Tribological behavior and frictional fatigue damage peculiarities in thin $a$-C and $a$-C:N coatings

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Abstract. The mechanical and tribological properties of thin vacuum-arc deposited coatings of amorphous carbon in an unalloyed state and alloyed with nitrogen have been investigated especially the peculiarities of their frictional fatigue failure.

1. Introduction

Alloying of diamond-like carbon (DLC) coatings is widely used to improve their properties, to decrease internal stress level and to prevent the film parameters from temporal degradation [1, 2]. Numerous plasma-assisted PVD and CVD technologies may be applied to alloy DLC films with numerous chemical elements, nitrogen being one of them. The interest to N-DLC systems has been stimulated by theoretical predictions [3] of a hypothetic $\beta$-C$_3$N$_4$-phase with a predicted strength higher than the diamond one. The most of N-DLC films being investigated are hydrogenised ($a$-C:H-based), i.e. have been reactively obtained from the mixtures of gaseous or vaporized hydrocarbons with nitrogen. The high antifriction properties of these $a$-C:H:N coatings may be associated with graphitization of amorphous carbon structure alloyed with nitrogen – the DLC structure becomes more “graphite-like” due to $sp^3/sp^2$-ratio decrease with the nitrogen concentration increase. Alloying with nitrogen also decreases residual stresses as compared with unalloyed $a$-C:H. The maximum positive effect on adhesion, antifriction and wear properties of $a$-C:H:N has been observed for nitrogen contents ~8...12 at. % (see, for example [4]).

Hydrogen-free amorphous carbon coatings alloyed with nitrogen ($a$-C:N) are in general less studied than $a$-C:H:N PVD films. Nevertheless the investigations of micromechanical and tribological properties of $a$-C and $a$-C:N coatings deposited by ion-beam assisted deposition (IBAD) of graphitic target [5] or closed-field unbalanced magnetron (CFUBM) sputtering of graphite [6] have demonstrated the possibility to improve the film characteristics by nitrogen alloying.

The aim of the present work was to study micromechanical and tribological properties of thin $a$-C and $a$-C:N coatings deposited by cathode-arc evaporation in vacuum and the peculiarities of their frictional fatigue failure.
2. Experimental

The coatings of amorphous carbon have been deposited using a cathode-arc impulse plasma source with graphitic cathode. The vacuum-arc deposition unit (CreepService SARL, Switzerland) used by the authors and the details of deposition are described in [7]. The 12Kh18N10T (AISI 321 type) stainless steel disc-shaped substrates (35 mm in diameter, 1.5 mm thick), polished ($R_s = 0.06 \mu m$) and ultrasonically cleaned have been used for deposition. Their surfaces were subjected to ion-cleaning by argon and titanium ions bombardment. A titanium transition layer Ti-C is deposited by nitrogen injection into the deposition chamber simultaneously with graphite cathode evaporation. The thickness of coatings was ~150 nm (for unalloyed a-C films) and ~500 nm (for films alloyed with nitrogen).

The resulting coatings have been subjected to a comprehensive investigation of their composition, structure, chemical bonding, micromechanical properties, coefficient of friction and tribological performance. To investigate microstructure, wear track morphologies and chemical composition of coatings the scanning electron microscope (JSM 6610 LV, JEOL, Japan) with energy-dispersive X-ray microanalysis system (EDXA) has been used. The presence of hydrogen in coatings was ignored as the deposition technology doesn’t presume the presence of hydrocarbon precursor gases.

To determine the prevailing carbon allotrope type in coatings Raman spectroscopy has been used. The nanohardness and elastic modules have been measured with “NanoScan-3D” (NT-MDT, Russia) scanning nanohardness tester by the Oliver-Pharr method.

A ball-on-disc tribometer has been used to estimate tribological parameters at sliding on air without lubricant. This type of tribometers is usually used for frictional contact fatigue studies of structural materials [8]. The ball – spherical silicon nitride indenter 6 mm in diameter was motionless and the disc sample with coating rotated with a constant rotation frequency (100 rev/min). The tests at each load $P$ were conducted over 1 h. The results were the average over a series of three tests. The coating performance was estimated as an integer number $N$ of the disc rotations preceding the abrupt friction force variation. Traditionally this abrupt change is assumed to be associated with moment of the coating’s fracture initiation.

3. Results and their discussion

The data on the chemical composition of $a$-C and $a$-C:N coatings are presented on figure 1. They demonstrate that the light element’s concentration ratio $\frac{[N]}{[C]+[N]}$ in $a$-C:N is about 0.11, i.e. $[N]$ and $[C]$ are about 10 and 90 at. % respectively.

![Figure 1. Chemical composition of $a$-C (1) and $a$-C:N (2) coatings deposited on 12Kh18N10T steel substrates as determined by EDXA. The presence of small amounts of metals from the substrate and titanium transition layer may be explained by the film’s small thickness.](image)

The Raman spectra of coatings with two characteristic features known as D- and G-bands are presented on figure 2. The G-band is associated with optical vibrations of carbon atoms in the basal plane of graphite crystal lattice. If some degree of structural disorder is introduced in the structure of graphite phase the G-band becomes broader and shifts in direction of smaller wave vector values. The D-band is characteristic to all disordered $sp^2$-type structures. The position of this band with $sp^2$-disordering changes is stable but its intensity may change strongly. At low degrees of disorder the D-band may have the form of a “shoulder” at the left side of the graphitic G-band or may take form of an
independent spectral maximum if the disorder increases. The position and the width of the D-band as well as the intensity ratio $I_D/I_G$ and the G-band width may to the opinion of some authors be used to estimate the “graphitization index” – the degree of DLC coating structure graphitization.

