Effect of diamond-like carbon coatings alloying with chromium and molybdenum on the lubricating properties of oils during friction in pair with steel

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Abstract. The results have been presented of an experimental study of the tribological behavior of diamond-like carbon coatings (DLC) doped with chromium and molybdenum obtained by reactive magnetron sputtering. The effect of alloying with these metals on the tribological characteristics of boundary lubrication of a DLC coating / steel contact has been studied for the case of three model lubricants (inactive, surfactant, and chemically active). It has been shown that doping with chromium and molybdenum improves both the tribological characteristics of coatings under dry friction and the lubricating properties of the model oils, while alloying with molybdenum provides lower coefficients of friction and less wear at dry and boundary friction than alloying with chromium.

1. Introduction

It is well known that the material of the contacting elements of the friction pair may strongly affect the effectiveness of the antifriction and wear-protective action of oils that lubricate friction units operating under boundary lubrication conditions. These materials determine both the durability of the lubricated friction units and the level of energy losses during their operation in the boundary lubrication regime of friction in which any lubricated contact can operate continuously or periodically (e.g. in the start-stop mode, during overloads, etc.) [1].

One of the methods of stimulating the formation of strong boundary layers that can provide moderate energy losses and low wear rate of the rubbing parts of the friction units is the modification of their surfaces, e.g. by chemical and/or heat treatment or by antifriction coating/layer deposition. Deposition of diamond-like carbon (DLC, “hard carbon”) coatings is one of the promising methods to solve the problem.

These coatings are characterized by a unique combination of chemical inertness, high hardness, and high wear-resistance with rather low coefficient of friction (COF) values [2, 3]. At the same time, the chemical inertness of DLC coatings prevents them from the interaction with the lubricating medium, except the thinnest surface layer where the processes of friction-induced carbon graphitization take place. These processes result in formation of a positive gradient of mechanical properties over the coating depth and thus a noticeable antifriction effect may be realized.

Another method to ensure the high level of antifriction properties of DLC coatings is to dope them
with certain chemical elements (e.g. tungsten, titanium, silicon, fluorine, nitrogen, etc.). [6–8]. This alloying may provide a “beneficial” tribological effect increasing the ability of these coatings to interact with the lubricating medium, which result in formation of strong boundary layers that reliably separate the rubbing surfaces thus improving the antifriction and wear-resistant behavior of lubricated tribological joints. The most significant antifriction effect of alloying on the lubricated boundary friction of DLC coatings in pair with steel has been achieved in the case of DLC coatings alloyed with the two carbide-forming elements – tungsten [7] and molybdenum [8]. These metals belong to the VI A subgroup of the Periodic Table of Elements, all the elements of which demonstrate a high ability to form carbides. Thus it may be expected that DLC coatings alloying with chromium also might be used for their antifriction and wear characteristics optimization.

Unfortunately the number of publications on the influence of the DLC coatings alloying with chromium and molybdenum on the tribological behavior of steel parts intended for friction units operating in the boundary lubrication regime is limited [8, 9]. Nevertheless though some encouraging results were obtained the question about the influence of chromium and molybdenum on the antifriction characteristics of lubricants during friction in the boundary lubrication regime remains open. These problems may be of interest both for tribologists and materials scientists since they allow one to expand the understanding of the influence of the DLC coatings alloying on the lubricating ability of oils in the boundary lubrication regime and for technologists engaged in choosing the optimal materials for friction units.

The aim of this work was to study the effect of chromium and molybdenum alloying on the antifriction and wear-protective properties of diamond-like carbon coatings deposited onto the steel surfaces of friction parts operating in boundary lubrication mode in specific lubricating media with no chemically nor surface-active agents (named “inactive” in further), with both surfactant or chemically active additives, and in the conditions of unlubricated contact of coated steel surface with steel.

2. Materials and methods of investigations
Three model compositions were used as lubricants to assure that the different mechanisms control the processes of boundary friction: an inactive lubricant (PAO-4, the pure polyalphaolefin oil), PAO-4 with a surfactant addition (PAO-4 + 1 wt. % of oleic acid (OA)), and PAO-4 with a chemically active sulfur-containing additive (PAO-4 + 2 wt. % of DF-11™, a ZDDP (zinc dialkyldithiophosphate)-based additive). The tribological behavior of the lubrication compositions was compared with that of an unlubricated frictional contact of the Cr- and Mo-alloyed DLC coatings deposited on steel with the steel surface of the counterpart.

