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INFLUENCE OF PARAMETERS OF MAGNETRON SPUTTERING PROCESS ON PHASE COMPOSITION AND STRUCTURE OF CARBON NITRIDE COATINGS

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ABSTRACT

Deposition of CN_x-coatings was carried out using two magnetron devices with titanium and graphite targets in the mixture of Ar/N_2 gases. The influence of gas mixture (Ar/N_2) composition, pressure (0.35, 1 and 2 Pa) and temperature (100–200 °C) on the structure of the CN_x coating were investigated. It was found that the structure of the coating represents an amorphous disordered graphite-like structure with sp^3-, sp^2- and sp^1 electron bonds of carbon. The most ordered structure is observed in the CN_x coatings (the least ID/IG = 1.16 and 1.2), produced at a pressure of 0.35 Pa, the temperature of the specimen is 130 °C, the content of nitrogen is 40 and 58 %. The influence of a titanium sublayer and a transition TiCN layer on adhesive properties of the CN_x coating was studied. When a titanium sublayer and a transition TiCN layer are used together, the adhesion of the coating to the bases of titanium and Khl8N10T steel grows at a thickness of the coating being 2–3 μm.

KEYWORDS: magnetron sputtering, CN_x coating, structure, phase composition, Raman spectroscopy

INTRODUCTION

Over the last decade, the carbon nitride CN_x coating has attracted a considerable attention [1]. In 1989, Liu and Cohen theoretically calculated a new superhard structure, carbon nitride C_3N_4 [2]. By then, numerous efforts were aimed at the synthesis of this new material. Carbon nitride amorphous film was one of the results of such studies. It was found that it has higher hardness and wear resistance [3] as compared to the film made of a diamond-like carbon. Amorphous coatings have already found a widespread use as protective coatings on hard drives and read-write heads [4] due to their excellent properties. As compared to hydrogenated diamond-like carbon coatings, CN_x has a higher wear resistance at a low friction coefficient [5]. Another advantage of nitrogen incorporation in the coating is an increase in surface energy, which in turn provides a high wettability [6].

CN_x films are mainly composed of carbon and nitrogen, and also can be alloyed with hydrogen. Since these elements are widespread in a living body, the coatings have the properties of biocompatibility [7].

CN_x coatings can be synthesized by such methods as plasma chemical deposition from acetylene with nitrogen gas mixture; vacuum-arc spraying in nitrogen medium from carbon plasma flows generated by cathode spots of vacuum-arc discharges [8]. The use of reactive magnetron sputtering of a graphite target in the mixture of Ar/N_2 gases for this purpose is also interesting [9]. Under certain conditions of deposition, the magnetron CN_x coating can be of great importance of a normalized H/E hardness (more than 0.12), which determines its elasticity and wear resistance under friction conditions (in tribotechnical contact) [10]. In [11] it is proposed to evaluate the elastic properties of the CN_x coating during indenting by the percentage of elastic recovery $R(\%) = (h_{max}–h_{res})/h_{max}\cdot 100$, where h_{max} is the depth of introducing indenter in the coating at a maximum load; h_{res} is the depth after relieving the load. Due to elastic properties, the CN_x coating was called a “superhard rubber”. In [12], the results of studying mechanical and tribotechnical properties of the CN_x coating, deposited on titanium bases, which confirm its high resistance to plastic deformation, are presented. Thus, while depositing the CN_x coating to titanium, elastic surface recovery (R, %) increases from 30 to 81 %.

Wear resistance and adhesive strength of the CN_x coating depends on the effect of ion bombardment conditions [13]. In [14], the technology of producing the CN_x coating with a high adhesion to the surface of the bases of stainless steel with the use of a chromium sublayer is considered. To deposit chromium, the method of high-power impulsed magnetron sputtering (HIPIMS) was used. A distinctive feature of HIPIMS is a high level of ionization of a sprayed material and a high level of dissociation of gas molecules.

