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Influence of Technological Parameters of Deposition on Physical and Mechanical Properties of Vacuum-Arc Multilayer Nitride Coatings Based on Chromium and Niobium

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Establishing the regularities of the structure and phase formation of vacuum-arc multilayer nitride coatings at different technological parameters is important for the predicted obtaining of the required properties of multilayer systems. To analyse the influence on the physical and mechanical properties, the following technological parameters of deposition vacuum-arc multilayer nitride coatings are chosen: pressure of the reaction gas in the vacuum chamber (0.08–0.27 Pa), constant negative voltage on the substrate (70–200 V), layer thickness (17–150 nm) and number of layers (68, 270, 1080). Chromium and niobium nitrides, which are promising materials in many fields of application, are chosen as components of vacuum-arc coatings. The research show that vacuum-arc multilayer nitride coatings CrN/NbN obtained under different technological conditions have high planarity of layers and practically no drop phase in the volume of the coating. The analysis of heterogeneity of the structural and phase state of the coatings is carried out by the root-mean-square deviation

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of the vacuum-arc coating microhardness. The trends in changes in physical and mechanical properties are evaluated based on the average values of microhardness, contact modulus of elasticity, and others ratios.

Key words: vacuum-arc coatings, multilayer coatings, microhardness, surface morphology, physical and mechanical properties.

Встановлення закономірностей структуро- та фазоутворення вакуумно-дугових багатошарових нітридних покриттів за різних технологічних параметрів нанесення є важливим для прогнозованого одержання потрібних властивостей багатошарових систем. Для аналізи впливу на фізико-механічні властивості були обрані наступні технологічні параметри нанесення вакуумно-дугових багатошарових нітридних покриттів: тиск реакційного газу у вакуумній камері (0,08–0,27 Па), постійна неґативна напруга на підкладинці (70–200 В), товщина шарів (17–150 нм) і кількість шарів (68, 270, 1080). В якості складових вакуумно-дугових покриттів були обрані нітриди Хрому та Ніобію, які є перспективними матеріялами у багатьох галузях застосування. Проведені дослідження показали, що одержані за різних технологічних умов вакуумно-дугові багатошарові нітридні покриття CrN/NbN мають високу планарність шарів і практично відсутність крапельної фази в об'ємі покриття. Аналізу неоднорідности структурно-фазового стану покриттів проводили за середньоквадратичним відхилом мікротвердости одержаних вакуумно-дугових покриттів. Оцінювання тенденцій змін фізико-механічних властивостей виконувалося за середніми значеннями мікротвердости, контактного модуля пружности та інших співвідношень.

Ключові слова: вакуумно-дугові покриття, багатошарові покриття, мікротвердість, морфологія поверхні, фізико-механічні властивості.

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1. INTRODUCTION

In recent years, the development of vacuum-arc coatings for various fields of application is based on the combination of coating components with different physical and mechanical, electrical, magnetic, optical properties and the complication of the vacuum-arc coating structure. Thus, over the past two decades, a wide range of multicomponent [1–5] and multilayer [6–10] coatings have been created and researched. These studies showed the perspective and limitless possibilities of creating vacuum-arc coatings for various purposes.

One of the important factors affecting the functional properties of multilayer vacuum-arc coating is the state of the interphase boundary between layers of materials with different phase composition and structural state. This becomes especially significant when the thickness of the layers is reduced to tens of nm [11, 12]. In addition, the thickness of individual layers and their total number also make a significant contribution to the processes of controlled formation of vacuum-arc coatings with the necessary properties [13, 14].

In order to obtain predictably the required properties of multilayer systems, it is important to establish the regularities of structural and phase formation of vacuum-arc multilayer coatings under different deposition technological parameters, namely, the pressure of the reaction gas in the vacuum chamber, the constant negative voltage on the substrate, the thickness and number of layers. Despite the large number of studies in this direction and taking into account the infinite number of possible combinations of multilayer systems, this task is still relevant.

Nitrides of transition metal of IV group (Ti, Zr, Hf) [15–17], V group (V, Nb, Ta) [18–20] and VI group (Cr, Mo, W) [21–23] are mainly used as components of a multilayer system. For example, chromium nitride has good wear and corrosion resistance, high temperature stability, and a lower friction coefficient than titanium nitride [24]. Due to this, it is used as a protective coating on a cutting tools operating at high cutting speeds. In turn, niobium nitride has high hardness and electrical conductivity, good heat resistance and chemical inertness [25], and is used in microelectronic devices, superconductor detectors and other fields. When these two materials are combined, it becomes possible to obtain new properties of vacuum-arc multilayer coatings and expand the field of their application.

This paper presents the results of studies of the influence of deposition technological parameters on the physical and mechanical properties of vacuum-arc multilayer coatings based on chromium and niobium.

2. MATERIALS AND METHODS

2.1. Materials and Deposition

Vacuum-arc nitride multilayer coatings based on chromium and niobium were deposited in a modified installation 'BULAT-6'. The evaporator materials were pure metals of vacuum melting: chromium (Cr99N1) and niobium (Nb1). Cathodes were made of rods with a diameter of 60 mm.

AISI 430 BA + PVC stainless steel samples with a mirror-polished surface were used as substrates for deposition of coatings. Surface roughness of these samples R_a was lower than 0.05 μm. The dimensions of the samples were 18×18×2 mm. They were used to determine the physical and mechanical, tribological properties of coatings.

Previously, the samples were washed with an alkaline solution in an ultrasonic bath for 10 minutes, and then with Nephras C2-80/120. During the deposition of the coatings, the samples were placed on both sides on a vertically located metal substrate-holder in the vacuum-arc chamber of the installation. Substrate-holder was in the form of a rectangle with dimension 220×300 mm. It was placed on the same horizontal level as the evaporators and rotated around its vertical axis. The evaporators themselves were located opposite each other, as shown in Fig. 1.

Before deposition of the vacuum-arc coatings, the vacuum chamber with the samples was pumped to a pressure of $P = 1.3 \cdot 10^{-3}$ Pa. After this, the ionic cleaning and activation of the sample surface were carried out by bombardment with metal ions with continuous rotation of the substrate-holder and a constant voltage on it −1.1 kV. The process of samples cleaning and heating lasted for 10 minutes. After these processes, an underlayer of pure metal (Cr, Nb) was deposited to improve the adhesive properties of the coatings.

To study the influence of technological deposition parameters on the physical and mechanical properties of vacuum-arc multilayer nitride coatings based on chromium and niobium, three series of coatings were obtained: with continuous rotation of the substrate holder with samples at a speed of 12 revolutions per minute (series I), at the interval of the substrate holder rotation of 80 seconds (series II), at the interval of the substrate holder rotation of 20 seconds (series III).

Control of the technological installation units (motor of substrate holder rotation and power sources of the evaporators) during the deposition of vacuum-arc coatings of the second and third series was car-

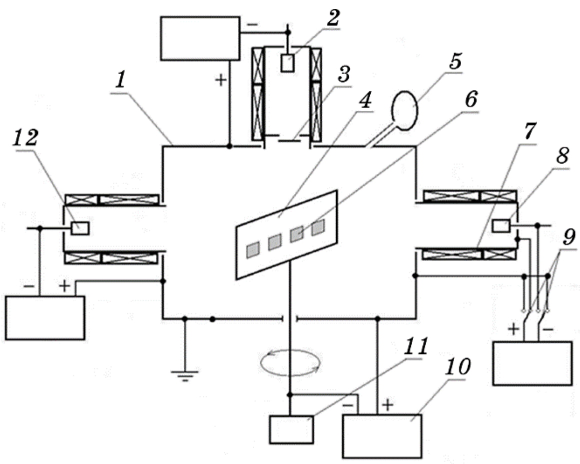

Fig. 1. Scheme of the installation for deposition of vacuum-arc multilayer nitride coatings: *1*—vacuum chamber, *2*—vacuum-arc evaporator (titanium), *3*—shield, *4*—substrate holder with samples, *5*—gas inlet, *6*—substrates (samples), *7*—vacuum-arc evaporator frame—the anode for the gas discharge, *8*—vacuum-arc evaporator (chromium), *9*—switching relay for connection of evaporator power supply, *10*—high negative voltage source U_S, *11*—system for controlling the deposition of nanolayer vacuum-arc coatings, *12*—vacuum-arc evaporator (niobium).

ried out using the system for controlling the deposition of nanolayer vacuum-arc coatings [26]. During the deposition of the second and third series of coatings, the evaporators were turned off during the rotation of the substrate-holder by 180°. This made it possible to obtain clear boundaries between the layers.

