Influence of the electronic structure of carbon (diamond-like) thin films on tribological characteristics

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Abstract. This study takes a new look at carbon-based ion-plasma coatings (DLC) deposited on a steel substrate from acetylene and methylsiloxane gas mixture. The most remarkable result to emerge from X-ray photoelectron spectroscopy is a surface-to-substrate decrease in the ‘diamond’ electron configuration of carbon sp3. A set of tribological tests showed a noticeable decrease in the coefficient of friction. Surprisingly, there was no increase in wear resistance when using DLC coatings on the contact surfaces of nitrided nitralloy steel in a loaded friction unit.

1. Introduction
Vacuum ion-plasma coatings have received much attention over the last three decades. The studies commonly focus on multi-component systems of metal, nitride, oxide, carbon systems and their compositions [1, 2]. Their specificity, inter alia, lies in the ability to provide high functionality (e.g., hardness, thermal, wear, or corrosion resistance) with a small thickness (up to several micrometers), and high adhesion to the substrate. Among the variety of existing coatings, carbon diamond-like coatings (DLC) are distinguished by the smallest thickness and variability of properties due to the formation of various typologies of electronic configurations of carbon and their stabilization with light elements (H, B) [3, 4].

In the overwhelming majority of studies, the characteristics of DLC have not been dealt with in depth. Hence, our work aims to extend our current knowledge of DLC coatings [5, 6]. This applied research concentrates on a specific type of substrate designed for industrial use and the tribotechnical functionality of a DLC coating exploited in loaded friction units.

2. Research method
Vacuum ion-plasma carbon coating technology included cleaning the sample surface by Ar ion bombardment at a temperature of 300°C, ion implantation with Nb ions to increase the adhesion of the coating, and the actual deposition of the coating using acetylene and methylsiloxane gas mixture at a temperature of 180 ... 250°C at a deflection voltage of 100 V. The sequential preliminaries were carried out in the working chamber of a two-cathode plant with 10 kW arc evaporators. 38Cr2MoAl
nitrided steel (nitr alloy) was employed as the substrate. The given steel is widely used in heavily loaded gear and spline gears of transport engineering. Depending on the deposition time, the thickness of the obtained DLC coatings was in the range of 0.4 ... 1.8 μm.

In order to investigate the coating microstructure in the cross-section and over the surface, we applied a two-beam (electron/ion) scanning electron microscope (SEM) equipped with built-in energy-dispersive X-ray spectroscopy (EDAX). The study of the coating electronic structure was performed by the SPECS system for surface analysis using X-ray photoelectron spectroscopy (XPS) techniques in a deep vacuum (8·10⁻¹⁰ mbar). The chemical composition of the coating and the configurations of carbon chemical bonds were defined from the survey spectra taken from the surface. The distribution of carbon electron configurations over the coating depth was achieved through a sequential ion-beam etching (profiling) of the coating in the vacuum chamber of the SPECS system. Then, the differential components of the experimental survey spectra obtained at each profiled depth of the coating were analyzed as detailed in [7–9] by built-in specialized software.

The mechanical properties of the coatings (hardness $H$, modulus of elasticity $E$, as well as $H/E$ and $H^3/E^2$ ratios) were determined by continuous nanoindentation using a Berkovich indenter. The tribological properties of the coatings were identified by a set of sliding friction tests following DIN 50324 and ASTM G99 methods. We measured the coefficient of friction $\mu$, the volumetric wear rate of both the coated sample $J$ and the WC – Co alloy-made 6.35 mm-diameter ball $K$, acting as a counterbody. Test mode was as follows: pin-plate scheme; the load on the pin is equal to 10 N; the frequency of the reciprocating motion of the coated plate is 10 Hz; amplitude is 800 μm; test duration is 50,000 cycles.

3. Results and discussion
The studied DLC coatings are characterized by microstructural homogeneity. Neither optical nor electron microscopy show any differences in their structure (figure 1). Based on the results of energy dispersive analysis, the average chemical composition of the coating has an approximate ratio (in mass fractions): C/Si = 4.5/1. C$_2$H$_2$ and CH$_3$-Si-O gas mixture used in the ion-plasma DLC deposition technology leads to an uneven silicon distribution in the coating. Its higher content is detected in the substrate-adjacent layer, which in figure 1 is seen lighter than the rest of the coating cross-section.

![Figure 1](image-url)

**Figure 1.** Microstructure of the experimental DLC coatings (SEM): (a) cross-section with surface relief (sample tilt towards the observer); (b) cross-section with coating thickness markers.

The state of the carbon electronic structure over the DLC coating depth was examined by XPS methods by sequential profiling (etching, evaporation) of the coating to the substrate surface and obtaining survey spectra from each profiled surface. To analyze the types of carbon electron hybridization in the form of $sp^3/sp^2$ ratio, we exploited the C (KLL) Auger spectra isolated from the
survey spectra. Figure 2a reports the data on spectra collected after 10, 20, 30, 70, 90, and 130 minutes of profiling. These data allowed determining the values of the $d$ parameter. The methods detailed in [10, 11] and the calibration reference spectra of graphite and diamond helped to calculate the fractions of the carbon $sp^3$ and $sp^2$ states at different depths of the diamond-like coatings. The parameter $d$ (eV) is the distance between the positive and negative extrema of the C (KLL) differential spectra. In figure 3a, it is the distance between the dotted lines.