For the vacuum-arc technology used in this investigation the $I_D/I_G$ ratio is significantly ~5 times, higher for coatings alloyed with nitrogen (see table 1 where the characteristics of other nitrogen-doped typically hydrogenised films are also presented for comparison). Thus nitrogen leads to significant changes of the coating’s Raman spectrum (figure 2).

![Figure 2. Raman spectra $I_D(\delta_R)$ of $a$-C (a) and $a$-C:N (b) coatings.](image)

The data collected in table 1 demonstrate that alloying with nitrogen leads not only to DLC structure graphitization but also significant changes of mechanical characteristics are observed. The trend of these changes may be different depending on the type of deposition technology used by the authors.

| Coating type | [N], at. % | Thickness, nm | $I_D/I_G$ | $H_c$, GPa | $E_c$, GPa | $H/E$ | Carbon source (technology) | Issue |
|--------------|------------|--------------|-----------|-----------|-----------|-------|--------------------------|-------|
| $a$-C        | 0          | 150          | 0.21      | 28        | 178       | 0.157 | Graphitic cathode (vacuum cathode arc) | Present work |
| $a$-C:N      | 10         | 500          | 1.14      | 35        | 146       | 0.24  | | |
| $a$-C:H      | 0          | 1500         | 0.97      | 14.4      | 105       | 0.137 | | |
| $a$-C:H:N    | 12         | 1900         | 0.98      | 8.6       | 87        | 0.099 | C$_2$H$_2$ + CH$_4$ (CFUBM) | [3] |
| $a$-C:H:N    | 29         | 2300         | 2.51      | 4.2       | 41        | 0.102 | | |
| $a$-C:H      | 0.1        | –            | 1.5       | 14.3      | 125.5     | 0.114 | CH$_4$ (PA CVD) | [8] |
| $a$-C:H:N    | 3.8        | –            | 2.5       | 13        | 109.5     | 0.119 | | |
| $a$-C:H      | 0          | 160–276      | –         | 38        | 460       | 0.083 | Graphitic target + C$_2$H$_2$ (PVD) | [9] |
| $a$-C:H:N    | max        | –            | 21.5      | 330       | 0.065     |       | |

It may be concluded for example that using graphite targets or cathodes it becomes possible to obtain DLC coatings whose hardness exceeds 30 GPa, these values being more typical for the coatings of tetrahedral amorphous carbon ta-C [2]. At the same time the hardness of $a$-C:H and $a$-C:H:N films obtained by reactive deposition of hydrocarbon gases is typically less than 15 GPa. The type of technology may also influence the “index of plasticity” $H/E$ values, $H/E < 0.1$ in combination with high hardness may certify the DLC coating’s ability to be crack resistant [9]. Thus it may be concluded that the process of friction-induced damage of vacuum-arc deposited coatings with $H/E > 0.15$ have to be brittle.

The results of tribological tests (figure 3) have demonstrated the low antifriction properties of unalloyed $a$-C film ($f = 0.3…0.7$, and the $f$ value gradually grows with increasing $P$). Alloying with nitrogen improves the antifriction behavior reducing $f$ to about 0.2…0.3 for all the loads.

The performance of $a$-C was extremely low, less than 100 cycles for all $P$ values, and the alloying with nitrogen significantly changed the situation: the durability of $a$-C:N period of friction coefficient stability increased to $N > 6000$ for $P = 0.02$ and 0.05 N and was $N \approx 1000$ for $P = 0.1$ N.
The nature of surface friction and wear induced damage the coatings have been studied with SEM. It was established that that the surface of DLC coatings both in unalloyed and nitrogen-alloyed state inherits the grain structure morphology of the 12Kh18N10T steel substrate. The secondary-electron SEM images presented on figure 4 demonstrate that the local defects on the wear track surfaces leading to further fracture damage develop along the grain boundaries of the substrate and at ternary junctions of these boundaries. The friction damage-induced fracture of both types of coatings was brittle.

Figure 3. Load dependence of coefficient of friction $f$ (a) and of $N$ – number of cycles preceding the of friction fatigue-induced damage initiation (b) for coatings: $a$-C (1); $a$-C:N (2) and for substrate material (12Kh18N10T stainless steel) (3).

Figure 4. Surface damage evolution with load in $a$-C:N film: wear tracks at $P = 0.10$ (a) and at $P = 0.15$ N (b).

4. Conclusions
The mechanical and tribological properties of thin vacuum-arc deposited hydrogen-free amorphous carbon $a$-C and $a$-C:N coatings have been studied. Their extremely high micromechanical properties have allowed us to suppose that the amorphous carbon in both unalloyed and nitrogen-alloyed coatings of this type has tetrahedral amorphous structure of $ta$-C. The tribological tests have demonstrated that alloying with nitrogen significantly improves of performance of $a$-C:N coatings as compared with $a$-C.

The investigations of coating surfaces with scanning electron microscopy have shown that their morphology is inherited from the steel substrate and that the processes of the coating’s frictional fatigue-induced damage and cracking initiates in the vicinity of these “substrate-determined” boundaries and of their ternary junctions.

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