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Thermal Effects on the Surface Morphology of an Ion-plasma Coating

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The dependence of the surface morphology of ion-plasma coatings on the temperature influence in vacuum was investigated. The coatings were formed by vacuum-arc method with the use of pulsed high-frequency stimulation of deposition. To compare the frictional properties, Ti-Hf metal coatings obtained in argon medium and (Ti-Hf-Si)N composite coatings were investigated. The coatings were annealed in a high temperature vacuum oven. The roughness of the coatings was investigated using a profilometer. In order to detail the structure of the surface of coatings before and after annealing, a study was carried out using an atomic force microscope. It is established that thermal influence on the surface of nanostructured coatings significantly changes the surface morphology. Such changes lead to the evolution of the structural and physico-mechanical characteristics of the coatings. The results of tribotechnical studies of Ti-Hf and (Ti-Hf-Si)N coatings are presented. The results of thermal influence on the samples of (Ti-Hf-Si)N nanocomposite coating are analyzed. The results of the study of the surface of these coatings are compared. A decrease in the (Ti-Hf-Si)N coating roughness was found by annealing and an increase in hardness to 55.7 GPa. The evolution of the surface morphology of the coatings is the result of changes in the coating structure and recrystallization processes. The studied statistical characteristics of the relief of the surface of the coatings are consistent with other experimental results.

Keywords: Vacuum-arc coatings, Surface morphology, Statistical characteristics of surface topography, Thermal impact.

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1. INTRODUCTION

Increasing the efficiency of wear-resistant coatings based on transition metal nitrides is possible by creating nanostructured compositions. Due to a significant increase in the volume fraction of the division boundaries, such coatings show a unique combination of properties: high hardness, wear resistance, heat resistance and, at the same time, a relatively low coefficient of friction [1, 2].

Nanocomposite coatings based on transition metal nitrides in several compositions are significantly superior in physical and mechanical properties to coatings based on titanium nitride. The most effective way to improve coatings based on transition metal nitrides is to change their structure and physical and mechanical properties by introducing alloying elements Si, B, Al, Y, etc., as well as to form multilayer nanostructured coatings, which allow to take into account complex physical and chemical processes occurring in the "coating-base" system [1, 4, 7].

Temperature influence on the formed vacuum-arc coatings initiates diffusion processes of mass transfer of elements in coating layers, from substrate to coating and vice versa, which may lead to the formation of metal nitrides and dispersed phases of implementation [3].

Ion-plasma flows initiate the formation of surface stresses, diffusion activation, change in dislocation structure and phase state. The development of these processes leads to the modification of the surface topography. It is necessary to consider the integral result of the interaction of these processes of the forming relief with the processes of spraying, ion-stimulated segregation, desorption, etc. Coatings obtained by vacuum-arc deposition are characterized by complex surface topography. In this connection it is of great interest to study the influence of temperature on changes in surface morphology of multicomponent ion-plasma coatings, in particular, on the basis of Ti-Hf and (Ti-Hf-Si)N systems [5-7].

The atomic force microscopy allows to estimate statistical characteristics of relief and degree of surface roughness experimentally. Methods of mathematical statistics allow to analyze and predict physical processes in the formed vacuum-arc coatings.

The aim of the work is to study the dependence of surface morphology of ion-plasma coatings based on Ti-Hf and (Ti-Hf-Si)N on the annealing temperature in argon medium using atomic force microscopy and statistical analysis of surface topography.

2. EXPERIMENTAL PROCEDURE

To investigate tribotechnical characteristics, coatings based on Ti-Hf were formed by vacuum-arc spraying of Ti + Hf cathode in argon medium at 0.7 Pa pressure and $U_{bp} = -200$ V displacement potential. The coating thickness was 3 μm.

(Ti-Hf-Si)N coatings of 1.2 μm thick were formed by vacuum-arc method on polished surfaces of steel samples (steel 45) with 5.0 mm diameter and 2.0 mm thick by spraying the cathode made of Ti + Hf + Si alloy. The high-frequency bias potential was applied to the substrate from a HF oscillator, which generated pulses of damped oscillations with a frequency < 1 MHz, duration of each pulse of 60 ms, repetition frequency of 10 kHz. The nitrogen pressure at application was $P_N = 0.7$ Pa. The applied displacement potential was $U_{bp} = -200$ V.

