Hard carbon coatings antifriction properties improvement by alloying

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Abstract. The efficiency of hard carbon coatings with different structure to improve the tribological performance of contacting surfaces of machine parts working in heavily loaded conditions has been analyzed. The possibility of increasing the antifriction and wear-resistant characteristics of these coatings by doping them with metals of the chromium subgroup of the Periodic table has been demonstrated. The possible mechanisms of hard carbon coatings dry and boundary friction tribological properties improvement by alloying have been considered. The possible role of alloying elements choice, structural and tribochemical factors has been discussed.

1. Introduction

A large number of carbon structure variants have been experimentally observed [1]. This carbon polymorphism is explained by the ability of the sp³-, sp²-, sp¹-hybridized states of external electron shells of carbon atoms to form different types of covalent bonds. The structure and properties of carbon coatings deposited in vacuum are largely influenced by the energy of atoms, ions and radicals, the substrate temperature and to a much smaller degree by the structure and chemical composition of the substrates [2]. Solid hydrocarbons and the products of gaseous hydrocarbon cracking – carbon, hydrogen and various groups of hydrocarbon radicals – are deposited on the substrate when plasma-assisted deposition technologies from gaseous hydrocarbon precursors (both PVD and CVD) are used for coating fabrication. Hydrogen and other chemical elements introduced into the solid carbon films during deposition may have a great influence on their properties. Creation of thus alloyed hydrogenless or hydrogenated nanostructured carbon coatings with diamond-like, graphite-like, nanodiamond, etc., structure is one of the most promising directions of modern tribology. By this way one may both reduce the energy losses during the operation of friction units of machines, increase their durability and expand the allowable ranges of their working loads and temperatures.

The solid carbon coatings, in particular, the diamond-like ones, are of interest because of their combination of high strength, wear-resistant and antifriction properties being unusual for traditional tribological materials and their capability of effective operation both under dry friction and in the boundary lubrication regime [2-4]. In the latter case the contact surfaces are not permanently separated by a continuous layer of liquid lubricant. It’s worth mentioning that many friction units of modern machines work in such conditions at certain moments of time (at start-stop, in the "dead" points of the mechanisms with reciprocating motion, etc.) or permanently (at low speeds of mutual motion, at high specific loads, temperatures and geometries, complicating the liquid lubricant access).
The modern methods of vacuum deposition make possible to obtain a wide range of hard carbon coating compositions doped with both non-metallic elements (Si, N, F, P, O) and metals (W, Cr, Mo, Ti, etc.) [5, 6]. alloying of solid carbon coatings with additional components can be performed either by the use of some standard vacuum deposition methods (magnetron sputtering, vacuum-arc deposition, ion plating, etc.) in hydrocarbon-based reactive atmospheres, either by the use of composite metal-graphite targets or with “hybrid” technologies. The modern deposition technologies may allow to obtain coatings with modulated (layered) or nanocomposite structure. Such methods of coating alloying can significantly modify the properties of coatings, but the nature of the influence of certain additives on their phase composition, microstructure, mechanical and tribological properties remains unclear. The peculiarities of the nanocrystalline structure existing in hard carbon coatings doped with different elements, the nature of the nanostructured state and the effect of their phase composition on tribological properties have not been sufficiently studied. Since the structure of coatings can significantly affect functional properties the study of its features, micromechanical, strength and tribological properties of metal-carbon nanostructured systems is of considerable interest, both in terms of the possible practical use and from the point of view of the development of scientific bases of materials science of such nanocomposites and physical mechanisms of their micromechanical behavior and strength.

The authors of this paper have tried to analyse the possible effects that alloying may produce on functional and tribological behavior of solid carbon coatings of different types tested in dry and boundary friction conditions. The analysis is based on both literature and the authors’ own results especially on alloying with the chromium subgroup elements.

