Complex study of structural state and properties of ion-plasma functional coatings

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Abstract. Based on the justified methodological complex the study of the multilevel structural state of coatings and surface layers created by the ion-plasma modification was made. A comparative quantitative assessment of structural changes and the chemical composition of coatings by SEM, XPS, EDX methods and the physical and mechanical properties of coatings based on titanium nitride was carried out. It was found that for all variants of coating formation there is no titanium in the metallic state and, therefore, the formation of a droplet phase does not occur. Layer-by-layer XPS analysis has determined that coatings are heterogeneous in its composition in depth. It is shown that the modification of steel surfaces with a TiN-based composition can be used to form wear-resistant coatings on the working bodies of road milling machines that are actively used in the overhaul and maintenance of the highways.

1. Introduction
The progressive approaches that allow industrial enterprises to carry out production and business activities more efficiently and competitively include the creation of new materials and coatings based on the surface modification of parts and tools. Surface modification provides significant savings in scarce and expensive alloying elements used in traditional alloy production operations. Functional coatings make it possible to obtain new properties of products due to the formation of a special structural phase state of materials, which leads to an increase in the operational stability of machine parts and tools and, as a result, to a decrease in the need of spare parts [1, 2].

The development and implementation of new resource-saving technologies require complex laboratory and bench research and testing methods to minimize the laboriousness (time and labor) of performing research work in the interests of enterprises in the manufacturing sector of the economy.

Methods of studying the structure and properties of materials and coatings should be considered and applied considering a systematic analysis of the relationship of micro-, meso-, macrostructural states with operational characteristics of surfaces that enter into frictional interaction. At the same time, the methods chosen for research should complement each other, since none of the individual methods provides a complete account of the numerous factors affecting the change in structure during surface modification and coating formation.

Fig. 1 shows a methodological complex for studying the structure and physio mechanical properties of coatings and materials with coatings at various structural levels. The proposed systematic set of research methods will make it possible to make a reasonable choice of testing equipment for specific
tasks and to unify the instrumental apparatus for studying materials and coatings obtained by using various surface modification technologies.

![Methodological complex of coating research](image)

**Figure 1.** Methodological complex of coating research

2. **Problem statement**

Comprehensive studies of modified materials and coatings are based on the relationship of the structure at different levels of the hierarchy and operational properties (Fig. 1). Moving from bottom to top according to this scheme, from the physical and mechanical properties of coatings to enhanced performance characteristics (wear resistance, corrosion resistance, etc.), each stage can be considered as a basis for moving to the next stage, which gradually approaches the necessary properties.

By stage-by-stage studying of coatings at various structural levels, it is possible to obtain information on the real structure of materials, which is a complex dynamic system with the properties of nonlinearity and nonequilibrium. The main methods for studying the microstructure are scanning electron microscopy (SEM), x-ray photoelectron spectroscopy (XPS), energy-dispersive x-ray spectroscopy (EDX).

The results obtained earlier and disclosed in the publications of our research group [3–9] on determining the interconnections and interdependencies of micro-, meso- and macro-structural levels made it possible to determine the range of materials, the modification of the surface and surface layers of which allows achieving the required values of the product performance.
The purpose of the work is the application of a well-grounded comprehensive research method, including the study of micro-, meso- and macrostructural levels of materials, to solving problems of reducing the wear rate of modified surfaces and coatings on products demanded by production using the example of working bodies of construction equipment.

3. Materials and methods
In the present work, Hadfield austenitic steel 110G13L (GOST 977-88) was used as the material modified by applying an ion-plasma coating, from which the working bodies and cutting parts of various industrial products are made.

Hadfield austenitic steel 110G13L contains 11-14.5% Mn, 0.9-1.3% C, has high wear resistance at high pressures and shock loads, and it also has high ductility.

Ion-plasma modification was carried out on a modernized installation NNV-6.6, using a three-cathode system that allows surface activation by spraying it at different angles, as well as applying coatings of various compositions [1, 4].

Samples of Hadfield austenitic steel with TiN-based ion-plasma coatings doped with Al were processed in different covering times (15, 35, and 50 min). It is known, that the presence of aluminum reduces the likelihood of the formation of a droplet phase of titanium metal in the coating due to the prevention of prolonged burning and the growth of cathode spots [10, 11].

