Structure and tribological behavior of titanium-based coatings deposited by reactive magnetron sputtering

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Abstract. The structure and functional properties of coatings deposited by reactive magnetron sputtering of titanium in acetylene-nitrogen mixtures of different composition have been studied. It has been established that all the coatings contain the amorphous (diamond-like) carbon phase, and different types of stoichiometric and non-stoichiometric titanium carbide, nitride and oxide phases. The tribological tests for friction fatigue have demonstrated that the coefficient of friction values for coatings were rather low and that they remained operational at contact pressures up to 450 MPa.

1. Introduction
The development of coatings for machine parts surface strengthening and the study of their functional properties are one of the structural materials science basic problems. Films and coatings based on titanium carbides and nitrides are widely used in machinery manufacturing and instrument making as strengthening, corrosion-resistant, thermo-barrier and decorative layers. The diamond-like carbon (DLC) coatings and nanocomposites modified by titanium are also a promising tribological material that provides a combination of high wear-resistant and antifriction properties [1]. In their previous publications the authors have studied the behavior of chromium-doped nanocomposite DLC coatings obtained by magnetron sputtering in a mixture of acetylene and nitrogen reactive gases [2]. They have demonstrated that nitrogen when added during Cr–DLC film sputtering significantly improves mechanical and antifriction properties, at the same time reduces the frictional-fatigue resistance and the adhesion strength of the coatings [3].

Thus, the aim of the present study has been to obtain coatings with titanium by magnetron sputtering of titanium metal target in acetylene and nitrogen reactive gas mixtures and to investigate the peculiarities of phase composition and structure of these coatings, supposed to contain the diamond-like carbon, as well as their mechanical and tribological behaviors.
2. Experimental methods

The technology of magnetron sputtering deposition analogous to that described by us in [2] has been used. The coatings were deposited on substrates made from 12Kh18N10T (AISI 321-type) steel. Data on the composition of the reactive gas mixture, chemical composition and thickness of coatings are presented in table 1. The coatings obtained by magnetron sputtering were characterized by a significant level of internal stresses which might result in their delamination and peeling that in particular had prevented from obtaining a titanium-based coating in pure acetylene. To avoid this undesired effect the thickness of coatings with nos. 2–4 has been made significantly less than that of the no. 1.

| No. | Reactive gas content, vol. % | Chemical element concentration, at. % | Thickness, µm |
|-----|--------------------------------|-------------------------------------|---------------|
| 1   | 80 C₂H₂, 20 N₂                | [Ti] 13.4, [C] 86.6, [N] –, [O] –   | 4.0           |
| 2   | 60 C₂H₂, 40 N₂                | [Ti] 29.5, [C] 5.2, [N] 65.3, [O] – | 0.6           |
| 3   | 40 C₂H₂, 60 N₂                | [Ti] 23.1, [C] 3.5, [N] 43.5, [O] 30.0 | 0.7           |
| 4   | 20 C₂H₂, 80 N₂                | [Ti] 28.8, [C] –, [N] 34.5, [O] 36.7 | 0.6           |

The coatings then have been subjected to a comprehensive study by means of X-ray powder diffractometry, Raman spectroscopy, instrumented nanoindentation and tribologically tested for friction-fatigue. The nanohardness of coatings and their elastic moduli have been studied on a NHT (CSM International) nanohardness tester using the Oliver-Pharr method. Tribological tests of coatings were performed on a “sphere-on-disk” tribometer. The tests were carried out in air in dry friction mode; the counterbody material – silicon nitride; the test base – 6000 cycles; the load \( P = 0.02–0.20 \) N and Hertzian contact pressures – 230–450 MPa. The Raman spectra were obtained using an “Horiba LabRam” spectrometer with exciting laser radiation wavelength – 532 nm.

The X-ray investigation has been performed in symmetric \( \theta–\theta \) and asymmetric geometry on the Thermo ARL XTRA and the Empyrean (Malvern Panalytical) diffractometers, respectively. The latter instrument equipped with a highly sensitive semiconductor detector and with parallel beam optics has been used because the X-ray intensity curves taken in symmetric geometry, even after their processing by the method described in [4], turned out to be uninformative and very difficult to interpret. The use of asymmetric technique with the incident beam glancing the coated surface has significantly increased the "effective" layer thickness involved in formation of a scattered X-ray intensity distribution. The diffraction patterns thus obtained have been quite informative (see figure 1) which have made possible the analysis of phase composition of coatings and even quantitative estimates of the phases content in the near-surface layer.

![Figure 1](https://example.com/figure1.png)

**Figure 1.** The X-ray intensity curve for the sample no. 1 measured in asymmetric geometry (incidence angle – \( \alpha =-2 \) deg) and its deconvolution. Symbols (colored in online version) with the reflections indices above them correspond to the phases observed in coating.
The diffractograms of coatings have been processed using the “Origin-8.5” and “Fityk-0.9” computer programs and the phase composition determinations by means of the “MDI Jade 6” program with the ICDD PDF-2 database used as a source of X-ray reference data. To estimate the size of the coherent diffracting domains \(D\) the coating diffraction pattern was decomposed into the constituent phases’ intensity peaks and then the Scherrer equation [5] was used to determine the \(D\) values of all the reflections observed. The data concerning the phase composition of coatings and the coherent diffracting domains sizes are given in table 2.