The technological process of deposition vacuum-arc multilayer nitride coatings to the samples took place within 1.5 hours. The pressure of the reaction gas (nitrogen) in the vacuum chamber varied from 0.08 to 0.27 Pa. The constant negative voltage on the substrate was −70 V and −200 V. The arc current of evaporators was 80 A (for chromium) and 100 A (for niobium). The evaporators had plasma flow focusing by a magnetic field 5 mT. The distance from the evaporators to the axis of substrate-holder rotation was 500 mm.

2.2. Structural Characterization

Planar raster electron microscopic images were obtained using a Tescan Vega 3 SBU in secondary electron mode at an accelerating voltage of 30 kV. The samples were examined without applying any coatings. A standard technique was used to study the cross sections, which consisted of cutting the sample (STRUERS Secotom-50 saw), fixing it in a polymer matrix, and successive mechanical grinding and polishing (STRUERS Tegramin 25 device). Cross sections were examined in a field emission scanning electron microscope (Zeiss ULTRA Plus) at an accelerating voltage of 2 or 10 kV. An in-lens detector of secondary electrons and a wide-angle detector of backscattered electrons were used.

2.3. Mechanical Testing

The study of physical and mechanical characteristics of coatings on stainless steel samples was carried out by the microindentation method using CMS hardness measurement equipped by standard Vickers pyramid. Microhardness numbers were determined under indentation loads not higher than 1.0 N. Microtester capable for load-displacement measurements and equipped by trihedral Berkovich pyramid was used to determine Young’s modulus, E, according to the test method procedure originally proposed by Oliver and Pharr.

3. RESULTS AND DISCUSSION

3.1. Structural Characterisation of Vacuum-Arc Multilayer Nitride Coatings CrN/NbN

Technological parameters of deposition of vacuum-arc multilayer nitride coatings: arc current of chromium evaporator I_{A1} and niobium I_{A2}, constant negative voltage on the substrate U_S, pressure of reaction gas (nitrogen) P_N are presented in Table 1.

Three series of vacuum-arc multilayer nitride coatings were obtained by using of different technological modes: coatings with different thicknesses of individual CrN and NbN layers and bilayer period (CrN–NbN), number of layers (68 and 270 layers) and kind of the interface between the layers (clear boundary or transition layer).

Figure 2 demonstrates SEM images for the surface morphology of vacuum-arc coatings of three series, obtained under the same technological conditions (constant negative voltage on the substrate $U_S = -200$ V and pressure of the reaction gas (nitrogen) $P_N = 0.08–0.09$ Pa).

The use of different technological deposition modes of vacuum-arc coatings, namely turning off the power sources of the evaporators (chromium and niobium cathodes) after 20 s and 80 s for the time of turning the substrate holder (5 s) and permanently switched on evaporators, affect the processes occurring on the cathodes surface and in the near cathode zone (width up to $2\cdot10^{-4}$ cm [27]). The formation processes of cathode spots of the I and II types and the duration of their

TABLE 1. Technological parameters of deposition of vacuum-arc multilayer nitride coatings based on chromium and niobium.

Series of coatings	No. sample	Coating composition	I_{A1}, A	I_{A2}, A	U_S, V	P_N, Pa	Technological mode
I	I-1	CrN/NbN	80	120	−70	0.27	Constant rotation
	I-2	CrN/NbN	80	120	−200	0.27	Constant rotation
	I-3	CrN/NbN	80	100	−200	0.09	Constant rotation
II	II-1	CrN/NbN	80	100	−200	0.27	Rotation interval – 80 s, 68 layers
	II-2	CrN/NbN	80	100	−70	0.27	Rotation interval – 80 s, 68 layers
	II-3	CrN/NbN	80	100	−70	0.08	Rotation interval – 80 s, 68 layers
	II-4	CrN/NbN	80	100	−200	0.08	Rotation interval – 80 s, 68 layers
III	III-1	CrN/NbN	80	100	−200	0.27	Rotation interval – 20 s, 270 layers
	III-2	CrN/NbN	80	100	−70	0.27	Rotation interval – 20 s, 270 layers
	III-3	CrN/NbN	80	100	−70	0.08	Rotation interval – 20 s, 270 layers
	III-4	CrN/NbN	80	100	−200	0.08	Rotation interval – 20 s, 270 layers

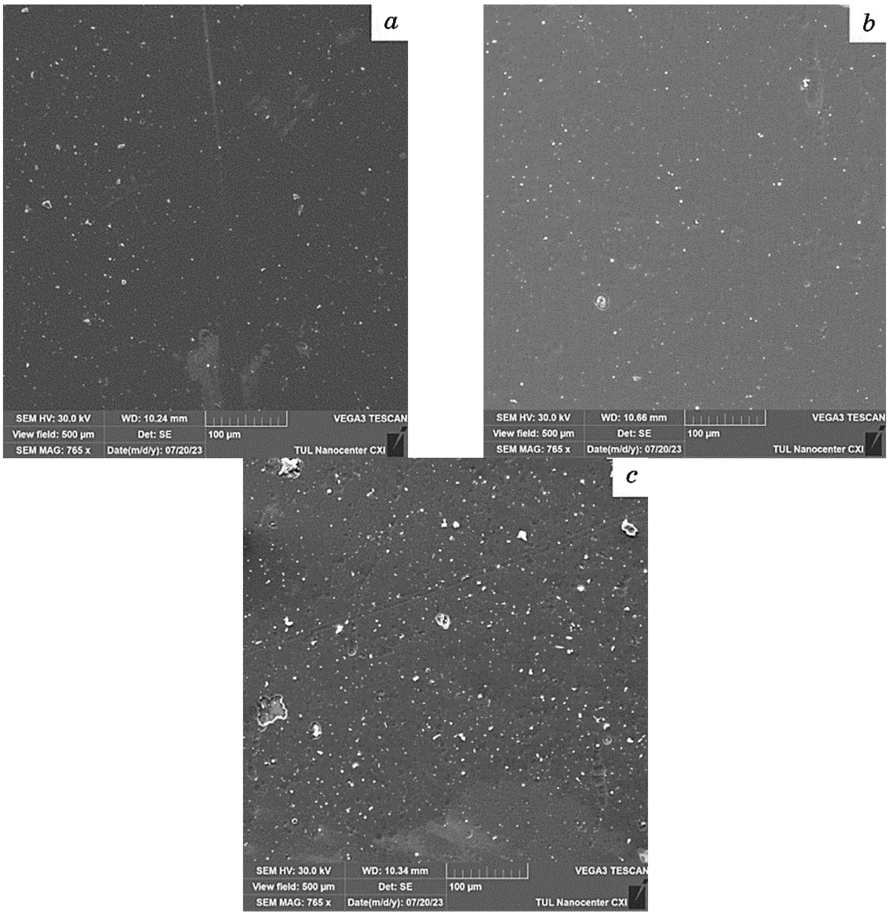

Fig. 2. SEM images of the surface morphology of vacuum-arc multilayer nitride coatings CrN/NbN obtained at the same technological conditions ($U_S = -200$ V, $P_N = 0.08–0.09$ Pa): I series—sample I-3 (*a*), II series—sample II-4 (*b*), III series—sample III-4 (*c*).

existence on the cathode surface, the temperature of the cathodes, the composition and state of the metal component of the plasma depend on these conditions. Thus, even a relatively small change in the temperature of the cathode leads to a significant decrease in the average energy and multiplicity of metal component ions of the plasma [27], which, in turn, further affects the deposition processes of the vacuum-arc coating, the structural-phase state, and the physical and mechanical properties of the vacuum-arc coatings.