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The obtained coating samples were annealed in a vacuum furnace at temperatures of 500 °C, 800 °C and 1000 °C [2]. Analysis of coating surface topography was carried out in the air using atomic force microscope produced by NT-MDT Company. NSG10/W2C Si-cantilevers with 30 nm thick W2C hard conductive coating were used.

Coating surface roughness was measured using automated precision contact profiler SURTRONIC 25.

The study of mechanical characteristics of (Ti-Hf-Si)N-based coatings was carried out by nanoindentation using the Nanoindenter G200 device (MES Systems, USA) with the use of Berkovich trihedral diamond pyramid with a radius of curvature at the apex of about 20 nm.

Tribological tests were carried out on the automated friction machine “Tribometer”, CSM Instruments in the air according to the “ball-disc” scheme at a temperature of 20 °C. A 6 mm diameter ball made of sintered certified material (Al_2O_3) was used as a counterbody. Coated discs were made of steel 45 (HRC = 55) with a diameter of 50 mm and a thickness of 5 mm. The load was 3.0 N and the sliding speed was 10 cm/s.

Precise sizing of coating surface parts at the submicron level is important for modern technology in determining grain size, coating structure evolution and surface roughness. All of the above tasks require precision at the nanometer level.

In the work, statistical methods of the analysis of the surface of the formed coatings and annealed samples are applied that allows to detail the surface structure and to specify physical and mechanical characteristics of the coatings. Statistical characteristics are obtained as a result of atomic force microscopy of coating samples.

3. RESEARCH FINDINGS

Roughness of the coatings is an important characteristic of the quality of protective coatings. The coefficient of friction is closely related to the roughness of friction surfaces. A known way to determine the roughness of surfaces of coatings is application of profilometers. The results of measuring the roughness of Ti-Hf and (Ti-Hf-Si)N coatings are given below.

It has been experimentally determined that the application of Ti-Hf coatings in argon medium by vacuum-arc deposition on the polished surface of a steel disk leads to an increase in the roughness (see Fig. 1a and Fig. 1b) due to the formation of a drip component from the plasma flow.

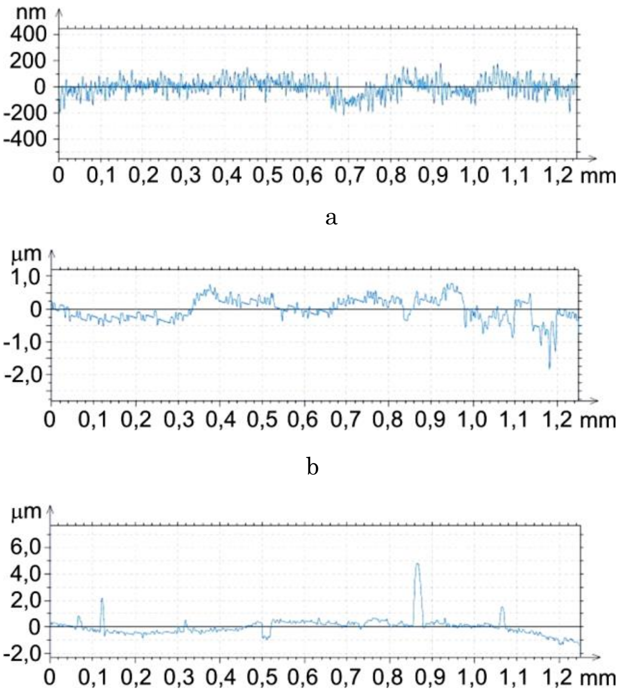
The results of friction tests of Ti-Hf-based coatings are given in Table 1. According to the results of the tests, it was found that coating of the steel substrate surface provides increased wear resistance of the steel surface.

Fig. 1c shows a profile diagram of the nanocomposite (Ti-Hf-Si)N coating system obtained from a straight-flow plasma flow. The curve bursts indicate the presence of a drip component of the coating.

Composite (Ti-Hf-Si)N coating obtained by silicon alloying is characterized by a significantly lower degree of roughness compared to Ti-Hf coating, which improves the performance of the first coating.

