Thermal stability, mechanical and tribological behavior of Ti-Al-Si-N ion-plasma coating

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Abstract. It is shown that the elemental and phase composition does not change, and the architecture with clearly defined layer boundaries is preserved when annealing the amorphous-nanocrystalline Ti-Al-Si-N multilayer coatings in the vacuum at temperatures of 700-1100 °C. At the same time, the coherent scattering regions of X-ray radiation increase from 8.5-9.5 to 11-12 nm while the microstrains in the crystal lattice decrease from 1.1 to 0.6-0.7%. Structural changes are accompanied by a slight decrease in hardness. Thermal treatment does not change the nature of cohesive fracture of coatings and does not affect their adhesive strength. The decrease in wear resistance after thermal treatment of coatings, manifested in the increasing wear and friction coefficient, is probably due to the changing nature of the cohesive fracture accompanied by the appearance of large fragments that act like high-abrasive particles between friction surfaces. Ti-Al-Si-N coating is characterized by partial oxidation when heated in air up to 800 °C and complete nitride phases transition to oxides and oxynitride compounds at 900 °C.

1. Introduction
At the present time, Ti-Si-N is one of the most intensively studied systems for coating formation. According to [1–2], nc-TiN/am-Si3N4 nanocomposite coatings, in which TiN grains of approx. 4 nm are embedded in an amorphous Si3N4 matrix that forms a continuous mesh with the layers of 0.3-0.5 nm, have high-performance mechanical properties. Such a structure can be achieved if the silicon content makes 6-10 at.% of the coating. The resulting coatings are thermally stable at up to 1000 °C while maintaining a high hardness of about 45 GPa. In addition, the annealing may even add some extra hardness.

Recrystallization of TiN phase in these composites occurs in the range from 800 to 1200 °C, and the temperature of the recrystallization onset increases with the crystallite size decreasing from 10 to 2 nm [3–4]. Crystallization of amorphous Si3N4 phase occurs at temperatures from 1300 to 1700 °C with the formation of α-Si3N4 and β-Si3N4 structure [5].

Another architectural type of nanostructured coatings produced in this system and representing alternating nc-TiN and am-Si3N4 layers is described in [6]. According to the authors, the transition to such a structure makes it possible not only to increase the hardness of the coatings but also ensure their improved fracture toughness. These assumptions result from the general concept, according to which such a morphology influences the fracture toughness of a multilayer structure of coatings due to the possibility of cracks bending at the layer interfaces through shielding the crack tips as a result of elastic deformations at the layer interfaces, forming a more stable distribution of residual stresses and curving the crack.
Creating a more complex architecture of multilayer coatings with alternating layers of nanocrystalline and amorphous phases, for example, by introducing the nanoparticles into the structure of the amorphous layer, can strengthen the coating material and increase its fracture toughness [7]. It seems to be relevant to develop superhard thermally stable nanostructured Ti-Al-Si-N multilayer coatings by introducing nanocrystallites into amorphous Si-N layer.

The present research study examines the thermal stability of such coatings and their physical and mechanical, as well as tribological behavior.

2. Research methods
Coating depositions were carried out with filtered cathodic vacuum arc deposition installation with two disposed flat arc cathodes in the atmosphere of the nitrogen reaction gas. The first cathode was made from titanium and the second one from 80 at.% Al and 20 at.% Si alloy. Evaporating arc current (I) at the cathodes remained constant (120 +/- 5 A). The bias voltage (Ub) ranged from -60 to -120 V.

A coating with a thickness of ~3.5 μm and a modulation parameter of 17-18 nm characterized by a hardness of 48±3 GPa was thermally treated in the vacuum of 10⁻³ Pa at temperatures of 700-1100 °C and in air at temperatures of 700-900 °C for 1 hour.

To determine the phase composition and substructure of the coatings, there was performed the imaging using Ultima 4 Rigaku diffractometer with CoKα radiation and embedded diffracted-beam graphite monochromator in asymmetric geometry (the angle between the incident beam and the sample surface was 5°). Stresses were determined using the sin²Ψ method.

JEM 2100 high-resolution transmission electron microscope was used to conduct structural examinations of the coatings.

Hardness (H), elastic modulus (E), and work of plastic deformation (Wp) of the coatings were measured on Micro-Hardness tester. The progressive load mode CMC was carried out with the following conditions: unloading was allowed only up to 5% of the corresponding maximum applied load of 50mN.

Evaluation of adhesive/cohesive strength was performed by scratching, following the destruction of the samples at a certain load. Studies were carried out with Revetest. The surface to be studied was scratched with a Rockwell-type diamond indenter with a radius of curvature of 200 μm under continuously increasing load.