Figure 3 demonstrates SEM images for the surface morphology of vacuum-arc multilayer nitride coatings CrN/NbN of third series obtained under different technological conditions of deposition.

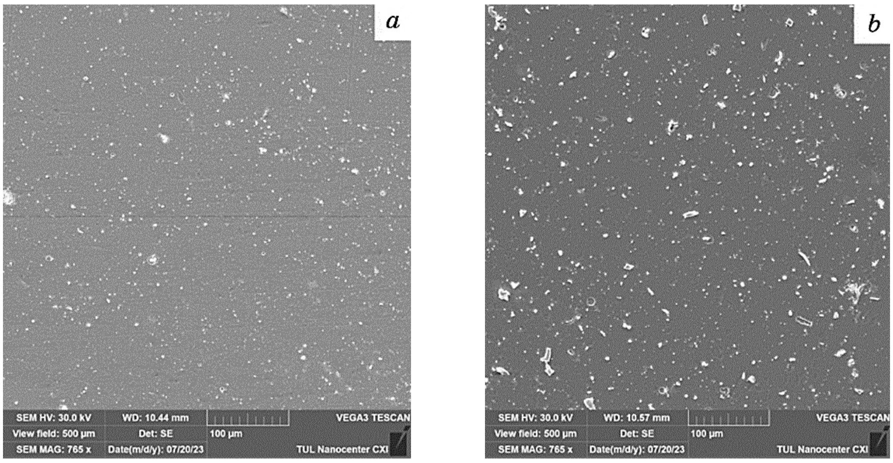

Fig. 3. SEM images of the surface morphology of vacuum-arc multilayer nitride coatings CrN/NbN of third series obtained under different technological parameters: sample III-1, $U_S = -200$ V, $P_N = 0.27$ Pa (*a*), sample III-3, $U_S = -70$ V, $P_N = 0.08$ Pa (*b*).

A transition layer of Cr–Nb–N is formed between CrN and NbN layers of the vacuum-arc nitride coatings in the mode of continuous rotation of the substrate holder with permanently switched on cathodes (series I). However, a clear boundary between CrN and NbN layers is formed when using a system for controlling the deposition of nanolayers vacuum-arc coatings (series II and III), due to turning off the cathodes for the time of turning the substrate holder.

Figure 4 demonstrates SEM images of cross-section of vacuum-arc multilayer nitride coatings CrN/NbN with different thicknesses of individual CrN and NbN layers and bilayer period (CrN–NbN), the number of layers (68 and 270 layers), and the kind of the interface between the layers (clear boundary or transition layer). The boundaries between the layers are clearly visible, as can be seen in Fig. 4.

Analysis of the cross-sections SEM images of the vacuum-arc multilayer nitride coatings CrN/NbN of three series with different number of layers showed that the total thickness of the coatings was 3.6 μm for the vacuum-arc coatings of the first series, which were obtained by continuous rotation of the substrate holder, and about 8 and 9 μm for vacuum-arc coatings of the second and third series, respectively.

Table 2 shows the geometric parameters of the vacuum-arc multilayer nitride coatings CrN/NbN of three series, namely the thickness of the chromium nitride h_{CrN} and niobium nitride h_{NbN} layers, the bilayer period h_b, the total coating thickness h, the number of bilayers (periods), and the total number of layers.

Evaluation of the thickness of individual chromium nitride layer

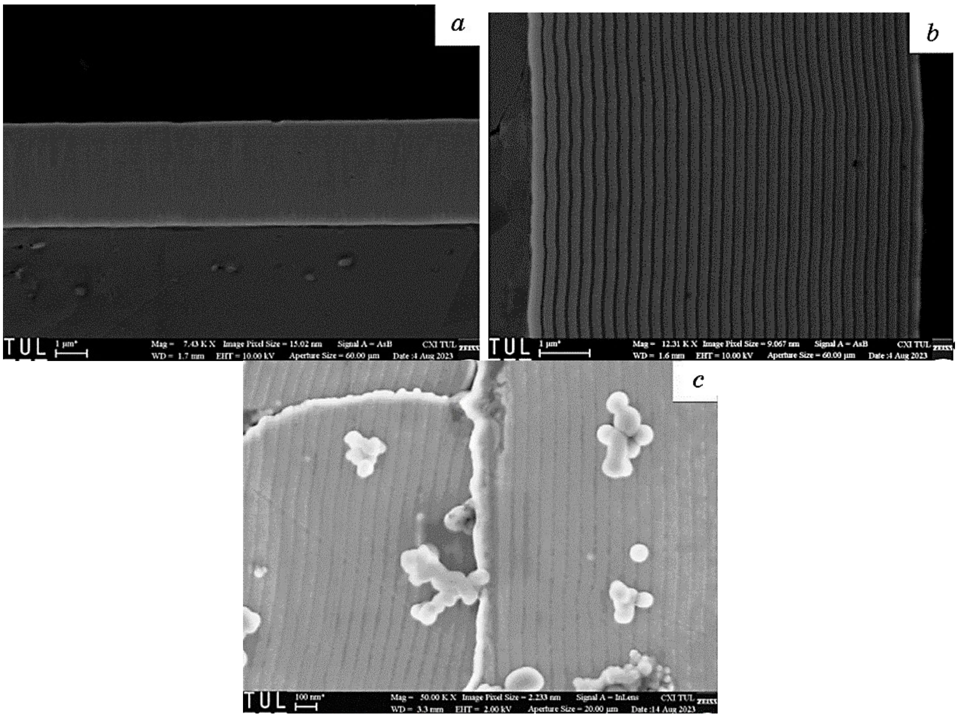

Fig. 4. SEM images of cross-section of vacuum-arc multilayer nitride coatings CrN/NbN of three series with different number of layers: I series (sample I-3)—constant rotation (*a*), II series (sample II-4)—68 layers (*b*), III series (sample III-1)—270 layers (*c*).

TABLE 2. Geometric parameters of vacuum-arc multilayer nitride coatings CrN/NbN of three series.

Series of coatings	Coating composition	h_{CrN}, nm	h_{NbN}, nm	h_b, nm	h, μm	Number of bilayers	Total number of layers
I series	CrN/NbN	–	–	6.7	3.6	540	1080
II series	CrN/NbN	80	150	230	7.8	34	68
III series	CrN/NbN	17	50	67	9	135	270

h_{CrN} and individual niobium nitride layer h_{NbN} for vacuum-arc multilayer nitride coatings of the first series (with constant rotation of the substrate-holder) was not carried out, since these coatings do not have clear transition boundaries between CrN and NbN layers due to the formation of a transition layer Cr–Nb–N.

In general, the resolution of the EDS technique is at the level of 1 μm.

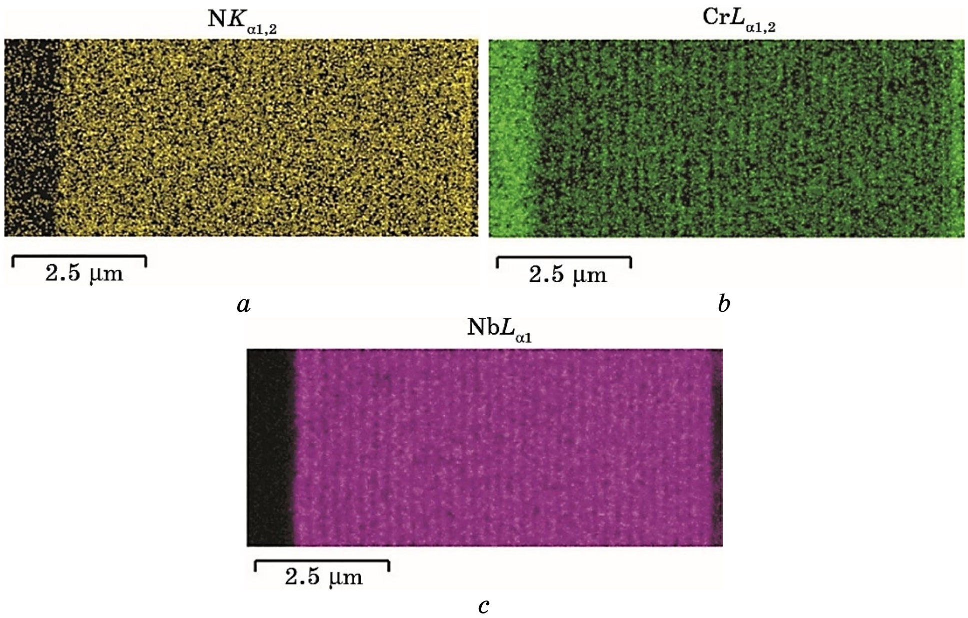

Fig. 5. Elements distribution of vacuum-arc multilayer nitride coatings CrN/NbN of the second series (sample II-4) by depth of the coating: nitrogen N (*a*), chromium Cr (*b*), niobium Nb (*c*).