Table 1 – Tribological characteristics of "45 Al_2O_3 steel substrate" and "Ti-Hf Al_2O_3 coating" systems

Sample	Coefficient of friction, μ		Wear factor $mm^3 \times H^{-1} \times mm^{-1}$	
	Initial	In testing	Counterbody ($\times 10^{-5}$)	Sample ($\times 10^{-5}$)
Steel 45	0.204	0.674	0.269	35.36
Ti-Hf coating	0.273	0.847	0.269	2.21



a

b

c

Fig. 1 – Roughness profile of the steel disc surface after polishing, $R_a = 0.088$ μm (a); surface profile of a Ti-Hf coated steel disc, $R_a = 0.36$ μm (b); results of surface roughness measurement of (Ti-Hf-Si)N-based coatings ($R_a = 0.228$ μm) obtained from direct-flow plasma flow (c)

The use of atomic force microscopy coatings in surface studies allows us to significantly detail the structural characteristics of the surface.

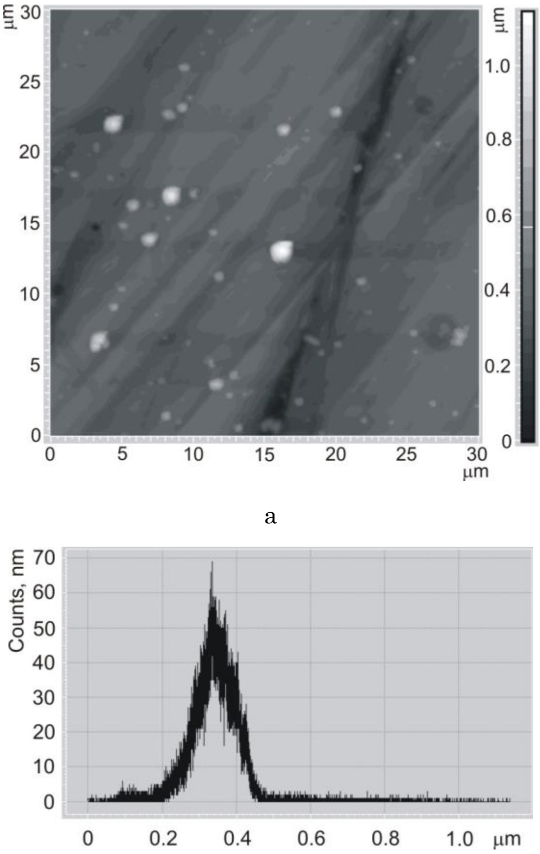
Fig. 2a illustrates an AFM image of the initial coated surface of (Ti-Hf-Si)N, which shows the presence of grain boundaries and nanostructured relief. The alternation of dark and light ledges and cones is observed, which indicates the change in the height of the surface relief.

More detailed information about the surface topography is provided by the analysis of AFM image profiles and statistical analysis of height distribution, shown in Fig. 2b. The statistical analysis showed that the average height of the projections is 90 nm. The lateral dimensions of the projections at the base are 200 nm and the width of the projections at half height is approximately 70 nm.

The initial (Ti-Hf-Si)N coating is characterized by a single-mode histogram of the relief height distribution (Fig. 2b) described by the function $Z(X, Y)$. The maximum quantitative value of the relief level is observed in the vicinity of 300 nm. The single value of the distribution indicates a significant uniformity of substructure formations.

Fig. 3 shows an AFM image of the surface of a nanostructured (Ti-Hf-Si)N coating after annealing at 500 °C with higher resolution. Compared to the original coating, the temperature-affected coating is characterized by smoothed structural fragments.

Fig. 4 shows histograms of the surface topography of (Ti-Hf-Si)N-based coatings obtained at 500 °C, 800 °C and 1000 °C annealing temperatures.



a

b

Fig. 2 – AFM image of the surface of nanostructured (Ti-Hf-Si)N coating with the field size of 3030 microns: a – 2D image of the coating surface; b – histogram of the relief distribution $Z(X, Y)$ in the substrate section – surface of the coating