The magnetron power with a chrome target was carried out from the pulsed voltage source: U = 500–= 1000 V, f = 150 Hz, t_p = 100 ms, the displacement voltage source had the following parameters: U_d = = 500–1000 V, f = 150 Hz , t_p = 100 ms. The CN_x coating was deposited by spraying the graphite target at DC at a negative displacement voltage U_d = –25 V. Determination of adhesive strength of the CN_x coating by scratching method showed that as compared to the variant when a chromium sublayer was deposited while powering the magnetron from the direct voltage source, the critical load of destruction of the CN_x coating more than 3 times increased.

In [13], it is noted that ion bombardment of amorphous CN_x films improves their mechanical properties, providing high hardness, high resistance to plastic deformation and high elastic recovery.

The aim of the work was the study of a reactive magnetron discharge with a graphite target in the mixture of Ar/N_2 gases, as well as the study and development of the process of producing the CN_x magnetron coating on stainless steel and titanium bases.

PROCEDURE OF EXPERIMENTS AND STUDIES

The coating was deposited using a modernized VU-1BS vacuum unit equipped with a DC magnetron sputtering module consisting of two magnetrons: magnetron 1 with a disc target (88 mm diameter, 4 mm thickness) made of MPG-7 graphite with a purity of 99.98 % and the magnetron 2 with a rectangular target (90×58×4 mm) made of VT1-0 titanium (Figure 1). The magnetrons are mounted on a one flange in such a way that the angle between the surfaces of the targets is equal to 150 °C. As a result, it was possible to simultaneously or alternately deposit coatings on a stationary base from two magnetrons with the same distance between the base and the targets, equal to 110 mm. The magnetron 2 was designed for the deposition of an adhesive sublayer of titanium on metal bases.

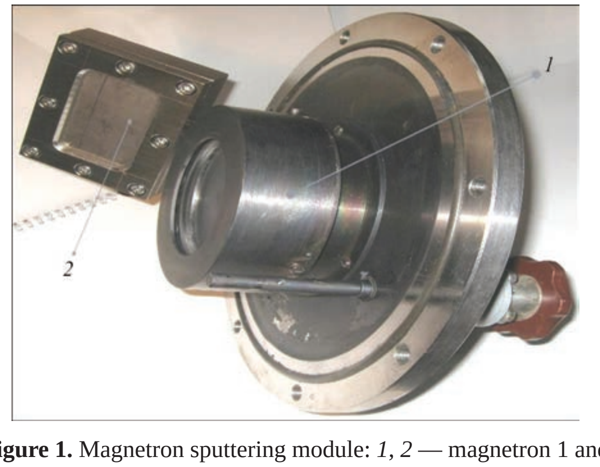

Figure 1. Magnetron sputtering module: *1*, *2* — magnetron 1 and magnetron *2*, respectively

The study of the characteristics of a reactive magnetron discharge with a graphite target was carried out at different values of the working pressure p, the mixture of Ar/N_2 gases, and the percentage of nitrogen in it.

For the initial experiments on studies of the process of the CN_x coating formation, glass bases (65×30×4 mm) were used. This choice was predetermined by the possibility of accurate measurement of the coating thickness using a profilograph-profilometer.

To study the process of forming the CN_x coating on metal materials, as a base, the specimens of Kh18N10T steel and VT1-0 titanium with a size of 65×30×0.5 mm, as well as the specimens of VT1-0 titanium with a diameter of 25 mm and a thickness of 5 mm were used. Before placing in the vacuum chamber, the specimens were cleaned in an ultrasonic bath, which is gradually filled with acetone and ethyl alcohol. In a vacuum at a pressure of $5.0 \cdot 10^{-4}$ Pa, the specimen was heated at a temperature of 150 °C for 20 min, then without turning off the heater, the surface of the specimen was cleaned by bombardment with argon ions (especially pure) in a direct current discharge at a pressure of 1.3 Pa, at a voltage of 1100 V for 20 min.

