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TRIBOLOGICAL PROPERTIES AT 20 AND 500°C OF TiN AND CrN CATHODIC ARC COATINGS DEPOSITED ON Ti-6Al-4V ALLOY

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Tribological properties of TiN and CrN coatings deposited by cathodic arc method at three different bias potentials -50, -150 and -300V on Ti-6Al-4V alloy in pair with alumina have been investigated. X-ray diffraction analysis showed that single-phase textured cubic nitrides of TiN and CrN were formed in these coatings. It is shown that the friction coefficient of the coatings is practically equal to that established for the Ti6Al4V alloy, but the wear rate is more than an order of magnitude lower than for the titanium alloy substrate. Coatings deposited at a potential of -50 V show optimal tribological properties at temperatures 20 and 500°C. Friction coefficients for TiN coatings are 0.4-0.8 at 20°C and 0,75 at 500°C; for CrN coatings they are 0.5 at 20°C and 0,7 at 500°C. Wear rates for TiN coatings are $0.86\cdot10^{-5}$ мм^3/Нм at 20°C and $3.56\cdot10^{-5}$ мм^3/Нм at 500°C; for CrN coatings they are $1.43\cdot10^{-5}$ мм^3/Нм at 20°C and $7.13\cdot10^{-5}$ мм^3/Нм at 500°C.
Keywords: *Titanium alloy; Cathodic arc deposition; Nitride coatings; Bias potential; Structure; Nanohardness; Friction coefficient; Wear*
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INTRODUCTION

One of the main factors determining the energy efficiency of nuclear and thermal power plants is the reliability of the steam turbine unit (STU) [1]. Ion-plasma surface modification and the use of protective coatings with high wear resistance can improve the reliability and longevity of titanium alloy components and extend the time between turbine overhauls. The high protective properties of TiN coatings deposited at elevated nitrogen pressure of 1...3 Pa allowed the selection of conditions for the synthesis of the optimal coating for the strengthening of steam turbine blades made of Ti-6Al-4V alloy [2]. The tribological properties of TiN and CrN coatings deposited by cathodic arc deposition have been extensively studied [3-7]. However, for specific technical applications of protective coatings, it is necessary to determine the influence of deposition process parameters on the wear resistance of the substrate-coating pair [8, 9]. One of the most important parameters in the cathodic arc coating process is the bias potential, which determines the energy of the deposited ions [10]. The ion energy determines the structure and properties of the coatings [11].

The aim of this work is to investigate the effect of deposition process parameters (bias potential) of protective nitride coatings TiN and CrN on the tribological properties of Ti-6Al-4V alloy.

EXPERIMENTAL DETAILS

Using a Bulat-6 type apparatus, the schematic of which is shown in Fig. 1, and two metal plasma sources, coatings were deposited on titanium alloy samples at a distance of 300 mm from the cathode. The cathodes were made of pure titanium (99.9%) and chromium (99.9%). The current of the vacuum arc discharge was 85 A for each cathode. The initial pressure in the vacuum chamber was 2×10^{-3} Pa. Before the deposition of the coating, the surface of the samples was subjected to sputtering with cathode material ions at a negative bias voltage of 1.2 kV. To improve the adhesion of the nitride layers, a thin metallic sublayer (titanium or chromium) of 0.1 µm thickness was deposited on the titanium alloy surface in vacuum (0.001 Pa) at a bias potential of -100 V. Negative bias potentials (U_b) of -50, -150 and -300 V were applied to the samples. The nitrogen pressure during the deposition of TiN and CrN coatings was 2 Pa. The temperature of the samples did not exceed 450°C. The thickness of the deposited coatings was 13-15 µm.

Deposited coatings were examined by X-ray diffraction using a DRON-UM1 diffractometer with filtered Cu-Kα radiation. To obtain a complete characterization of coatings, additional XRD tests were performed for the texture analysis and microstructural parameters estimation.

