Diamond-like carbon coatings alloyed with chromium – nanocomposite structure and tribological behavior in conditions of dry and boundary lubricated friction

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Abstract. The results have been presented of the vacuum deposited diamond-like carbon (DLC) coatings alloyed with chromium investigation devoted to elucidate the mechanisms of their friction and wear in the conditions of unlubricated and partially lubricated tribological contact. It has been demonstrated that in these coatings the features of their micro- and nanocomposite structure formed by the nanosized inclusions of metallic chromium and its interstitials in the DLC matrix have a significant influence on the tribological behavior under dry friction. In the case of a boundary lubricated contact the common practice is to associate the main role of alloying elements with the peculiarities of their tribochemical interaction with the chemically active components of the lubricant. However the present investigation has not confirmed the existence of such a synergistic effect of to tribochemical interaction of alloying metal and chemically active lubricant additives for the coatings obtained via magnetron sputtering of chromium in acetylene-based reactive atmosphere.

1. Introduction
Diamond-like carbon (DLC) coatings are of a considerable interest from a tribological point of view. They have a combination of high strength, wear-resistant and anti-friction properties that is unusual for the traditional tribological materials and are able to work both under dry friction and in a boundary lubrication mode, when the contacting surfaces are not permanently separated by a continuous layer of lubricant, and the frictional contact is partially "metallic" [1-3]. At the same time the DLC coatings have a number of disadvantages, which include a low adhesion to the substrate, a high level of compressive residual stresses and a high probability of the DLC structure and properties degradation with time during long-term storage in the environment. One way to reduce the impact of these negative factors is to dope DLC coatings with different elements. In this regard, the existing technologies of vacuum deposition make it possible to obtain coatings alloyed with both non-metallic elements (Si, N, O, F) and metals (Ti, W, Mo, Fe, Ni, Co, Ag, etc.) [4,5]. Alloying with metal elements, in particular, the carbide-forming ones, allows to significantly modify the properties of the DLC films, but the mechanisms of the influence of specific alloying elements on phase composition,
microstructure, mechanical and tribological properties of coatings are not usually discussed. The peculiarities of the nanostructure formed in doped DLC coatings and of their phase composition effect on tribological behavior have not been sufficiently studied. The tribochemical interactions of doping elements with components of the surrounding (external and lubricating) environment in which friction occurs are also of great interest. In our previous research [6] we have supposed that in the case of DLC coatings operating with boundary lubrication the main role of alloying elements may be related to the tribochemical interaction of the latter with the lubricant medium. In particular, it has been experimentally established that alloying of DLC and carbyne coatings (orientants) with tungsten [7, 8] and molybdenum [8] provides a significant reduction in the coefficient of friction in a sulfur-containing lubricant medium. Since tungsten and molybdenum both belong to the same subgroup of the Periodic table as chromium it was interesting to study the tribological effects that might occur when the DLC coatings alloyed with it are rubbed in a lubricant with the sulfur-containing tribochemically-active additives.

The aim of this work was a comparative investigation of the chromium-alloyed DLC (Cr-DLC) coatings deposited in vacuum (magnetron sputtering) devoted to identify the mechanisms that control the characteristics of unlubricated (dry friction) and partially lubricated friction contact.

2. Experimental

2.1. Coating deposition

The coatings were obtained by reactive magnetron sputtering. The scheme of the vacuum deposition unit is shown in figure 1. The details of this technology were described in our previous publications, e.g. [9]. The Cr-DLC coatings were deposited in three stages: at the first one the substrate was subjected to ion cleaning and surface activation by bombarding with argon ions, at the second – a chromium sublayer up to 0.5 μm thick to improve the adhesion was deposited by ion sputtering of a chromium target in argon; and at the third – the main coating with a thickness of 3 μm was reactively sputtered in a mixture of chemically active gases. Pure chromium (99.95%) was used as the cathode material. The reactive atmosphere consisted of argon (99.99%), nitrogen (99.9%) and acetylene of technical purity (99.1%). During the deposition process the argon flow rate was kept constant, and the volume ratio of acetylene and nitrogen gases was changed to obtain Cr DLC coatings with different compositions. The shape of the samples for coating deposition was cylindrical but their dimensions and material varied depending on the specific character of the tribological test unit (see below). Before sputtering the samples were washed with acetone in an ultrasonic bath. The coating was deposited onto a sample’s face plane prepolished to a roughness of Ra = 0.06.