The specified variants of the specimens treatment were one of the components of the process of increasing the adhesion of the CN_x coating to the base surface. The conducted preliminary experiments showed that in order to increase the adhesive strength of the CN_x coating on the specified bases, it is necessary to deposit an adhesive layer of titanium and an intermediate Ti–C–N layer on their surface. The latter was intended for smoothing the transition interface between materials with different physical characteristics of the base CN_x and adhesive layers of titanium.

Three stages of the process of forming the CN_x coating layers on the surface of Kh18N10T and VT1-0 titanium specimens were determined, as well as the ranges of changing deposition parameters of the layers:

- deposition of a titanium sublayer (δ = 0.3 μm) in argon at an operating pressure p = 0.35 Pa, specific power of a magnetron discharge with a titanium target Δ_{PTi} = 3.5 W/cm, deposition rate V_{Ti} = 25 nm/min and a change in the negative displacement on the base of U_d from –300 to –1400 V;
- deposition of the intermediate Ti–C–N layer (δ = = 0.25 μm) using joint reactive magnetron sputtering of graphite and titanium targets on a direct current in the mixture of Ar/N_2 gases at pressures of p = 0.35, 1 and 2 Pa, average values of Δ_{PC} = 10.4 W/cm and Δ_{PTi} = 3.4 W/cm, $U_{d\,CN_x}$ = 0– –40 V;

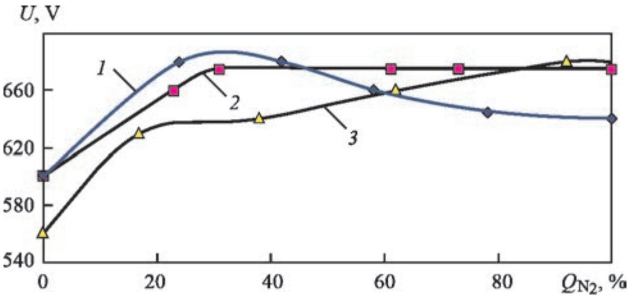

Figure 2. Dependence of the magnetron discharge voltage with a graphite target of MPG-7 on the content of nitrogen in the mixture of Ar/N_2 at $I = 1$ A, $p = 0.35$ (*1*), 1 (*2*), 2 (*3*) Pa

● deposition of the base CN_x layer ($\delta = 2.0$–3.9 μm) in the mixture of Ar/N_2 gases at $p = 0.35$, 1 and 2 Pa, $\Delta_{PC} = 10$ W/cm, $U_{\mathrm{d\ CN}_x} = 0$– –40 V, $T_b = 130$, 200, 350 °C.

The phase analysis of the coatings was carried out by the X-ray diffraction method using an X-ray diffractometer Philips X'Pert-MPD with a CuK_α X-ray source (wavelength $\lambda = 0.15418$ nm). X-ray diffraction spectra were taken in the Bragg–Brentano geometry (2Th-omega-scanning) — the full angular range of diffraction spectrum registration by $2\theta = 25$–75°.

The combining Raman spectroscopy method (CRS) was used to determine the configurations of carbon chemical bonds in the coating. The micro Raman spectra were measured in the reflection geometry at a room temperature using a triple Raman spectrometer T-64000 Horiba Jobin-Yvon equipped with a cooling CCD detector. For excitation, an Ar–Kr laser line with a wavelength of 488 nm was used. The radiation was focused on the specimen using a 50× objective, the power of the radiation falling on the specimen was about 0.25 mW.

RESULTS OF EXPERIMENTS AND THEIR DISCUSSION

In order to determine the optimal conditions for deposition of the CN_x coating, the characteristics of a DC magnetron discharge with a graphite target from MPG-7 in the mixture of Ar/N_2 gases were investigated. The experiments were carried out at $p = 0.35$, 1 and 2 Pa. It was found that at the indicated pressures the discharge is stable and breakdowns of a discharge gap at $P = 11$ W/cm are absent.