2. The effect of doping of carbon coatings on tribological characteristics at dry friction

The tribology of dry friction of hard carbon coatings, in particular diamond-like has been investigated by many authors but only in a relatively small number of publications the effect of the structural state and phase composition of doped diamond-like coatings on tribological behavior has been studied (see e.g. [6]). It is possible to mention a number of works, studying DLC films doped with titanium and chromium from this point of view [7-9]. These elements have a tendency to form interstitial phases in particular carbides, therefore in coatings alloyed with them the easy formation of nanosized inclusions of both metal and carbide phases is possible. In addition to this chromium is able to form a whole range of carbides. To this connection the structure of a-C:H:Cr coatings obtained by reactive magnetron sputtering of chromium in acetylene-nitrogen gas mixtures and its effect on mechanical and tribological properties has been investigated in [10]. It was found that with an increase in the nitrogen content the formation of carbide phases occurs in the sequence Cr$_{23}$C$_6$ (in pure acetylene) → Cr$_7$C$_3$ → Cr$_3$C$_2$ → CrC (in a mixture with 80 vol. % nitrogen.) The size of the coherent diffracting domains (CDD) being in fact the size of the corresponding phases inclusions shown in figure 1. It has been experimentally found (figures 2–4), that the size of the chromium metal inclusions has a noticeable effect on mechanical, tribological behavior [10] and adhesive strength [11] of these coatings. The results of [10] have confirmed the structural model [9] of the Cr-DLC structure consisting of nanosized inclusions of chromium and its phases in the amorphous carbon matrix.

It was found that the nanohardness dependence on the size of chromium inclusions in a-C:H:Cr coatings follows the "inverse" Hall-Petch law, i.e. the strength increases when the chromium CDD size increases (figure 2). Simultaneously with the increase in strength, the antifriction properties are improved – the value of $f$ decreases to ~ 0.1 (figure 3), but the friction fatigue performance of coatings in the test on a one-ball tribometer characterized by the number of cycles $N$ until the onset of the coefficient of friction (COF) instability dependence (figure 4) decreases. The critical (threshold) loads of formation of the specific types of surface damage measured in adhesion strength test shown in figure 2 (digitals correspond to: 1 – transition from cohesive to adhesive coating damage; 2 – multiple cracking of coating surface; 3 – local chipping) decrease too. To some extent this situation is similar with that for bulk ceramic materials and coatings when the material being less strong but more plastic is more wear-resistant than the stronger one.
Figure 1. Dependence of the coherent diffracting domain (CDD) sizes for (1) chromium, (2) chromium carbide, and (3) nitride phases on the volume content of nitrogen in acetylene-nitrogen mixture [12].

In [12] its authors besides the abovementioned diamond-like \( a\)-C:H:Cr have also investigated another type of chromium-carbon nanocomposite coatings obtained by magnetron sputtering of composite chromium-nanodiamond targets whose structure was different from the DLC one and compared the structure, phase composition and functional characteristics of both.

It has been found that the inclusions of chromium and its carbides in chromium-carbon coating that have demonstrated the maximal performance when tribologically tested at high contact pressures have almost the same size $\geq 10$ nm, whereas in the structure of \( a\)-C:H:Cr coatings reactively sputtered in acetylene-nitrogen mixtures the nanosized inclusions of chromium of $\sim 10$ nm and the inclusion of chromium carbides and nitrides less than 2 nm have been observed. In the abovementioned chromium-carbon coating the matrix composition was chromium and C$_7$C$_3$ carbide phases, and the carbon phase was present in the form of sufficiently large (micron-sized) graphite-like agglomerates. In process of friction these agglomerates were rolled out and formed a protective layer playing the role of a solid lubricant in contrast to, where the amorphous carbon acts as a matrix phase "reinforced" by nanosized inclusions of chromium and its intersitial phases. It was found that the friction fatigue performance of hard chromium-carbon “nanodiamond-based” coatings was higher ($N > 4000$ cycles at $P = 0.2$ N) than that of \( a\)-C:H:Cr. The COF of Cr-DLC was low $\sim 0.1$÷0.15, whereas in chromium carbon coatings it was above $\sim 0.3$.