2.2. Methods of coating characterization

The Cr-DLC coatings were subjected to a comprehensive investigation of their structural state and phase composition, micromechanical and adhesive strength properties. Optical and scanning electron microscopy (SEM), X-ray energy-dispersive microprobe analysis (EDX), and Raman laser spectroscopy were used to study the morphology of tribological surfaces and wear scars. Micromechanical properties and adhesion were studied using instrumented nanoindentation (NanoHardness Tester, CSM International) and scratching (REVETEST scratch-tester with a 200 μm Rockwell C indenter tip radius, CSM International), respectively. Some of the results especially those on dry friction have been described earlier [9-11]. In process of this work we also used them to select the Cr-DLC composition for the further boundary lubrication tribological tests.

2.3. Methods of tribological testing

To study the Cr-DLC dry friction a tribometer with a "sphere-on-disk" geometry was used. During dry friction tests the disk-shaped KhN35VT steel samples (diameter 30, thickness 3.5 mm) were used. A silicon nitride ceramic sphere 6 mm in a diameter was used as a counterpart. Tests were performed in air. The disk sample rotation speed was 100 rpm with a maximum number of cycles being equal to
6000. The applied load varied from 0.02 to 0.2 N (the hertzian maximum contact pressure varies from 290 to 620 MPa, respectively).

The boundary lubrication tribological tests were carried out on the KT-2 laboratory test machine. They were performed in “rotating ball – three roller face planes” geometry [12] (figure 2).

![Diagram of the magnetron sputtering unit](image1)

**Figure 1.** Diagram of the magnetron sputtering unit: 1 – magnetron for reactive sputtering; 2 – sample holder; 3 – vacuum chamber; 4 – ion source for the substrate ion-cleaning; 5 – vacuum pumping; 6 – electrically-controlled throttle; 7 – pressure gauge; 8 – magnetron for a metallic sublayer deposition; 9, 10 – flow gauges for reactive gases supply; 11 – flow gauge for argon supply.

**Figure 2.** Diagram of the sample contact during the boundary lubrication tribological tests on a KT-2 machine.

For boundary lubrication tribological tests standard ShKh-15 (AISI 52100 type) steel bearing balls (diameter 12.7 mm) as a counterpart and ShKh-15 steel rollers (diameter 5. height 8 mm) as experimental samples were used. The face planes of these rollers were coated with Cr-DLC. The spindle of the KT-2 test machine with a ball clamped in it under a load of 108 N was pressed against the end planes of the rollers which were installed in a mandrel the plane of which was perpendicular to the spindle axis. The speed of the spindle rotation was 1 rpm. During a 60 min. test with one set of samples (ball + 3 rollers) the values of the friction force moment were recorded with torsion dynamometer. The experimental results were presented as the coefficient of friction $f$ time dependencies. The final $f$ values were obtained by averaging the results of three independent tests. To assess the nature of the frictional damage the worn surfaces of the samples and wear scars on them were explored optically and with SEM.

To assess the effect of chromium doping on the anti-friction properties of a ShKh-15 – Cr-DLC coating pair, comparative tribological tests under various lubrication conditions were performed: (i) – without lubricant (dry friction contact); (ii) – in an lubricant (polyalphaolefin base oil PAO-4 ($v_{100} = 4\text{ mm}^2/\text{s}$)); (iii) – in a surfactant-doped lubricant (PAO-4 with the addition of 1% oleic acid) and (iv) – in a lubricant with a chemically active additive (PAO-4 with the addition of 2% ZDDP (zinc dialkyldithiophosphate, $\text{Zn}[(\text{S}_2\text{P(OR)}_2)_2]$ additive DF-11™).