The most complete idea of the nature of a magnetron discharge burning with a graphite target in the mixture of Ar/N_2 gases is given by the dependence of the voltage on a percentage content of nitrogen N_2 consumption in the mixture, which is determined by the ratio of nitrogen consumption to the sum of argon and nitrogen consumption — $Q_{N_2}/(Q_{N_2}+Q_{Ar})100$ (Figure 2). At $N_2 = 0$, with an increase in the pressure to 2 Pa, the discharge voltage decreases from 600 to 560 V. At $p = 0.35$ Pa with an increase in N_2 to 24 %, the discharge voltage reaches a maximum $U = 690$ V, and further decreases at $N_2 = 100$ % $U = 640$ V. A somewhat different character of the change in the discharge voltage was detected at pressures equal to 1 and 2 Pa. Thus, at $p = 1$ Pa and $N_2 = 24$ %, the voltage also reaches a maximum $U = 675$ V, but does not change further to $N_2 = 100$ %.

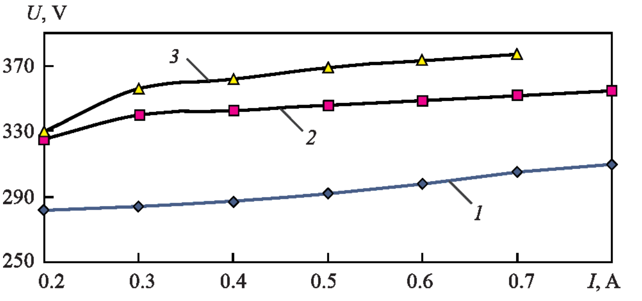

Figure 3. VACh of a magnetron discharge with a titanium target in the mixture of Ar/N_2 gases at $p = 0.35$ PA: *1* — $N_2 = 0$; *2* — 25.6; *3* — 45 %

The volt-ampere characteristics (VACh) of a direct current magnetron discharge with a VT1-0 titanium target (magnetron 2) in the mixture of Ar/N_2 gases at $p = 0.35$, 1, 2 Pa were also studied. The voltage of discharge burning increases with an increase in N_2 due to the formation of a TiN film on the surface of the target (Figure 3).

During a simultaneous operation of two magnetrons, the surface of a titanium target is partially dusted with a carbon film, which also leads to an increase in the voltage of a discharge burning and a sharp increase in the ignition voltage. For $p = 0.35$, 1, and 2 Pa, the corresponding boundary values of N_2 were determined, equal to 45, 73, and 66 %, at which a stable excitation and maintenance of the discharge with a titanium target was provided.

Figure 4 shows the dependences of the rate of depositing CN_x coating on glass substrates on the nitrogen content in the Ar/N_2 mixture under the following conditions: working pressures $p = 0.35$, 1 and 2 Pa, discharge current $I = 1$ A. At each of the specified pressures, the coating was deposited at six values

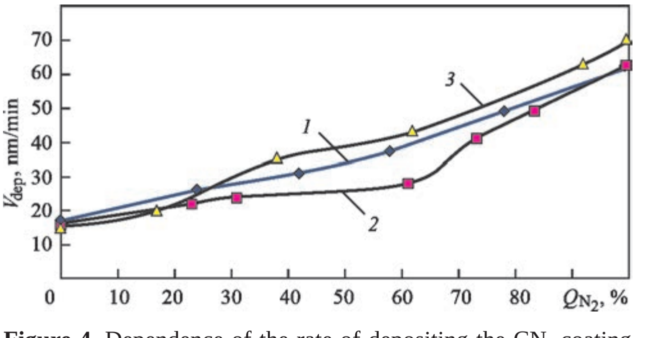

Figure 4. Dependence of the rate of depositing the CN_x coating on the content of nitrogen in the mixture of Ar/N_2 at $p = 0.35$ (*1*), 1 (*2*), 2 (*3*) Pa