Figure 3. The COF dependence on load for \( a\)-C:H:Cr coatings deposited in pure acetylene (1) and in gas mixtures with 80 (2), 40 (3) and 20 (4) vol.\% of C$_2$H$_2$.

The another fact related to the influence of the peculiarities of the nanostructured state of diamond-like carbon coatings on their tribological behavior was observed in [13] where the diamond-like
coatings doped with the metals of the chromium subgroup of the Periodic table, chromium, molybdenum and tungsten, have been studied, and the existence of a possible correlation between the degree of the nanocrystalline structure perfection of such coatings and their tribological characteristics at dry friction has been supposed. The coatings that during deposition have retained a certain degree of long-range order in their nanocrystalline structure and whose "correlation radius" (the radius of the decay of the pair distribution function oscillations) was more than 10 nm have demonstrated sufficiently high tribological performance and antifriction properties, while the coatings in an X-ray amorphous state with a correlation radius less than 1 nm have shown a much lower tribological efficiency.

3. The effect of hard carbon coatings alloying on their tribological characteristics at boundary lubrication

It was found that the high wear-resistant and antifriction properties of hard carbon coatings in boundary lubrication conditions [3, 4, 14, 15] are due to the fact that the lubricating fluid protects the friction contact zone of surfaces with hard carbon coatings deposited on them from the uncontrolled environmental effects, ensures the removal of wear products, and also provides the contact zone cooling which is especially important for hard carbon coatings being operative at relatively low working temperatures below about 220°C.

This section analyzes the tribological effects associated with tribochemical interactions between hard carbon coatings and their components and chemically active components of lubricating oils. This effect largely depends on the regime of the friction unit lubrication. According to [13-16] hard carbon coatings deposited on conjugated surfaces of the contacting bodies have the greatest impact on the antifriction properties of oils during sliding friction in the boundary lubrication mode. Some aspects of the tribological behavior of different types of hard carbon coatings alloyed with chemical elements for work at boundary lubrication are discussed.

The high antifriction properties of tetrahedral amorphous carbon coatings that do not contain hydrogen (ta-C) rub in similar combination and with lubricants containing alcohol groups were demonstrated in [17, 18]. The test results are shown in Table 1. They have shown that the COF of hydrogen-less ta-C coatings tested in similar combination for the boundary lubrication regime can achieve ultra-low \( f \) values. This phenomenon (“superlubricity”) is achieved as a result of the interaction of a ta-C coating with an ether-containing oil due to the formation of the thinnest boundary layer on the coating with minimal shear resistance due to the interaction of the alcohol \(-OH\) functional group contained both in glycerol and GMO molecules.

Table 1. The coefficients of friction for steel and diamond-like carbon-coated samples tested in a solution of glycerol monooleate (GMO) in polyalphaolefin (PAO), and in pure glycerol [18].

| Friction pair       | GMO + PAO | Glycerol |
|---------------------|-----------|----------|
| Steel / Steel       | 0.15      | 0.11     |
| \( a-C:H / a-C:H \) | 0.125     | 0.155    |
| \( ta-C / ta-C \)   | 0.03      | >0.01    |