![Figure 2. C (KLL) differential spectra (a) and the distribution of the $d$ parameter and $sp^3/sp^2$ ratio (b) over the DLC coating depth, obtained after different ion profiling time intervals, min: 1 – initial (non-profiled) surface of the coating; 2 – 10; 3 – 20; 4 – 30; 5 – 70; 6 – 90 minutes of Ar ion profiling.](image)

Figure 2 b reports on the distribution of the $d$ parameter and the corresponding $sp^3/sp^2$ ratio values of the coating. It is well known [9, 10] that the $sp^3/sp^2$ ratio determines numerous properties of carbon materials. Its decreasing distribution over the cross-section of the coatings in figure 2 b indicates the amorphization of the carbon fine structure with an increase in the fraction of the graphite-like component approaching the substrate. An increase in the fraction of the $sp^3$ electronic configuration in the near-surface layer characterizes this surface as diamond-like. It gives reason to assume a significant decrease in the coefficient of friction of the coating during tribological tests.

Table 1 illustrates the properties of DLC-coated and uncoated 38Cr2MoAl nitrided steel samples. The $H/E$ and $H^2/E^2$ ratios were obtained by calculation. In comparison with nitrided steel, the studied carbon coatings have a comparable level of hardness and significantly higher resistance to both elastic $H/E$ and plastic $H^2/E^2$ deformation. In terms of these parameters, they may well compete with wear-resistant ion-plasma nitride coatings (see data in [12]).

As detailed in table 1, the DLC coatings on nitrided steel do not lead to an increase in the wear resistance $J$, while other tribological properties are improved, for instance, the coefficient of friction $\mu$ decreases by about 1.5 times, and the wear of counterbody $J_K$ decreases to 2.0 times. Similar experimental data on tribological tests of identical DLC coatings deposited on a 12Cr2Ni4 carburizing
steel substrate demonstrate a decrease in all friction parameters $\mu$, $J$, $J_K$. It is worth noting that $\mu$, $J$, $J_K$ values experience the largest decrease as well [5].

| Feature   | Mechanical properties | Tribological properties |
|-----------|------------------------|-------------------------|
|           | $H$, GPa | $E$, GPa | $H/E$ | $H/J^2$, GPa | $\mu$ | $J$, $10^{-7}$ mm$^3$/N/m | $J_K$, $10^{-7}$ mm$^3$/N/m |
| Substrate | 12       | 231     | 0.0398  | 0.02975 | 0.53 | 4.50 | 3.96 |
| DLC       | 13.4     | 182.3   | 0.0739  | 0.0753  | 0.36 | 6.65 | 1.92 |

4. Conclusions
The evidence from this study implies that the effect of increasing the wear resistance of loaded friction units when using DLC coatings much depends on the combination of substrate and coating materials. Due to high adhesion, the contact of homogeneous materials (carburized steel and carbon coating) is more preferable than a dissimilar "substrate-coating" contact interface (nitrided steel and carbon coating), whose adhesion is not even improved by the implantation of Nb ions.

We have obtained comprehensive results proving that DLC coatings actually reduce the coefficient of friction. However, in coatings with a $sp^3$ diamond electronic configuration it occurs due to ultra-high hardness, while in coatings with a mixed electronic structure and a gradient distribution of the $sp^3/sp^2$ ratio, the lubricity of amorphous graphite is realized.

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References
[1] Cavaleiro A and de Hosson J T 2007 Nanostructured Coatings (New York: Springer Science & Business Media) 752 p
[2] Charitidis C A, Koumoulos E P and Dragatogiannis D A 2013 Lubricants 1 (2) 22–47
[3] Ren Zh, Qin H, Dong Y, Doll G L and Chang Y Wear 2019 436–437 203031
[4] Huang B, Zhou Q and Zhang E 2020 Coatings 10 (3) 243
[5] Kolesnikov V I, Vereskun V D, Kudryakov O V, Manturov D S, Popov O N and Novikov E S 2020 Journal of Friction and Wear 41 (2) 169–73
[6] Kudryakov O V, Varavka V N, Kolesnikov I V, Novikov E S and Zabiyaka I Yu 2021 IOP Conf. Ser.: Materials Science and Engineering 1029 (1) 012061
[7] Lascovich J C, Giorgi R and Scaglione S 1991 Applied Surface Science 37 17
[8] Me’rel P, Tabbal M, Chaker M, Moisa S and Margot J 1998 Applied Surface Science 136 105–10
[9] Mezzi A and Kaciulis S 2010 Surface and Interface Analysis 32 1082
[10] Dementjev A P and Petukhov M N 1996 Surface and Interface Analysis 23 517
[11] Kumar N, Sankaran K J, Kozakov A T, Sidashov A V, Nicholski A V, Haenen K and Kolesnikov V I 2019 Diamond & Related Materials 97 107372
[12] Kolesnikov V I, Kudryakov O V, Zabiyaka I Yu, Novikov E S and Manturov D S 2020 Physical Mesomechanics 23 (6) 570–83