Texture study was carried out by analyzing the ratio of the integral intensities of the diffraction peaks according to [12]. The texture coefficient $Tc_{(hkl)}$ was used to quantify the preferred orientations:

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$$Tc_{(hkl)} = \frac{I_{(hkl)}/I_{0(hkl)}}{(1/N)[\sum_N I_{(hkl)}/I_{0(hkl)}]}, \quad (1)$$

where $Tc_{(hkl)}$ – texture coefficient; $I_{(hkl)}$ – measured intensity of the peak *(hkl)*; $I_{0(hkl)}$ – intensity of the peak *(hkl)* in randomly oriented sample (taken from ICDD PDF-2 database); N – number of analyzed diffraction peaks.

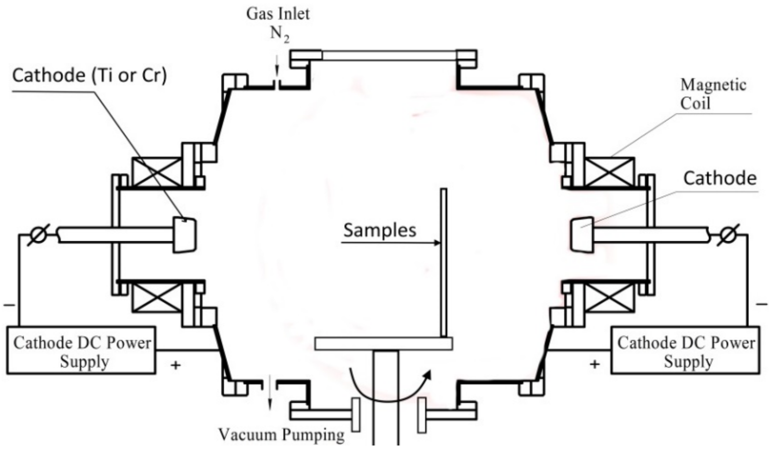

Figure 1. Scheme of the Bulat 6 type apparatus

Williamson-Hall method was applied for the estimation of microstructural parameters (crystallites size CSD and microstrains) of coatings:

$$\beta = \frac{\lambda}{D \cdot \cos(\theta)} + 4 \cdot \varepsilon \cdot \mathrm{tg}(\theta), \quad (2)$$

де β – true physical broadening; λ – X-ray wavelength; D – crystallite size; θ – diffraction angle; ε – microstrains. The instrumental function was obtained from a reference sample of recrystallized silicon.

The mechanical properties of the coatings were investigated by nanoindentation methods using a device Nanoindenter G200 with a CSM module with Berkovich indenter at 300 nm indentation depth [13].

The wear tests were carried out using a reciprocating device consisting of a pair of coated plates (dimensions 20×36×3 mm) and a 10 mm diameter ball of alumina with a hardness of 19 GPa. The friction coefficient was determined at a temperature of 20°C and of 500°C for 30 minutes using a force of 2 N to press the ball against the sample. The wear of the coatings was evaluated using the "Calibre C-265" profilograph-profilometer to measure the area S of the wear track profile [14].

RESULTS AND DISCUSSION

The TiN and CrN coatings deposited on the titanium alloy are golden and gray in color, typical of the cathodic arc deposition method. XRD analysis revealed (Fig.2, Table 1) that both types of coatings are single phase and consists of strongly textured nitrides TiN and CrN, respectively, with preferred orientation of grains with crystallographic planes {111} parallel to the surface. The lattice parameters of both nitrides are significantly large then literature data (a = 4.239 Å for TiN and a = 4.148 Å for CrN). The fact of increased lattice parameters can be explained by the presence of residual stresses in the coatings.

