Tribological behavior of coatings deposited by reactive magnetron sputtering of silicon in acetylene-nitrogen gas mixtures

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Abstract. The composition, micromechanical properties and tribological behavior of silicon-based coatings obtained by reactive magnetron sputtering of silicon have been investigated. The results of the friction fatigue tests and the peculiarities of the friction surface failure in several types of vapor-deposited silicon-based coatings have been discussed.

The use of silicon for diamond-like carbon (DLC) coatings alloying has become widespread due to the ability of this kind of alloying to reduce internal stresses that cause the appearance of microcracks and damaged areas on wear tracks, improve the temperature stability of functional properties, corrosion- and wear-resistance [1, 2]. The presence of silicon also allows reducing the effect of the environmental humidity on the DLC coatings coefficient of friction, which is associated with the easy formation of silicon hydroxides during friction [3]. Taking this into account the investigation of DLC coatings alloyed only with silicon and with a silicon-molybdenum combination obtained by the method of plasma-assisted chemical vapor deposition (PACVD) from organosilicon precursor gases was performed by the authors [4]. It has shown the low antifriction properties of these coatings whose coefficient of friction $f$ was $>0.5$ that made impossible to use them as tribological coatings.

Taking into account that the authors have already managed to obtain by reactive magnetron sputtering in acetylene-based atmospheres some DLC chromium-[4] and titanium-alloyed [5] coatings that have demonstrated their high tribological performance, the aim of the present research was to use reactive magnetron sputtering to obtain silicon-based coatings whose tribological characteristics may allow to use them in friction units.

The magnetron sputtering unit and the technology of reactive magnetron sputtering deposition were similar to those used by the authors earlier [4, 5]. Argon was used as a sputtering during; pure acetylene, nitrogen and their mixtures with 20, 40, 60 and 80 vol. % nitrogen were used as a reactive atmosphere; the target material was silicon. At the same time, only coatings deposited applied at 40,
80 and 100 vol. % of nitrogen turned out to be mechanically stable after deposition. (all other coatings have delaminated a short time after the extraction from the vacuum chamber due to a high level of internal stresses in them). The characteristics of coatings suitable for further study and tribological testing are given in table 1 (nos. 1–4), the data on two silicon-doped PACVD coatings studied earlier [4] are presented for comparison (nos. 5–6).

Table 1. Reactive atmosphere composition, chemical composition, thickness, nanohardness $H$ and elastic moduli $E$ of coatings.

| No. | Reactive gas mixture composition, vol. % | Chemical composition, at. % | Chemical formula and structure type (in parentheses) | Coating thickness $^{(1)}$, $\mu$m | $H$, GPa | $E$, GPa |
|-----|----------------------------------------|-----------------------------|------------------------------------------------------|-----------------------------------|---------|--------|
| 1   | C$_3$H$_3$ 60, N$_2$ 40, [Si] 42, [C] 51, [N] 7 | Si$_{0.42}$C$_{0.51}$O$_{0.07}$ (SiC) | 4.0 | 18 | 190 |
| 2   | 20, 80, 88, 88, 3  | Si$_{0.88}$O$_{0.12}$ (Si) | 2.5 | 28 | 216 |
| 3   | – 100, 57.5, 1.5, 41, – | Si$_{0.58}$N$_{0.41}$ (Si$_3$N$_4$) | 4.4 | 17.6$^2$ | 304$^2$ |

Plasma-assisted CVD from organosilicon precursor gases [4, 5]

| No. | Reactive gas mixture composition, vol. % | Chemical composition, at. % | Chemical formula and structure type (in parentheses) | Coating thickness $^{(1)}$, $\mu$m | $H$, GPa | $E$, GPa |
|-----|----------------------------------------|-----------------------------|------------------------------------------------------|-----------------------------------|---------|--------|
| 4   | a-CHSiO 14, 66, 2, 17 | Si$_{0.14}$C$_{0.66}$O$_{0.17}$N$_{0.02}$ | 0.5-1.0 | 8 | 70 |
| 5   | a-CHSiMoO 36, 40, 8 | Si$_{0.36}$Mo$_{0.16}$C$_{0.4}$O$_{0.08}$ | 0.5-1.0 | 15.4 | 147 |

Notes: $^{(1)}$ the thickness of coatings nos. 1–3 is calculated from the weight gain in the deposition process based on the density of the corresponding crystal phases (given in parentheses);

$^{(2)}$ $H$ and $E$ values from [7] used as estimates.

