HYBRID METHODS FOR HARDENING OF SUPERHARD VACUUM COATINGS

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Abstract:*Physicomechanical and adhesion characteristics, specific surface energy of vacuum coatings formed on high-speed steels of the P6M5 type subjected to processing at cryogenic temperatures are investigated. The structural transformations occurring in vacuum coatings formed on steel substrates with subsequent processing at low temperatures were studied. A change in the tribological characteristics of titanium nitride coatings during subsequent processing in a cryogenic liquid is shown.*

KEYWORDS*: MORPHOLOGY, COATINGS, MICROHARDNESS, ADHESION, CRYOGENIC TREATMENT*

1. Introduction.

The formation of coatings for various functional purposes allows to significantly change the physico-mechanical characteristics of the modified materials. Of particular interest at present are nanostructured composite coatings. The introduction of nanodispersed particles into thick and thin coatings leads to significant structural changes, a network of labile physical bonds is formed, which leads to a significant increase in physicomechanical characteristics, including at doping concentrations of nanomodifier. One of the main tasks of modern materials science is the creation of new materials with enhanced performance characteristics. For this, various physical, chemical methods of substance formation are used, as well as their combination. One of the common technological methods is the surface modification of materials. That is application of thin-layer coatings of a gaseous, liquid, solid state on the working surfaces of products, which leads to an increase in their operational characteristics.

Modern engineering makes extensive use of tools, on the working surface of which composite coatings are applied. Among the most common coatings for metalworking tools include zirconium nitrides and zirconides, which is applied using vacuum technology. Zirconium nitride coating provides high wear resistance of the tool for cold deformation of metal workpieces by preventing the setting and seizure phenomena. When applying zirconium carbonitide coatings to a metal cutting tool (drills, milling cutters, taps, countersinks, etc.), the effect increases dramatically Nanocrystalline compounds based on titanium aluminum nitrides are promising coatings. These coatings sustain hich can temperatures up to 700 ° C without noticeable oxidation, while maintaining a hardness of 25-30 GPa. In the formation of vacuum coatings, various methods of activating the substrate surface are used: mechanical method, corona discharge, thermal heating, ion flow in a neutral gas medium, etc. This preparation allows you to significantly change the adhesive properties of the formed coatings, strength and tribological characteristics The creation of composite coatings based on titanium nitride with subsequent cryogenic treatment will reduce the increase in resistance to aggressive coatings and increase the values of physical and mechanical characteristics.

The aim of the work is to study the structure and physicomechanical characteristics of composite coatings based on titanium nitride, modified by low-temperature processing.

2. Preconditions and means for resolving the problem.

Composite coatings based on titanium nitride were applied on a UVNIPA-1-001 vacuum unit equipped with a cathode-arc evaporator with a plasma electromagnetic filtering system and an II-4-0.15 ion source. As the substrate used steel grade P6M5. The surface of the steels was subjected to hardening and grinding to a cleanliness of at least grade 11. Before application, the surface of the sample was cleaned and heated by titanium ions under the following conditions: evaporator current, A - 105-110; potential on the sample, kV –1.0. The coating was deposited at a stabilizing coil current of 1.7 A, a control coil current of 2.0 A, and an arc current of 90 A. The pressure of the reaction gas (nitrogen) was in the range (0.87-5) × 10^{-2} Pa. During deposition of the coating, a bias voltage from minus 50 V to minus 100 V was applied to the substrate. The studied coatings were processed in liquid nitrogen at a boiling point T = 77.4 K for 1-24 hours.