3. Results and discussion

3.1. The influence of structural and phase composition peculiarities on the behavior under dry friction
The Cr-DLC coatings have a nanocomposite structure in which the tiny inclusions of chromium, chromium carbide and nitride phases (the size of the coherent diffracting domains (CDD) of which is ~ 2-15 nm) are randomly distributed in the matrix of hydrogenated amorphous carbon a–C:H [9]. The chromium metal phase CDD size \( D \), nanohardness \( H \) and \([N]\) – the atomic concentration of nitrogen are presented in figure 3 as a function of the acetylene volume content in the acetylene-nitrogen reactive gas mixture used in process of these coatings deposition. The value of \([N]\) is shown here to demonstrate the character of the chromium nitride phase volume concentration changes produced when the reactive atmosphere composition varies. One can see that the CDD size, nanohardness and \([N]\) increase with decreasing volume fraction of acetylene in the reactive gas mixture. In particular this indicates that the formation of nanometric nitride inclusions in Cr-DLC coatings makes them mechanically stronger.

![Figure 3](image_url)

Figure 3. Dependencies of the chromium metal CDD size \( D \) (1), nanohardness \( H \) (2), and nitrogen atomic concentration \([N]\) (3) on the acetylene volume content in \( \text{C}_2\text{H}_2–\text{N}_2 \) reactive gas mixture used for the Cr-DLC coating deposition (after [9]).

Figure 4 shows the values of the coating coefficient of friction \( f \) averaged over the time interval when the friction is steady and the number of cycles \( N \) above which the friction becomes unstable. This coefficient of friction instability is commonly considered as a manifestation of the coating’s catastrophic failure process initiation [13]. At the same time as it was noted in [9] it is not always possible to detect the characteristic traces of such a serious damage on the Cr-DLC coatings wear tracks which is probably due to relatively small contact stress values in these specific experiments.

![Figure 4](image_url)

Figure 4. Dependencies of the tribological characteristics of the Cr-DLC coatings on the volume content of \( \text{C}_2\text{H}_2 \) in a reactive gas mixture and on the hertzian maximum contact pressure obtained in the dry friction tests: (a) – the coefficient of friction; (b) – the number of cycles \( N \) above which the friction becomes unstable.
The results of tribological tests for dry friction are presented as the three-dimensional histograms in the coordinates “tribological parameter” – “acetylene volume fraction in the C2H2–N2 gas mixture” – “the hertzian maximum contact pressure $p_0$”. The dependence of the latter on the applied load $P$ was estimated as

$$p_0 = \left[ \frac{6PE^*}{\pi R^3} \right]^{1/3},$$

where $R$ is the counterpart radius; $E^*$ – the reduced elastic modulus of the counterpart material and the substrate steel [14].

It follows from these data analysis that the influence of the reactive gas mixture composition on the tribological properties of the magnetron sputtered Cr-DLC coatings is expressed quite clearly. There is an obvious tendency for the coefficient of friction reduction with a decrease in the acetylene content and/or an increase in nitrogen content in the reactive gas mixture. This means that the coatings obtained in a gas mixture with 80 vol. % N₂ have the highest antifriction properties. The antifriction properties of coatings deposited in atmospheres with less than 60 vol. % N₂ are significantly lower. At the same time the tribological performance (period of the coefficient of friction stability characterized by the number of working cycles $N$) of these coatings is higher than that of coatings obtained in the nitrogen-rich mixtures. The comparison of these facts with the results of nanohardness tests (figure 3), demonstrates that the dry friction performance of more “soft” Cr-DLC coatings is higher than that of more “hard” ones, while the antifriction characteristics of the latter are higher. The adhesive strength of coatings behaves similarly – is higher for the more “soft” ones [11]. Thus it may be concluded that for the Cr-DLC coatings obtained by magnetron sputtering the state of their nanocomposite structure and their phase composition determined by the technological conditions of the deposition process, the composition of reactive gas mixture in this case, can have a significant effect on their tribological behavior at dry friction.

3.2. The peculiarities the Cr-DLC coatings tribological behavior at boundary lubrication

The problem was investigated in two aspects. The first was to answer whether the alloying of DLC coatings with chromium affects the partially lubricated frictional contact tribological characteristics. The second – to assess the magnitude of this effect for a typical set of model lubricants: the base engine oil in pure form and in combination with chemically inert and chemically active additives using those of them that have demonstrated the antifriction behavior improvement in previous experiments with W- and Mo-doped DLC coatings [6-8]. As a first approximation it was decided to ignore the possible influence of various aspects of the vapor deposition technological process, say the plasma discharge parameters or the reactive atmosphere composition. We have limited ourselves to the case of DLC coatings obtained by reactive magnetron sputtering of chromium in the presence of pure acetylene. This type of coatings as we mentioned earlier has demonstrated a high working performance in our dry friction experiments although the antifriction properties were slightly worse ($f \sim 0.2$) than those obtained in nitrogen-rich C₂H₂–N₂ gas mixtures. Since the friction coefficient is usually lower in the conditions of boundary lubrication than that of an unlubricated contact, it seems reasonable to use the Cr-DLC coatings deposited by reactive magnetron sputtering in a 100 % acetylene atmosphere in this section of our research devoted to boundary lubrication tribology.

