Influence of ion bombardment of a substrate on the quality of vacuum-plasma Ti-TiN coatings

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Abstract. The characteristics of the quality of multi-layer vacuum ion-plasma coatings Ti-TiN such as roughness and adhesion strength are investigated. It is shown that additional ion bombardment promotes the production of high-quality coatings. Ion bombardment has a significant effect on the state of the surface layer of the metal. In the process of ion bombardment, conditions are created for the formation of active adsorption centers and the formation of a fine-grained structure, nanoscale grains and layers.

1. Introduction
Characteristics of the quality of a surface with a vacuum ion-plasma coating (VIPC) under ion bombardment conditions largely depend on the initial surface, as well as on preliminary preparation before coating deposition. Preliminary preparation allows to clean the surface of all kinds of contaminants, and includes modification, thermal activation of the surface and the formation of active nucleation centers. That, first of all, promotes high adhesion of coatings. Existing traditional methods of preliminary preparation of the substrate surface (mechanical, electrochemical and chemical polishing, ultrasonic cleaning, combined methods) do not always guarantee a high degree of purification [1, 2].

The purpose of this work was to investigate the effect of additional ion bombardment (AIB) on the stage of the surface pre-cleaning and deposition of coatings on the quality characteristics of the synthesized VIPC of Ti-TiN system.

2. Results and discussion
Heat-resistant steel of the martensitic class of Russian brand 13H11N2V2MF was chosen as the object of research. Coatings with additional ion bombardment were applied to flat samples with a diameter of 20 mm, a thickness of 3 mm. Samples were polished.

Synthesis of multilayer coatings was implemented on the upgraded installation of NNV-6.6-I1 using the following technology, including [3, 4]:
– preparation of the surface for spraying;
– preliminary cleaning and heating of the surface using the plasma generator “PINK”;
– formation of a multilayer coating of the Ti-TiN system;
– cooling of the vacuum chamber for a predetermined time.

To realize additional ion bombardment, a plasma generator “PINK” was used. It realizes a non-self-sustaining high-current diffusion discharge (NSDD). The generator was used both at the stage of preliminary treatment and activation of the surface, and for the synthesis of protective coatings in the
plasma assisting mode. Use of the “PINK” allows to significantly increase the adhesive strength and to form a better coating, as well as to reduce the temperature of the formation of layers. On the stage of coating deposition, application of the plasma generator provides significant additional acceleration to the ions of the plasma-forming gas and also promotes the acceleration of diffusion processes in the near-surface layers of the substrate. Plasma assisting involves the bombardment of ionic coatings during their formation and growth by high-energy ions, providing a significant improvement in the adhesion strength, microstructure and stoichiometry of coatings, as well as the formation of structures with pronounced anisotropy of properties, reducing the deposition temperature without deteriorating the level of physicomechanical properties of the surface layer [5–7].

The formation of multilayer coatings is realized by successive deposition of Ti and TiN from an arc discharge plasma. The plasma generator “PINK” was used for simultaneous plasma assisting in the deposition of coatings. The uniformity of the distribution of the thickness of the formed coatings is achieved by planetary rotation of the work part simultaneously around the axis of the table and relative to its own axis [7, 8].

Conducting an AIB with a plasma generator “PINK” allows:

– to ensure high energy efficiency of the process of generation of low-temperature bulk plasma;

– to reduce the fraction of the microdrop fraction in the plasma flow of vacuum electric arc evaporators;

– to produce plasma cleaning, etching and activation of the surface without spraying by vapors of the cathode material;

– to provide complex processing of products in a single vacuum cycle, including processes of final cleaning, activation, electron-ion-plasma nitrider of the surface and spraying of functional coatings with plasma assisting;

– to ensure the formation of micro- and nanostructured coatings with high hardness, increased wear resistance, improved corrosion resistance.

Ionic purification and activation of adsorption centers on the processed surface of NSDD is carried out in an inert gas (argon) medium under following conditions: the pressure is $10^{-1}$ Pa, displacement on a substrate is negative (900–1100 V), discharge current is 30–40A, processing time is 1...2 min. The end of the processing was fixed by stopping the occurrence of micro-arcs. This made it possible to avoid the introduction of plasma ions during the process of modifying and activating the surface, including the pre-cleaning.

The thickness of the deposited multilayer coatings, according to microstructural analysis, was 5...7 μm. These data are consistent with the results of calculations of the weighting method. The use of a multilayering of coating ensures:

– smooth reduction of residual stresses in thickness;

– decrease in porosity and defectiveness of the coating;

– increase in the integral thickness of the coating without reducing the performance characteristics;

– providing a smooth transition from a soft base to a hard functional layer.

Modification of the surface and its activation by means of a plasma realized by the plasma generator allows to increase the rate of spraying the surface, to reduce the processing time, to reduce the temperature of the coating formation, and to achieve uniform heating of the surface, which in turn ensures high adhesion strength of the VIPC.

