The effect of structure on tribological behavior of chromium-carbon coatings obtained by plasma-assisted physical vapor deposition

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Abstract. Two different kinds of chromium-carbon vacuum-deposited coatings have been investigated. The coatings were obtained by magnetron sputtering of chromium in a reactive argon-acetylene-nitrogen atmosphere and by non-reactive sputtering of a sintered chromium-nanodiamond target in argon. The structure of reactively sputtered coatings consisted of a diamond-like hydrogenated carbon matrix with nanosized inclusions of pure chromium and chromium carbide and nitride phases and that of non-reactively sputtered was a mixture of nanosized chromium and Cr₇C₃ carbide. Carbon observed in the former case was in form of agglomerates few microns in size whose degree of graphitization varied from agglomerate to agglomerate. The existing coating structure–functional properties correlations are discussed.

1. Introduction
Diamond-like carbon (DLC) PVD coatings are perspective materials for highly loaded tribological contacts [1]. To improve their properties the alloying with different chemical elements is widely used [1, 2]. Earlier the authors have studied DLC coatings alloyed with chromium (Cr-DLC) and have found them to considerably improve the tribological behavior [3].

Detonation synthesis nanodiamonds (DSND) are the other type of new nanostructured carbon materials [4]. DSND or synthetic “combustion” nanodiamonds (ND) are the product of solid explosives utilization. The DSND structure consists of a distorted “diamond” core 4–6 nm in diameter surrounded by a shell 0.4–1 nm thick of highly disordered graphite phase whose structure is composed of chemically bonded sp²- and sp³-hybridized carbon atoms, and of a surface layer with heteroatoms of N, H, and O that in combination with carbon may form a wide spectrum of functional groups.

DSND or their additions are used in industry to improve the wear-resistant, abrasive, lubrication and other properties of materials. They are also used in metal-nanodiamond (Me-ND) composite coatings obtained by electrolytic co-deposition of ND with different metals. These electrodeposited coatings are characterized by high microhardness and adhesion, corrosion- and wear-resistance, low friction, etc. [4]. In [5] the existence of a composite structure with nanosized “diamond phase” inclusions in
Me-ND coatings deposited by plasma-assisted PVD has been suggested.

The aim of this work was to estimate the influence of microstructure and phase composition peculiarities of reactively-sputtered Cr-DLC and the coatings deposited by Cr-ND targets sputtering on certain functional parameters (coefficient of friction (COF); tribological performance characterized by the number of frictional contact cycles $N$ before the coating failure; nanohardness and adhesion).

2. Experimental

The technologies of coating deposition have been described in previous publications on Cr-DLC [3] and coatings sputtered from Cr-ND targets [6]. In [6] we have studied different Cr-ND coatings to find the technology and coating composition optimal from a tribological point of view. The coatings deposited from the sintered targets of chromium and ND powders with nanohardness ~ 30 GPa were found to be convenient to these criteria: COF ~ 0.3; period of a friction pair stable work ~ 4000 cycles at maximal contact pressure ~ 450 MPa.

All the chromium-carbon coatings have been subjected to a comprehensive structure, mechanical and tribological properties investigation. The experimental methods used and the details may be found in [3, 6]. The dry sliding tribological tests were performed in ambient air using a ball-on-disc tribometer [7]. A silicon nitride ball 6 mm in diameter was used as a counterpart. The investigations of adhesive strength were performed on a REVETEST (CSM International) scratch-tester with a conical Rockwell C indenter with tip radius 200 μm (load $L$ varied from 1 to 60 N; the score length was 4.92 mm). The scores were examined by optical microscopy and by SEM. The state of coating’s carbon was studied by Raman spectroscopy.

