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Properties of Coatings Based on Carbon and Nitrogen-Doped Carbon Obtained Using a Pulsed Vacuum Arc Method

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Abstract—Diamond-like carbon coatings on hard-alloy substrates, including coatings doped with nitrogen about 1.0 μm thick have been obtained using a pulse vacuum-arc method. Three types of coatings have been investigated: a carbon diamond-like coating (C), a carbon coating doped with nitrogen (C : N), and a composite coating based on (C : N + C) layers. The coatings have been annealed in atmospheric air at a temperature of 400°C. The tribological characteristics (wear resistance and friction coefficient change dynamics), the adhesion strength, and the microhardness of coatings in the initial state and after annealing have been studied. The composite coating consisting of C : N + C layers surpasses the constituent coatings in properties, both in the initial state and after annealing at a temperature of 400°C.

Keywords: amorphous carbon coatings, pulsed vacuum arc method, annealing, wear resistance, microhardness, adhesion, Raman spectra

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INTRODUCTION

The production of carbon nitride films attracted the attention of many researchers after the theoretical prediction of a potential existence of structural state β-C_3N_4 [1] that should rank over natural diamond in mechanical properties. However, a large number of experimental studies have not allowed one to unequivocally confirm this assumption.

The authors of [2] reported the results of studies concerning carbon nitride superhard and elastic films obtained using a vacuum-arc method with plasma flow filtration. The ions were ionized and accelerated using a high-frequency ion source. The nitrogen pressure in the vacuum chamber was maintained at a level of 2×10^{-4} Torr. It was established that, as the energy of nitrogen ions increased to 100 eV, the microhardness, the modulus of elasticity, and the elastic recovery exhibited an increase to 47 GPa, 400 GPa, and 87.5%, respectively. Any further increase in the energy of nitrogen ions resulted in a deterioration of these properties, which was attributed by the authors to an increase in the size of graphite clusters.

The pulse vacuum arc technique for obtaining diamond-like carbon coatings [3] has a number of advantages over other methods. The authors of [4] reported the results of complex studies concerning the structure and properties of nitrogen-doped amorphous carbon coatings (a-C:N) obtained in vacuum using a pulsed carbon plasma flow. It was established that the nitrogen doping of a carbon coating leads to an increase in electrical conductivity, to a decrease in internal stresses, to a decrease in density, hardness, and elastic modulus, and to a change in the structure, surface morphology, and tribological characteristics as compared to an undoped coating (ta-C). It was shown that the a-C:N coatings are significantly inferior to ta-C coatings in the values of hardness and modulus of elasticity, but they are more elastic and are not subjected to brittle fracture in the form of cracks and chips.

The effect of annealing in vacuum exerted on the tribological characteristics of nanoscale carbon coatings doped with nitrogen was studied by the authors of [5]. It was established that the annealing of these coatings in vacuum at a temperature of 600°C resulted in a threefold increase in their wear resistance.

The results of the studies presented in [6] are of particular interest, since they indirectly confirm the existence of a theoretically predicted new species of crystalline carbon nitride β-C_3N_4 [1]. Crystalline carbon nitride was obtained via magnetron sputtering with additional ion irradiation and subsequent annealing in a nitrogen atmosphere. The microstructure of the coating was investigated using X-ray diffraction (XRD) and transmission electron microscopy (TEM). The film was shown to contain a very dense and uniform distribution of crystalline grains, the crystal lattice parameters and the type of crystal lattice being in good agreement with the parameters of theoretically predicted carbon nitride crystalline species β-C_3N_4.

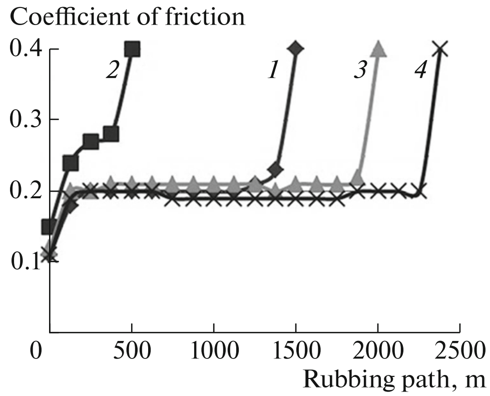

Fig. 1. Tribological characteristics of carbon coatings before and after annealing: (*1*) C400; (*2*) C:N400; (*3*) C:N + C; (*4*) (C:N + C)400.

