Effect of structure and deposition technology on tribological properties of DLC coatings alloyed with VIA group metals

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Abstract. The results of a comprehensive research on atomic structure, phase composition, micromechanical and tribological characteristics of alloyed DLC coatings have been presented. The coatings have been deposited by reactive magnetron sputtering in acetylene-nitrogen gas mixtures of different compositions (a-C:H:Cr), by plasma-assisted chemical vapor deposition in atmospheres of silicone-organic precursor gases (a-C:H:Mo:Si), and by nonreactive magnetron sputtering of a composite target (a-C:H:W).

1. Introduction
Diamond-like carbon (DLC) coatings having amorphous carbon (a-C) structure are one of advanced materials for surface strengthening machine and mechanisms wear parts. They are characterized by high wear resistance and low friction even at high contact pressures. The active research is carried out on further improvement of wear resistance and reduction of the residual stresses in such coatings by alloying them with different metallic and nonmetallic elements.

The aim of the present work was to study the peculiarities of nanocomposite structure of plasma-assisted vapor deposited DLC coatings alloyed with chromium, molybdenum and tungsten and its relationship with deposition technology, as well as with mechanical and tribological characteristics.

2. Methods of coating characterization and synthesis
The investigations of fine atomic structure, phase composition, nanomechanical and tribological properties of DLC coatings obtained by plasma-assisted chemical vapor deposition from gaseous silicon-organic “precursors” (a-C:H:Mo:Si), by reactive magnetron sputtering in atmospheres containing acetylene (a-C:H:Cr) [1, 2] and by non-reactive magnetron sputtering of “mosaic” W/C targets (a-C:H:W) have been studied. The coatings deposited on steel substrates have been studied by X-ray diffractometry, energy-dispersive electron-probe microanalysis, instrumented nanoindentation. Raman spectroscopy has been used to estimate the state of carbon phase in coatings. Tribological tests have been performed in conditions of dry friction using a one-ball “sphere-on-disc” tribometer at 0,02 to 0,2 N loads. Immovable silicon nitride ceramic spherical indentor (6 mm in diameter) has been used as counterpart.

Experimental X-ray spectra of coatings have been treated by the method described in [3] that made it possible to eliminate the contribution of the substrate in scattering intensity. To estimate the coating phase composition JCPDS PDF-2 and the “Match!” software have been used.
3. Results and discussion

3.1. Coating structure peculiarities

Table 1 and figures 1–3 represent the results of structural investigations. In \(a\)-C:H:Cr coating the formation of a complex structure formed by nanometer sized (~ 10 nm) chrome inclusions, carbide and nitride phases has been established (figure 1).

| Coating type | Element concentration, at. % | Structure type | Phase composition | \(H,\) GPa |
|--------------|-----------------------------|----------------|-------------------|------------|
| \(a\)-C:H:Cr | 100% \(C_2H_2\) | | \(Cr_{23}C_6 + Cr\) | 10 |
| \(a\)-C:H:Cr | \(C_2H_2/N_2 = 20/80\) | nanocrystalline | \(Cr_3C_2 + Cr_2N + Cr\) | 29 |
| \(a\)-C:H:Mo:Si | 40 / 8 / 36 / 16 | amorphous | \(Mo_5Si_3 + Mo\) | 15 |
| \(a\)-C:H:W | 75 / 2 / 0.9 / 17 | amorphous | \(W + WC + W_2C\) | 20 |

In coatings alloyed with molybdenum and tungsten the structure might be characterized as “X-ray amorphous”. The proper diffuse scattering intensity for these coatings is presented in figures 2 and 3. Their modulations prove the absence of long-range order with conservation of short-range order elements at the distances of some nearest coordination spheres.

For the \(a\)-C:H:Mo:Si coatings this might be explained by the presence of ultra-dispersed inclusions of molybdenum, molybdenum carbide and silicide phases with size less than 0.5 nm the formation of which might be explained by the use of silicon-organic precursors during their synthesis. In DLC coatings alloyed with tungsten the structure might consist of metallic inclusions, tungsten carbides and \(a\)-C domains of sub-nanometer size.

These data demonstrate that the nature of nanocrystalline state in Me-DLC coatings may depend on the type of vacuum deposition technology used in their synthesis. So, one may conclude that reactive magnetron sputtering used for \(a\)-C:H:Cr deposition will result in a composite structure of nanosized domains of chromium and its interstitial phases that sustain the rather perfect long-range order in the matrix of amorphous carbon. As it has been shown in [2] the additional alloying of \(a\)-C:H:Cr with nitrogen leads to formation of chromium nitrides and is accompanied by the increase in nanomechanical and tribological properties.
3.2. Tribological properties of coatings

The results of tribological tests are summarized on figure 4. The DLC coatings alloyed with chrome have demonstrated highest tribological parameters. For these coatings the friction coefficient \( f \) was lower than \( f = 0.2–0.35 \), and their complementary doping with nitrogen has allowed to make it lower, about \( f \approx 0.1 \) or less. At the same time the coating performance characterized by the number of cycles \( N \) before the fracture process initiation has reached its highest level for coatings deposited in pure acetylene and doping of coatings with nitrogen making \( f \) lower also at high contact pressures has been accompanied by a noticeable \( N \) decrease.