However, as we can see from Fig. 5, which shows the EDS map of sample II-4, the observed map demonstrates the layered state of the sample. The given elemental maps do not contain indications of a violation of the layered structure homogeneity in the depth of the coating.

The elements distribution of the vacuum-arc multilayer coating on the surface of sample II-4 is shown in Fig. 6. It can be seen that the coating is quite homogeneous in composition. The analysis of the images showed that the obtained coatings of the II and III series have high planarity of layers and practically no droplet phase in the volume of the multilayer vacuum-arc nitride coatings CrN/NbN, as can be seen in Fig. 4, *b* and *c*.

The chemical composition (on the surface) of the vacuum-arc multilayer nitride coatings CrN/NbN of the second series (sample II-4) is: 25.1 at.% niobium, 32.5 at.% chromium, 42.4 at.% nitrogen.

3.2. Mechanical Characteristics of Vacuum-Arc Multilayer Nitride Coatings CrN/NbN

3.2.1. Microhardness of Vacuum-Arc Nitride Coatings CrN/NbN

In order to compare the physical and mechanical properties of vacuum-arc multilayer nitride coatings CrN/NbN with the properties of pure metals (Cr and Nb), nitrides and individual nitride coatings (CrN and NbN) and to further establish the regularities of the influence of the technological deposition parameters, their properties are shown in Table 3 (microhardness H_μ and modulus of elasticity E_μ) [28–34].

The microhardness of the studied vacuum-arc multilayer nitride coatings based on chromium and niobium is presented in Table 4 in the form of the minimum H_{min} and maximum H_{max} values of the microhardness, the range of the obtained values ΔH, the average value H_{med} and the root mean square deviation (RMSD). Evaluation of the microhardness was carried out by eight measurements at a distance of 100 µm between them, with a total measurement length of 0.7 mm.

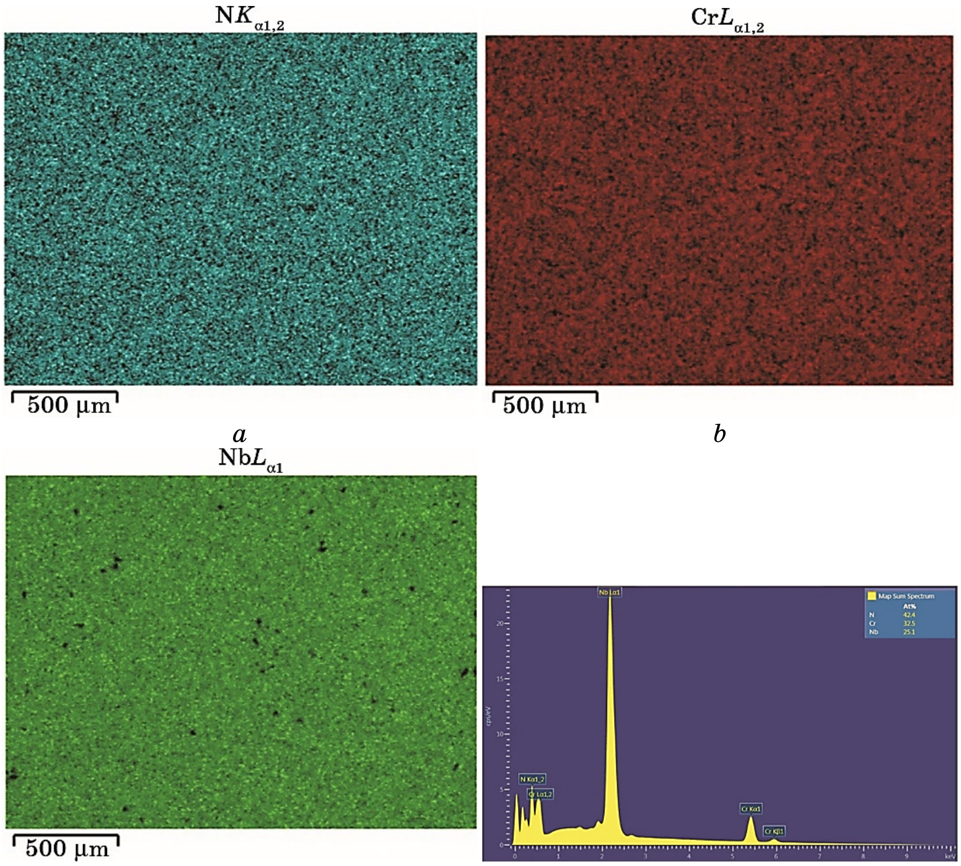

Fig. 6. Element maps of vacuum-arc multilayer nitride coatings CrN/NbN of the second series (sample II-4): nitrogen N (*a*), chromium Cr (*b*), niobium Nb (*c*), energy dispersive spectrum (*d*).

TABLE 3. Properties of pure metals (Cr and Nb), nitrides and individual nitride coatings (CrN and NbN).

No	Phase	H_μ, kg/mm^2	H_μ, GPa	E_μ, kg/mm^2	E_μ, GPa	Reference
			Pure metals			
1	Cr	142–250	1.4–2.5	24000	235.4	[28, 30]
2	Nb	87	0.87	16000	157	[28, 30]
			Nitrides			
3	Cr_2N	1571 ± 49	15.4 ± 0.48	–	310	[29]
4	CrN	1093 ± 93	10.7 ± 0.9	–	319.8	[29]
5	Nb_2N	1720 ± 100	16.9 ± 1	–	–	[29]
6	$NbN_{0.75}$	1780	17,5	–	–	[29]
7	$NbN_{0.97}$	1525 ± 136	15 ± 1.3	–	–	[29]
8	NbN	1461	14.3	49300 ± 2000	493 ± 2	[29, 31]
			Vacuum-arc nitride coatings			
9	CrN	–	16–23	–	298 ± 11	[32, 33]
10	NbN	–	22.7–38.2	–	343–437	[34]

When analysing the obtained microhardness values, the values related to the droplet phase of vacuum-arc coatings with microhardness values less than 2.5 GPa were excluded. These microhardness values correspond to the maximum value of microhardness among pure metals (cathodes), namely chromium (Table 3).

TABLE 4. Microhardness of vacuum-arc multilayer nitride coatings based on chromium and niobium.

Series of coatings	No. sample	Coating composition	H_{min}, GPa	H_{max}, GPa	ΔH, GPa	H_{med}, GPa	RMSD, GPa
I	I-1	CrN/NbN	22.274	24.922	2.648	23.716	1.044
	I-2	CrN/NbN	16.607	24.996	8.389	22.31	2.552
	I-3	CrN/NbN	16.972	19.914	2.942	18.766	0.896
II	II-1	CrN/NbN	15.76	31.717	15.957	22.481	4.338
	II-2	CrN/NbN	10.402	17.176	6.774	14.531	2.958
	II-3	CrN/NbN	18.884	31.916	13.032	24.055	3.472
	II-4	CrN/NbN	23.076	29.579	6.503	25.188	1.994
III	III-1	CrN/NbN	21.889	25.562	3.673	23.435	1.389
	III-2	CrN/NbN	15.33	34.994	19.664	23.723	7.16
	III-3	CrN/NbN	23.059	28.019	4.96	25.045	2.062
	III-4	CrN/NbN	21.574	24.913	3.339	23.054	1.15

The analysis of the average microhardness values of the obtained vacuum-arc coatings CrN/NbN by series (I–III) depending on the technological deposition parameters (constant negative voltage on the substrate U_S and the pressure of the reactive gas (nitrogen) P_N) are presented in the form of graphs, as can be seen in Figs. 7, 8. These graphs show trends in changes in the microhardness of vacuum-arc coatings depending on changes in technological parameters, but do not take into account the heterogeneity of the structural-phase state of each vacuum-arc coating. This heterogeneity is characterized by the spread of the microhardness values and the root mean square deviation (RMSD). Thus, a larger value of RMSD indicates a greater spread of microhardness values in the obtained data set, while a smaller value, respectively, indicates that the obtained values are grouped around the average value of microhardness.