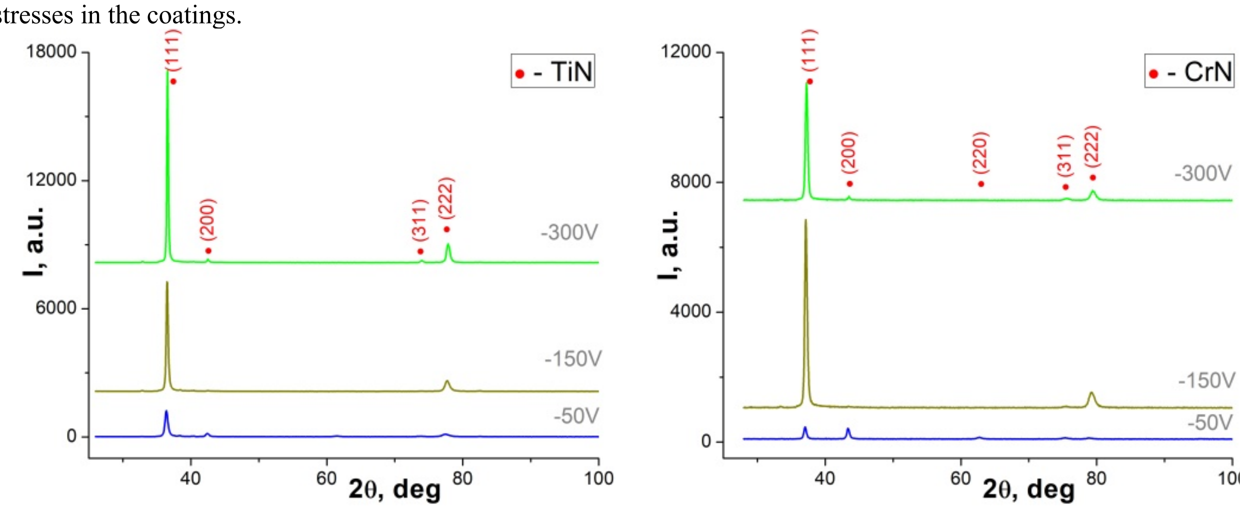

Figure 2. Diffraction patterns of Ti-6Al-4V samples with TiN (left) and CrN (right) coatings deposited at different substrate bias

Table 1. Phase composition and microstructural characteristics of investigated coatings

Coatings	U_b, V	Phase	Lattice parameter, Å	CSD size D, nm	Microstrains, ε	*Tc(111)*
TiN	-50	TiN	4.267	26.0	$4.2 \cdot 10^{-3}$	4.7
		Ti-α	a = 2.93; c = 4.68	-	-	-
	-150	TiN	4.256	49.0	$3.3 \cdot 10^{-3}$	6.0
		Ti-α	a = 2.93; c = 4.68	-	-	-
	-300	TiN	4.250	92.8	$2.7 \cdot 10^{-3}$	5.7
CrN	-50	CrN	4.181	35.4	$4.2 \cdot 10^{-3}$	2.0
	-150	CrN	4.186	36.5	$3.6 \cdot 10^{-3}$	6.0
	-300	CrN	4.177	35.8	$3.2 \cdot 10^{-3}$	5.5

An increase in the substrate bias potential U_b leads to monotonous decrease in the lattice parameter of TiN nitride (from a = 4.267 Å at U_b = -50 V to from a = 4.250 Å at U_b = -300 V). At the same time, crystallite size (CSD) increases considerably (from D ≈ 26 nm to D ≈ 93 nm) while the microstrains decrease. The magnitude of the bias potential also affects the texture of the TiN nitride: texture coefficient $Tc_{(111)}$ increases with U_b increasing, but has maximum $Tc_{(111)}$ = 6.0 at -150 V.

The evolution of structural and microstructural parameters of CrN nitride with the change in bias potential is significantly different from the results obtained for TiN nitride. Thus, with the increase in the substrate bias the lattice parameter first increases, reaching a maximum a = 4.186 Å at -150 V, and then decreases down to a = 4.177 Å. Microstrains in CrN nitride slightly decrease with the increase in U_b potential (from $4.2 \cdot 10^{-3}$ to $3.2 \cdot 10^{-3}$), while the crystallites size doesn't depend on bias changes and equal D ≈ 36 nm. More significantly, U_b potential affects the preferred orientation of CrN grains: it changes from week texture with $Tc_{(111)}$ = 2.0 at U_b = -50 V to strong texture with $Tc_{(111)}$ = 5.5 at U_b = -300 V.

Friction coefficient measurement data as a function of test time and temperature, as well as wear track profilograms of the Ti6Al4V alloy with TiN and CrN coatings deposited at bias potentials of -50, 100 V and -50, -150 V, respectively, compared to the uncoated alloy are shown in Figure 3 and Figure 4.