The results of the comparative tribological tests of rollers coated with Cr-DLC deposited in pure acetylene are presented in figure 5. We have also included the results of uncoated steel rollers tests. It follows from this figure that the coefficient of friction of both the uncoated and coated steel surfaces is maximum for an unlubricated contact ($f > 0.7$), and the Cr-DLC coating reduces $f$ only by $\sim 0.1$–0.2. In tests with pure PAO-4 lubricant the reduction of the coefficient of friction was more serious especially in the experiment with the Cr-DLC coated rollers for which the value of $f$ was as low as $\sim 0.15$.

Note that the KT-2 machine boundary lubrication tests were performed at the vertical force $P = 108$ N, thus the normal load acting on the roller face plane equal to $\sim 44$ N and the hertzian maximum contact pressure $\sim 1.7$ GPa that is significantly higher than in our Cr-DLC dry friction experiments on the ball-on-disk tribometer described above. Therefore this time one may expect to find more serious surface damage especially when friction occurs in the conditions of unlubricated contact.
Figure 5. Time dependencies of the coefficient of friction measured in tests on the KT-2 machine in pair with a ShKh-15 steel counterpart: (a) 1 – ShKh-15 steel roller surface without lubrication; 2 – ShKh-15 lubricated with PAO-4; 3 – Cr-DLC coating without lubrication; 4 – Cr-DLC with PAO-4; (b) 5 – Cr-DLC with PAO-4 + 1% oleic acid; 6 – Cr-DLC with PAO-4 + 2% ZDDP-based DF-11™ additive.

Really the results of optical microscopy and SEM studies of wear scars on steel surfaces coated with Cr-DLC have revealed traces of this surface damage. Both single arc-shaped cracks and multiple through thickness cracks leading to local coating spallations were detected (figure 6). The character of this crack damage allows to conclude that they are the result of high compressive stresses generated in coating ahead the moving contact by the effect of friction traction [15].

Figure 6. SEM microphotographs of the wear scar surface defects due to the unlubricated frictional contact of the ShKh-15 steel counterpart with the Cr-DLC coated roller’s face plane (microphotograph (a) is obtained in secondary electrons and (b) – in backscattered electrons composition regime (BEC)).

The tribological behavior of the Cr-DLC coatings tested in PAO-4 with additives is shown in figure 5(b). The range of observed changes in the value of the coefficient of friction here is about ± 0.1 so the scale on the ordinate axis for this figure is increased. In this enlarged scale it is easy to see that the coefficient of friction for the PAO-4 lubricant increases to 0.19 at the beginning of the test, then decreases, after which it stabilizes at the level of ~ 0.15-0.16. In a lubricating medium containing ZDDP in the form of DF-11™ additive, the coefficient of friction gradually increases. After 35 min. of testing / becomes even higher than when the friction occurs in PAO-4 base oil without additives.

From figure 5(b) it follows that the maximal coefficient of friction reduction was observed when testing the Cr-DLC coatings in PAO-4 base oil with the addition of a surfactant – oleic acid. The value
of the coefficient of friction in this case was in the range 0.125-0.13.

Typical micrographs of wear scars obtained during tests on the KT-2 machine without lubrication and in PAO-4 based lubricants are presented in figure 7. The surface of Cr-DLC coating tested in dry friction conditions without lubrication (figure 7(a)) is seriously damaged. This may be the single arc-shaped and short linear cracks (figure 6(a)), multiple through thickness cracks, spallations and irregularities of the surface relief due to rubbing (figure 6(b)). The formation of linear cracks and surface relief irregularities is associated with rolling and dragging of the third body particles formed during friction from the coating and counterbody wear debris and the products of the counterbody oxidative wear. Traces of the coating surface damage are also visible on the micrograph of the sample tested in PAO-4 (figure 7(b)). In this case attention is also drawn to the modified layer and the dark flat particle partially damaged in the process of friction lying on top of it. This particle material according to the EDX analysis data contains a significant amount of iron and oxygen. The latter indicates that it was formed most likely during the counterbody ShKh-15 steel oxidative wear.