Increasing the constant negative voltage on the substrate U_S from −70 to −200 V leads to:

– the reduction of the average microhardness value of vacuum-arc

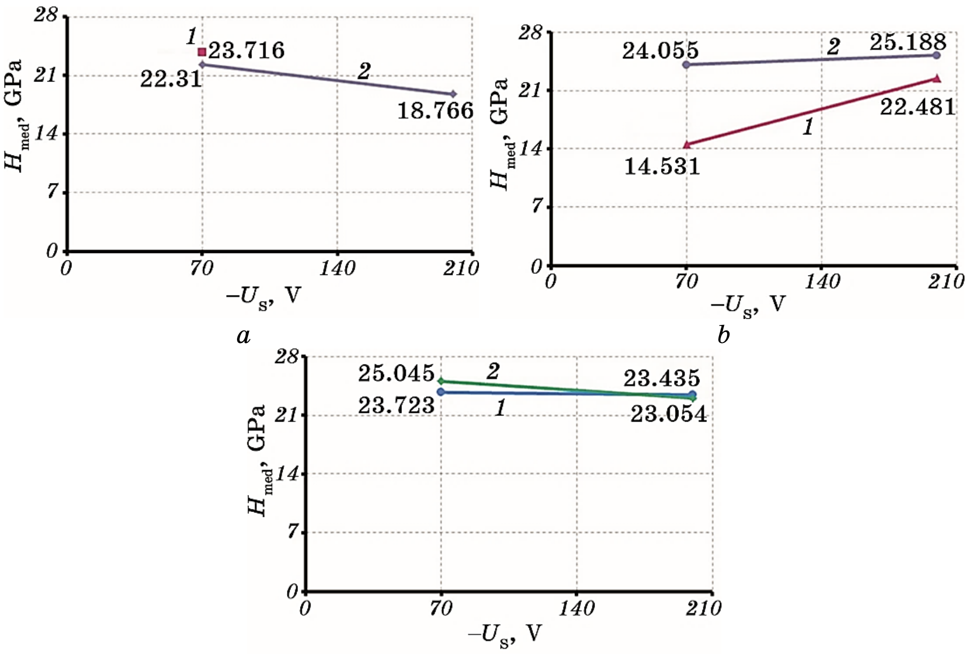

Fig. 7. Dependence graphs of the average microhardness value H_{med} of vacuum-arc multilayer nitride coatings CrN/NbN to the constant negative voltage on the substrate U_S at constant values of the nitrogen pressure in the vacuum chamber P_N: series I (*1*—$P_N = 0.27$ Pa, *2*—$P_N = 0.09$ Pa) (*a*), series II (*1*—$P_N = 0.27$ Pa, *2*—$P_N = 0.08$ Pa) (*b*), series III (*1*—$P_N = 0.27$ Pa, *2*—$P_N = 0.08$ Pa) (*c*).

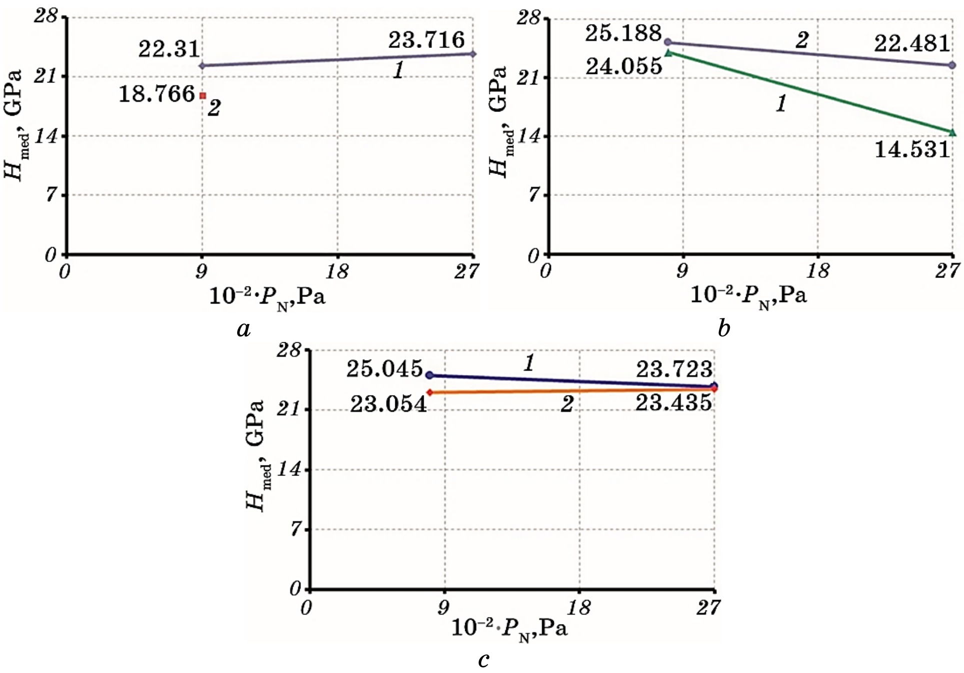

Fig. 8. Dependence graphs of the average microhardness value H_{med} of vacuum-arc multilayer nitride coatings CrN/NbN to the nitrogen pressure in the vacuum chamber P_N at constant negative voltage on the substrate U_S: series I (*1*—$U_S = -70$ V, *2*—$U_S = -200$ V) (*a*), series II (*1*—$U_S = -70$ V, *2*—$U_S = -200$ V) (*b*), series III (*1*—$U_S = -70$ V, *2*—$U_S = -200$ V) (*c*).

multilayer nitride coatings CrN/NbN of the first series by 3.5 GPa at the pressure of the reaction gas (nitrogen) $P_N = 0.09$ Pa, as can be seen in Fig. 7, *a*;

– an increase in the average microhardness value of the second series of vacuum-arc multilayer nitride coatings CrN/NbN by 8 GPa at the pressure of the reaction gas (nitrogen) $P_N = 0.27$ Pa and by 1 GPa at the pressure of the reaction gas (nitrogen) $P_N = 0.08$ Pa, as shown in Fig. 7, *b*;

– the preservation of the average microhardness value of vacuum-arc multilayer nitride coatings CrN/NbN of the third series at the pressure of the reaction gas (nitrogen) $P_N = 0.27$ Pa and a decrease of 2 GPa at the pressure of the reaction gas (nitrogen) $P_N = 0.08$ Pa, see Fig. 7, *c*.

An increase in the pressure of nitrogen in the vacuum chamber P_N from 0.08 to 0.27 Pa leads to:

– an increase in the average microhardness value of vacuum-arc multilayer nitride coatings CrN/NbN of the first series by 1.4 GPa at a constant negative voltage on the substrate $U_S = -70$ V, see in Fig. 8, *a*;

– the decrease in the average microhardness value of the second series of vacuum-arc multilayer nitride coatings CrN/NbN by 9.5 GPa at a constant negative voltage on the substrate $U_S = -70$ V and by 2.7 GPa at a constant negative voltage on the substrate $U_S = -200$ V, as shown in Fig. 8, *b*;

− the decrease in the average microhardness value of vacuum-arc multilayer nitride coatings CrN/NbN of the third series by 1.3 GPa at a constant negative voltage on the substrate $U_S = -70$ V and preservation of the value at a constant negative voltage on the substrate $U_S = -200$ V, as can be seen in Fig. 8, *c*.

