Structure, chemical composition, mechanical properties of fluorine-containing coatings based on diamond-like carbon

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Abstract. The report contains the results of the study of structure and properties of coatings based on diamond-like carbon (DLC) containing fluorine atoms deposited from the products of pulsed vacuum cathodic-arc discharge with graphite cathode under the inflow of octafluorocyclobutane into the vacuum chamber. For the coatings deposited, the fluorine content reaches approximately 30 atomic %. The presence of C-F and C-F₂ chemical bonds is shown. The morphology of the coatings is characterized by the presence of smooth regions and surface formations with increased content of fluorine chemically bonded to carbon. The hardness and Young’s modulus of the DLC-F coatings are lower in comparison with the undoped DLC coatings deposited under analogous conditions. The DLC-F coatings demonstrate low friction coefficient and high wear resistance in dry friction tests.

1. Introduction
Deposition of coatings based on diamond-like carbon (DLC) in the medium of a chemically active gas is an effective way to change their properties, especially when depositing multilayer and gradient systems. Using such approach, it is possible to improve coating adhesion and lower internal stress, enhance its biocompatibility or increase electric conductivity [1, 2].

The present report is dedicated to the study of structure, composition, and properties of fluorine-containing DLC coatings (DLC-F) deposited in vacuum from the products of erosion of a graphite cathode by pulsed cathodic-arc discharge in the medium of a fluorine-containing gas.

2. Experimental methods
Octafluorocyclobutane (C₈F₈) was used as the fluorine-containing gas for coating deposition. The octafluorocyclobutane gas was let in into the vacuum chamber up to the pressure of 0.1–0.4 Pa. The coatings were deposited onto silicon monocrystal wafers and polished ball bearing steel plates with 50-nm-thick sublayer of titanium that was preliminary deposited using filtered constant-current cathodic-arc discharge with titanium cathode. The thickness of the coatings was approximately 300 nm.

Morphology of the coatings was studied by scanning electron microscopy (SEM) using a Hitachi S-570 microscope in the secondary electron detection mode. The microscope was as well equipped with an energy-dispersive X-ray spectroscopy (EDS) detector. No additional conductive coatings were deposited to perform the measurement.
On a finer level, the morphology was studied by atomic-force microscopy (AFM) using a Nanoscope-IIIa scanning probe microscope. The measurement was performed in the tapping mode of probe cantilever oscillation. Topography and phase contrast images were recorded during the measurement. Mapping the phase contrast allows showing differences in adhesion forces between the probe tip and the surface across the scan as well as reveals finer details of the surface hidden in the topography images because of the height-based coloring.

Chemical composition of the coatings was studied by X-ray photoelectron spectrometry (XPS) using a Kratos AXIS Ultra DLD spectrometer. Etching the sample surface before the XPS measurement by the Ar ions showed insignificant influence on the XPS spectra of the coating. Hence, the spectra obtained without etching were recorded and analyzed.

Structure of the coatings was studied by Raman spectrometry using a Confotec NR350 3D laser scanning confocal Raman microscope. The wavelength of the Raman excitation laser was 473 nm; its power was 1.5 mW. The usage of the confocal Raman microscope allowed measuring the spectra of characteristic micrometer size features of the coating surface.

Mechanical properties of the coatings were studied by nanoindentation using a TriboIndenter nanomechanical test system. The indentation depth was less than 15 % of the coating thickness during the measurements performed. Hence, the influence of the substrate can be neglected.

Tribological properties of the coatings were studied using an MTM-1 sphere-on-plane reciprocating friction tribometer. The counterbody sphere 5.95 mm in diameter was made of ball bearing steel with TiN coating. The load of 0.98 N was applied to the sphere; the average sliding speed was 16.9 mm/s; the friction track length was 13 mm. The tests were conducted under dry conditions without lubrication. For each cycle of the reciprocating motion, average value for the central part of the friction track and maximum value of the coefficient of friction was calculated.

3. Results and discussion
The morphology of the DLC-F coatings is characterized by the presence of both smooth regions of nanometer-range roughness and surface formations that have the lateral size ranging from hundreds of nanometers to about two micrometers (figures 1 and 2). The surface formations occupy approximately 1.5 % of the coating surface.