In the group of the magnetron sputtered coatings presented in table 1 only the coating no. 1 has a composition close to a silicon carbide SiC stoichiometry with a small admixture of oxygen. The coating no. 2 contains almost 90 at. % silicon. The coating no. 3 composition is close to Si$_3$N$_4$, i.e. an excess of silicon in it indicates that it possibly may have a two-phase Si + Si$_3$N$_4$ structure.

The organosilicon-based PACVD coatings $a$-C:H:Si:O and $a$-C:H:Si:Mo:O previously studied in [4] are denoted in table 1 by nos. 4 and 5. The nanohardness values of coatings 1, 2, 4 and 5 were measured on the NHT Nanohardness tester (CSM International). For the coating no. 3 the values of $H$ and $E$ for a hot-pressed Si$_3$N$_4$ ceramics were used as an estimate [6]. Tribological tests of all coatings were carried out on a single-ball tribometer according to the ball-on-disk scheme with a silicon nitride ceramic counterpart. To estimate the tribological performance of coatings the tribological test for friction fatigue was used [7]. The results of tribological testing of coatings nos. 1–4 are presented in figure 1 (the data for the silicon-molybdenum alloyed coating (no. 5) being significantly worse than those of coating no. 4 are not presented).

The SEM micrographs of the wear tracks for coatings nos. 1 and 3 are presented in figure 2. One may see that a rather high porosity of these coatings. As it follows from figure 2(a) no significant traces of surface failure are observed in coating no. 1 for the entire range of loads (P = 0.02–0.2 N) used in tribological tests. In contrast to this in coating no. 3 certain signs of surface failure are visible even at minimal loads (figure 2(b)).

The comparison of figures 1 and 2 clearly demonstrates the behavior of the coefficient of friction correlates with the nature and degree of surface failure observed during friction. For example, in coating no. 3 the nature of surface damage is brittle starting with $P = 0.05$ N – the areas with a well developed relief appear. This relief may be explained by numerous chipping of the near-surface layer of this coating. In some areas, small near-surface chips are observed already at $P = 0.02$ N (figure
2(d)). Simultaneously with the beginning of this type of brittle failure on may see a sharp increase in the coefficient of friction $f$ for coating no. 3 (figure 1(a)).

![Graph](attachment:graph.png)

**Figure 1.** The dependences of: the coefficient of friction $f$ (a) and the number of the tribological test cycles $N$ (b) preceding the coating failure initiation on load $P$ (the coating numbers are the same as in table 1).

![Micrographs](attachment:micrographs.png)

**Figure 2.** Micrographs of wear tracks of coatings no. 1 (a, b) and no. 3 (c, d): (a, c) – general views (the load $P$ increases from 0.02 to 0.2 N when moving from the periphery to the center of coatings); (b, d) – wear tracks at $P = 0.02$ N.

In contrast to this in coating no.1 mainly the plastic deformation of the surface layer is observed during friction (figure 2(b)). As the load increases the width of the observed wear track grows which is explained by the increase of the contact area diameter. Thus at $P > 0.1$ N smearing of the coatings’
material may be noted. This smearing is accompanied with the decrease in the coatings’ pore size especially for pores located in the central (middle) part of the wear track and the process of the wear surface smoothing. At the same time the filling up of the open surface pores with wear products having the same composition as the main coating takes place. The coefficient of friction of coating no. 1 changes little with load remaining close to $f \sim 0.35$, which is about half that of the PACVD coating no. 4. One may conclude that the coating no. 1 has shown high friction fatigue performance in the entire range of loads $P$ (figure 1(b)). The sufficiently high value of $f \sim 0.35$ observed in this case seems to be explained by the coating no. 1 composition close to that of silicon carbide SiC. This is consistent with the data on the coefficient of friction of coatings obtained by PACVD technology in a mixture of SiCl$_4$-methane in [8]. Note that the minimum coefficient of friction $f \leq 0.1$, according to these authors, should be observed in coatings with (15÷25) at. % Si.