3. Results and discussion
The study of the morphology of Ti-Al-Si-N coating surfaces before and after the annealing have demonstrated that it shows no noticeable changes and is characterized by a dense mesh structure as it imitates the substrate surface relief, on which noticeable roughness is formed after preliminary gas abrasive treatment (Ra of approx. 0.1 μm).

The initial elemental composition of the coatings, containing Si, Al, Ti and N in the amount of 3.5, 9.8, 37.4 and 49.3 at.% respectively, after thermal treatment in the vacuum does not change.

According to the results of X-ray diffraction analysis of sample coatings before and after annealing, it can be clearly stated that only TiNx phase is presented, since the analyzed X-ray diffraction lines can be attributed to both TiN and AlN because of their overlap, except for titanium nitride line (220). No silicon phases were detected using this method. Electron diffraction studies of the phase composition of the examined TEM coatings made it possible to establish the presence of aluminum nitride with the ZnS wurtzite structure in the coating in addition to titanium nitride (figure 1). X-ray photoelectron spectroscopy method was used to perform the additional studies of the phase composition and determine the state of silicon in the coatings before and after annealing.

Obtained Ti2p3/2, Al2p, Si2p binding photoelectron energies of Ti-Al-Si-N sample coatings remained virtually unchanged before and after annealing. Ti2p3/2 (454.9 eV) and Al2p (74.0 eV) binding energies correspond to TiN and AlN phases, while Si2p (101.6-101.9 eV) correspond to Si3N4 phases. As there are no diffraction lines the silicon phase on X-ray diffraction patterns and electron
diffraction patterns, it can be concluded that Si\(_3\)N\(_4\) is amorphous in coatings before and after annealing.

X-ray structural studies of the characteristics of the coating substructures subjected to heating at 1000 and 1100 °C showed slightly increased coherent scattering regions of X-ray radiation for the TiN phase from 8.5-9.5 to 11-12 nm, with a simultaneous decrease in the microstrains from 1.1 to 0.6-0.7%.

**Figure 1.** Images and electron diffraction patterns of the Ti-Al-Si-N coating before and after annealing.

TEM images show the presence of well-defined multilayer structure in the Ti-Al-Si-N coatings before and after annealing in the entire temperature range (figure 1). There are no blurred boundaries of the coating layers after annealing caused by possible diffusion processes. The thickness of the nanocrystalline TiN layer (dark areas) is about 20 nm, and that of amorphous Si\(_3\)N\(_4\) with nanocrystalline AlN grains (light areas) is about 23 nm.

The values of stresses undergo significant changes in the process of thermal treatment of the studied coatings. The study of the stress state of Ti-Al-Si-N coatings before and after thermal treatment at 900 and 1100 °C shows its decrease from -4.6 to -2.5 and -0.6 GPa, respectively.

Measured hardness, elastic modulus, the work of plastic deformation of sample coatings before and after annealing, as well as calculated H/E and H\(^3/E^2\) parameters, which characterize the resistance of the coating material to elastic and plastic deformations, are shown in table 1.

**Table 1.** Mechanical characteristics of Ti-Al-Si-N coating samples before and after annealing.

| Sample          | H, GPa | E, GPa | H/E | H\(^3/E^2\), GPa | Wp, % |
|-----------------|--------|--------|-----|------------------|-------|
| Before annealing| 48±3   | 462±49 | 0.103 | 0.52             | 36    |
| After annealing | 43±2   | 473±50 | 0.091 | 0.36             | 42    |

As can be seen from the table above, the hardness decreases slightly after annealing at maximum temperature applied in this research. E changes within the measurement error. The portion of the work of plastic deformation increases slightly at nanoindentation of samples, while H/E and H\(^3/E^2\) parameters decrease. This can be explained by a decrease in stresses in the coating material and microstrains in the crystal lattice after annealing.

According to the results of the scratching of Ti-Al-Si-N coating samples measured before and after annealing in the study-specific temperature range, adhesion strength does not undergo significant changes (figure 2). No stripping occurs while scratching, i.e. the coatings are destroyed by a cohesive mechanism associated with plastic deformation and the formation of cracks in the coating material, which distribution is limited to a layered structure.

Discrete touching of the coating surface due to its roughness and subsequent broadening and smoothing of the scratch is accompanied by an increase in acoustic emission under loads up to 51.5 and 27.8 N for the initial and thermally treated surfaces respectively. These loads correspond to the
appearance of the first cracks (Lc1) in the respective corresponding sample coatings. This is demonstrated by a sharp increase in signal intensity in the acoustic emission curve.