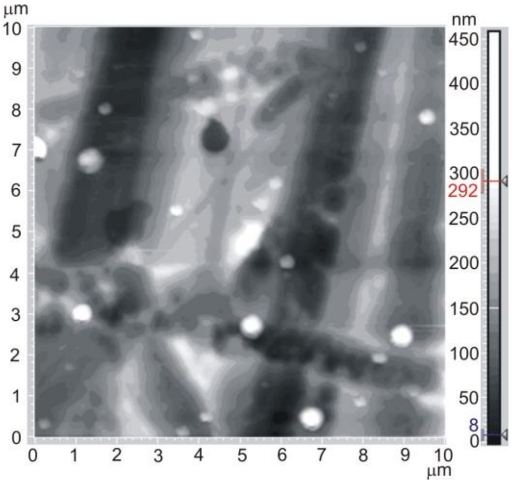
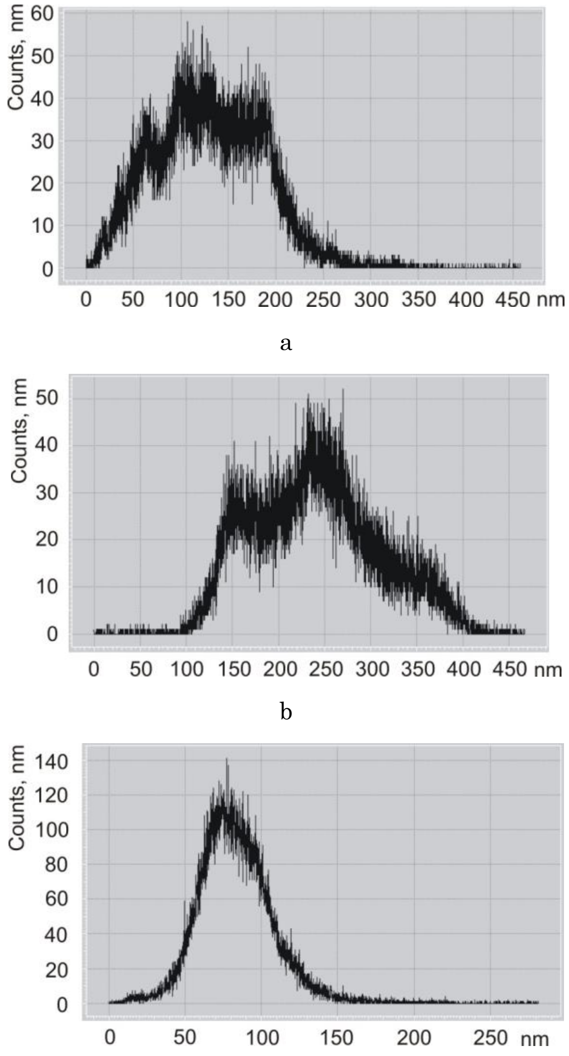


Fig. 3 – AFM image of the surface of nanostructured coating (Ti-Hf-Si)N after annealing at 500 °C (field size 1010 μm)



a

b

c

Fig. 4 – Histogram of relief distribution $Z(X, Y)$ on the substrate section – surface of (Ti-Hf-Si)N coating after annealing: a – 500 °C, b – 800 °C, c – 1000 °C

In contrast to the initial coating, the histogram of the annealed surface image at 500 °C is characterized by multimodality. There are characteristic peaks of height distribution in the vicinity of 70, 100, 130 and 170 nm values. This indicates a peculiar uneven structure of the surface formed after annealing. The range of the image histogram is about 250 nm.

The same situation is observed in the case of annealing the surface at 800 °C. However, the number of image histogram modes is reduced to three in the vicinity of 150, 250 and 350 nm. Thus, there is a trend towards a more even distribution of surface structure elements. The range of the histogram increases to 300 nm.

The histogram of the image of the (Ti-Hf-Si)N coating surface after annealing at 1000 °C is similar in nature to the histogram of the image of the original coating surface. The histogram is single-mode with slight asymmetry close to the Gaussian distribution. This histogram indicates uniformity in the distribution of substructural elements of the coating. This surface structure is characterized by a reduced degree of roughness.

From the analysis of statistical characteristics of $Z(X, Y)$ surface topography distribution it follows that temperature influence significantly changes the system surface morphology of (Ti-Hf-Si)N. The average roughness of the initial coating is 50 nm; for annealed coating samples at 500 °C, 800 °C and 1000 °C the average roughness is 46, 55 and 19 nm, respectively. Thus, annealing at 1000 °C reduces the coefficient of friction, which promotes the use of this coating as a protective for friction pairs of machine parts.

The coefficient of excess γ_2 of $Z(X, Y)$ distribution for the initial coating is 14.4. The values of γ_2 are significantly different. For coating samples after annealing at temperatures of 500 °C, 800 °C and 1000 °C, the distribution coefficient of excess takes, respectively, the following values: 0.2, – 0.46 and 4.93. The values of γ_2 differ significantly. The coefficient of excess determines the measure of acuteness of the random value distribution.