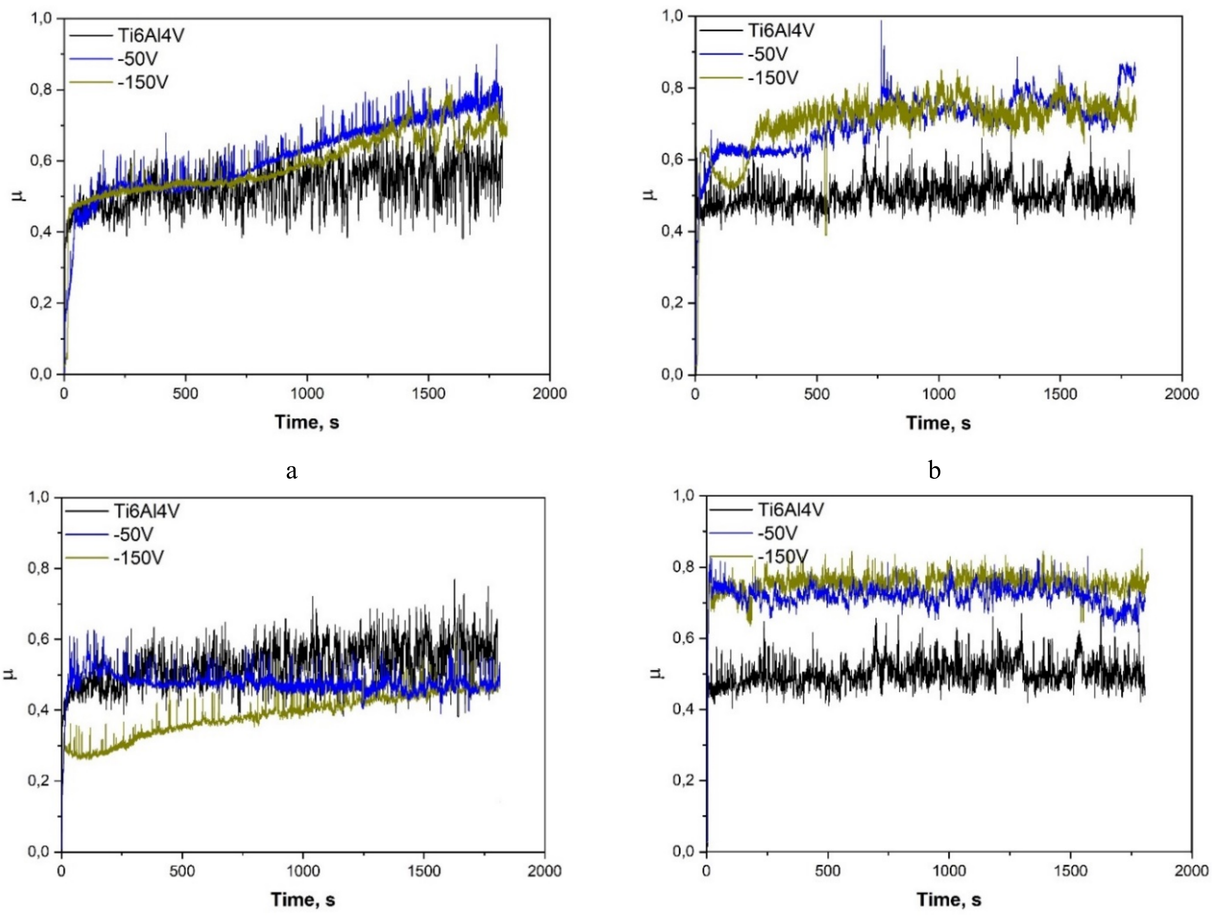

Figure 3. Friction coefficients of the Ti6Al4V with TiN (a, b) and CrN (c, d) coatings at temperatures 20°C (a, c) and 500°C (b, d).

