The tribological characteristics and structural state of Ti-Al-Si-Cu-N coatings in temperature range test to 300 °C

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Abstract. The study of tribological characteristics and the structural state of Ti-Al-Si-Cu-N gradient-layer coatings has found that, for temperatures up to 100 °C, these coatings are subject to abrasive and oxidative wear. Increase in their coefficient of friction is associated with cracking, tribofilm formation, and delamination of tribofilm and coating, with the formation of track relief due to localization of substrate deformation. An increase in the test temperature to 300 °C results in adhesive wear.

1. Introduction
Currently, synthesis of wear-resistant coatings is focused on creating a structure and architecture of multi-element compositions on the basis of the emerging technology for producing gradient [1, 2] and/or adaptive coatings [3] with specific functional layers or separate phases. Characteristics of deformation and destruction of these layers are associated with characteristics of a defect microstructure, phase composition and alloying elements of a coating, which can contribute to contact stress relaxation, i.e. improving the wear resistance of a coating due to the activation of specific deformation mechanisms, formation of plastic phases or antifriction surface films. In this connection, the paper is aimed at studying tribological characteristics, and microstructural deformation and destruction patterns of titanium nitride coatings doped with Al, Si and Cu, with a structure combining submicrocrystalline and surface nanocomposite layers.

2. Experiment
The coatings were produced by magnetron sputtering of targets Ti (VT1-0 alloy), Al_{60}Si_{40} alloy and commercial purity copper in argon and nitrogen by assisting two sources of gas (nitrogen) plasma on a HSS substrate. The substrate surface was cleaned and heated with argon ions at a bias potential of $U_s = -350$ V. A titanium sublayer was deposited and nitrided in a nitrogen gas discharge with a negative bias of 6 kV. The coatings were deposited at a bias potential $U_s = -200$ V and substrate temperature ~150 °C. The sputtering power of the copper target was varied in the range of 0.1–0.35 kW. The thickness of the coating with the sublayer was about 1.2 μm.

Tribological tests were performed with a high-temperature tribometer (THT) manufactured by CSM Instruments with a counterbody made of W-Co alloy in the form of a ball with a diameter of 6 mm, at a load of 1 N, linear velocity of 5 cm/s, track length of 100 m, and humidity of 65% in the temperature range of 100–300 °C.

3. Results
Based on known regular effects of deposition conditions on the composition and structure, gradient-
layer coatings (see [4] for details) were synthesized, with thickness-variable elemental and phase compositions corresponding to the formation of a two-phase titanium nitride–copper mixture in the surface layer.

Tribological tests of coatings at room temperature have shown that the coefficient of friction increases from ~0.18 to 0.55. Oscillations of its value indicate localized deformation and destruction. The profilometry of the track surface shows the formation of a surface relief with the height difference between its points not exceeding 0.7 μm. These findings are confirmed by microscopy results, indicating that the surface relief is formed by a tribofilm with a thickness up to ~500 nm in some areas (figure 1(a)) and with insignificant wear (no more than 100 nm) of the coating. It has been found that the tribofilm has an amorphous structure and includes elements of the coating, counterbody and oxygen. Oxygen concentration can reach ~50 at. %.

Figure 1. Coating structure in the tribotrack zone at room temperature: (a) – transmission electron microscopy in cross section: 1 – tribofilm, 2 – coating; (b) – scanning electron microscopy of the track surface: 1 – clusters of cracks, 2 – delaminated region.

The tribofilm is cracked and cannot be found in some surface regions, suggesting that it has been removed from the friction surface, which affects wear and coefficient of friction. Clusters of cracks formed on the friction surface are spaced at about 100 μm. In some of them, there are delaminations of the coating ~10 μm (figure 1(b)). It has been found that the delamination mechanism of the coating is as follows: the coating is pressed into the substrate (figure 1(a)) with the formation of steps across the slip. The pressure on steps increases; these steps are cracked and filled with the tribofilm material, the action (pressure) of which opens the crack and initiates cracking along the coating-substrate interface. For destruction zones, it has been found that the bending-torsion of the crystal lattice in nanocrystals remains unchanged, but average sizes of crystals decrease by ~50% to ~4.5 nm compared to the non-deformed state.