The noticeable chemical inertness of carbon-based coatings makes it difficult to lubricate them with oils containing chemically active additives. However, there are certain types of additive compositions that provide a fairly noticeable anti-friction effect. These include molybdenum dithiocarbamate (MoDTC) and zinc dithiophosphate (ZDTP). It can be assumed that in a mixed solution of MoDTC + ZDTP or only with MoDTC in conditions of a tribological contact the products of tribochemical decomposition of the additive are formed (in particular, sulfur and molybdenum) which when “planted” on the DLC coated surfaces in the result of secondary reactions taking place directly on the surface of the coating form molybdenum disulfide that improves anti-friction and wear-resistant properties [19].
Despite the high tribological characteristics of hard carbon coatings there are practical problems in their use associated both with their low adhesion and with insufficient lubricity of coated surfaces due to their chemical inertness. One way to improve the functional properties of hard carbon coatings is alloying with various chemical elements [20]. In [21] the effect of dehydrogenized DLC coatings alloying with Si, Co, Ni, Cr, Ti on the tribological characteristics was studied for surfaces lubricated with pure PAO and with PAO with the addition of 1% glycerol monooleate (GMO) (PAO + GMO). The authors have shown that the most significant effect of the COF decrease to \( f = 0.02 \) was observed for DLC coatings alloyed with cobalt. The unalloyed coating under similar test conditions has demonstrated \( f = 0.10-0.12 \). The authors of [21] explain the reduction of friction in cobalt doped DLC coating by the interaction of cobalt with the lubricant and nanolayers with low shear resistance formed on surfaces in the zone of friction contact. According to the results of [16, 22] the DLC carbon doped with tungsten in process of friction against steel in the environment of PAO with sulfur-containing additive the partial transfer of the coating to the steel surface was observed after this in the result of the tribochemical reaction of tungsten with sulfur deliberated in the process of additive’s decomposition WS\(_2\), an effective anti-friction material, forms. This leads to a COF decrease from 0.13 in the test oil without additive to 0.10 after the introduction of a 10% sulfur-containing additive to PAO oil.

The most pronounced beneficial effect of alloying may be observed in hard carbon coatings whose structure was specially designed for work in the conditions of a boundary lubricated contact. The method of such a structural modification oriented to ensure a high level of orientation (alignment) of the lubricant molecules on the interface of the liquid and solid phases has been developed. This approach is based on the fact that the solid surface with a high degree of structural long-range order might induce some degree of spatial ordering in the neighboring boundary lubricant layer. To realize this hard carbon coatings with a specific self-organized structure have to be deposited onto a protected, presumably steel, surface. This highly organized carbon coating must possess a homeotropic oriented two-dimensional ordered linear-chain structure [23] that ensures the formation of a highly ordered homeotropically oriented boundary layer with a sufficiently wide range of high antifriction properties thermal stability. This type of carbon structures is known in home literature under the names of “single-crystal hard carbon” (SCHC) structures or “hard carbon coatings-orientants” [24]. These SCHC coatings may be obtained by the method of pulsed carbon plasma condensation in combination with argon ions bombardment [25]. In the experiments described below they have been alloyed with tungsten, molybdenum and silicon, and. have demonstrated very high nanohardness (~ 60-90 GPa), good adhesion and satisfactory thermal stability [24].

In particular the deposition of alloyed SCHC coatings may improve wear-resistance of contacting surfaces, e.g. the deposition of a SCHC coating doped with tungsten (W-SCHC) on a surface of a steel slab decreases the volume wear of these slabs by 15-20 times in UMT-3MT vibro-tribometer tests in normal tetradecane lubricant. Thus on a surface of an uncoated steel slab the deep wear traces have been left by the wearing steel spheres (figure 5(a)). Their depth is confirmed by the fact that they cross the traces of grinding on the surface of the slab and significantly deepen into it. For samples whose surface was protected with a W-SCHC film the traces of grinding may be recognized even under the wear track through a transparent coating, and the coating surface itself has been only slightly damaged in process of friction (figure 5(b)).

The boundary lubrication of unalloyed and a number of alloyed SCHC coatings ~ 1.2-1.5 \( \mu \)m thick has been studied in [26]. The tests under boundary lubrication conditions were carried out on an improved KT-2 test machine with the “ball vs three rollers” friction test geometry. According to this scheme three cylindrical rollers were installed in the mandrel perpendicularly to the axis of the spindle with a spinning ball. The mandrel structure is shown in figure 6. The ShKh-15 tool steel bearing ball (diam. 12.7 mm) surface was in contact with the SCHC-coated lateral sides of three 100Cr6 steel rollers (diam. 8 mm). The friction test parameters: axial load – 108 N, spindle speed – 1 min\(^{-1}\).
Figure 5. Micrographs of steel plate surfaces: (a) – in uncoated and (b) – in W-SCHC coated states after the tribological tests in normal tetradecane on a UMT-3MT vibro-tribometer (oscillation frequency – 1 Hz; maximum contact load – 51 N; test duration – 60 min).

