных покрытий.

Одним из наиболее эффективных технологических путей повышения прочностных характеристик изделий является нанесение на рабочую поверхность различных покрытий. В работе рассмотрены особенности технологии нанесения однослойных декоративно-защитных покрытий на базе Ti-Al-N. Проведена серия экспериментов по созданию однослойных многокомпонентных ионноплазменных покрытий вакуумным напылением в среде аргона и азота. В экспериментальных исследованиях использовали два источника маталлической плазмы – электродуговой испаритель и магнетрон. Были получены декоративно защитные покрытия, имитирующие по цвету золото. В качестве предметов исследований были определены изменения структуры и микротвердости пленок в зависимости от химического состава покрытий. Методом наноиндентирования получены значения микротвердости декоративно-защитных покрытий. С помощью энергодисперсионного микроанализа исследована структура поверхности покрытий и их химический состав. Экспериментальным путем получено покрытие с устойчивыми адгезионными характеристиками. Покрытие исследовано на коррозионную стойкость в условиях атмосферы. Нанесение вакуумного ионно-плазменного декоративно защитного покрытия позволило повысить прочностные характеристики поверхности напыляемого материала. Значение показателя микротвердости пластины из нержавеющей стали, благодаря защитным свойствам данного вакуумного ионноплазменного декоративного покрытия на базе Ti-Al-N, увеличилось в 1,53 раза.