Table 2. Phases observed in coatings, the size of coherent diffracting domains \(D\) and phase content (estimated from the results of XRD intensity measurements in asymmetric geometry).

| No. | Phase type | \(D\), nm | Phase content, vol. % | Phase type | \(D\), nm | Phase content, vol. % | Phase type | \(D\), nm | Phase content, vol. % |
|-----|------------|----------|----------------------|------------|----------|----------------------|------------|----------|----------------------|
| 1   | C\(^a\)    | 1–1.5    | 20                   | (TiO\(_{1.20}\))\(_{3,12}\) | 1–2       | 59                   | TiC        | 1–4      | 16                   |
| 2   | –          | –        | –                    | TiO        | 2–7      | 46                   | TiN        | 3–7      | 54                   |
| 3   | –          | –        | –                    | Ti\(_{3}O\(_{5}\)\) | 4–23     | 47                   | TiO\(_{0.34}\)N\(_{0.74}\) | 8–20     | 53                   |
| 4   | \(\beta\)-C\(_{3}\)N\(_{4}\) | 2–8    | 64                   | TiO        | 1–3      | 18                   | TiN        | 2–15     | 18                   |

\(^a\) PDF Card # 01-074-2328.

3. Experimental results and discussion

Data on the chemical composition of coatings (table 1) indicate that of all the studied coating to the only no. 1 obtained in a mixture with 80 vol. % acetylene can be attributed to the carbon-based ones. At the same time the phase composition of the coatings determined by x-ray diffractometry is according to table 2 a combination of stoichiometric and non-stoichiometric titanium oxides and nitrides. The carbonaceous phases were found only in samples nos. 1 and 4. The rather large concentration of oxide phases observed in coatings including those with no oxygen in their chemical composition to our opinion might be explained either by oxidation of titanium present in near-surface layer of coating due to its interaction with air from environment, or by the presence of water vapor in residual vacuum during deposition. As the interpretation of experimental X-ray intensities in this investigation has used only the results obtained in asymmetric geometry that is aimed to lengthen the path of the incident X-ray radiation in the coating material, the first variant seems to be preferred because the information on the structure of the near-surface layers of material prevails in X-ray intensity detected in asymmetric geometry with small values of incidence angles [6].

Investigation of the Raman spectra of coatings (figure 2) has revealed the presence of D and G peaks typical for a disordered diamond-like (amorphous) hydrogenated carbon \(a\)-C:H structure in all them. The intensity of Raman scattering \(I_R\) measured in sample no. 1 deposited at 80 vol. % of C\(_2\)H\(_2\) was large proving the presence of a high concentration of diamond-like phase. For samples no. 2–4 deposited at acetylene contents from 60 to 20 vol. % the intensity \(I_R\) was much weaker, and the volume concentrations of \(a\)-C:H in them should be much lower being presumably less than 5 %. The D and G peak intensities ratio \(I_D/I_G\) for all the coatings was rather large that means a high level of amorphous hydrocarbon phase graphitization. The linear size of the regions with preferred sp\(^2\)-type graphite-like coordination of carbon atoms in this \(a\)-C:H phase has been estimated by means of an empirical formula proposed in [7] to calculate it from \(I_D/I_G\) experimental values and was found to be about 5 nm.

The results of nanohardness and tribological tests are shown in figure 3. The nanohardness values of coatings are in the range between 10 and 20 GPa and change unmonotonously with reactive gas concentration – the nanohardness of coatings deposited in gas mixtures with 20 and 80 vol. % of acetylene is less than that of coatings sputtered with 40 and 60 vol. % C\(_2\)H\(_2\).

The tribological tests performed at contact pressures varying from 230 to 450 MPa (at load from 0.02 to 0.2 N) have shown that the performance of all coatings was higher than \(N = 6000\), the maximum number of cycles used in this investigation. The coefficients of friction of coatings were in
principle higher than those of Cr-DLC coatings reactively sputtered in C_2H_2–N_2 mixtures of the same composition [2, 3]. Nevertheless their values were enough low (f ~ 0.2...0.3) to conclude that these titanium-based coatings may have good perspectives of their use in friction parts of machines.

![Figure 2.](image)

**Figure 2.** Raman spectra of coatings: (a) – no. 1 (I_D/I_G = 4.1), (b) – no. 2 (I_D/I_G = 4.8) and (c) – no. 4 (I_D/I_G = 3.5).

![Figure 3.](image)

**Figure 3.** The coating nanohardness variation with acetylene content in an acetylene-nitrogen reactive gas mixture (a) and the coefficient of friction dependence on load (b). The coatings are numerated in accordance with table 1.
4. Conclusions
Coatings obtained by reactive magnetron sputtering of titanium in acetylene and nitrogen mixtures have been demonstrated to possess nanocomposite structures based on the carbide/nitride and oxide phases of titanium whose coherent diffracting domains size varies from 1.5 to 20 nm.
Raman spectroscopy of coatings has shown the presence of diamond-like carbon phase whose amount decreased with the increase of nitrogen content both in reactive gas mixture and in coatings. The value of nanohardness of coatings ranges from 10 to 20 GPa and behaves unmonotonously with acetylene-nitrogen gas mixture composition. The results of tribological tests have shown that the coefficient of friction is about 0.2–0.3 and its dependence on load is weak. The coatings have demonstrated high performance when working in regime of a heavy-loaded friction contact.

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