The strength of adhesion of the coatings to the base before and after annealing (Lc3) makes approx. 82-72 N. The substrate partially opens under these loads, which is accompanied by a change in the color of the material at the bottom of the scratch and a sharp change in the growth of force intensity and friction coefficient under the load. Full abrasion of the original and annealed coatings does not occur under a load of less than 90 N.

![Figure 2](image1.png)

**Figure 2.** Variation in the friction force (F, H), the friction coefficient (µ), the relative intensity of the acoustic emission signal (AE,%) with respect to the scratch length and the applied load for Ti-Al-Si-N coatings samples and the type of their fracture.

At the same time, the cohesive coating fracture mechanism before and after thermal treatment is somewhat different. After annealing, coating fracture is followed by the separation of relatively large fragments of material and the appearance of numerous cracks at the bottom of the scratch.

When this occurs, the AE amplitude increases under the significantly lower loads on the indenter than those accompanying the scratching of the non-annealed samples (28 N vs. 51 N). This may be due to a decrease in the resistance of the coating material to the occurrence and development of cracks during deformation due to a change in the stress state. It is known that layered coatings are fairly resistant to the crack propagation progress (i.e. they possess high energy threshold for cracks occurrence). At the same time, they are characterized by critical compressive stress, which influences both the resistance to the crack propagation progress, as well as the hardness of the coating material.

It is the relaxation of the stress state, i.e. the decrease in the compressive stresses in the coatings after annealing from -4.6 to -0.6 GPa, that can be the cause of the observed phenomenon when scratching coating samples. The absence of a noticeable decrease in the hardness of the coatings, which have not undergone noticeable changes in the annealing process, as indicated above, argue for the great impact created by their multilayering and nanostructure.

![Figure 3](image2.png)

**Figure 3.** Variation in the friction coefficient of the Ti-Al-Si-N coating with respect to friction length and path.

Tribological tests were carried out to study the effect of thermal treatment on wear and friction coefficient of the coatings under consideration. The friction coefficient and wear of the coating after
annealing increase from 0.51 to 0.69 and from 2.1 to 3.8·10⁻⁵ mm⁹/(N·m). The decrease in wear resistance after thermal treatment of coatings can be not only due to a relatively small decrease in hardness but also due to the changing nature of their cohesive fracture, accompanied by the appearance of relatively large fragments that act as high-abrasive particles between the friction surfaces. The decrease in wear resistance after thermal treatment of the Ti-Al-Si-N coatings correlates with the decrease in H/E and H'/E' parameters during the annealing, which characterizes the resistance of the coating materials to the elastic and plastic deformation. According to some authors, these parameters identify the wear resistance of the coatings. The variation in the friction coefficient with respect to the Ti-Al-Si-N coating friction path length before and after annealing at 1100 °C is shown in figure 3.

The Ti-Al-Si-N coating is characterized by partial oxidation when heated in air to 800 °C and the complete oxidation of nitride phases at 900 °C. This can be judged by the results of the elemental analysis and by the concentration profiles of the distribution of coating elements, including oxygen (table 2). No oxidation of the substrate material occurs.

| Temperature, °C | Ti  | Al  | Si  | N  | O  |
|----------------|-----|-----|-----|----|----|
| 800            | 25.1| 9.5 | 1.7 | 8.7| 55 |
| 900            | 24.9| 9.4 | 1.6 | 0  | 64.1|

4. Conclusions
The elemental and phase composition of the amorphous-nanocrystalline Ti-Al-Si-N multilayer coatings, being annealed in the vacuum at temperatures of 700-1100 °C, undergo no changes. They preserve the structure with clearly defined layer boundaries after thermal treatment.

The coatings heated in the vacuum at 1000 and 1100 °C are characterized by the coherent scattering regions of X-ray radiation increased from 8.5-9.5 to 11-12 nm, and microstrains in the crystal lattice decreased from 1.1 to 0.6-0.7%.

Thermal treatment neither changes the nature of cohesive fracture of coatings and nor affects their adhesive strength. After annealing, the nature of sample fracture changes slightly. It is accompanied by the appearance of the larger fragments of coating material during scratching associated with a change in the stress state of the “substrate-substrate” composite, in turn, accompanied by a decrease in compressive stresses from -4.6 to -0.6 GPa in the original coating and after annealing at a temperature of 1100 °C respectively.

The decrease in wear resistance after thermal treatment of the coatings manifested in increased wear and friction coefficient is associated not only with a relatively small decrease in hardness but also with the changing nature of their cohesive fracture accompanied by the appearance of relatively large fragments that act as high-abrasive particles between friction surfaces.

The Ti-Al-Si-N coating is characterized by partial oxidation is heated in air to 800 °C and complete transition of the nitride phases to oxides and oxynitride compounds at 900 °C. No oxidation of the substrate material occurs.

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