The study of the antifriction and wear-resistant characteristics of the abovementioned model lubricants was carried out on a KT-2 test machine [10] according to the scheme of friction “rotating ball-on-three rollers face planes” provided for the Russian GOST 23.221-84 Standard. The ball and the rollers were installed according to this scheme in the mandrel unit shown in figure 1. It consists of a housing (1) in which a conical separator (5) is installed. In it, at an angle of 35°30±5’ to the vertical axis, three grooves are made evenly spaced around the circumference, in each of which a cam (3) is installed. Between this cam and the flat surface of the separator slot, the test samples (4) are placed, which are pressed against the flat surface of the slot through the pressure ring (2) with a cap nut (not shown in figure 1) and fixed in this position.

The mandrel assembly is placed in the oil bowl of the KT-2 test machine filled with the liquid lubricant to be tested, then the face planes of the samples (4) are brought into contact with the spherical counterpart (6) fixed in the machine spindle, the test unit is loaded with a given axial load and the engine which drives the spindle into rotation is turned on. According to the GOST 23.221-84 Standard the spindle speed is equal to 1 min⁻¹, the axial load is 108 N, and the test duration is 60 min. These test conditions with high initial contact pressure about 1.7 GPa, relatively low viscosity of the base oil; and low speed of relative movement – 0.37 mm/s ensures the implementation of the boundary lubrication regime of friction. During the tests the current COF values were recorded; and the
diameters of the wear scars formed on the coated face planes of the rollers (4) being in point contact with the steel ball (6) were measured after the end of each test.

The rotation bodies of the standard antifriction bearings were used as samples: the diameter of a ball was 12.7 mm, the rollers were 5 mm in diameter, and their length was equal to 8 mm. The both were made of the ShKh-15 (analogue of AISI 52100) tool steel. Their material is characterized by a significant uniformity of composition and structure. The DLC coatings alloyed with chromium and molybdenum (Cr-DLC and Mo-DLC, respectively) with a thickness of 3 μm were deposited by the method of reactive magnetron sputtering onto the pre-polished (Ra = 0.06) face planes of the rollers. The targets made of bulk chromium and molybdenum metals were used for deposition. Acetylene of technical (99.1 %) purity was used as reactive, and argon of 99.993 % purity as sputtering gas. The design of the magnetron sputtering unit and the details the deposition technology have been described earlier [11].

3. Results and discussion

In process of this study the impact on the antifriction characteristics and wear behavior of both the type of metals used for the DLC coatings alloying (Cr or Mo), and the type of model lubricants used in boundary lubrication tests has been evaluated. The tests of the Cr-DLC and Mo-DLC coatings in unlubricated contact with the ShKh-15 steel have been also performed for comparison. The results of the tribological experiment are presented in figures 2 and 3 showing how the COF value varies during the boundary lubrication tests of the ShKh-15 steel rollers coated with Cr-DLC and Mo-DLC.

**Figure 1.** The KT-2 test machine mandrel assembly: 1 – mandrel body, 2 – clamping ring, 3 – cam, 4 – roller (bottom sample), 5 – separator, 6 – wearing ball (upper sample).

**Figure 2.** The COF dependencies on time measured during the tribological tests of the Cr-DLC coatings in pair with ShKh-15 steel: 1 – without lubricant and 2 – with PAO-4 oil lubrication, and for the Mo-DLC coatings tested: 3 – without lubricant, and 4 – with PAO-4.

**Figure 3.** The COF dependencies on time measured during the tribological tests of the Cr-DLC coatings in pair with ShKh-15 steel: 1 – lubricated with PAO-4 + 1% OA; 2 – with PAO-4 + 2% DF-11™, and for the Mo-DLC coatings tested: 3 – with PAO-4 + 1% OA; 4 – with PAO-4 + 2% DF-11™.
In figure 4 the histogram of the averaged values of the diameters of wear scars formed on the DLC-coated face planes of rollers (the “bottom” samples (4) in figure 1) tested on the KT-2 test machine is presented.