The structural features of composite heat-resistant coatings subjected to various types of processing were analyzed using a MDS 1600T universal metallographic microscope. The structural features of the boundary layers in functional composite coatings were studied using modern methods of physicochemical analysis: IR spectroscopy, X-ray diffraction analysis, atomic force microscopy. Tribotechnical studies were carried out on an FT-2 type friction machine, which operates according to the “finger-disk” scheme under dry friction of three spherical samples with a radius R = 1.5 mm on a flat surface of a disk (counterbody) made of steel and sanded on a flat plane surface with an emery cloth or grinding paste to an arithmetic mean deviation of the surface profile Ra = 0.1 - 0.3 microns. The tests were carried out at a normal load of 20 to 100 N and a linear sliding speed of 0.1-0.5 m / s. To measure the microhardness of coatings formed on metals, a PMT-3 microhardness meter was used. The operating principle of the device is based on a change in the linear magnitude of the diagonal of the imprint c obtained from the indentation of the diamond pyramid into the test material under a certain load. Adhesion characteristics were determined by scratch analysis. To calculate the energy parameters of vacuum coatings, we used the direct-shadow method for determining the wetting angle. We used liquids of different polarity to study the wetting and calculation of the adhesion forces, polar and dispersion components of the surface energy. Titanium nitride - the interstitial phase δ (TiN) - has a face-centered cubic lattice of the NCl type. Titanium nitride has a wide homogeneity region and can be considered as an interstitial solution with an excess of atoms in the TiN lattice. The microhardness of titanium nitride depends on the degree of nitrogen filling of the octahedral pores. However, depending on the degree of ionization, plasma energy, and ultimately plasma temperature, the plasma-chemical reaction will proceed at different rates, and the resulting structure, composition and microhardness of the coating will be different. Thus, surface microhardness is determined by the pressure of the reactive gas and the temperature of the process. Figure 1 shows the X-ray diffraction patterns of titanium nitride before and after cryogenic processing

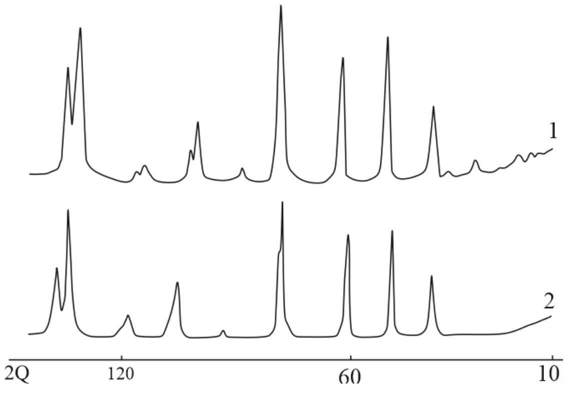
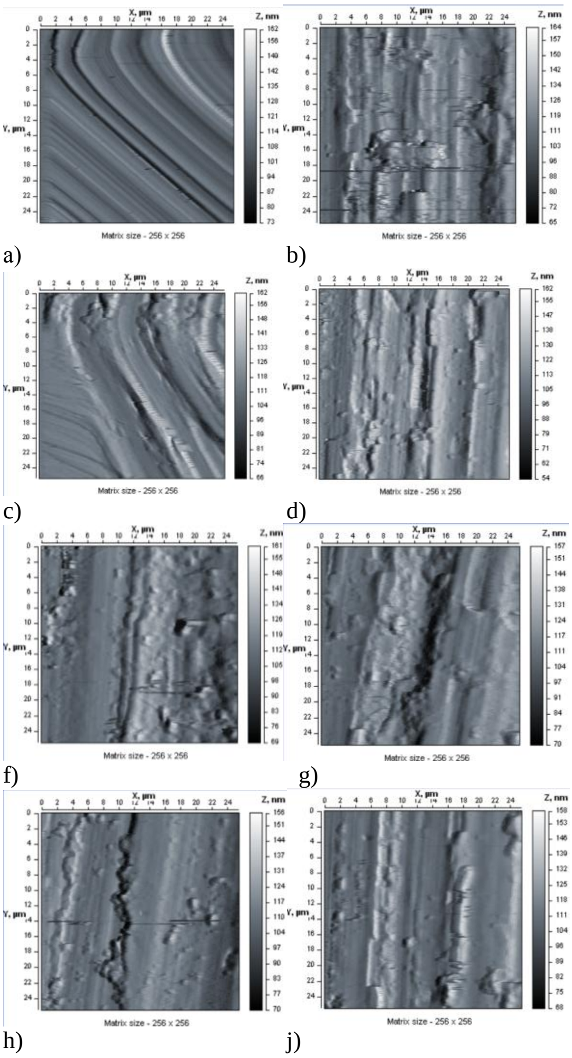


Figure 1 - X-ray diffraction patterns of titanium nitride coating: 1 - initial coating, 2- coating after cryogenic treatment for 360 minutes

Diffraction maxima lying at angles 2θ=65°; 78°10′; 78°30′; 112°; 137°30′; 138°20′ correspond to the diffraction maxima of titanium nitride. Also, titanium nitride samples exhibit diffraction maxima at angles of 2θ=44°40′; 99°; 99°30′, corresponding to iron, and the maxima lying at angles 2θ=116°30′; 117° correspond to Fe_3C [2].