Figure 7(c) shows the wear scar on a sample tested in PAO-4 base oil lubricant with the addition of oleic acid as a surfactant. The wear scar has smooth contours in contrast with the wear scar on a sample tested in a chemically active additive DF-11™-containing lubricant that was smeared (figure 7(d)). The modified layer formed by friction is clearly visible on the surface of the both wear scars.

![Figure 7. Wear scars on the Cr-DLC coated roller face planes tribologically tested in pair with ShKh-15 steel: (a) – unlubricated contact (optical microphotography) and contacts lubricated with: (b) – PAO-4; (c) –PAO-4 + 1% oleic acid; (d) – PAO-4 + 2% ZDDP-based DF-11™ additive (the magnification of all microphotographs is the same).](image)

The wear scars average diameters are compared in figure 8. The maximal wear was observed for both the uncoated and the Cr-DLC-coated ShKh-15 samples tested without lubricant. Lubrication
reduces the wear scar size in all cases. The possibility exists to further reduce the wear using additives. For the Cr-DLC coatings the reduction was maximal when using oleic acid.

From figure 8 it follows that there exists a certain correlation between the coefficient of friction of boundary lubricated coatings and the diameter of wear scars observed on their surface i.e. the wear is likely to be higher for samples with high values of coefficient of friction.

The results presented above demonstrate that the Cr-DLC coatings have a potential to improve the tribological and antifriction characteristics. The correct selection of lubricant may be very important in this case. Our experiments have demonstrated that there are no obvious synergistic or antagonistic effects from the interaction of chromium in coating with specific components of the lubricant media. The effect of using additives as it can be seen from the coefficient of friction time dependencies and the surface morphologies of the wear scars may not be a definitely positive one.

For example, the DF-11™ chemically active additive in a concentration of 2% does not have a significant effect in reducing friction and wear. The reason for this to our opinion follows from the Cr-S system phase diagram [16]. As we know [3, 6] the reason for the Mo- and W-DLC high antifriction properties with sulfur-containing additives is the formation in the result of tribochemical reactions of hexagonal MoS2 and WS2 layered structures with a low shear stress resistance. In the case of the Cr–S binary system the chromium chalcogenide compounds with the CrS2 stoichiometry and layered structure with weakly interacting atomic layers do not exist. Thus in the case of the Cr-DLC coatings tribochemical reactions between the alloying element and the chemically active sulfur-containing additive (ZDDP in this case) if they occur may not result in the formation of compounds with a beneficial effect on friction.

At the same time it was established that 1% of a surfactant (oleic acid) added to a lubricant medium can effectively reduce the Cr-DLC-coated surfaces friction and wear. To understand the mechanism of this reduction further investigation of wear products and modified surface layers formed in process on boundary friction of coatings may be needed.

4. Conclusions
The use of the DLC coatings alloyed with chromium deposited by the reactive magnetron sputtering allows reducing of friction and wear in the case of both the dry friction and the boundary lubricated friction. The reduction effect observed in the case of dry friction is explained by the nature of the nanocomposite structure formed in these coatings during the technological process of their deposition.

The boundary lubrication tribological tests have shown that the type of lubricant medium may contribute to a reduction of coefficient of friction of chromium-alloyed diamond-like carbon coatings. The PAO-4 base oil in itself does not reduce the friction significantly. The use of PAO-4 with a chemically active sulfur-containing additive DF-11™ at a concentration of 2% also does not have a further reduction effect. A noticeable effect of friction and wear reduction is achieved in PAO-4 with a surfactant (oleic acid) additive.
The reason for the lack of a noticeable reduction in friction in tests of chromium-alloyed diamond-like carbon coatings in experiments with the sulfur-containing additive DF-11™ is due to the fact that in the chromium-sulfur system the formation of chemical compounds suitable to facilitate friction (e.g. layered structures with weak interlayer interaction) does not occur.

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