Morphology of multilayer metal-carbon coatings with different arrangements of functional layers

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Abstract. The surface morphology of multilayer metal-carbon coatings before and after annealing in the air atmosphere at temperature of 350°C for 60 minutes was investigated by atomic force microscopy. The coatings were obtained by the arc discharge method. The surface morphology, roughness, and adhesion forces largely depend on the type of deposit layers and their sequence (architecture). Annealing in air at temperature of 350°C differently affects the properties of coatings of different designs.

1. Introduction
During the last decades, metal-containing diamond-like coatings (Me/α-C or α-C:Me) deposited by various methods of physical spraying (PVD) or chemical vapour deposition (CVD) have become widespread in various engineering industries due to their high hardness as well as wear- and chemical resistance. The wide use of such coatings in pure form is limited by the low adhesion to the substrate.

Various methods are used to increase the adhesion of such coatings by controlling their structure. One of them is the inclusion of metal and nitride layers in the coating. They perform the function of adhesion and damping layers [1]. Metal and nitride layers make it possible to increase the strength of the adhesive bond between the coating and the substrate. It was found that the residual stress in α-C coatings decreased and adhesion increased after depositing a carbon coating on a sublayer of a carbide-forming metal (chromium or titanium) [2].

There are various ways of investigation and control of the thin multilayer coatings properties. Atomic force microscopy (AFM) is one of the multifunctional methods. It allows evaluating the parameters and properties of the surface [3-8]: roughness, average grain size, elastic modulus, adhesion forces, deformation, and others. AFM allows carrying out tests for wear and friction [9-13].

The aim of this work was to investigate the influence of annealing and coating design on morphology, roughness, and adhesion force of the surface of multilayer metal-carbon coatings.

2. Experimental details
Two- and three-layers metal-carbon coatings were produced: Ti-(Ti+α-C) – № 1; Ti-(Ti+α-C)-α-C – № 2; Ti-(TiN+α-C)-α-C – № 3; Ti-(TiN+α-C) – № 4; TiN-(Ti+α-C) – № 5 (Fig. 1).

The carbon component of the coating was deposited by a pulsed arc-cathodic method at the pulse frequency of 15 Hz and the discharge voltage of 350 V. The alloying with the nitrogen was due to the sputtering at the nitrogen partial pressure in the chamber of 5×10⁻² Pa. The metal component was...
formed using the direct current arc discharge at the arc current of 70 A. The titanium of the VT-100 grade was used as a cathode. The thickness of the coatings depended on its architecture and was in the range from 300 to 500 nm. Two- and three-layers metal-carbon coatings were formed on silicon single crystal substrates with the (100) preferred crystallographic orientation. The samples annealing was carried out in the air atmosphere at the temperature of 350°C for 60 minutes.

The surface morphology, roughness $R_a$ and adhesion forces $F_{ad}$ measurements were performed using Dimension FastScan AFM (Bruker, USA) in the PeakForce Tapping QNM (Quantitative Nanoscale Mechanical Mapping) mode with the standard silicon probe type MPP-12120-10 (Bruker, USA) with the curvature radius 42 nm and the cantilever stiffness of 6.2 N/m.

3. Results and discussion

The surface images of multilayer metal-carbon coatings before and after annealing were obtained by AFM (Fig. 2). The surface is the "smooth coating" with particles evenly distributed over the surface. The "smooth coating" consists of cluster formations of 50-70 nm in size with undefined boundaries. Such morphology is typical for nanocomposite multilayer metal-carbon coatings.

Annealing in air at 350°C affects the metal-carbon coatings differently. The particles quantity on the surface of some coatings decreases: Ti-(Ti+α-C), Ti-(TiN+α-C)-α-C, and Ti-(TiN+α-C). In other coatings Ti-(TiN+α-C)-α-C and TiN-(Ti+α-C), amount and particles size increase. After annealing, the cluster formations size of the "smooth coating" increases or remains unchanged.

The coatings surface roughness $R_a$ (Table 1) during annealing decreases almost for all samples. The growth of $R_a$ was only on TiN-(Ti+α-C) coatings surface. This is due to the increase in the amount of submicron-particles of 100-230 nm after annealing on the surface of TiN-(Ti+α-C).

The particle size on the surface of Ti-(Ti+α-C)-α-C coating decreases after the annealing from 100-370 nm to 36-97 nm. So, the roughness $R_a$ decreases from 1.04 to 0.15 nm. The same changes proceed in Ti-(TiN+α-C) coating. Annealing practically did not change the properties of Ti-(Ti+α-C) coating.

The adhesion forces of coatings during annealing decrease or increase either. The adhesion forces increase from 1.33 to 4.60 nN and from 3.19 to 6.97 nN, respectively, in the two-layer TiN-(Ti+α-C) coating and the three-layer Ti-(TiN+α-C)-α-C coating. Annealing leads to the decrease in the adhesion forces all the other coatings.
Figure 2. Surface morphology of multilayer coatings before (a,b,c) and after (d,e,f) annealing: (a,d) – №3 (Ti-(TiN+α-C)-α-C); (b,e) – № 4 (Ti-(TiN+α-C)); (c,f) – № 5 (TiN-(Ti+α-C)).

Table 1. Surface roughness $R_a$ and adhesion forces $F_{ad}$ of investigation coatings before and after annealing (scanning area 2x2 $\mu$m$^2$).

| №  | Multilayer coating           | Before annealing | After annealing |
|----|-------------------------------|-----------------|-----------------|
|    |                               | $R_a$, nm       | $F_{ad}$, nN    | $R_a$, nm       | $F_{ad}$, nN    |
| 1  | Ti-(Ti+α-C)                   | 0.11±0.01       | 1.55±0.08       | 0.17±0.01       | 1.03±0.05       |
| 2  | Ti-(Ti+α-C)-α-C               | 1.04±0.05       | 6.39±0.03       | 0.15±0.01       | 1.53±0.08       |
| 3  | Ti-(TiN+α-C)-α-C              | 0.46±0.02       | 3.2±0.2         | 0.40±0.02       | 7.0±0.4         |
| 4  | Ti-(TiN+α-C)                  | 0.21±0.01       | 2.8±0.1         | 0.14±0.01       | 0.32±0.02       |
| 5  | TiN-(Ti+α-C)                  | 0.20±0.01       | 1.33±0.07       | 0.63±0.03       | 4.6±0.2         |

The increase in the adhesion forces of Ti-(TiN+α-C)-α-C and TiN-(Ti+α-C) coatings during annealing can be due to diffusion between TiN and α-C layers. It is assumed that the annealing increases the adhesion forces of the entire multilayer coating: the adhesion between the layers and the adhesion of the coating to the substrate.

4. Conclusion
The influence of the architecture, the type of deposited layers and the annealing on the morphology of the surface, roughness, and adhesion forces were investigated by atomic force microscopy. It was established that the annealing in air at 350°C differently affected the coatings of various designs. The particles number on the surface and roughness decreased for Ti-(Ti+α-C)-α-C and Ti-(TiN+α-C)
coatings. Annealing of Ti-(TiN+α-C)-α-C and TiN-(Ti+α-C) coatings led to the increase of surface adhesion. It was assumed that during annealing process diffusion occurred between TiN and α-C layers. Therefore, it is possible to reduce the surface roughness and increase the adhesion of the multilayer metal-carbon coatings after annealing considering their architecture.

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