For the vacuum-arc multilayer nitride coatings CrN/NbN of the third series with the largest total number of layers (270 layers) and the smallest bilayer period ($h_b = 67$ nm), the preservation of the average microhardness value is observed when the nitrogen pressure in the vacuum chamber changes (at a constant negative voltage on the substrate $U_S = -200$ V) at the level of 23.05 GPa (sample III-4)—23.43 GPa (sample III-1) and when the negative voltage on the substrate changes (at constant pressure of the reaction gas (nitrogen) $P_N = 0.27$ Pa) at the level 23.72 GPa (sample III-2)—23.43 GPa (sample III-1).

A change in voltage on the substrate at a constant nitrogen pressure leads to a change in the temperature conditions for deposition of vacuum-arc coatings due to a change in the energy of metal ions bombarding the substrate. In turn, an increase in the pressure of the reaction gas (nitrogen) in the vacuum chamber at a constant voltage on the substrate leads to an increase in the dispersion of the droplet phase of the plasma metal flow and can affect the energy of metal ions and thereby also regulate the temperature conditions of coating deposition. Thus, most likely, during the deposition of vacuum-arc coatings on samples III-1, III-2 and III-4, the same temperature conditions were created with different technological parameters, which affected the processes of the formation of nuclei centres and the directionality of the chemical reaction during film formation.

The dependence of the average microhardness value of vacuum-arc multilayer nitride coatings CrN/NbN on the number of layers N is presented in Fig. 9. For vacuum-arc coatings of the first series (constant rotation of the substrate-holder), based on the technological conditions of coating deposition (deposition time is 1.5 hours, the rotation speed of the substrate-holder is 5 s, the thickness of the coating is 3.6 μm), the approximate calculated values of the number of layers and the bilayer period were 1080 layers (revolutions of the substrate-holder) and 6.7 nm, respectively.

An increase in the number of layers from 68 to 270 leads to an increase in the average microhardness value H_{med} by 4–39% at various technological deposition parameters of vacuum-arc multilayer nitride coatings CrN/NbN, except for the mode at $U_S = -200$ V, $P_N = 0.08$–0.09 Pa, when H_{med} decreases by 8.5%. These changes are associated

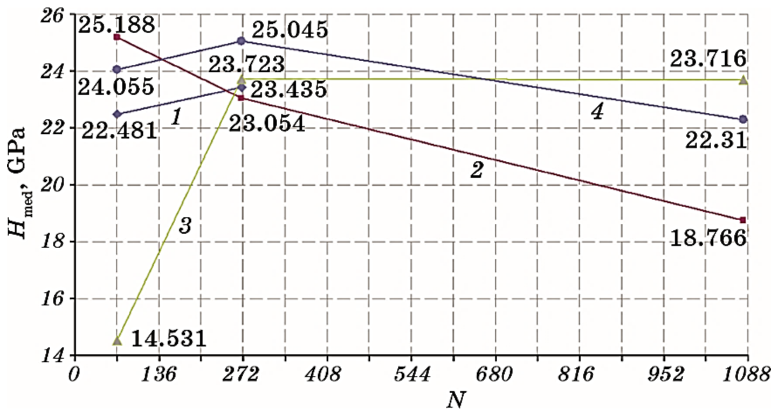

Fig. 9. Dependence graphs of the average microhardness value H_{med} of vacuum-arc multilayer nitride coatings CrN/NbN on the number of layers N at various technological parameters: *1*—$U_S = -200$ V, $P_N = 0.27$ Pa, *2*—$U_S = -200$ V, $P_N = 0.08$–0.09 Pa, *3*—$U_S = -70$ V, $P_N = 0.27$ Pa, *4*—$U_S = -70$ V, $P_N = 0.08$–0.09 Pa.

with an increase in the number of interphase boundaries, which affect the processes of deformation of individual layers and diffusion between them. This leads to increased crack propagation resistance and elastic properties of vacuum-arc multilayer nitride coatings. The nature of the boundaries between CrN and NbN layers also affects the physical and mechanical properties of the coatings. Thus, vacuum-arc multilayer nitride coatings with a transition layer Cr–Nb–N (series I) between layers CrN and NbN have average microhardness values by 11–19% lower than coatings with clear transition boundaries CrN/NbN (series III).

The maximum of the average microhardness value $H_{med} = 25.188$ GPa of vacuum-arc multilayer nitride coatings CrN/NbN was obtained at a constant negative voltage on the substrate $U_S = -200$ V, the pressure of the reaction gas (nitrogen) in the vacuum chamber $P_N = 0.08$ Pa and the total amount layers $N = 68$ with a bilayer period $h_b = 230$ nm. It should be noted that the maximum of the absolute value of the microhardness $H_{max} = 34.994$ GPa, as can be seen in Table 4, among the studied vacuum-arc coatings CrN/NbN has the coating sample III-2, which consists of 270 layers with a bilayer period $h_b = 67$ nm, but at the same time it has the maximum spread of the microhardness values RMSD = 7.16 GPa.

3.2.2. The Root Mean Square Deviation of Microhardness of Vacuum-Arc Multilayer Nitride Coatings CrN/NbN

As it was noted earlier, the average microhardness value of vacuum-arc multilayer nitride coating does not reflect the heterogeneity of the structural phase state of the coating, but only summarizes the properties. To evaluate this heterogeneity, we can use the spread of the obtained microhardness values of the coatings and RMSD. The analysis of these values can help to establish a connection between the technological deposition parameters of vacuum-arc multilayer nitride coatings CrN/NbN and the processes of formation of the structural phase state. Figures 10 and 11 show the influence of the technological conditions of coating deposition on the spread of microhardness values of vacuum-arc multilayer nitride coatings CrN/NbN.

An increase in the constant negative voltage on the substrate from −70 V to −200 V at a constant pressure of the reaction gas (nitrogen) in the vacuum chamber leads to a decrease in the spread of microhardness values of vacuum-arc multilayer nitride coatings CrN/NbN of all three series, respectively, this indicates that, that the obtained values cluster around the average value of microhardness. Thus, when the voltage

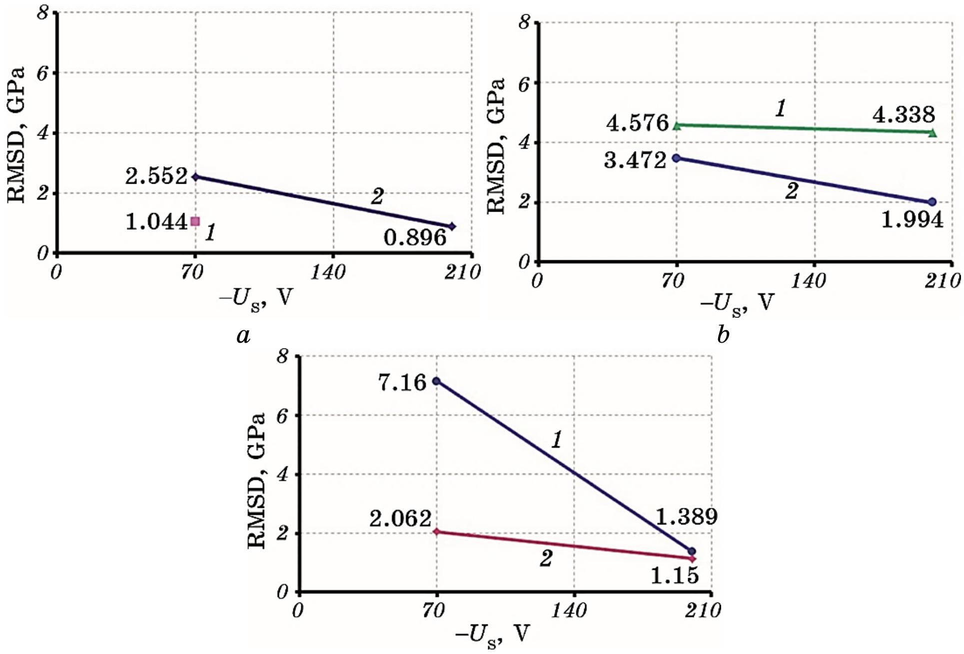

Fig. 10. Dependence graphs of the root mean square deviation RMSD of microhardness of vacuum-arc multilayer nitride coatings CrN/NbN to the constant negative voltage on the substrate U_S at constant values of the nitrogen pressure in the vacuum chamber PN: series I (*1*—P_N = 0.27 Pa, *2*—P_N = 0.09 Pa) (*a*), series II (*1*—P_N = 0.27 Pa, *2*—P_N = 0.08 Pa) (*b*), series III (*1*—P_N = 0.27 Pa, *2*—P_N = 0.08 Pa) (*c*).