It has been shown that the coefficient of friction at a test temperature of 100 ºС has higher values both at the beginning (~0.28) and at the end (~0.90) of the test than that at room temperature, and its behavior during the test is similar at both temperatures. Images of the track surface demonstrate an increase in its width, the presence of a coarser relief with well-defined “scratches” at their greater density and length compared to the test at room temperature (figure 2(a)). The relative area of darker regions on the friction surface increases (by ~60–70 %) (figure 2(a)). The elemental analysis of these regions suggests higher oxygen concentration (~ 40–50 at. %). Therefore, these findings indicate the intensification of oxidative and deformation (“ploughing”) components of wear, but the density of delaminated regions becomes lower with a more uniform distribution of cracks.

The results of electron microscopic studies show that significant (~50%) wear can be found in highly deformed regions of the substrate, which forms the relief. At the same time, the tribofilm on relief steps is either very thin or cannot be detected, while submicron cracks are formed in the coating itself: vertical (when the coating shifts to the substrate) or horizontal (along the boundaries of the layered structure) (figure 2(b)). The study of the defect microstructure of the friction surface shows
that the average size of crystals increases near the surface (up to 100 nm), with a slight decrease in the value of bending-torsion of the lattice in crystals. There is a correlation between this decrease and the increase in the size of the crystal.

![Figure 2](image)

**Figure 2.** Coating structure in the tribotrack zone at a test temperature of 100 °C (a), (b) and 300 °C (c), (d): (a): 1 – steps of the surface topography, 2 – cracks; (b): 1 – crack along the interface of layers; (d): 1 – worn particles of the coating, 2 – tribofilm; (a), (c) – scanning electron microscopy of the track surface, (b), (d) – transmission microscopy in cross section.

It has been found that, with an increase in the temperature of the tribological test to 300 °C, changes in the coefficient of friction become quasi-cyclic with an oscillation amplitude ~ ±0.15 around the mean value ~ 1.0. Large (hundreds of microns in length) regions of coating delamination (up to ~30% of the surface) have been found on the track surface. The adjacent areas have topographic elevations up to 100 μm in size (figure 2(c)) with decreased density and size of cracks. The track coating has a uniform color, suggesting that different regions of the surface have similar elemental compositions.

The analysis of the elemental composition shows that elevated regions have a low concentration of the coating elements, but large (~10–20 at. %) concentrations of the counterbody elements (W and Co) and oxygen (~40 at. %). In adjacent regions, the concentrations of these elements decrease by 2–3 times, but the content of the coating elements increases accordingly. The study of the surface structure shows that the residual coating in elevated regions is pressed into the substrate, while a thick two-phase layer has formed on the top. It is composed of coating fragments of various sizes (up to 400 nm), which are randomly distributed in the amorphous tribofilm (figure 2(d)). The study of the bending-torsion of the crystal lattice in highly destructed regions of the coating shows that its value has increased by about 2 times with a 1.5-fold decrease in the size of the crystals.

### 4. Conclusions

The presented patterns of the tribological behavior of the Ti-Al-Si-Cu-N coating system for tests at room temperature suggest that the wear of the coating is abrasive and oxidative, while oscillations of the coefficient of friction are associated with cracking, tribofilm formation, and delamination of the
tribofilm and the coating. When the temperature of the tribological test rises to 100 ºC, an increase in the coefficient of friction and wear heterogeneity is observed. This process is associated with more intense surface oxidation and tribofilm formation, as well as with the formation of a relief due to localization of substrate deformation. A further increase in the temperature of tribological tests to 300 ºC results in adhesive wear, which leads to high coefficient of friction due to more intense coating destruction and transfer of the counterbody material, as an abrasive, to the friction zone.

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