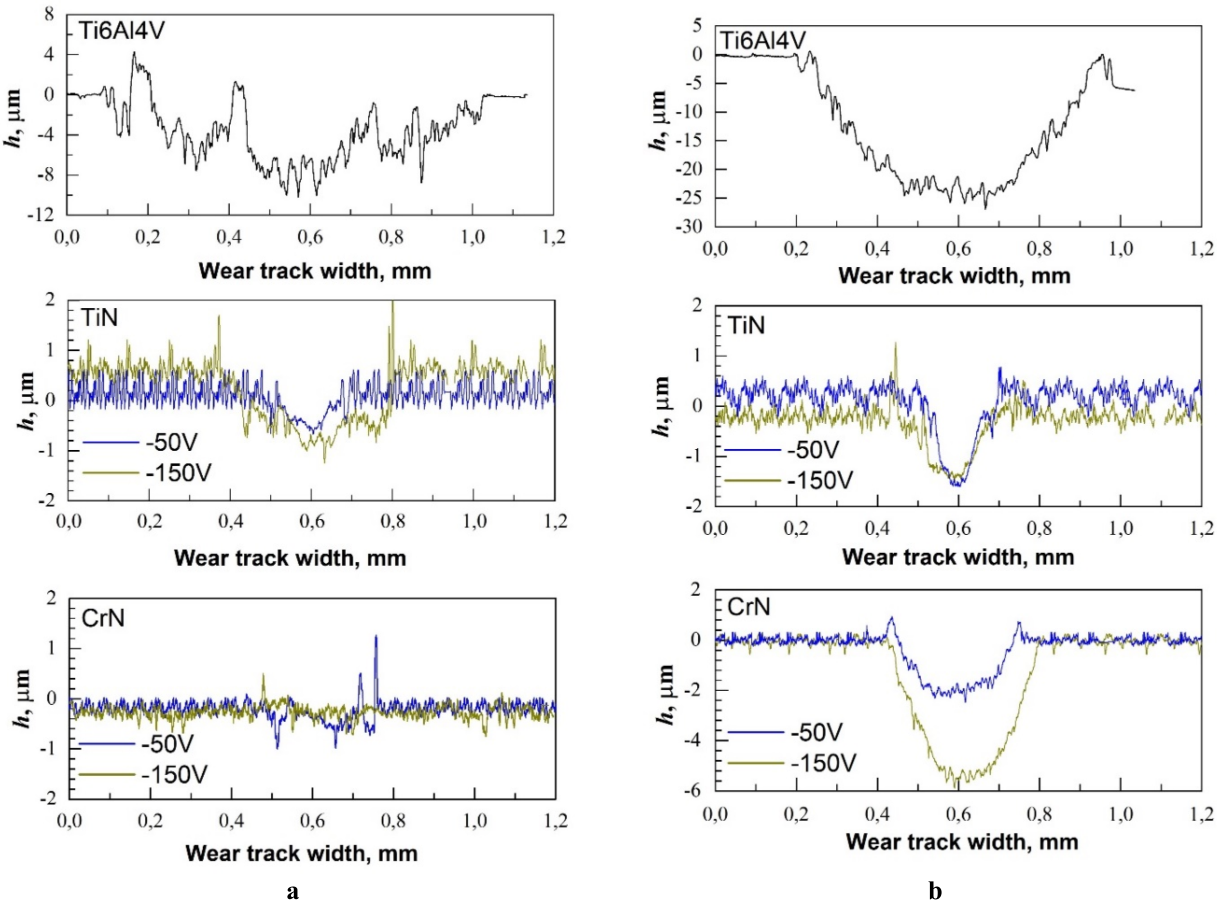

Figure 4. Wear profiles of the Ti6Al4V with TiN and CrN coatings at temperatures 20°C (a) and 500°C (b)

The initial nanohardness of the titanium alloy is 4 GPa, and the coefficient of friction remains constant at 0.55 throughout the test period at a temperature of 20 °C (Fig. 3 a). This value is very close to the literature values of μ = 0.55-0.6 for the Ti6Al4V alloy-alumina pair at a load of 2 N [15]. The wear intensity for the alloy in the initial state is 6.32×10^{-4} mm³/Nm, and the depth of the friction track reaches a maximum of 10 μm (Fig. 4a). At a test temperature of 500 °C, the friction coefficient increases to 0.6 and the wear rate to 1.87×10^{-3} mm³ N/m (Table 2).