Figure 6. The mandrel of the improved KT-2 test machine: 1 – roller, 2 – mandrel body, 3 – separator, 4 – ball. The coupling nut presses the rollers to the mandrel casing through a clamping ring (are not shown for visibility).

Figure 7 shows the coefficient of friction $f$ variation with time for uncoated and SCHC-coated steel surfaces tested in a chemically active sulfur-containing (PAO + DF-11 additive) and in a surface-active (PAO + OK additive) lubricating media.

Figure 7. Time dependences of the coefficient of friction $f$ of unalloyed and alloyed hard carbon coatings tested in pair with steel in solutions: (a) – with the DF-11 sulfur-containing additive and (b) – with the OK surface-active additive. Nomenclature: 1 – steel on steel; 2 – SCHC coating on steel; SCHC coatings doped with: 3 – silicon (Si-SCHC) on steel; 4 – tungsten (W-SCHC) on steel and 5 – molybdenum (Mo-SCHC) on steel.

The analysis of the experimental results presented in figure 7 shows that if the lubricating medium contains sulfur, it reacts with molybdenum (or tungsten) present in coating thus forming molybdenum
or tungsten disulfides that results in a significant reduction of COF. This effect is observed only if the carbon-based coating is doped with these specific metals and only in presence of sulfur-containing liquid lubricants. To understand this one can compare the test results for steel counterparts tested in pairs with unalloyed “single-crystal hard carbon” (SCHC) coating and with SCHC coatings alloyed with silicon, tungsten and molybdenum in solutions with a DF-11 additive that contains sulfur. The kinetics of the tungsten and molybdenum disulfides formation may be understood from the analysis of the curves’ 4 and 5 shape variations in figure 7(a), i.e. as these solid lubricants form the COF values decrease. One may also see that alloying of SCHC-coatings with silicon does not practically affect the value of $f$, while SCHC doping both with molybdenum and tungsten significantly reduces friction. At the same time doping of SCHC with silicon, molybdenum and tungsten does not affect the antifriction properties coatings when tested in the surface-active OK lubricating medium (figure 7(b)). This means that only the formation of molybdenum and tungsten disulfides (higly effective solid lubricants) in the result of appropriate tribochemical reactions is able to provide a noticeable increase in the anti-friction properties of the rubbing bodies.

Thus, the alloying of carbon coatings with tungsten and molybdenum during friction in sulfur-containing media with boundary lubrication can significantly reduce friction losses in heavily loaded friction units. Doping of coatings with elements that do not form a compound with the components of the lubricant that can play the role of a solid lubricant does not have a noticeable effect on its antifriction properties.

4. Conclusion
A comparative analysis of the results of a comprehensive investigation of the several types of hard carbon coatings alloyed with the chromium subgroup metals (diamond-like, metal-carbon and single-crystal hard carbon coatings-orientants) structural state, mechanical and tribological properties has been performed.

It has been demonstrated by numerous tribological experiments that alloying of all these types of coatings might have a noticeable effect on the peculiarities of their tribological behavior at dry and boundary friction.

For the hard carbon coatings working in dry friction regime the peculiarities of the alloyed coating’s micro- and nanocomposite structure, the structure and the character of carbon phase distribution in them may strongly influence tribological behavior.

For the case of boundary lubricated contact the principal effect of the hard carbon coating alloying is presumably due to tribochemical interactions of specific alloying elements with the components of lubricating liquid environment.

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