As a result of the cryogenic treatment of heat treatment, diffraction peaks appear at angles 2θ=24°40′ и 82°20′, which according to the data of [3] correspond to titanium oxide compounds TiO_2. In the diffraction patterns of titanium nitride coatings, at some diffraction maxima, their splitting is observed, which is most likely due to structural changes in the crystal lattice of this compound itself.Studies on the morphology of titanium nitride coatings formed on substrates made of P6M5 steel show that during cryogenic treatment (Figure 2), structural components are transformed [4-5].



a) b)

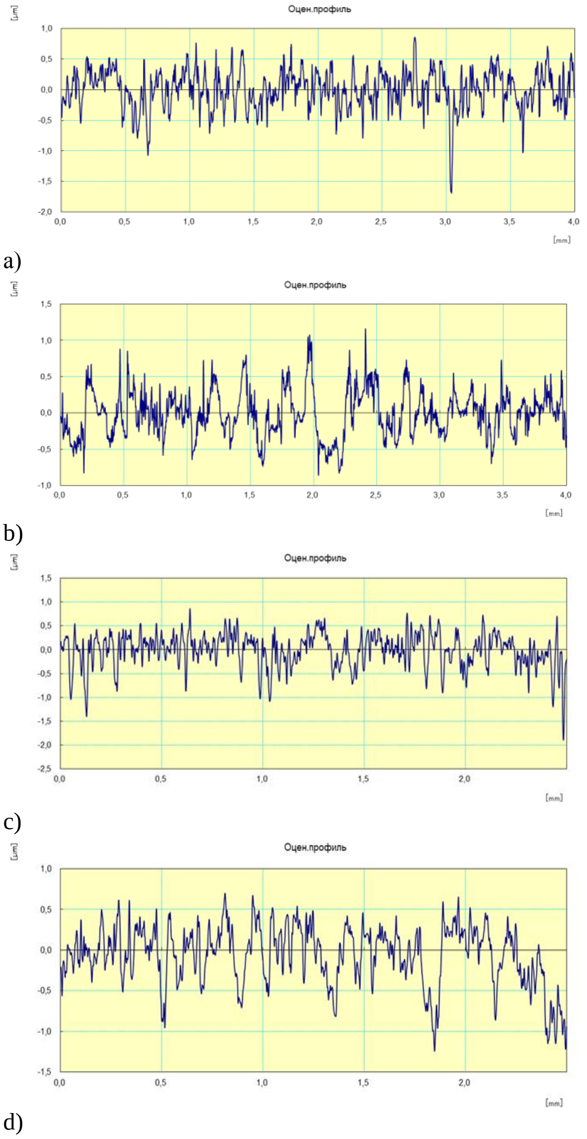
c) d)

f) g)

h) j)

Figure 2 *Morphology of titanium nitride coatings subjected to cryogenic temperatures: a-initial steel P6M5, b-coating of titanium nitride formed on a substrate of steel P6M5, c - coating of titanium nitride, treated for 30 minutes in a cryogenic liquid, d - coating of nitride titanium, treated for 60 minutes in a cryogenic liquid, f-coating of titanium nitride, treated for 120 minutes in a cryogenic liquid, g-coating of titanium nitride, treated for 360 minutes in a cryogenic liquid, h-coating of titanium nitride, treated for 720 minutes in a cryogenic liquid, j-coating of titanium nitride, treated for 1440 minutes in a cryogenic liquid*

