Evolution via friction of properties of DLC nanofilms on steel

T A Kuznetsova1, V A Lapitskaya1, E V Torskaya2, T I Muravyeva2, A M Mezrin2, V Y Samardak3, A V Khabarava1, R E Trukhan1 and S A Chizhik1

1 A V Luikov Heat and Mass Transfer Institute of NAS Belarus, 220072 Minsk
2 Ishlinsky Institute for Problems in Mechanics, RAS, 119526 Moscow
3 School of Natural Sciences, Far Eastern Federal University, 690920 Vladivostok

E-mail: kuzn06@mail.ru

Abstract. The results of the diamond-like carbon (DLC) coatings surface investigation with thickness of 100, 300 and 500 nm, applied on hardened steel via laser ablation methods and pulse arc discharge are presented. Topography, roughness, adhesion forces and specific surface energy of coatings before and after tribotests were studied using atomic force microscopy (AFM). The changes in the elastic modulus E and microhardness H of the surface after dry sliding friction have been established by nanoindentation method (NI).

1. Introduction
Surface modification of tribotechnics steel parts by coatings application is a more efficient solution compared to the volume modification by nanoscale additives [1, 2]. The idea to combine high wear resistance with a low friction coefficient may be realized if specific surface structures are obtained due to friction; the properties of the structures are very important subject of studying. The secondary structures formed during friction significantly reduce the friction coefficient and protect the surface from wear. In the last decade, to reduce wear and friction of the working surfaces of the contacting parts, DLC [3] has been widely used. The expansion of the DLC applications was greatly facilitated by doping with metals (Ti, Cr, Mo, W, Ni, Al, Cu, Ag, Ta) and the use of the adhesive sublayers that provide strong adhesion and industrial employment of the coatings. The evolution of the coating properties during the friction is taken into account at selection of optimal technological modes of application and operation [4]. The morphology of the modified surface can explain the tribological properties of the parts. The mechanism of wear of diamond at the nano scale during the friction is discussed in [5]. The flat amorphous “flakes” with a diameter of about 50 nm and a thickness of one atom move from the diamond tip to the friction zone; the process is shown using transmission electron microscopy. Amorphization contributes to reduction of friction coefficient in the tribopairs made of composite materials using diamond and diamond-like structures [6]. In [7], the visualization of the secondary tribostructures of DLC doped with Ti was performed by AFM, which shows a significant plastic deformation of the surface layers. Using AFM with highly sensitive force recording allows to evaluate simultaneously the morphology, adhesion forces between the probe and the surface and roughness. Taking into account the nano-roughness of DLC allows to explain the high normal stresses in the contact [8], which contribute to the mechanochemical reactions and the secondary structures formation.
The aim of this work is an experimental investigation by the methods of nanoindentation and atomic force microscopy (AFM) of changes in the morphology and mechanical properties of DLC coatings different thickness (100, 300 and 500 nm) due to friction.

2. Experimental details
DLC samples were deposited on the substrates made of polished hardened steel by Pulse laser deposition (PLD) and laser arc PVD deposition on a SWISSNANOCOAT PVD COATING SYSTEM (NCI-Swissnanocat, Switzerland). Before the DLC deposition, a titanium sublayer with a thickness of about 800 nm was created for the samples of 300 and 500 nm thickness for better adhesion. The sample of 100 nm thickness does not have a sublayer. The tribological tests were carried out using the generally accepted “ball-disk” friction pattern with rotational motion (ASTM G99), implemented on serial friction machines UMT-2 from CETR (USA). As a counterbody a SiC ball with a diameter of 4 mm was used, the sliding velocity was 0.1 m/s, and the load was 0.1 N.

The morphology and chemical composition of the coatings were examined using a scanning electron microscope (SEM) FEI Quanta 650 (Netherlands) with the analytical device EDAX (USA).

Investigations of the topography, deformation and adhesion forces of the coatings surface were carried out using Bruker Dimension FastScan microscope in the PeakForce QNM (Quantitative Nanoscale Mechanical Mapping) mode using standard silicon cantilevers of the NSC-11 type (manufactured by MicroMash, Estonia) with the tip radius of 10 nm and console stiffness of 4.8 N/m. The QNM mode using a silicon probe allows to estimate the distribution of adhesive forces over the surface of these hard coatings and thus to identify better the various phases and crystallite boundaries. The adhesion force between the AFM tip and the surface was determined by the maximum force of the tip separation from the samples surface according to the force curves of the “approach-withdrawal” QNM. Specific surface energy was estimated by the adhesion value, taking into account the contact surface of the tip. The roughness of the coatings (Ra, Rq, and Rz), the adhesion force and deformation in the QNM mode were assessed over an area of 5 × 5 μm².

The microhardness (H) and elastic modulus (E) of DLC coatings were measured by introducing Berkovich diamond pyramid with continuous recording of deformation curves on 750 Ubi model nanoindenter (Hysitron, USA).

The depth of the wear tracks (on each track at three locations) was measured with a Surftest SJ-210 contact profilometer (Mitutoyo, Japan). The wear value of the coatings could not be established, since the depth of the friction track was lower than the sensitivity of the profilometer (20 nm).