Figure 4. The dependence the coefficient of friction \( f \) (a) and the number of cycles \( N \) (b) before the coating fracture initiation on load for: 1 – \( a \)-C:H:Cr (deposited in pure acetylene); 2 – \( a \)-C:H:Cr (deposited in acetylene – nitrogen 20/80 gas mixture); 3 – \( a \)-C:H:Mo:Si; 4 – \( a \)-C:H:W coatings on KhN35VT substrates.
DLC coatings alloyed with W that have been deposited by non-reactive sputtering of a composite W/C target when tested have demonstrated $f \sim 0.2–0.4$ for all the load values, that might be compared with $f$ values for coatings deposited in pure acetylene but the results of their durability tests have been rather low.

The a-C:H:Mo:Si coatings as compared with the other ones have shown the highest $f$ values and low durability. To our opinion this decrease of tribological parameters might be explained by the presence of molybdenum silicides MoSi$_x$ in them and/or by the processes of silicon hydroxides formation during friction in air environment. The presence of these hydroxides having low strength characteristics [1] leads to a coating mechanical strength decrease. The way to improve the tribological properties of these coatings might probably consist in lowering the contact pressures/ changing contact geometry or using lubricants [1].

In general the results of the present investigation on the structure of DLC coatings alloyed with metals are in agreement with the known facts on the influence of the plasma-assisted deposition conditions on it. Thus the problem of nanocomposite structure formation in magnetron sputtered films of a-Cr-C has been discussed in [4] and the authors concluded that the structure with nanosized carbide inclusions is typical for reactive magnetron sputtering and the amorphous one – for a non-reactive technology.

3.3. Radial distribution function analysis

To our opinion to define the nature of phases formed in these conditions more precisely the analysis of the radial distribution functions $G(r)$ of coatings might be useful. These functions described the probably to find a pair of atoms at a distance $r$ between them and the maxima of $G(r)$ correspond to atomic distances values being the most probable for a particular structure.

The “PDFgetX3” software [5] has been used to calculate $G(r)$ from the experimental X-ray diffuse scattering intensity $I(2\theta)$ spectra:

$$G(r) = \frac{2}{\pi} \int^{q_{\text{max}}}_{q_{\text{min}}} q[S(q) - 1] \sin(qr) dq,$$

where $q = \frac{4\pi \sin \theta}{\lambda}$; $\theta$ – the diffraction angle; $\lambda$ – the radiation wavelength; $q_{\text{min}}$ and $q_{\text{max}}$ correspond to $\theta_{\text{min}}$ and $\theta_{\text{max}}$ values respectively; $S(q)$ – Faber–Ziman type structure function:

$$S(q) = 1 + \left[ I_{\text{coh}}(q) - \sum_i c_i f_i(q)^2 \right] \left[ \sum_i c_i f_i(q) \right]^2,$$

$c_i$ – atomic concentration; $f_i(q)$ – atomic factor of the $i$-th atom; $I_{\text{coh}}(q)$ – experimental diffuse scattering intensity.

The $G(r)$ functions for the coatings under study are presented on figure 5. One may notice that the doping element type and the deposition technology have a rather strong influence on the pair distribution function behavior and the local $G(r)$ maxima positions that might coincide with certain atomic pair distances characteristic for the crystal structures of the corresponding nanocomposite components. The radial distribution functions presented on figure 5 for $r \leq 10$ Å demonstrate strong oscillations that might decay at longer interatomic distances.

The analysis of the behavior of radial distribution functions $G(r)$ for Cr-DLC has demonstrated that in these coatings the oscillations of $G(r)$ decay only at $r > 100–120$ Å (10–12 nm) that is close to the size of the coherently scattering domains, i. e. the elements of long-range order exist even for rather long interatomic distances. To our opinion this fact proves that the nanosized metallic and interstitial phase inclusions in chromium-based diamond-like nanocomposites retain the structure of their “parent” phases. For DLC coatings doped with tungsten and molybdenum (figures 5(c) and 5(d) respectively) the $G(r)$ oscillations decay at $r$ about 8–10 Å and in their case only short-range correlations exist with a “correlation radius” not exceeding 1 nm.
Figure 5. Radial distribution functions $G(r)$ for DLC coatings alloyed with VIA group metals:
(a) – $a$-C:H:Cr (100 % C$_2$H$_2$); (b) – $a$-C:H:Cr (20 % C$_2$H$_2$ + 80 % N$_2$); (c) – $a$-C:H:Mo:Si;
(d) – $a$-C:H:W.

4. Conclusions
The results of this investigation have confirmed the correlation of the structural state of diamond-like carbon coatings alloyed with VIA group transition metals with the technology of their deposition as well as with their tribological properties.

Nanocomposite DLC coatings alloyed with chromium whose structure consists of metallic inclusions $> 10$ nm in size and nanometer chromium carbide and nitride inclusions have demonstrated the highest tribological characteristics. The DLC coatings alloyed with Mo and W had an amorphous type structure and their friction and durability parameters were considerably lower as compared with Cr-DLC.

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