The conditions of coating deposition, chemical and phase composition, the size of coherently scattering chromium inclusions $D_{Cr}$, nanohardness, critical load of cohesive to adhesive (C→A) failure mode transition, coefficient of friction and numbers $N^*$ of cycles before an abrupt increase of COF (both – for coatings tested at contact stress ~ 450 MPa) are presented in table 1.

| No. | Target type | Sputtering atmosphere | [C], at.% | Phase composition | $D_{Cr}$, nm | $H$, GPa | $L_{C→A}$, N | COF | $N^*$ |
|-----|-------------|-----------------------|-----------|-------------------|-------------|---------|-------------|-----|-------|
| 1   | Cr          | Ar+C$_2$H$_2$         | 80.4      | Cr+Cr$_7$C$_3$+α-C:H | 8.1         | 10      | 33.3        | 0.15 | 3500  |
| 2   | Cr          | Ar+C$_2$H$_2$+N$_2$ (80:20) | 64.3      | Cr+Cr$_7$C$_3$+α-C:H | 8.7         | 12.9    | 41.1        | 0.08 | 2400  |
| 3   | Cr          | Ar+C$_2$H$_2$+N$_2$ (20:80) | 27.4      | Cr+Cr$_7$C$_3$+CrN+ +α-C:H | 13.4       | 29.1    | 15.9        | 0.12 | 1000  |
| 4   | Cr + ND     | Ar                    | 40.6      | Cr+Cr$_7$C$_3$     | 13          | 29.6    | 36          | 0.29 | 4100  |

3. Structure peculiarities

As it was supposed in [5] (the results have been obtained using SPM technique) the structure of Cr-ND PVD coatings is nanocomposite with metallic subgrain size about 30-70 nm and the “nanodiamond phase” particles segregated at the boundaries of these subgrains. The results of our X-ray studies [6] have demonstrated the different type of structure: nanosized phases of Cr and Cr$_7$C$_3$ carbide (both ~13-14 nm) and no lines of diamond phase being detected that may mean its low volume content.

The Cr-NA coating’s microstructure reported in [6] is different from that of α-C:Cr and α-C:H:Cr with chromium and chromium interstitial phase nanosized inclusions randomly distributed in an amorphous matrix of non-hydrogenated or hydrogenated carbon [2, 3]. The inclusion sizes observed in [3] are in agreement with the transmission electron microscopy (TEM) data [8]. These authors by high-resolution TEM have also confirmed the carbon in matrix phase of Cr-DLC to be amorphous.
This means that the structures of Cr-DLC and of chromium-carbon coatings deposited by Cr-ND target sputtering represent two different types of metal-carbon nanocomposite structure. As their constitution may influence the material characteristics the study of the respective micromechanical, tribological, adhesion, strength and other parameters may be interesting both from practical and fundamental points of view.

4. Results and discussion

From the data presented in table 1 it follows that the Cr-DLC coatings reactively sputtered in acetylene-rich atmospheres (1 and 2) and the coating 4 deposited from sintered Cr-ND targets all demonstrate $N^* > 2500$ in friction fatigue tests with similar test conditions. The Cr-DLC film 3 deposited in acetylene-poor mixture ($C_2H_2$–80 vol. % $N_2$) with nanohardness 29.6 GPa, significantly higher than that of coatings 1 and 2, keeps its tribological functionality during only $N^* \sim 1000$ cycles when tested at a maximal load $P = 0.2$ N (contact pressure $p_{\text{max}} \approx 450$ MPa). One can note that the structure of coatings numbered as 1, 2 and 3 is significantly different [3]. In the first two coatings deposited at high concentrations of $C_2H_2$ the chromium inclusions ~ 10 nm and of $Cr_2C_6$ less than 2 nm in size are present. alloying of coatings with a large amount of nitrogen leads to the increase of chromium inclusions size to 13 nm and to formation of nanosized $Cr_7C_3$ and $CrN$ phases accompanied with a nanohardness increase from 10 to 29 GPa. Thus from the viewpoint of their hardness the Cr-DLC coating 3 and the coating 4 deposited by Cr-ND compact sputtering are similar. Nevertheless the COF of Cr-ND is ~ 0.3 i.e. much higher than in all abovementioned Cr-DLC coatings. The period of the COF stability of this coating is sufficiently higher than that of number 3, the appropriate number of cycles $N^*$ is compatible to that of Cr-DLC coating 1 deposited in pure acetylene.