The X-ray photoelectron spectroscopy (XPS) also confirmed the presence of sp^3-hybridized C–N bonds in the film. The concentration of particles of crystalline carbon nitride in the film is 43.91%, which is higher than that obtained in previous works. The interest in this work is also caused by the fact that we published a paper [7] in which we described a new phase of crystalline carbon formed upon annealing in vacuum at a temperature of 600°C in an amorphous carbon matrix obtained using a pulsed vacuum arc technique. Thus, the same approach to the modification of the structure of carbon coatings can be traced.

It is of interest to obtain a combined coating based on a-C:N and ta-C layers, followed by annealing in atmospheric air, as well as to study the properties of this coating in the initial state and after the action of an elevated temperature.

This work was aimed at obtaining, studying, and comparatively analyzing the tribological characteristics, microhardness, and adhesion strength of carbon coatings (C, C:N, and combined ones on the basis of C:N + C layers) before and after annealing at 400°C.

EXPERIMENTAL

The carbon coatings were obtained using a UVNIPA-1-011 experimental facility modernized in the part of power supply units and equipped with an ion source, a vacuum arc source of a metal plasma with a plasma flow separation system, and a pulse carbon plasma source. The samples represented disks made of solid alloy (WC) based on tungsten carbide and cobalt with a diameter of 20 mm and a thickness of 3 mm. The samples were polished using diamond pastes; then they underwent a cleaning operation in an ultrasonic bath and drying in an oven at a temperature of 100°C. The vacuum chamber was pumped to a pressure no higher than 5×10^{-5} mmHg.

Further, ion purification was carried out using accelerated argon ions at a pressure of 5×10^{-3} mmHg, a discharge voltage of 2.0 kV, and a discharge current of 100 mA for 10 min. After that, a purification by titanium ions and an application of a titanium sublayer was performed. Next, a carbon diamond-like coating was deposited using a pulsed vacuum arc method in the following modes: charge storage voltage 300 V, charge storage capacitance 2000 μF, pulse repetition rate 5 Hz. The coating thickness was 1.0 μm. A carbon coating doped with nitrogen was produced via nitrogen injection into an ion source for ionization at a pressure of 5×10^{-3} mmHg.

The following three types of coatings were investigated: a carbon diamond-like coating (C), a nitrogen-doped carbon coating (C:N), and a layer-based composite coating (C:N + C). The coatings were annealed in an air atmosphere at a temperature of 400°C for 10 min. For annealing, a Nabertherm LT5/12/B170 muffle furnace was used. The tribological characteristics (the wear resistance and the changing dynamics of the friction coefficient), the adhesion strength, and the microhardness of coatings in the initial state and after annealing were studied. The wear resistance of the coatings was tested using a laboratory bench according to a scheme "disk–flat coated sample" under conditions of dry friction until the coating was completely worn, which was fixed by an abrupt increase in the coefficient of friction.

The counterbody represented a disk with a diameter of 10.0 mm made of of the corrosion-resistant steel (Fe–0.12C–0.90Mn–0.025P–0.01S–16Cr–0.20Cu, all in wt %). The load on the disk was 50 g. The investigations were carried out at a relative slip velocity of 0.5 m/s. The hardness of the coatings was studied using a technique of "instrumental indentation" (Russian State Standard ISO 14577–1:2002) using a Shimadzu DUH-211S ultra microhardness meter. The indentation was carried out at an indentation load of 100 and 200 mN. To determine the adhesion of the coating to the substrate, a sclerometric (scratching) test was used. In this case, a Revetest scratch tester (CSM Instruments) was used to determine the adhesion/cohesion strength and scratch resistance, as well as to determine the fracture mechanism.

The moment of the adhesive or cohesive destruction of the coatings was registered after the testing visually by means of an optical microscope equipped with a digital camera, as well as according to change in the acoustic emission and the coefficient of friction. As a result of the tests, the minimum (critical) load Lc which led to the coating destruction was determined. To study the structural changes caused by the action of temperature, Raman spectroscopy was applied using a LabRAM HR Evolution Raman spectrometer (laser wavelength 532 nm, power 50 mW).

