Chromium-nanodiamond coatings obtained by magnetron sputtering and their tribological properties

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Abstract. Peculiarities of structure, chemical and phase composition, micromechanical and tribological properties of chromium-based coatings obtained by magnetron-sputtering of composite and/or compacted chromium-nanodiamond targets have been investigated.

1. Introduction

It is well known that the composite coatings obtained by electrolytic codeposition of nanodiamonds with metals typically possess high wear resistance and hardness in combination with low porosity, high corrosion resistance and low friction, and also demonstrate good adhesion and cohesion [1, 2]. The time of life of the units with these coatings is typically sufficiently (2 to 10 times) higher than that of uncoated ones and their wear rate may be significantly decreased by increasing the nanodiamond phase content in them. It has been demonstrated that the chrome-nanodiamond coatings obtained by ion-assisted and PVD methods have nanocomposite structure with grain size typically of about 30–70 nm and that the nanodiamond phase segregates at the boundaries of these metallic nanosized grains [3], i.e. the structure of such chromium-nanodiamond (Cr-ND) coatings must significantly differ from that of metal-alloyed nanocomposite diamond-like carbon (DLC) coatings where the nanostructured metallic and carbide phase inclusions are randomly distributed in an amorphous carbon matrix [4, 5].

The investigation of the micromechanical, tribological and strength properties of such Cr-ND coatings, the comparison of their structure and phase composition with that of alloyed Cr-DLC coatings is of high interest both from the practical point of view and as a scientific base for non-equilibrium synthesis of nanocomposite structural materials with high mechanical properties and strength.

The analysis of peculiarities of the structural state, phase composition and functional properties of magnetron-sputtered chromium-nanodiamond coatings has been the aim of the present investigation.

2. Coating deposition and characterization techniques

The deposition unit equipped with an ion-source for ion-cleaning and with two magnetron sputtering units has been used for deposition of Cr-ND coatings in argon and/or argon-reactive gas mixtures. The polished substrates of AISI 430 have been used to deposit Cr-ND coatings 6–10 μm thick. The
magnetron technology was similar to that used for $a$-C:H:Cr:N coatings deposition [6, 7]. The bulk chromium targets with blind holes symmetrically arranged in the zone of maximal target erosion and filled with detonation nanodiamond powder to form the “inclusions” of ND material have been used as well as the Cr-ND targets obtained by powder metallurgy methods. The bulk targets with the nanodiamond “inclusions” will be mentioned below as “composite” (sometimes also called “mosaic”). For comparison with them the coatings obtained by sputtering pure chromium targets have been also investigated.

Structure and phase composition of coatings have been studied by X-ray powder diffractometry technique. The details of X-ray experiment and the methods of XRD patterns interpretation have been analogous to those used earlier [6, 7]. The chemical composition of coatings has been investigated by energy-dispersive X-ray microanalysis (EDXA) on a JSM 6610 LV (JEOL) scanning electron microscope. Nanohardness and elastic modules have been measured by instrumental nanoindentation with an NHT nanohardness tester (CSM International) by the standard Oliver-Pharr method. Tribological tests have been performed on a ball-on-disc tribometer with the scheme used to estimate frictional fatigue of materials [8]. The ball of silicon nitride ceramics 6 mm in diameter has been used as counterpart. The tests have been performed on air during 1 h (disc rotation speed – 100 rev/min, the maximum number $N$ of disc revolutions (“cycles”) being 6000) at loads $P = 0.02–0.2$ N (contact pressures of about 0.2–0.45 GPa). The number of cycles preceding an abrupt change of the coefficient of friction $f$ that is usually associated with the beginning of coating fracture has been registered.

3. Results and discussion

The data on target type, sputtering conditions, technology parameters, coating chemical and phase compositions are presented in table 1. The results of nanohardness tests are presented on figure 1 and those of tribological tests – on figure 2.