In this case, large values of γ_2 indicate an acute peak of distribution, i.e. the surface relief is characterized by the concentration of structural elements near the mean value. Coating samples annealed at temperatures of 500 °C and 800 °C are characterized by a significant spread of structural elements relative to the mean value. Note that the entropy of all surfaces differs slightly and is 11.4, 11.2, 11.5, and 10.04, respectively, for the initial coating and samples annealed at 500 °C, 800 °C and 1000 °C.

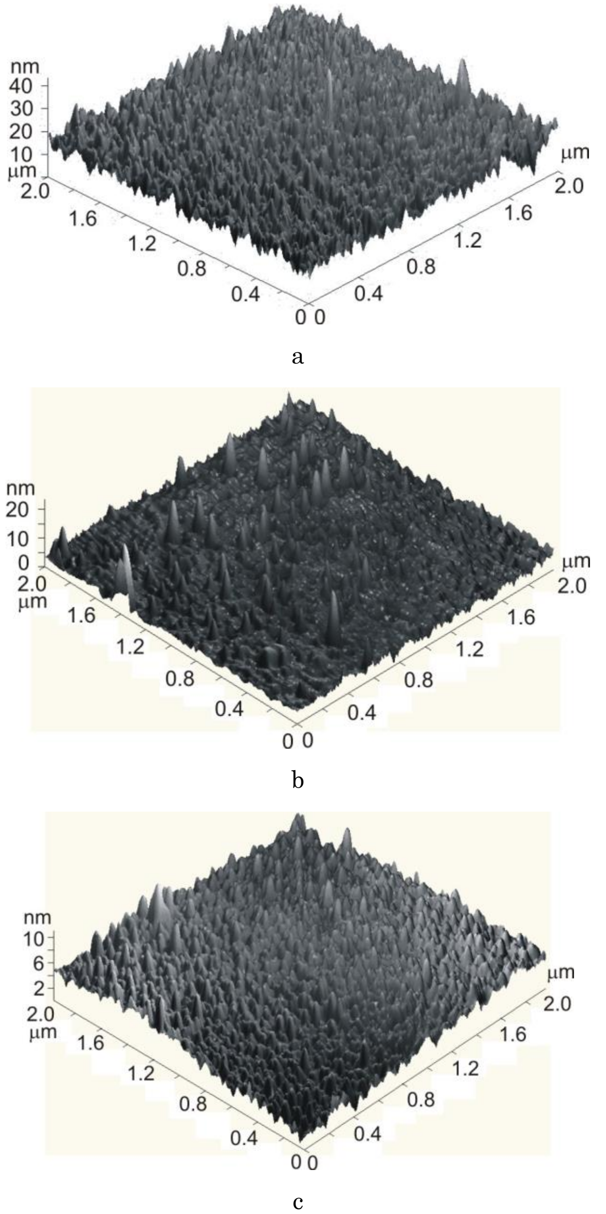
Fig. 5 shows a 3D image of the initial (Ti-Hf-Si)N coating surface and the surface after annealing at temperatures of 800 °C and 1000 °C. Visually, the surface of the coating after annealing at 800 °C is characterized by a large number of abnormal emissions in comparison with the depicted surfaces in Fig. 5a and Fig. 5c. This is consistent with the results of statistical analysis of the $Z(X, Y)$ relief histograms.

Fig. 6 shows a graph of the maximum relief value $Z(X, Y)$ of the surface of (Ti-Hf-Si)N coatings (broken line A) and the average relief value $Z(X, Y)$ (broken line B) for samples of the initial coatings and for samples of the coatings annealed at temperatures of 500 °C, 800 °C and 1000 °C. It follows from the graph that the thermal impact on the (Ti-Hf-Si)N coating samples leads to a decrease in the level of abnormal projections, i.e., smoothes the coating surface. This leads to a decrease in the surface roughness of the coatings and consequently to a decrease in the coefficient of friction.