The image of the initial surface (sample made of P6M5 steel) has a relief clearly oriented along the polishing direction with a height characteristic Ra = 175.3 nm over a field of 25 x 25 μm. The relief elements are elongated stripes with a characteristic size of 30 x 1.5 microns. The deposition of a nitride layer closes the initial relief and forms a developed relief with no distinct shape of the type of "poor wetting" (Fig. 2 b). The film has pores with a diameter of several micrometers. The elevation characteristic of the relief increased after applying the layer to Ra = 277.4 nm. Subsequent processing of the steel substrate and coating of titanium nitride in a cryogenic liquid for 30 minutes leads to the formation of a smoother relief with Ra = 160.6 nm. In the coating, inclusions with a lateral size from 0.75x0.75 microns to 2x2 microns are observed. An increase in the exposure time of the studied samples with the coating in liquid nitrogen leads to a decrease in the values of Ra = 198 nm, smoothing of the initial relief and the formation of a finely dispersed phase with a diameter of ~ 1 μm. A further increase in the exposure time of TiN coatings in liquid nitrogen leads to some smoothing of the initial relief with an increase in the concentration of low-dimensional phases of a globular type. The studies on the topography of TiN coatings by profilometry showed a similar dependence of the topographic characteristics similarly obtained by atomic force microscopy (.Figure 3)



a)

b)

c)

d)

Figure 3 Topography of the surface layers of titanium nitride coatings subjected to processing in a cryogenic liquid: a - initial P6M5 steel, b-TiN coating formed on a substrate of P6M5 steel, c - TiN coating formed on a substrate of P6M5 steel and exposured in liquid nitrogen in within 120 minutes, d - TiN coating formed on a substrate of P6M5 steel and exposured ubated in liquid nitrogen for 360 minutes.

The arithmetic average of the profile for the studied samples varies depending on the exposure time in the cryogenic liquid. The initial

Ra value for P6M5 steel is 0.245 μm. The formation of a coating on a steel substrate leads to an increase of Ra value to 0.303 μm. The exposure of the coatings in liquid nitrogen for 120-360 minutes reduces the Ra value to 0.27-0.28 microns. The increase of exposure time (720-1440 minutes) in the cryogenic liquid leads to an increase of Ra value to 0.30-0.313 μm. Based on the data obtained, it can be assumed that under the influence of cryogenic temperatures on titanium nitride coatings, recrystallization processes occur in them, accompanied by a change in the morphology of the coatings. The structural and morphological changes that occur in titanium nitride coatings formed on the steel substrate P6M5 should lead to changes in the physicomechanical characteristics of the coatings. Studies on the strength characteristics of TiN coatings confirm this assumption. So the determination of microhardness values by the Vickers method show an increase in the values of this parameter depending on the exposure time of the nitride coating in liquid nitrogen at the boiling point (table 1).

Table 1: *The microhardness of titanium nitride coatings after cryogenic treatment.*

Type of coating	The values of microhardness, N (GPa)
Original steel P6M5	3,4
TiN coating formed on a steel (P6M5) substrate	8,1
TiN coating aged in liquid nitrogen for 30 minutes	8,2
TiN coating exposured in liquid nitrogen for 60 minutes	8,4
Покрытие TiN, выде TiN coating exposured in liquid nitrogen for 120 minutes	8,6
TiN coating exposured in liquid nitrogen for 360 minutes	10,2
TiN coating exposured in liquid nitrogen for 720 minutes	9,4
TiN coating exposured in liquid nitrogen for 1440 minutes	9,1

The optimum is the exposure of titanium nitride coatings formed on P6M5 steel for 6 hours in liquid nitrogen. An increase in the microhardness of the modified samples by ~ 21% with respect to the initial coating is observed. One of the main characteristics that determine the operational characteristics of ceramic vacuum coatings is the adhesive interaction of the deposited layers with the surface of the substrate. The adhesion characteristics of vacuum coatings were determined by scratch analysis. A preliminary modification of coatings in a cryogenic liquid leads to an increase in the adhesive interaction between the coating and the substrate. Studies on the effect of cryogenic treatment on the specific surface energy (SSE) values of TiN coatings treated in a cryogenic liquid show a decrease in SSE values with an increase in the exposure time of plasma-chemical coatings in liquid nitrogen. A decrease in the coefficient of friction of modified TiN coatings by 18-24% with respect to the initial coating is also observed.

3.Conclusion

Thus, it was found that when processing plasma-chemical coatings of titanium nitride formed on a steel substrate P6M5, an increase in the values of physicomechanical characteristics is observed. The processing modes in TiN coatings in cryogenic liquids have been optimized to increase the wear resistance of a metalworking tool made of high speed steel. It was shown that the treatment of steel samples with titanium nitride-coatings in liquid nitrogen increases the adhesive interaction between the substrate and the coating. The influence of low temperatures has a positive effect on the tribotechnical characteristics of the studied plasma-chemical coatings.

4. Literature

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