The results of the mechanical property studies (nanohardness, Young's modulus, H^3/E^2 coefficient, friction coefficient, and wear rate) of the initial Ti6Al4V alloy and TiN and CrN coatings are presented in Table 2.

Table 2. Mechanical properties of Ti6Al4V alloy samples with TiN and CrN coatings.

Materials	U_b, V	H, GPa	E, GPa	H^3/E^2, GPa	Friction coefficient, μ		Wear rate, $\times10^{-5}$ мм³/Нм	
					20 °C	500 °C	20 °C	500 °C
Ti6Al4V	-	4	120	0.004	0.55	0.6	63.2	187
TiN	-50	24	437	0.072	0.5-0.8	0.75	0.86	3.56
	-150	30	470	0.122	0.4-0.8	-	2.73	-
	-300	25	428	0.085	0.4-0.7	-	2.83	-
CrN	-50	25	359	0.121	0.5	0.7	1.43	7.13
	-150	18	296	0.066	0.3-0.5	0.75	1.85	22.3
	-300	19	318	0.067	0.4-0.5	-	1.58	-

TiN coatings have a high nanohardness of 24-30 GPa. Titanium alloy with TiN coatings has a μ coefficient in the range of 0.4-0.8. Depending on the bias potential, there is a slight decrease in the μ coefficient for TiN coatings: at a potential of -50 V, it is 0.5-0.8, and at a potential of -300 V, it is 0.4-0.7. The wear rate of TiN coatings is more than an order of magnitude lower than that of the initial alloy (Table 2). The minimum wear rate of 8.61×10^{-6} mm³/Nm is observed for coatings deposited at a bias potential of -50 V. An increase in the bias potential (-150 and -300 V) results in an increase in the wear rate, which is $2.73\text{-}2.83\times10^{-5}$ mm³/Nm. The values obtained for the coefficient of friction and the wear rate are in the range of the known values for TiN coatings deposited by the cathodic arc method and alumina balls (0.58 and 6×10^{-6} mm³/Nm) [3]. Tests at a temperature of 500 °C were performed only on the TiN-coated sample (-50 and -150 V), which showed minimum wear at a temperature of 20 °C (Fig. 4 a, b). The coefficient of friction for the TiN coating remained at 0.75 at this temperature, and the wear rate increased slightly to 3.56×10^{-5} mm³/Nm.

The titanium alloy with CrN coatings shows a similar trend in the change of mechanical and tribological properties depending on the bias potential (Table 2). The nanohardness of CrN coatings decreases with increasing bias potential from 25 to 18-19 GPa. The coefficient of friction is 0.3-0.5 and weakly depends on the bias potential. CrN coatings applied at a bias potential of -50 V show the lowest wear rate (1.43×10^{-5} mm^3/Nm). Increasing the bias potential (-300 V) leads to a slight increase in the wear rate to 1.58×10^{-5} mm^3/Nm. Tests at 500°C were performed on two samples with CrN coatings deposited at potentials of -50 and -150 V because the wear rates at room temperature were very similar in value (Fig. 4 a). These tests clearly showed a lower coefficient of friction and a significantly lower wear rate (7.13×10^{-5} mm^3/Nm) for the coating deposited at -50 V compared to the coating deposited at a bias potential of -150 V (Fig. 4 b), for which the wear rate is 2.23×10^{-4} mm^3/Nm.

The correlation between the H^3/E^2 ratio [16] and the wear resistance of coatings was found only for chromium nitride coatings, confirming that the higher the ratio, the higher the wear resistance of the coating (Table 2). There is no such correlation for TiN coatings, which was also noted by the authors of [17].