The hardness of the initial coatings varies between 38 and 48 GPa. Thermal influence on (Ti-Hf-Si)N coating samples increases hardness up to 54.2-55.7 GPa, as in the case of (Zr-Ti-Si)N nanocomposite system coatings [2]. X-ray structural studies have revealed the formation of a two-phase system: the solid solution of substitution (Ti, Hf)N and the peak spectrum of the second phase Si_3N_4. The coefficient of friction of (Ti-Hf-Si)N coatings as a function of the structural-phase state when tested under the scheme "disc-coated – ball Al_2O_3" in the air is 20 % lower than the coefficient of friction for coatings based on (Ti, Hf)N solid solution.

The increase in size, number of cones and their formation on the surface of coatings, according to the authors [3], are the result of processes generated by ion-induced stresses and associated with the movement of atoms in the surface layer.

In the works devoted to research of results of energy impact on the surface of condensed media, namely temperature [3, 6], it is shown the occurrence of defective deformation instability. This leads to the realization of critical conditions for the manifestation of a synergistic effect, leading, among other things, to the development of surface structures of the relief. In our case, the influence of temperature on the evolution of surface topography is characterized by the processes of changing the structural state of the surface, which leads to the modification of the topography as a system of nanostructured protrusions.



a

b

c

Fig. 5 – 3D AFM surface image of nanocomposite (Ti-Hf-Si)N coating: a – initial; b – annealed at 800 °C; c – annealed at 1000 °C

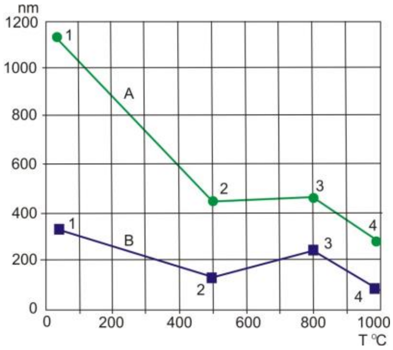


Fig. 6 – Maximum relief values $Z(X, Y)$ of the surface of coating (Ti-Hf-Si)N (broken line A) and average relief values $Z(X, Y)$ (broken line B) determined for the initial sample of coatings (point 1) and annealed samples of coatings at temperatures of 500 °C (point 2), 800 °C (point 3) and 1000 °C (point 4)

4. CONCLUSIONS

It is shown that nanocomposite (Ti-Hf-Si)N coating is characterized by better frictional properties in comparison with metal Ti-Hf coating.

The temperature effect on the (Ti-Hf-Si)N system coating significantly changes the surface morphology. Annealing at 1000 °C reduces the roughness of the formed coating and helps to increase coating hardness and reduce friction coefficient.

Statistical characteristics of surface topography distribution histograms $Z(X, Y)$ testify to the surface morphology modification as a result of thermal influence at the level of coating surface structural elements.

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Термічний вплив на морфологію поверхні іонно-плазмового покриття

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Досліджено залежність морфології поверхні іонно-плазмових покриттів від температурного впливу у вакуумі. Покриття формувалися вакуумно-дуговим методом із застосуванням імпульсної високочастотної стимуляції осадження. Для порівняння фрикційних властивостей досліджувалися металеві покриття Ti-Hf, отримані в середовищі аргону, і композитні покриття (Ti-Hf-Si)N. Покриття відпалювалися у високотемпературній печі у вакуумі. Шорсткість покриттів досліджувалася за допомогою профілометра. З метою деталізації структури поверхні покриттів до і після відпалювання здійснювалося дослідження за допомогою атомно-силового мікроскопа. Встановлено, що термічний вплив на поверхню наноструктурованих покриттів істотно змінює морфологію поверхні. Такі зміни призводять до еволюції структурних і фізико-механічних характеристик покриттів. Наводяться результати триботехнічних досліджень покриттів Ti-Hf та (Ti-Hf-Si)N. Проаналізовано результати термічного впливу на зразки нанокомпозитного покриття (Ti-Hf-Si)N. Порівнюються результати дослідження поверхні зазначених покриттів. Виявлено зниження шорсткості покриття (Ti-Hf-Si)N за результатами відпалювання і підвищення твердості до значення 55,7 ГПа. Еволюція морфології поверхні покриттів відбувається в результаті змінювання структури покриття і процесів рекристалізації. Вивчені статистичні характеристики рельєфу поверхні покриттів узгоджуються з іншими експериментальними результатами.

Ключові слова: Вакуумно-дугові покриття, Морфологія поверхні, Статистичні характеристики рельєфу, Термічний вплив.