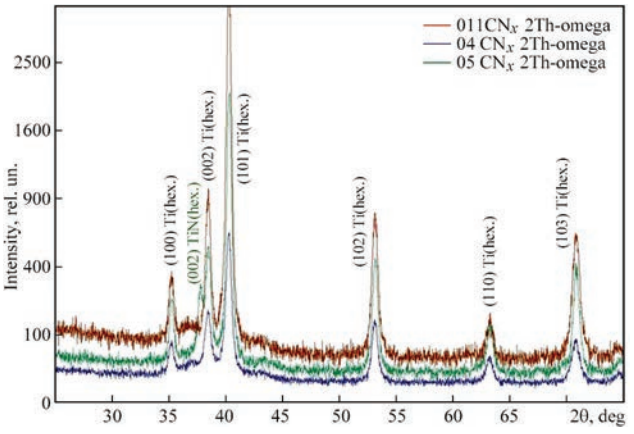

Figure 5. X-ray patterns of specimens 04CN$_x$, 05CN$_x$ and 011CN$_x$ produced in the geometry of Bragg–Brentano

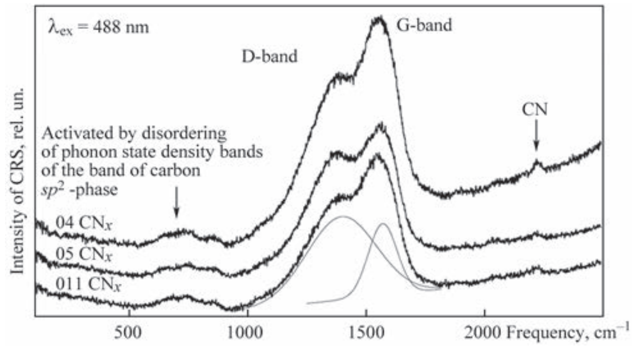

Figure 6. CRS spectra of CN$_x$ coating specimens (in all CRS spectra two D- (≈ 1390 cm^{-1}) and G-bands (≈ 1580 cm^{-1}) are recorded, which are characteristic of inelastic light scattering in carbon structures)

of the N_2 nitrogen content consumption in the Ar/N_2 mixture. At the same time, the specific power of the magnetron discharge P varied within the ranges of 9.3–11.4 W/cm.

As is seen from Figure 4, with an increase in the nitrogen content in the mixture of gases at all pressures, the deposition rate increases. At p = 0.35 and 2 Pa, the growth is uniform. At p = 1 Pa, an increased growth in the deposition rate occurs with an increase in N_2 from 60 to 100 %. At N_2 = 0, in the argon atmosphere, a carbon coating was deposited on the base at a rate V_C = 16 nm/min (0.96 μm/h). At N_2 = 100 %, the CN$_x$ coating was formed with the maximum nitrogen content at an average rate V_{CN_x} = 60 nm/min (3.6 μm/h). Therefore, when N_2 changed from 0 to 100 %, the rate of the coating deposition increased by 3.8 times, and the specific power of the discharge, proportional to which the rate of ion sputtering of materials usually changes, increased by only 1.2 times (from 9.3 to 11.4 W/cm).

A significant difference in the degree of the specific power and deposition rate indicates a more complex mechanism of spraying graphite in the mixture of Ar/N_2 gases. The work [15] states that an increase in the deposition rate is possible with an increase in the spraying coefficient of a graphite target due to a reduced cohesive bonding of carbon atoms during the chemical reaction between nitrogen and carbon atoms. In addition, flying CN radicals can be formed, that are easily sprayed on the target surface.

The results of X-ray structural analysis of the magnetron CN$_x$ coatings are presented in Figures 5, 6. The parameters of the process of depositing CN$_x$ coatings are given in Table 1.

As is seen from Figure 5, on the spectra of X-ray diffraction from all specimens 04CN$_x$, 05CN$_x$ and 011CN$_x$ the presence of the titanium (hexagonal) phase, which corresponds to the presence of the adhesion layer of titanium (δ = 0.35 μm) is seen. In the specimen 05CN$_x$, a TiN phase is also present, which most likely formed due to an increased deposition temperature. No reflexes from the layers of CN$_x$ and Ti–C–N are observed, which indicates their amorphous state.