The Raman spectra investigation of the Cr-DLC coatings performed in [3] has shown that the carbon phase for these coatings has a disordered diamond-like structure. The two well resolved D and G peaks of equal intensity were observed in all Raman spectra.

The analysis of adhesive strength tests of coatings is presented in figure 1 and in table 2. The critical loads $L_i$ correspond to the threshold load values of different types of surface damage.

![Figure 1](image_url)

**Figure 1.** Types of score’s surface damage and specific threshold loads $L_i$ of their generation (in N) for Cr-DLC coatings 1 and 3. The specific values of $L_i$ associated with the specific types of surface damage (described in table 2) correspond to a middle point of a score fragment image. The length of each score fragment microphotograph equals 250 μm.

The analysis of high magnification SEM and optical microphotographs allows to expose typical forms of damage associated with surface chipping, formation of cracks of coating bulk material, exfoliation of coating fragments and flakes provoked by unloading following the scratching indenter pass, wear of coating material by mechanical rubbing, the process of substrate uncovering.

The analysis of the typical scratch-test induced surface damage types observed in chromium-carbon coatings shows that the process of surface failure may be divided into 5 consecutive stages: (1)
formation of single thin cracks → (2) local chipping of coating surface → (3) formation of multiple cracks localized in the volume of coating → (4) local substrate uncovering by the process of coated layer rubbing → (5) total substrate uncovering. From figure 1 one may conclude that at stages (1)–(3) the process of damage is limited by the volume of coatings and can be accordingly to [9] classified as “cohesive” but with the increase of load applied to indenter the damage becomes heavier and at stages (4)–(5) the coating–substrate interface and the substrate become involved and the failure takes “adhesive” character. Based on this the threshold load of substrate partial uncovering due to the coated surface rubbing in terms of [9] might be considered as critical for “cohesive” to “adhesive” (C→A) failure mode transition, and designated as $L_{C\rightarrow A}$. The abovementioned damage types (1)–(5) are presented in figure 1 of scratch-tested Cr-DLC samples 1 and 3. From table 2 one may see that in all their aspects the behavior of coatings 1–4 was similar except that for the coating 4 the stage (2) was not observed.

**Table 2.** The results of coating scratch-test.

| Number of sample | 1  | 2  | 3  | 4  | Failure mode [9]                  |
|------------------|----|----|----|----|-----------------------------------|
| Type of coating  | Cr-DLC | Cr-ND |    |    |                                   |
| Surface damage description | Critical load $L_i$, N |    |    |    |                                   |
| Formation of single thin cracks | 2.7 | 2.2 | 2.9 | 1.9 | Cohesive                          |
| Local chipping   | 6.5 | 6.5 | 6.7 | -  | Cohesive                          |
| Multiple cracking | 16.1 | 19.4 | 9.1 | 10.4 | Cohesive                          |
| Local substrate uncovering | 33.3 | 41.1 | 15.9 | 36.0 | Cohesive → Adhesive               |
| Total substrate uncovering | 52.1 | 50.1 | 41.9 | 51.8 | Adhesive                          |

The basic results for Cr-DLC and Cr-ND-based chromium-carbon coating are collected in figure 2.

**Figure 2.** Functional properties of coatings 1 – 4: (a) – atomic concentration of carbon in coatings; (b) – nanohardness; (c) – $N^*$ – number of cycles preceding the abrupt growth of force of friction measured at contact pressure equal to 450 MPa; (d) – critical loads of surface damage: $L_{C\rightarrow A}$ (I) – local substrate uncovering (transition from cohesive to adhesive coating damage); $L_{mult}$ (II) – multiple cracking of coating surface; $L_{chip}$ (III) – local chipping.

From the analysis of figure 2 one can suppose that there might be a certain correlation between the carbon content, the number of test cycles preceding the sudden friction force growth indicating coating
friction fatigue failure, and the critical loads (threshold values) of adhesive strength. At the same time the distinct correlations between composition and mechanical properties, between high mechanical properties, low performance and low friction observed in Cr-DLC coatings [3] are not applicable to the Cr-ND coatings. The best tribological performance in this case was demonstrated by a coating with nanohardness ~ 30 GPa and a rather large COF ~ 0.3 which in contrast with Cr-DLC is independent on composition, hardness and elastic modulus of Cr-ND coatings.