Table 1. Coatings obtained by magnetron sputtering of chromium-nanodiamonds (ND) targets, their chemical and phase composition.

| No., target type          | Technological parameters | Chemical composition, at. % | Phase composition                  |
|---------------------------|-------------------------|------------------------------|-----------------------------------|
| 1. Cr                     | Ar                      | Cr 90.7 C 9.3 N 0 O         | Cr                                |
| 2. Cr+ND (composite)      | Ar                      | Cr 91.3 C 8.7 N 0 O         | Cr                                |
| 3. Cr                     | Ar + N$_2$ (5:1)        | Cr 78.2 C 7.5 N 12.2 O 2.0  | Cr + Cr$_3$N                      |
| 4. Cr+ND (composite)      | Ar + N$_2$ (5:1)        | Cr 75.0 C 7.6 N 14.3 O 2.2  | Cr + Cr$_3$N                      |
| 5. Cr+ND (composite)      | Ar + N$_2$ (7:1)        | Cr 72.5 C 16.4 N 8.1 O 3.1  | Cr + Cr$_3$N$_{0.35}$C$_{0.61}$   |
| 6. Cr+ND (composite)      | Ar + N$_2$ (7:1) $U_b = -60$V | Cr 78.6 C 8.0 N 11.6 O 1.8  | Cr + Cr$_3$N                      |
| 7. Cr+ND (composite)      | Ar + air                | Cr 82.5 C 0 N 14.6 O 2.9    | Cr + Cr$_3$N                      |
| 8. Cr+ND (sintered)       | Ar                      | Cr 58.5 C 40.6 O 0.9        | Cr + Cr$_3$N$_{0.35}$C$_{0.61}$   |

Note. If not otherwise stated, the negative bias voltage $U_b$ is zero.

From the analysis of these data it may be concluded that:

1. The carbon content [C] is less than 10 at. % in coatings Nos. 1–4;
2. The structure of coatings sputtered in pure argon (Nos. 1 and 2) is bcc;
3. The nitrogen content [N] in coatings Nos. 3 and 4 deposited in the presence of nitrogen is about 12–14 at. % and their structure is bcc Cr + Cr$_3$N chromium nitride.

The tribological tests of coatings Nos. 1–4 have demonstrated that they failed practically at the beginning even at loads being less than 0.1 N (figure 2). The tribological parameters of coatings Nos. 5–7 have been better. In particular at $P = 0.1$ N their behavior has been stable. The noticeable friction coefficient fluctuations due to friction fatigue damage being observed at $P = 0.15$ N (figure 2(b)). This is possibly due to the nitrogen carbide phases formed in nitrogen-argon gas mixture.

The coating No. 5 with [C] $\sim$ 15 at. % and [N] $\sim$ 10 at. % contained a carbonitride phase Cr$_3$N$_{0.35}$C$_{0.61}$. In coating No. 6 the nitrogen content was $\sim$ 11 at. %, the same as in coatings Nos. 3 and
4, but their tribological properties were better probably as a result of ion bombardment of growing film due to non-zero negative bias potential \( U_b = -60 \text{ V} \) being applied during deposition. The fact of coating densification and porosity decrease in the presence of ion bombardment stimulated by the negative bias applied to the substrate is well known from the literature [9].

The coating No. 7 deposited in argon-air gas mixture and having \([\text{N}] > 14 \text{ at. \%}\) was decarburized. Despite of this decarburization the tribological properties of the coating were close to those of coatings Nos. 5 and 6 that may be explained by the presence of chromium nitrides. The absence of carbon in No. 7 may be due to the oxygen present in air and to carbon monoxide \( \text{CO} \) formation during reactive magnetron sputtering in nitrogen-air mixtures [7].

![Figure 1. Nanohardness of coatings (the coating numbers are the same as in table 1).](image1)

![Figure 2. The dependence of the coefficient of friction \( f \) (a) and the number of cycles \( N \) (b) before the coating fracture initiation on load \( P \) (the coating numbers are the same as in table 1).](image2)

The results of coating Nos. 1–7 performance tests at high contact pressures (figure 2(b)) may be compared with the results of nanohardness measurements (figure 1). It may be noticed that the most of the abovementioned coatings posses nanohardness that doesn’t exceed 17 GPa. In particular the hardness of chromium coatings Nos. 1 and 2 is close to 4 and 7 GPa respectively. It may be concluded that the low micromechanical characteristics may be a sign of poor tribological performance at high contact pressures. In this connection one can notice that the performance of coatings Nos. 6 and 7 with nanohardness close to \( \sim 25 \text{ GPa} \) is higher than that of other coatings deposited by magnetron sputtering of composite targets. The fact may indicate that there is a close correspondence between high micromechanical properties of Cr-ND coatings and their high tribological performance. In particular it may be supposed that the hardness of Cr-ND coatings with high tribological efficiency must be close to 30 GPa or better.