3. Results and discussion
EDAX showed the presence of Ti in DLC coatings applied to the titanium sublayer. The 300 nm thick coating contained 1% Ti and the 500 nm thick coating contained 3% Ti. An increased oxygen content is found in some wear microparticles at the edges of the wear tracks. The results of the friction test of the DLC coatings are shown in figure 1. At the initial stage of testing (up to 80 sec), the best values of the friction coefficient (COF) were observed for the coating of 100 nm thickness (0.36). Around the middle of the test, the most stable COF becomes for the 500 nm thick coating (0.60) and then practically does not change. The average COF for coatings of 100 nm and 500 nm thickness is practically the same, however, the range of values of 100 nm is much greater. The unstable frictional force indicates the brittle destruction of the coating. The wear particles are powder at the edges of the wear track without signs of the plastic deformation. The 500 nm thick coating contains 3% titanium, the count of particles are lower, the particles contain lot of titanium, they are located in the track, and according to their shape and the values of H and E the particles have signs of the plastic deformation (figure 2).

The features of the coatings surface in the initial state and after the friction tests are very similar, and SEM does not allow to detect differences (figure 2.b). AFM shows a globular surface structure and with an increase in the coatings thickness from 100 to 500 nm, the size of individual large globules (microparticles) slightly increases (figure 2.). The roughness Ra is 15.7, 14.1 and 14.5 nm for
coatings with thicknesses of 100, 300 and 500 nm, respectively. AFM revealed differences in the morphology between the initial surface and the wear track, which are manifested in an increased number of microparticles of 20-200 nm after the tribological tests. After the tribotesting, the size of the globules (microparticles) in each coating decreases. At the same time, the surface morphology of the wear tracks is very close to the original, isometric, without signs of material texturing due to the plastic deformation, Ra increases by no more than 1.4 times and is 18.2, 20.1, and 16.2 nm for coatings with a thickness of 100, 300 and 500 nm, respectively. The specific surface energy in the initial coatings was 0.7 N/m for 100 nm thickness, 0.8 N/m for 300 nm thickness, and 0.6 N/m for 500 nm. After the tribotests, the values of the specific surface energy decreased and amounted to 0.3 N/m for 100 nm thickness, 0.1 N/m for 300 nm thickness, and 0.3 N/m for 500 nm thickness. The DLC surface deformation by the AFM probe in the QNM mode was 1.7 nm (100 nm), 3.4 nm (300 nm), and 2.5 nm (500 nm) for the initial coatings. After the tribotests, the deformation values were 2.2 nm (100 nm), 1.1 nm (300 nm), and 1.5 nm (500 nm). Hereof it follows that the surface hardness of the 100 nm coating slightly increased, while for 300 and 500 nm coatings it decreased. The AFM deformation results correspond to the NI data. Slight changes in the properties defined by NI, as well as changes in the deformation of the surface layer performed by the AFM probe in the QNM mode, were caused by transformations occurring in the nanometer layers of the DLC films under the counterbody action during the friction. These changes in the properties of nanoscale surface layers are associated with the accumulation of point defects and dislocations in them. Moreover, defects can not only "soften" the surface layer as in 100 nm DLC, but also "strengthen" it as in 300 nm and 500 nm DLC. The "softening" can be judged by increasing the depth of deformation.

The E and H values are 192 and 17.4 GPa for 100 nm, 205 and 19.8 GPa for 300 nm, 175 and 17.3 GPa for 500 nm and correspond to the values for coatings deposited on a titanium alloy and containing Ti addition [9]. The values of E and H in the wear track are 194 and 18.0 GPa for 100 nm, 190 and 17.4 GPa for 300 nm, 177 and 17.9 GPa for 500 nm. The properties of DLC with a thickness of 300 nm decreased more significantly than other coatings. The H/E ratio of the coatings was 0.09 – 0.10 and did not decrease in the wear track.

![Figure 1](image)

**Figure 1.** The dependences of COF on time according to the ball-disk test scheme at load N = 0.1 N, speed v = 0.1 m/s with table of average values. Slider (SiC) is a ball of ø4 mm.

The obtained results indicate a change in the microstructure and properties of the thin surface layer in the DLC coatings on steel under the influence of the tribological tests. The type of layer morphology practically does not change, and changes can be judged only by a decrease in the size of microparticles and a decrease in the values of E and H detected by NI. The most sensitive to the changes in the properties of the surface layer in the wear track were the specific surface energy and deformation obtained by the QNM AFM mode.
Figure 2. Images of the 100 nm thick DLC coating: a – coated sample; b – SEM image of the wear track, x 500; c-h – AFM images; c, d, e – the initial surface; f, g, h – the wear track; c, d, f, g – topography; e, h – adhesion contrast.

4. Conclusions
The surface morphology and the mechanical properties of DLC films of various thicknesses on steel substrate in the initial state and after the tribotests were determined using the atomic force microscopy
and nanoindentation methods. Having the close roughness of 14.1–15.7 nm, the films showed the different character of changes in the surface properties after the tribotests associated with their doping with titanium.

It was found that the mechanical properties of undoped DLC of 100 nm thick after the tribotests increase, while the mechanical properties of DLC of 300 and 500 nm thick doped with Ti and on the titanium sublayer decrease.

The surface microstructure of the wear tracks detected by the ACM did not contain any damage or texture formed by deformation, but consisted of equi-axial microparticles, slightly smaller in size compared to the original surface and with greater uniformity in size.

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