A rough estimate based on chemical composition and the results of quantitative X-ray analysis of coatings obtained by the sintered Cr-ND target sputtering has shown that about 10-15 at. % of carbon in them might be in a non-bounded state. The results of this “free” carbon analysis are given below.

The investigation of Raman spectra in [10] has shown that the character of carbon distribution in Cr-ND was different from the uniform distribution in Cr-DLC [3] where amorphous form of carbon plays the role of matrix material with incorporated nanosized inclusions of chromium and its phases.

These results have given an argument to suppose that the matrix of chromium-carbon composite obtained by sputtering of Cr-ND targets is constituted from grains containing nanosized subgrains of chromium and its Cr7C3 carbide. Such a two- or three-dimensional ordered multiphase structure in general may be typical for many materials and coatings obtained by deposition in non-equilibrium conditions. One example are the PVD coatings of the Ti–N system [11]. Their TEM investigation has revealed the presence of a “stripped” contrast of TEM images of individual grains generated by the alteration of nanosized layers having different phase composition.

In contrast to the nanometer size of chrome and Cr7C3 phases the solid carbon in Cr-ND coatings accordingly to Raman spectroscopy results [10] has the form of rather large spherical particles or their agglomerates ~2–10 μm in size (figure 3(a)) with different types of graphite, and their graphite-like structure being characterized by the sp3/sp2-ratios for separate particles may vary strongly (figure 3(b)). Thus the presence of a specific “nanodiamond” structure supposed in [5] was not confirmed.

Figure 3. The results of Raman spectroscopy analyses of chromium-carbon coatings deposited by a sintered Cr-ND target sputtering: (a) – coating surface with carbon spherical particles and their agglomerates; (b) – Raman spectra of different agglomerates on the same coating surface; (c) – wear tracks and the products of solid graphite-like carbon phase wear (the arrow shows the direction of sliding).

One may suppose that the carbon particles few microns in size with different degree of graphitization would play the role of a solid lubricant. This graphitized carbon layer formed in process of dry friction will protect the surface of coatings and prevent catastrophic wear.

This supposition is based on the fact that the most intensive Raman spectra were observed in the vicinity of wear tracks formed during the coating tribological tests where large amounts of carbon material were present (figure 3(c)) that proves the possibility of friction-induced graphitization processes initialized at high contact stresses in conditions of a complex (“compression + shear”) loading.

5. Conclusions
At a microscopic level the structures of diamond-like carbon coatings alloyed with chromium and chromium-carbon coatings deposited by chromium-nanodiamond targets sputtering are significantly different. The
structure of diamond-like carbon coatings deposited by reactive magnetron sputtering in acetylene-nitrogen gas mixtures is characterized by the presence of nanosized inclusions of chromium (~10 nm), chromium carbides and nitrides (<2 nm) while in chromium-carbon coatings deposited from chromium-nanodiamond targets the domains of chromium and carbide are of equal size ~10 nm.

Amorphous carbon in Cr-DLC coatings plays the role of a matrix phase reinforced by the nanosized inclusions of chromium and its interstitial phases while in coatings sputtered from chromium-nanodiamond targets the matrix is composed of a mixture of metal and carbide nanosized grains and carbon exists in form of micron-sized spherical particles and/or their agglomerates that in process of friction may form a protective layer playing the role of solid lubricant.

Correlations exist between the carbon atomic concentration in coatings, the number of cycles before the film failure observed in tribological tests and the critical threshold loads for different types of surface damage observed during the coating scratch-tests.

The numbers of test cycles preceding coating failure and critical load values for specific types of local surface failure observed in scratch-tests of Cr-DLC coatings decrease significantly while the nanohardness and friction coefficient increase with the increase of nitrogen content in reactive atmospheres. For coatings obtained by chromium-nanodiamond targets sputtering the first two parameters are higher than those of Cr-DLC coatings reactively deposited in gas atmosphere rich with nitrogen.

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