On the nanometer-range level, both the smooth regions and the surface formations are characterized by a similar granular structure with the characteristic grain size of a few tens of nanometers as it can be seen from the phase contrast AFM image (figure 2(b)). Both the smooth regions and the surface formations demonstrate similar adhesion forces towards the AFM probe tip. Hence, the variation of the element composition across the surface is thought to be insignificant.
Indeed, the EDS element analysis performed during the SEM measurement showed that the content of fluorine ranges from 22 to 24 atomic % across the coating surface when Si and Ti contribution from the substrate and the sublayer is excluded from the calculations. The higher values of fluorine content from this range were obtained for the surface formations, whereas the lower values are characteristic of the smooth regions of the coating surface.

The XPS study (figure 3) of the element composition showed higher content of fluorine in the coatings in comparison with the EDS results. It was approximately 30 atomic %. It should be noted however that the XPS method allows avoiding the influence of the sublayers and the substrate on the coating element composition measurement results.

Besides the $sp^2$ and $sp^3$ C-C peaks, the C 1s XPS core level spectrum of the coating contains peaks characteristic of C-CF, C-F, and C-F$_2$ bonds [3]. The dominant peak in the F 1s spectrum can be attributed to F-C bonds thus confirming chemical bonding between carbon and fluorine in the coating material.

Analysis of the Raman spectra of the DLC-F coatings (figure 4) showed that the surface formations are characterized by a higher content of carbon in the $sp^3$-hybridized state in comparison with the smooth regions. It is known that the ratio of the intensity of the D peak (at around 1390 cm$^{-1}$) to intensity of the G peak (at around 1590 cm$^{-1}$) $I_D/I_G$ decreases with the increase of the $sp^3$ carbon content [4]. The $I_D/I_G$ ratio is lower for the spectrum measured at the center of the surface formation in comparison with the spectrum measured in the smooth region of the coating surface.
Figure 4. Raman spectra of the DLC-F coating measured in the smooth region (1) and in the centre of the surface formation (2). The inset contains the optical image of the coating surface with the spectrum acquiring points shown.

It is interesting to note that the increased content of the sp$^3$-hybridized carbon in the surface formations coincides with slightly higher fluorine content there according to the EDS measurement. Moreover, taking into account the large depth from which the EDS obtains the data, the difference of the fluorine content in the surface formations and in the rest of the coating is thought to be underestimates. Hence, the increase of the sp$^3$-hybridized carbon content in the surface formations is the result of higher content of fluorine chemically bonded to carbon rather than more diamond-like structure.

Study of the mechanical properties by nanoindentation showed that the hardness of the DLC-F coating ranges from 11 to 15 GPa, whereas the Young’s modulus ranges from 131 to 164 GPa (figure 5). It is approximately two times lower in comparison with the corresponding values for the DLC coating deposited using the same parameters of the vacuum pulsed cathodic-arc discharge without inflow of the fluorine-containing gas.

Figure 5. Loading and unloading nanoindentation curves for the DLC-F coating measured under the maximum load of 750 µN (a) and 1000 µN (b). The tables in the insets show the corresponding values of hardness and Young’s modulus calculated.
After the running-in period, the friction coefficient of the DLC-F coating on the polished steel surface against the TiN-coated ball counterbody stabilizes around 2–2.5 until the coating wearing-out at around the 90000th cycle when the coefficient of friction starts growing sharply owing to the friction of the counterbody against the pristine steel substrate.

**Figure 6.** Kinetics of the maximum and cycle-average values of the coefficient of friction during the friction of the TiN-coated ball against the polished steel plate with DLC-F coating.

4. Conclusions
The study of the coatings based on DLC, formed in the medium of octafluorocyclobutane, showed the chemical interaction of carbon and fluorine in the coating material with C-F and C-F$_2$ bond formation. The content of fluorine atoms in the coatings is around 30 %. Besides the smooth regions, the surface of the coatings contains characteristic surface formations with the height of tens of nanometers and lateral dimensions of up to approximately 2 µm. The surface formations are characterized by higher content of fluorine chemically bonded to carbon, corresponding to higher content of carbon in sp$^3$-hybridized state. Hardness and Young’s modulus of the DLC-F coatings are lower in comparison with the DLC coatings formed under analogous conditions without the octafluorocyclobutane gas. The DLC-F coatings are characterized by low coefficient of friction and high wear resistance during dry friction.

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