It is interesting to note that the wear rate of the alumina counterbody paired with a titanium alloy does not depend on the test temperature and is at the level of 1.2 - 2.1×10^{-3} mm^3/Nm. At the same time, this value is one order of magnitude lower for a pair with a TiN coating and is at the level of 1.31×10^{-4} mm^3/Nm at room temperature and increases slightly to 4.03×10^{-4} mm^3/Nm at a temperature of 500 °C. For CrN coatings, this value is even lower, 1.03×10^{-5} mm^3/Nm at room temperature, but increases to a value of 3.36×10^{-4} mm^3/Nm at 500°C, which is close to the wear rate in a pair with a TiN coating. This dependence of the wear rate of the Al_2O_3 ball on the test temperature and the material of the counterpart (plane) may be related to the peculiarities of the formation of abrasive particles and oxide layers in the contact zone. The wear pattern of the alloy, coatings and alumina ball corresponds to abrasive wear in general.

CONCLUSIONS

Titanium nitride and chromium nitride coatings were deposited on Ti-6Al-4V alloy by cathodic arc method at three different bias potentials -50, -150, and -300 V.

X-ray diffraction analysis has shown that single-phase textured cubic nitrides of TiN and CrN are formed in these coatings at bias potentials from -50 to -300 V. The level of microdeformations in the coatings decreases with increasing substrate potential.

TiN and CrN coatings have high nanohardness of 24-30 and 25-18 GPa, respectively. With an increase in the bias potential, the nanohardness of TiN coatings increases, while that of CrN coatings decreases.

The study of the tribological properties of the Ti6Al4V titanium alloy substrate and coatings at temperatures of 20 and 500°C in a pair with an Al_2O_3 ball showed that:

- for the Ti-6Al-4V alloy, the coefficient of friction is 0.55 and the wear rate is 6.32×10^{-4} mm^3/Nm at 20°C and 0.6 and the wear rate 1.87×10^{-3} mm^3/Nm at 500°C;

- TiN and CrN coatings deposited at a bias potential of -50 V have the lowest wear rate at 20°C: 8.61×10^{-6} mm^3/Nm and 1.43×10^{-5} mm^3/Nm, respectively. The coefficient of friction is in the range of 0.4-0.8 for TiN coatings and 0.5 for CrN coatings. The wear rate at 500 °C for these coatings increases to 3.56×10^{-5} mm^3/Nm and 7.13×10^{-5} mm^3/Nm, respectively, and the coefficient of friction increases to 0.75 and 0.7, respectively.

Thus, the research results indicate that TiN and CrN coatings can be used to increase the wear resistance of Ti6Al4V alloy in air at temperatures from 20 to 500 °C.

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ТРИБОЛОГІЧНІ ВЛАСТИВОСТІ ПРИ ТЕМПЕРАТУРАХ 20 ТА 500°C КАТОДНО-ДУГОВИХ ПОКРИТТІВ TiN ТА CrN, ОСАДЖЕНИХ НА СПЛАВ Ti-6Al-4V

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Були досліджені трибологічні властивості покриттів TiN та CrN, осаджених катодно-дуговим методом при трьох різних потенціалах зміщення -50, -150 і -300 В на сплав Ti-6Al-4V у парі з оксидом алюмінію. Рентгенівський аналіз показав, що у цих покриттях утворилися однофазні текстуровані кубічні нітриди TiN та CrN. Показано, що коефіцієнт тертя покриттів практично рівний тому, що відповідає для сплаву Ti6Al4V, але знос є більш ніж на порядок нижчим, ніж для підкладки з титанового сплаву. Покриття, осаджені при потенціалі -50 В, демонструють оптимальні трибологічні властивості при температурах 20 та 500 °C. Коефіцієнти тертя для покриттів TiN становлять 0,4-0,8 при 20°C та 0,75 при 500°C; для покриттів CrN - 0,5 при 20°C та 0,7 при 500°C. Знос для покриттів TiN становить $0{,}86\cdot10^{-5}$ мм^3/Нм при 20°C та $3{,}56\cdot10^{-5}$ мм^3/Нм при 500 °C; для покриттів CrN - $1{,}43\cdot10^{-5}$ мм^3/Нм при 20°C та $7{,}13\cdot10^{-5}$ мм^3/Нм при 500°C.

Ключові слова: *Титановий сплав; катодно-дугове осадження; нітридні покриття; потенціал зміщення; структура; нанотвердість; коефіцієнт тертя; знос*