![Figure 4. Histogram of the averaged values of the wear scar diameters for the combinations of the friction pair materials and the model lubricant compositions used in KT-2 tribological tests: 1 – without lubricant, 2 – lubricated with PAO-4, 3 – with PAO-4 + 2% DF-11™, and 4 – with PAO-4 + 1% OA.](image)

The analysis of this histogram shows that both the type of the alloying element and the composition of the lubricating medium may have significant effect both on the antifriction and wear-resistant behavior of a DLC coating contact with a steel counterpart. Figure 2 (curves 1 and 3) and the histogram presented in figure 4 demonstrate that in the case of unlubricated contact the type of the element used for alloying is dominant and the friction and wear characteristics of contact are fully determined by it.

The experimental results confirm that in the case of unlubricated (“dry”) friction the antifriction effect of DLC coating alloying with Mo is significantly greater than that of alloying with Cr (the Cr-DLC coating coefficient of “dry” friction is about 0.5, while alloying with Mo reduces COF to 0.38). The diameter of wear scars formed after the unlubricated contact of a Cr-DLC coating with steel is 483 μm, and 300 μm for a Mo-DLC / steel pair. The presence of lubricants dramatically reduces both friction and wear of DLC coatings alloyed with Cr and Mo. The differences between the COF values (figures 2 and 3) and the diameters of the wear scars (figure 4) for the friction pairs being in lubricated contact are significantly reduced as compared to the case of dry friction. Nevertheless one may certify that for Mo-DLC / steel the COF values and the wear scars diameters remain somewhat lower than those for Cr-DLC coatings in contact with steel.

The optical micrographs of the wear scars for Cr-DLC and Mo-DLC coatings tested in different conditions are presented in figure 5.

![Figure 5. Micrographs of wear scars observed in Cr-DLC (a, b, c, d) and Mo-DLC (e, f, g, h) coatings tested in pair with ShKh-15 steel: (a) and (e) – without lubricant; (b) and (f) – with PAO-4 base oil; (c) and (g) – with PAO-4 + 2% DF-11™; (d) and (h) – PAO-4 + 1% OA.](image)
The nature of the tribological processes in the lubricated DLC/steel contact may by indirectly supposed by the COF behavior presented in figures 2 and 3. The wear scar surfaces presented in figure 5 have allowed clarifying their specific character. Thus one may see that the use of even the inactive PAO-4 lubricant reduces the rough grooves and the local pullouts that occur during dry friction of the Cr-DLC/steel pair and may lead to the DLC coating integrity violation (figure 5(a)). The friction surface of the Cr-DLC coating tested with PAO-4 shown in figure 5(b) is significantly smoother and is disturbed only by some local relief heterogeneities of the modified surface film. The use of additives makes the Cr-DLC friction surfaces smoother, although the use of DF-11™ leads to roughening (figure 5(c)) accompanied by the increase of the coefficient of friction from 0.125 to 0.175 (see curve 2 in figure 3). For the Mo-DLC/steel friction pairs the wear scars are quite smooth even in the absence of a lubricant (figure 5(e)), and there are no any traces of the coating material pulling-out (figures 5(f)–(h)). In view of this it may be concluded that although the use of lubricants largely smoothens-out the difference in friction and wear behavior of DLC coatings alloyed with Cr and Mo the use of Mo-DLC coatings seems to be advantageous for the friction pairs operating in the limited lubrication mode.

4. Conclusion

The analysis of the experimental data has demonstrated that the antifriction and wear-protective properties of lubricants during the friction of diamond-like carbon coatings alloyed with chromium and molybdenum on steel are significantly affected by the presence of these metals in them. The use of DLC coatings alloyed with Mo, which provide lower friction coefficients and lower wear scars diameters than Cr-alloyed DLC coatings, is most effective in combination with surfactants and chemically active lubricants. To clarify the limits of the effectiveness of the antifriction action of chromium and molybdenum-doped diamond-like carbon coatings, it would be necessary to continue their laboratory and bench tests in a wide range of loads, speeds and temperatures.

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