To analyze the properties of the formed surface layer, microhardness studies were carried out. The tooling “PMT-3” was used. The measurements were carried out by successively pressing a diamond pyramid 136° with a square base with loads of 0.2, 0.5, 1.0 and 0.20 N. The stress lasted for 5–10 s. The diagonals of the prints were measured by a 30-hapiobjective OE-6 with aperture $A = 0.65$ and a 15-fold eyepiece micrometer AM9-3. It ensured a total magnification of 485 times. The microhardness value was identified from the tables by the lengths of the measured diagonals of the prints and the value of the applied load.

The depth of penetration of the indenter was calculated as the ratio of half the diagonal of the print to half the tangent of 136°. To estimate the true value of the measured value, the arithmetic mean was used.
For a sufficiently reliability of average result, the number of measurements was increased to 7. At different points of the sample, when estimating the arithmetic mean of the microhardness, the tests showed the same results (table 1).

**Table 1. Results of the study of the microhardness of coatings.**

| Material          | Coating type                              | Microhardness, GPa |
|-------------------|-------------------------------------------|--------------------|
| Initial condition |                                           | 16.3               |
| 13H11N2VMF        | Multilayer coating of Ti-TiN (3 layers)   | 17.8               |
|                   | Nanostructured multilayer coating          | 25.7               |

The nanostructured multilayer coating was formed from nanometer layers (up to 100–150 nm) by the number of layers up to several tens. Due to the peculiarities of the structure, the ultra-thin layer thickness and their large number, as well as the possibility of dense interfacing layers of different materials, these coatings combine the qualities of layered systems and the specific properties of nanoobjects.

The main influence of the effect of AIB in the process of modification and ionic cleaning on the properties of coatings is formed at the stage of coating initiation due to leveling of stresses upon exposure to the substrate and transformation of the crystal structure. The ion flux forms the point defects on the surface, these defects are active adsorption centers.

In comparison with the original polished surface of the substrate, its roughness after the synthesis of the coating increased. This is due to the peculiarities of the formation of layers under the conditions of additional ion bombardment, since active adsorption centers are formed and the ions of the coating material are deposited on the protrusions of the microrelief of the surface of the material being processed. Adhesive strength is determined by:

– composition, thickness, structure, residual stresses, that is, coating parameters;
– composition, microgeometry of the surface, type of preliminary machining, – i.e. parameters of the substrate and the type of its preparation;
– type of cleaning, preheating, – i.e. preparation of the surface for spraying;
– substrate temperature, accelerating voltage, gas composition and pressure, condensation rate and arc current, – i.e. technological modes of deposition of coatings.

Studies of adhesion strength were carried out by various methods. So, the study by bending samples using the VIAM technique showed excellent adhesion of the coating with respect to the main material. A study of a diamond pyramid imprint with an increase using an optical microscope showed that there was no cracking of the coating material near the exposure zone, which also indirectly indicates a high adhesion of the coating.

Investigations of the adhesive strength of deposited coatings, which were carried out by the VIAM method by bending samples at 90°, showed that the coatings have a high adhesion to the main material. In addition, adhesion was investigated by indenting the diamond pyramid indenter and studying its imprints. Indirect evidence of high adhesion of the coating to the main material was the absence of cracking of the coating material near the impact zone.

Figure 1 shows a photograph in the optical microscope of the beginning of the destruction of the Ti-TiN coating with an increase in the load on the indenter during the scratching process.

**Figure 1.** Evaluation of the adhesion strength of multi-layer Ti-TiN coatings by scratching.
The study of the adhesion strength of coatings on a scratch device by scratching method showed satisfactory adhesion. The observed minor cleavages along the edges of the scratch correspond to the requirements. The load on the tip was 3.0 N. In addition, the effect of surface pretreatment and the quality of preparation of the substrate surface was investigated by ionic cleaning directly in the vacuum chamber. In this case, the adhesive strength of the coatings on substrates was evaluated. It has been established that with a cleaning duration in a vacuum chamber of less than 30...45 s, the adhesion strength of Ti-TiN coatings is about 20 to 30 MPa.

Coatings formed at the minimum values of the duration of the ion-cleaning process are characterized by poor quality up to partial peeling off the substrate. This is explained by the fact that the removal of oxide films from the surface does not occur, and the temperature is insufficient for the effective course of plasma-chemical reactions. At optimal values of the cleaning duration, the coating has good characteristics of the adhesive interaction of the substrate and the coating. With an increase in the duration of cleaning, surface overheating and a decrease in adhesion strength are possible. Further overheating of the surface can lead to the formation of a columnar structure of the coating.

AIB has a significant effect on the physico-chemical state of the surface layer of the substrate. In the process of ionic exposure, surface contamination is removed. The substrate remains atomically pure until the formation of the main coating layer.

The process of ion cleaning and surface activation under the conditions of additional ion bombardment, realized by the plasma generator “PINK”, ensures the production of high-quality vacuum-plasma coatings.

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