The typical SEM micrographs illustrating the nature of surface failure modes observed in tribological tests of coatings nos. 4 and 5 obtained with organosilicon precursors are presented in figure 3. These coatings having X-ray amorphous structure are designated in table 1 as $a$-C:H:Si:O and $a$-C:H:Si:Mo:O, respectively. The presence of oxygen in their formulae is due to the decomposition of different organosilicon compounds used in their synthesis [2].

\[\text{Figure 3. Micrographs of coatings no. 4 (a, b) and no. 5 (c, d): (a, c) – selected segments of wear tracks with characteristic types of surface damage; (b, d) – typical forms of wear particles.}\]

It may be concluded from figure 3 that the nature of surface failure at dry friction on air for the coatings doped only with silicon (no. 4) and with a combination of silicon and molybdenum (no. 5) is significantly different. For the coating no. 4 (designated also as $a$-C:H:Si:O), the observed local delaminations of coating might be associated with the brittle fracture propagating along the coating–substrate interface when sufficiently large coating areas being delaminated (figure 3(b)) as relatively large fragments. At the same time the SEM micrographs obtained in the back-scattered electrons regime have demonstrated that there was no subsequent crushing of these fragments into smaller ones.
Unlike a-C:H:Si:O the surface wear of coating no. 5 (a-C:H:Si:Mo:O) was catastrophic in nature and was accompanied by the denudation of large substrate areas in places where the wear track surface has been subjected to severe contact deformations (figure 3(c)). In this case the considerable fragmentation of “primary” wear particles was also observed (e.g. figure 3(d)). The back-scattered electrons SEM micrographs of a-C:H:Si:Mo:O coating demonstrate that even the wear products observed in secondary electron mode as the relatively large particles may in reality be are actually agglomerates of smaller “secondary” wear particles. According to [4] these “secondary” products of the no. 5 (a-C:H:Si:Mo:O) coating catastrophic wear have a high concentration of oxygen and silicon, ~50 and ~ 30 at. %, respectively, which indicates the formation of silicon hydroxides, is associated with tribostimulated silicon oxidation processes occurring during mechanical fragmentation and further severe plastic deformation of the "third" body particles formed during the processes of dry friction on air.

It has been demonstrated that the tribological properties of the silicon-based coatings obtained by reactive magnetron sputtering in acetylene-nitrogen reactive gases mixtures are significantly higher than those of the previously studied CVD coatings obtained by organosilicon precursor gas decomposition. The coatings obtained by magnetron sputtering in a mixture of acetylene with about 40 vol. % nitrogen in heavily loaded tribological contact conditions have shown high friction fatigue resistance but their coefficient of friction as high as ~ 0.35, may be explained by their composition being close to SiC. Thus the further research directions should be aimed to reduce the Si/C ratio to ~ 0.2–0.25 and to ensure an acceptable level of internal stresses.

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References
[1] Khrushchov M M 2013 Doped diamond-like coatings for tribology Sovremennie tekhnologii modifikatsirovania poverkhnostei detaili mashin (Modern Technologies of Machine Parts Surfaces Modification), ed G V Moskvitin (Moscow: Lenand) pp. 78–113
[2] Meškinis Š and Tamulevičienė A 2011 Materials Science (Medžiagotyra) 17 358–70
[3] Oguri K and Arai T 1991 J. Surf. Coat. Technol. 47 710–21
[4] Levin I S, Khrushchov M M, Marchenko E A and Avdyukhina V M 2016 Moscow Univ. Phys. Bull. 71 186–92
[5] Khrushchov M M, Marchenko E A, Levin I S, Avdyukhina V M, Kashourkin E V, Atamanov M V, Petrzhik M V and Obraztsova E A 2019 J. Phys.: Conf. Ser. 1313 012028
[6] Gong J, Miao H, Peng Z and Qi L 2003 Mat. Sci. Eng. A 354 140–5
[7] Kombalov V S 2008 Metody i sredstva ispitaniy na trenie i iznos konstruktsionnykh i smazchynyh materialov (Methods and Tools for Friction and Wear Tests of Structural Materials and Lubricants) ed. K V Frolov and E A Marchenko (Moscow: Mashinostroenie)
[8] Oguri K and Arai T 1992 Thin Solid Films 208 L58–60