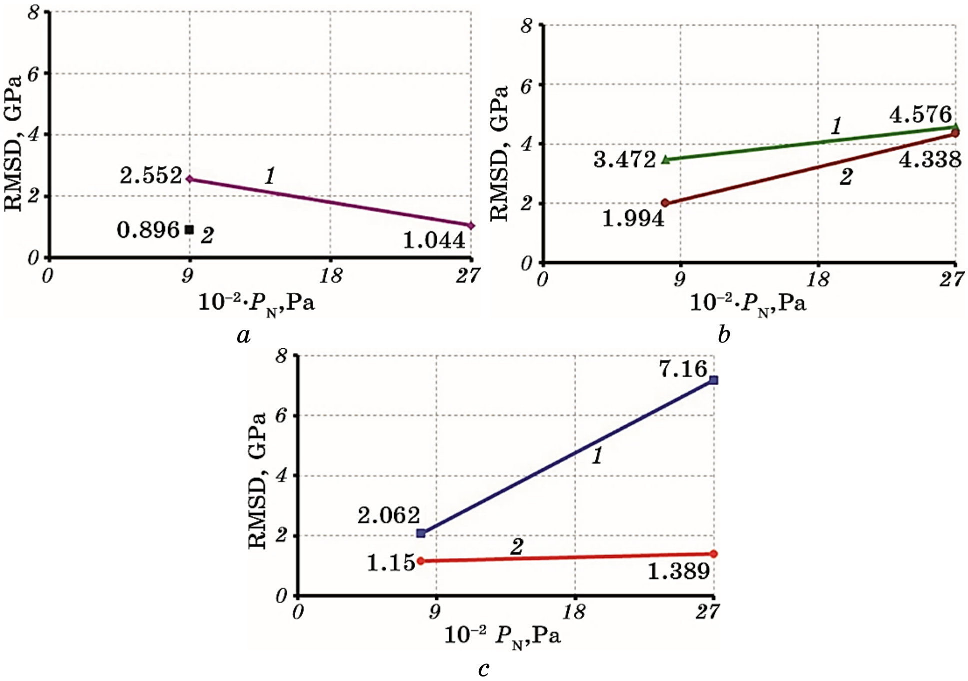

Fig. 11. Dependence graphs of the root mean square deviation RMSD of microhardness of vacuum-arc multilayer nitride coatings CrN/NbN to the nitrogen pressure in the vacuum chamber P_N at constant negative voltage on the substrate U_S: series I (*1*—$U_S = -70$ V, *2*—$U_S = -200$ V) (*a*), series II (*1*—$U_S = -70$ V, *2*—$U_S = -200$ V) (*b*), series III (*1*—$U_S = -70$ V, *2*—$U_S = -200$ V) (*c*).

on the substrate is increased, vacuum-arc multilayer nitride coatings with a more uniform structure are formed.

An increase in the pressure of the reaction gas (nitrogen) in the vacuum chamber from 0.09 Pa to 0.27 Pa with constant voltage on the substrate leads to a decrease in the spread of microhardness values of vacuum-arc multilayer nitride coatings CrN/NbN of the first series (with constant rotation of the substrate holder) and an increase in the spread of microhardness values of vacuum-arc multilayer nitride coatings of CrN/NbN of the second and third series.

The microhardness of the vacuum-arc nitride coating is determined mainly by the bonding forces between the metal and non-metal atoms. The properties related to the dynamics of the crystal lattice (root mean square amplitudes of thermal oscillations of the lattice structural complexes, melting temperature, elastic constants) are more influenced by the connection between the metal atoms themselves. Thus, an increase in the content of nitrogen atoms in Cr_xN_y and Nb_xN_y compounds leads to a decrease in microhardness (Table 3). An increase in microhardness occurs when the interatomic bond between metal atoms is strengthened, namely during the shear modulus decreases and shear deformations of the metal are difficult.

3.3. Elasticity Characteristics of Vacuum-Arc Multilayer Nitride Coatings CrN/NbN

Table 5 presents the average values of the elasticity modulus (elasticity contact modulus E_r, Young's modulus E) of vacuum-arc multilayer nitride coatings CrN/NbN, the H_{med}/E_r ratio, which characterizes the structural state of the vacuum-arc coating and the property of the material to resist mechanical impact, and the H^3_{med}/E^2_r ratio, which characterizes the material's resistance to plastic deformation [14].

Figure 12 demonstrates the dependence of the properties of vacuum-arc multilayer nitride coatings CrN/NbN on the number of layers, which was presented in Table 5.

The ratio of the average values microhardness to the contact modulus of elasticity H_{med}/E_r of the obtained vacuum-arc multilayer nitride coatings CrN/NbN lies in the range from 0.05 to 0.071, which corresponds to the nanostructural state of the coatings.

An analysis of the dependencies of elasticity contact modulus E_r on the technological deposition conditions of vacuum-arc multilayer nitride coatings CrN/NbN, as can be seen in Fig. 12, *a*, showed that when the number of layers in the coating increases from 68 to 270, the elasticity contact modulus E_r decreases by 6–8% when constant negative

TABLE 5. Physical mechanical characteristics of vacuum-arc multilayer nitride coatings based on chromium and niobium.

Series of coatings	No sample	Coating composition	H_{med}, GPa	E_r, GPa	E, GPa	H_{med}/E_r	H^3_{med}/E^2_r
I	I-1	CrN/NbN	23.716	300.45	372.95	0.064	0.148
	I-2	CrN/NbN	22.31	291.52	356.92	0.063	0.131
	I-3	CrN/NbN	18.766	250.22	291.36	0.064	0.106
II	II-1	CrN/NbN	22.481	317.96	403.72	0.056	0.112
	II-2	CrN/NbN	14.531	250.52	293.44	0.05	0.049
	II-3	CrN/NbN	24.055	279	336.88	0.071	0.179
	II-4	CrN/NbN	25.188	312.32	393.29	0.064	0.164
III	III-1	CrN/NbN	23.435	299.55	369.31	0.063	0.143
	III-2	CrN/NbN	23.723	335.33	439.54	0.054	0.119
	III-3	CrN/NbN	25.045	302.14	373.71	0.067	0.172
	III-4	CrN/NbN	23.054	286.13	347.15	0.066	0.15

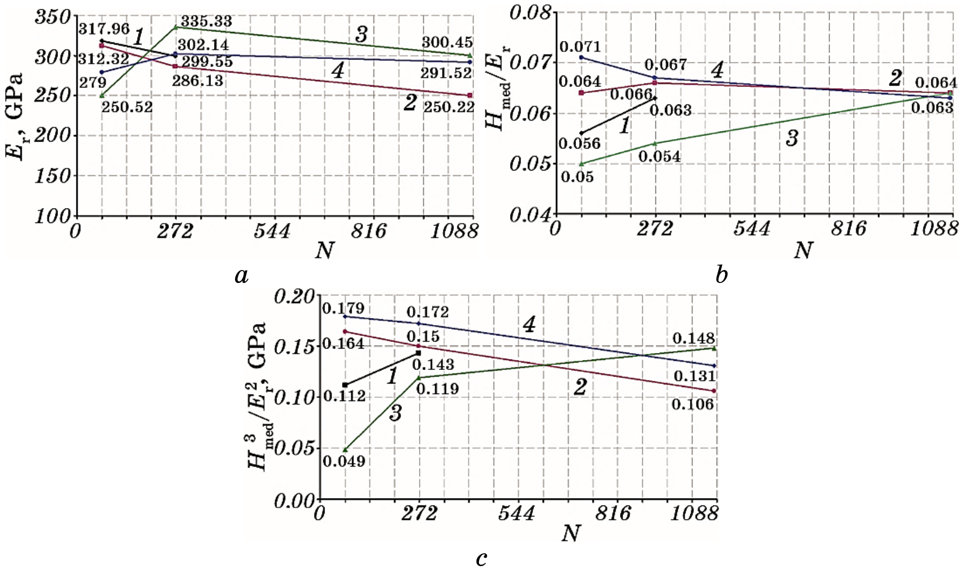

Fig. 12. Dependence graphs of the elasticity modulus E_r (a), ratio H_{med}/E_r (b), ratio H^3_{med} / E^2_r (c) on the number of layers N at various technological parameters: *1*—$U_S = -200$ V, $P_N = 0.27$ Pa, *2*—$U_S = -200$ V, $P_N = 0.08$–0.09 Pa, *3*—$U_S = -70$ V, $P_N = 0.27$ Pa, *4*—$U_S = -70$ V, $P_N = 0.08$–0.09 Pa.