RESULTS AND DISCUSSION

Figure 1 shows the results of studies concerning the tribological characteristics of carbon coatings before and after annealing until their total wear, which is

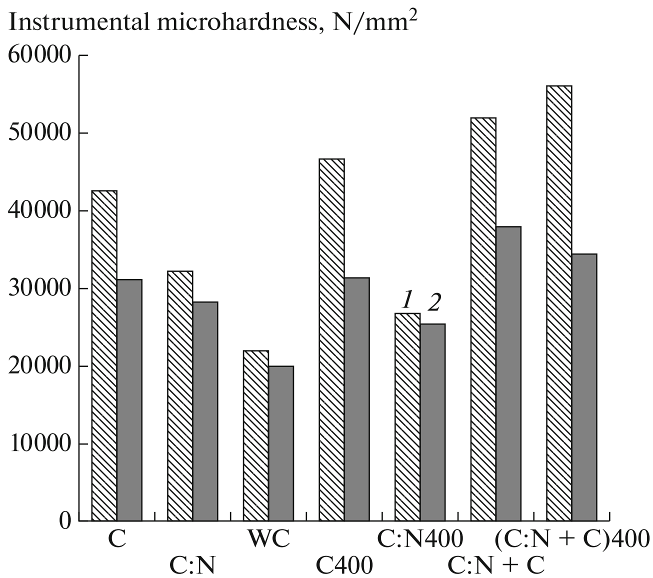

Fig. 2. Instrumental microhardness of coatings C, C:N, and C:N + C in the initial state and after annealing at a temperature of 400°C at different indentation loads: (*1*) 100 mN; (*2*) 200 mN.

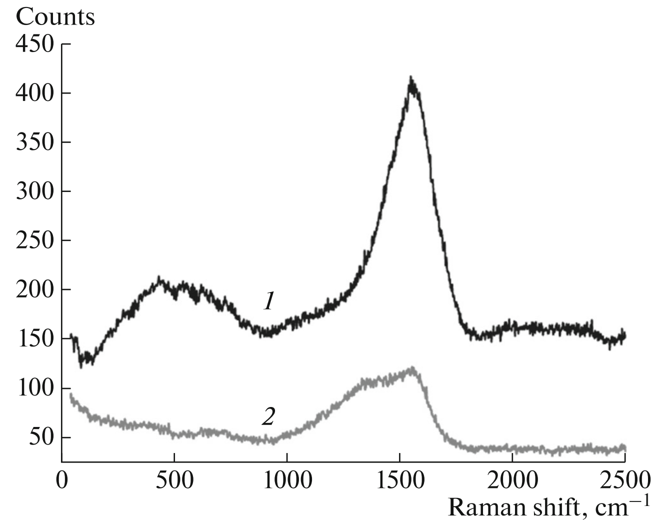

Fig. 3. Raman spectra of carbon coatings (*1*) and carbon coatings doped with nitrogen (*2*) after annealing at a temperature of 400°C.

indicated by an abrupt increase in the coefficient of friction. The C:N + C coating is the most wear-resistant one, both in the initial state and after annealing at a temperature of 400°C.

Figure 2 shows the results of measuring the instrumental microhardness of C, C:N, and C:N + C coatings in the initial state and after annealing at a temperature of 400°C. It should be noted that the composite coatings based on carbon and carbon layers doped with nitrogen (C:N + C) exhibit the greatest microhardness. An important result is the effect of increasing microhardness exerted by C and C:N + C coatings after annealing at a temperature of 400°C. A similar result has been obtained for the wear resistance of the same coatings.

The results of measuring the adhesion characteristics of carbon coatings are summarized in Table 1.

Analyzing the results given in Table 1, we should note that a C:N + C coating has the greatest adhesive strength in the initial state, whereas after annealing a C:N coating is the most adhesive one. In this case, the annealing leads to an increase in the adhesion strength of C and C:N coatings, but to a decrease in this value for the C:N + C coating.

Table 1. Adhesion characteristics determined for carbon coatings

No.	Coating	Critical load, N	
		in the initial state	after annealing
1	C	12	24
2	C:N	18	28
3	C:N + C	24	16

Figure 3 shows Raman spectra of carbon coatings (C) and carbon coatings doped with nitrogen (C:N) after annealing at a temperature of 400°C.

It should be noted that the spectrum of the carbon coating in the initial state does not differ from that shown in Fig. 3. The spectrum of the carbon coating doped with nitrogen in the initial state is characterized by a higher intensity of peaks.

The results obtained can be considered as a confirmation of the conclusions made by the authors of [7] that annealing leads to an improvement in the wear resistance of coatings as a result of structural changes associated with the phenomenon of local crystallization. This effect was established using a technique of high-resolution transmission electron microscopy (HRTEM).

CONCLUSIONS

It is established that the characteristics of a combined coating consisting of C:N + C layers ranks over the characteristics of the composing coatings, both in the initial state and after annealing at a temperature of 400°C. At the same time, the annealing does not worsen the properties of this coating, but on the contrary, it causes their properties to improve. This effect can be explained by the structural changes associated with local crystallization in the matrix of amorphous carbon. In addition, the results obtained have an applied value, since they make it possible to increase the tribological characteristics of diamond-like carbon coatings used in friction assemblies.

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