Table 1. Parameters of the process of depositing magnetron Ti + (Ti–C–N) + CN$_x$ coating (bases — VT1-0 titanium)

Specimen number	p, Pa	T_b, °C	Coating sputtering conditions					
			Ti		Ti–C–N		CN$_x$	
			P_{Ti}, W	U_d, W	N_2,%	P_C/P_{Ti}, rel. un.	N_2,%	P_C, W
03CN$_x$	0.35	200	184	–150	25.6	2.7	58	570
04CN$_x$	0.35	130	184	–150	25.6	2.8	58	560
05CN$_x$	0.35	350	184	–300	25.6	2.8	58	560
06CN$_x$	0.35	130	184	–300	–	–	58	580
011CN$_x$	0.35	130	184	–300	25.6	2.8	42	540
012CN$_x$	0.35	350	180	–300	25.6	2.8	42	540
07CN$_x$	1.0	130	190	–300	22.8	2.85	100	580
08CN$_x$	1.0	350	187	–300	22.8	2.9	100	560
010CN$_x$	1.0	200	180	–300	22.8	3.0	100	560
09CN$_x$	2.0	130	180	–300	66.0	2.75	100	560

Table 2. Frequency positions (ω), full width at half maximum (FWHM), ratio of integral intensities for D- and G-bands (ID/IG)

Specimen number	D-band (sp^2)			G-band (sp^3)			ID/IG
	ω, cm^{-1}	FWHM, cm^{-1}	FWHM, rel. un.	ω, cm^{-1}	FWHM, cm^{-1}	FWHM, rel. un.	
04 CN_x	1400.6	349.4	822	1574.5	140.2	683	1.20
05 CN_x	1393.3	336.1	621	1578.8	135.2	470	1.32
011 CN_x	1396.9	345.3	565	1570.6	142.6	488	1.16

The CRS spectra of the studied specimens are presented in Figure 6.

For modeling G- and D-bands, the Gauss functions with a preliminary subtraction of a modeled base line were used (Figure 6). Table 2 shows the results of the analysis of frequency positions, FWHM and ratios of integral intensity of D- and G-bands, which were performed by the decomposition of CRS spectra on the corresponding components. With regard to nitrogen-containing carbon films, in addition to the fluctuations caused by carbon C = C bonds, the contribution to the oscillatory lines is also made by the fluctuations of C = N bonds with the type of sp^2-configuration of chemical bonds. In the experimental CRS spectra in a general case, it is very difficult to divide these deposits. Changing the position and shape of these oscillatory bands occurs as a result of structural changes, formation of disordering, aromatic rings, microcrystalline graphite, etc. [15].

A weak signal in the area of 600–900 cm^{-1} is associated with an induced disordering of sp^2 structural carbon phase by scattering processes with the participation of phonons with non-zero wave vectors.

A Raman band with a spectral position of about 2220 cm^{-1}, which is observed in the CRS spectra of the CN_x coating is associated with the formation of triple C ≡ N chemical bonds with sp^1-hybridization in the studied structures.

The least value of ID/IG = 1.16 ratio indicates the highest carbon ordering in the structure of the CN_x coating (011CN_x specimen), produced at T_b = 130 °C and N_2 = 42 %.

CONCLUSIONS

1. The process of depositing a nanocomposite carbon nitride CN_x coating (2–3 μm thickness) on the bases of Kh18N10T and VT1-0 titanium with the use of the adhesive layer of titanium and intermediate Ti–C–N layer by the method of combined DC reactive magnetron sputtering of titanium and graphite targets in the mixture of Ar/N_2 gases was developed.

2. The studies of the CN_x coating showed that it has an amorphous disordering graphite-like structure with sp^3, sp^2 and sp^1 electron bonds of carbon. The most ordered structure was obtained in the CN_x coatings (ID/IG = 1.16 and 1.2) at p = 0,35 Pa and T_b = = 130 °C, N_2 = 40 and 58 %.

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CONFLICT OF INTEREST

The Authors declare no conflict of interest

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