voltage on the substrate $U_S = -200$ V and increases by 8–25% at a voltage $U_S = -70$ V and at different pressures of the reaction gas (nitrogen) $P_N = 0.08$–0.27 Pa. This may be due to a reduction in the energy of the ions bombarding the substrate and affecting the coating formation mechanisms. That is, the influence of the radiation factor on the properties of vacuum-arc coatings decreases.

The elasticity contact modulus E_r decreases by 3.5–12.5% at all investigated technological parameters of coating deposition for vacuum-arc multilayer nitride coatings with a transition layer of Cr–Nb–N between CrN and NbN layers. Thus, in the case of obtaining vacuum-arc multilayer nitride coatings of the first series with a total number of layers 1080 (with constant rotation of the substrate holder), the change tendency in the physical and mechanical properties H_{med} and E_r of the coatings is predominantly influenced by the nature of the boundaries formed between the layers CrN and NbN.

The maximum value of the elasticity contact modulus $E_r = 335.33$ GPa of the vacuum-arc coating CrN/NbN was obtained at a constant negative voltage on the substrate $U_S = -70$ V, the pressure of the reaction gas (nitrogen) in the vacuum chamber $P_N = 0.27$ Pa and the total amount of layers $N = 270$ with a bilayer period $h_b = 67$ nm.

Analysis of H_{med}/E_r ratio values with different number of N layers in the vacuum-arc multilayer nitride coating CrN/NbN, as can be seen in Fig. 12, *b*, demonstrated that the greatest influence of technological parameters of coating deposition is observed with the minimum number of layers ($N = 68$) with a bilayer period $h_b = 230$ nm. Thus, vacuum-arc coatings CrN/NbN of the series II with the same number of layers $N = 68$, but obtained under different technological deposition conditions, have more noticeable differences in the properties of the coatings than with other numbers of layers. Moreover, the vacuum-arc coatings CrN/NbN of the series I, which were obtained during constant rotation of the substrate holder and did not have clear boundaries between CrN and NbN layers, turned out to be the most structurally close to each other. This indicates that the reduction of the thickness of individual layers CrN (h_{CrN}), NbN (h_{NbN}) and the bilayer period h_b from 230 to 6.7 nm significantly affects the dependence of the properties of vacuum-arc multilayer nitride coatings CrN/NbN on the technological parameters of coating deposition.

The maximum value of the ratio $H_{med}/E_r = 0.071$ was achieved by vacuum-arc multilayer nitride coatings CrN/NbN, which were obtained at a constant negative voltage on the substrate $U_S = -70$ V, the pressure of the reaction gas (nitrogen) in the vacuum chamber $P_N = 0.08$ Pa and the total number of layers $N = 68$ with a bilayer period $h_b = 230$ nm.

4. CONCLUSION

Investigation of vacuum-arc multilayer nitride coatings CrN/NbN, which were obtained under different technological parameters of deposition (constant negative voltage on the substrate U_S is from −70 to −200 V, pressure of the reaction gas (nitrogen) in the vacuum chamber P_N is from 0.08 to 0.27 Pa, the total number of layers N (68, 270, 1080), the bilayer period h_b is from 6.7 to 230 nm) made it possible to expand the understanding of the technological deposition parameters influence on the physical and mechanical properties of the obtained vacuum-arc coatings. The obtained research results can be summarized in the form of the following conclusions.

1. The use of different technological modes made it possible to obtain three series of vacuum-arc multilayer nitride coatings with different thicknesses of individual CrN and NbN layers and bilayer period (CrN–NbN), number of layers (68 and 270 layers) and nature of the interface between the layers (clear boundary or transition layer).

2. Cross-sections analysis of vacuum-arc multilayer nitride coatings CrN/NbN of three series with different number of layers and bilayer period showed that the total thickness of coatings was 3.6 μm for vacuum-arc coatings of the first series, which were obtained by continuous rotation of the substrate holder, and about 8 and 9 μm for vacuum-arc coatings of the second and third series, respectively.

3. Elemental analysis using characteristic x-ray radiation showed that

the obtained coatings of series II and III have high planarity of layers and practically no droplet phase in the volume of multilayer vacuum-arc nitride coating CrN/NbN.

4. For vacuum-arc multilayer nitride coatings CrN/NbN of the third series with the largest total number of layers (270 layers) and the smallest bilayer period ($h_b = 67$ nm), the preservation of the average value of microhardness is observed when the nitrogen pressure in the vacuum chamber changes (at a constant negative voltage on the substrate $U_S = -200$ V) at the level 23.054 GPa (sample III-4)—23.435 GPa (sample III-1) and when the negative voltage on the substrate changes (at a constant pressure of the reaction gas (nitrogen) $P_N = 0.27$ Pa) at the level 23.723 GPa (sample III-2)—23.435 GPa (sample III-1).

5. An increase in the number of layers from 68 to 270 leads to an increase in the average value of microhardness H_{med} by 4–39% at various technological deposition parameters of vacuum-arc multilayer nitride coatings, except for the mode at $U_S = -200$ V, $P_N = 0.08$–0.09 Pa, when H_{med} decreases by 8.5%. These changes are associated with an increase in the number of interphase boundaries, which affect the processes of deformation of individual layers and diffusion between them. This leads to increased crack propagation resistance and elastic properties of vacuum-arc multilayer nitride coatings.

6. The maximum of the average microhardness value $H_{med} = 25.188$ GPa of vacuum-arc multilayer nitride coatings CrN/NbN was obtained at a constant negative voltage on the substrate $U_S = -200$ V, the pressure of the reaction gas (nitrogen) in the vacuum chamber $P_N = 0.08$ Pa and the total number of layers $N = 68$ with a bilayer period $h_b = 230$ nm.

7. An increase in the constant negative voltage on the substrate from −70 V to −200 V at a constant pressure of the reaction gas (nitrogen) in the vacuum chamber leads to a decrease in the spread of microhardness values of vacuum-arc multilayer nitride coatings CrN/NbN of all three series, respectively, this indicates on the fact that the obtained values cluster around the average value of microhardness.

8. During increasing the number of layers in the coating from 68 to 270, the elasticity contact modulus E_r decreases by 6–8% at a constant negative voltage on the substrate $U_S = -200$ V and increases by 8–25% at a voltage $U_S = -70$ V at various pressures of the reaction gas (nitrogen) $P_N = 0.08$–0.27 Pa.

9. The maximum value of the elasticity contact modulus $E_r = 335.33$ GPa of the vacuum-arc coating CrN/NbN was obtained at a constant negative voltage on the substrate $U_S = -70$ V, the pressure of the reaction gas (nitrogen) in the vacuum chamber $P_N = 0.27$ Pa and the total number of layers $N = 270$ with a bilayer period $h_b = 67$ nm.

10. The maximum value of the ratio $H_{med}/E_r = 0.071$ was achieved for vacuum-arc multilayer nitride coatings CrN/NbN, which were obtained at a constant negative voltage on the substrate $U_S = -70$ V, the

pressure of the reaction gas (nitrogen) in the vacuum chamber $P_N = 0.08$ Pa and the total number of layers $N = 68$ with a bilayer period $h_b = 230$ nm.

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