The carbon content in Cr-ND films deposited by magnetron sputtering of composite targets is not higher than 17 at. \% that is the problem is in obtaining coatings that contain more carbon and the way
to improve their characteristics is to fabricate targets with higher nanodiamond component contents. It is also desirable to obtain a target with an even distribution of chromium and nanodiamond components. To obtain this composition uniformity the methods of powder metallurgy have to be used for Cr-ND target fabrication. The targets of two types have been prepared: one was compacted by hot-pressing (type I) and the other – by sintering (type II).

The hot-pressed targets of type I possessed a rather heterogeneous loose structure with strong porosity. Their structure was composed of small faceted granules ~5…20 μm in size and of separate randomly distributed large formations of irregular shape (figure 3). The size of some of these formations reached ~50…70 μm and they were 100 % carbon. This was in contrast with small faceted granules rather rich in chromium (according to EDXA the [Cr] content in them varied from 40 to 80 at. %). Unfortunately the mechanical strength of the type I targets was low and they crumbled easily. It was impossible to use then as a source of sputtered material for Cr-ND coatings deposition.

![Figure 3](image-url)

**Figure 3.** The surface of a type I (hot-pressed) target with a carbon formation: images obtained in secondary electrons (a) and in characteristic X-ray radiations of chromium and carbon (in online version – superimposed areas colored in green and red respectively) (b).

The type II targets fabricated by sintering were more suitable for magnetron sputtering – they were less porous with characteristic granules size less than 5 μm and stronger than those of type I. Their structure was more uniform and suitable for magnetron sputtering. Their chemical composition and the composition of appropriate Cr-ND coatings No. 8 are presented in table 2.

**Table 2.** Compositions of a type II sintered Cr-ND-target and of coatings deposited by their sputtering.

| Chemical composition, at. % |  |  |
|-----------------------------|---|---|
| Cr  | C  | O  |
| Target | 59.3 | 23.5 | 15.6 |
| Coating | 58.5 | 40.8 | – |

One can see that the target in as fabricated state contains oxygen (about 16 at. %). This oxygen is eliminated from the final coatings probably due to the effects of preferential sputtering and as a result they contain only chromium and carbon. The carbon content in this type of coatings is large (about 40 at. %). This is close to values observed in Cr-DLC films reactively sputtered in argon-acetylene mixtures [5, 7] that have demonstrated a good working performance and antifriction behavior.

The results of tribological tests of coatings deposited from the type II sintered targets (No. 8 in figures 1 and 2) also were good. The coating No. 8 in spite of its rather high coefficient of friction ~0.3 has kept functionality ($N > 4000$ cycles for $P = 0.1…0.2$ N). This is much higher as compared with
other Cr-ND coatings (Nos. 1–7). To the author’s opinion this may confirm that the magnetron sputtering of targets fabricated by sintering is a promising technology that allows deposition of nanocomposite chromium-nanodiamond coatings for tribological applications. Further investigations devoted to study the Cr-ND nanocomposite film microstructure and their tribological behavior are desirable.

4. Conclusions

Chemical and phase composition, micromechanical and tribological properties of coatings deposited by magnetron sputtering of chromium-nanodiamond “composite” (mosaic) or powder-metallurgy fabricated targets have been investigated.

These coatings posses composite structure consisting of chromium with inclusions of chromium nitride, oxide or carbide phases formed during deposition as a result of chromium interaction with carbon or with reactive gases added to argon.

The highest tribological characteristics and performance in conditions of heavily loaded frictional contact have been demonstrated by the coatings deposited by non-reactive sputtering of targets fabricated by sintering of chromium and nanodiamond powders (type II).

Acknowledgements

The authors appreciate the financial support from the Russian Foundation for Basic Research, project no. 15-08-05264 and from the “MISiS Increase Competitiveness Program” of the Ministry of Education and Science of the Russian Federation (in part of nanohardness measurements).

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