To achieve this goal, studies were carried out using scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM), X-ray photoelectron spectroscopy (XPS) of the structural-phase state of the surface and surface layers of initial and modified samples of Hadfield austenitic steel.

To study the element composition and chemical state of atoms in the samples under study with different coatings on Hadfield austenitic steel, the surface sensitive method XPS was applied with the use of the Surface Science Center (Riber) analytical complex. To excite X-ray radiation, a source with an Al anode and an Al line energy of 1487 eV was used. XPS spectra were obtained under ultrahigh vacuum (~10^-9 Torr) using MAC-2 - two-stage cylindrical mirror analyzer. The diameter of the x-ray beam was ~ 5 mm, and the source power was 240 watts. The energy resolution in recording the core line spectra was 0.7 eV, the survey spectra were 1.2 eV and was constant over the entire range of measured energies. Layer-by-layer XPS analysis was carried out directly in the spectrometer chamber. The coating layer was affected by an argon ion beam with an average energy of 3 eV at a pressure in the spectrometer chamber of ~ 10^-5 Torr. The influence rate was ~1-3 nm / min. Quantitative analysis of the chemical composition of the studied samples was carried out using data obtained from the survey spectra using the formula:

\[ C_x = \frac{I_x}{S_x} \star 100 \]

where \( C_x \) is the atomic concentration of the element X, %; \( I_x \) – is the integrand peak area of element X, relative to unit; \( S_x \) – is the atomic sensitivity factor of element X, relative to unit;

\[ \sum_{\alpha} \frac{I_{\alpha}}{S_{\alpha}} \] – the sum of the integrand peak areas of all detected elements and the corresponding atomic sensitivity factors, relative to unit.

For quantitative analysis, the most intense lines of the corresponding elements were selected. The atomic sensitivity factor was determined in accordance with [12]. To average the data, the XPS spectra were measured at three different points on the surface.

Chemical analysis of the elements was carried out according to the spectra of the most intense lines measured with high energy resolution. To determine the background line, the Shirley method was used, which allows one to consider the contribution from inelastically scattered electrons [13].
spectra were fitted using a set of components represented by the convolution of the Gauss and Lorentz functions. Processing of XPS spectra was carried out in a licensed software package CasaXPS 2.3.16 [14].

According to the Framework Agreement on Scientific Cooperation, the equipment of the Center for the Shared Use of Scientific Equipment of the Scientific Center of the Siberian Branch of the Russian Academy of Sciences was used to perform the experiments: a JEOL JEM -2100 transmission electron microscope, a D-9 BRUKER X-ray diffractometer, an IR-Prestige 21 IR spectrometer, and a Specord VIS UV spectrometer.

The study of the mechanical characteristics of the samples was carried out by measuring the microhardness by the Vickers method on a PMT-3 microhardness meter with different loads on the indenter and, accordingly, with different thicknesses of the analyzed layer. The indenter load was 0.2, 0.5, and 1.0 N, which corresponded to an indentation depth of 0.9 to 3.0 μm. Five measurements were carried out at each load for all coatings.

For the practical application and testing of the obtained scientific results, coatings were applied on the surface of the road milling cutters and cold regenerators (recyclers), which are actively used in the process of capital and maintenance of roads with the aim of removing a layer of deformed asphalt concrete, preparing a reinforced base of pavement and many other operations. Comparative tribological tests of standard and modified with various compositions of cutters of road mills were carried out on a special stand, the description of which is given in [15].

The tests were carried out on concrete of grade M35 category V35 with an average compressive strength of 458 kgf / cm², the milling cutter rotation speed was 200 rev/min, the working width of the material being processed was 15 mm, the cutting depth was 6 mm, and the feed was 60 mm / min. The choice of concrete and bench performance were determined by comparative test methods and requirements to reduce the time of the experiment. At the same time, standard cutters and cutters of various compositions with modified coatings were installed on the stand, which provided the same conditions for their loading and wear.

4. Results and discussion

Fig. 2. presents XPS survey spectra for TiN coatings with different formation times.

![Figure 2. Survey XPS spectra for coatings on samples of and Hadfield austenitic steel 110G13L obtained at different formation times](image-url)
The spectra (Fig. 2) contain lines of titanium: Ti 2s (~555 eV), Ti 2p (~455 eV), Ti 3s (~57 eV) and Ti 3p (~57 eV); oxygen: O 1s (~530 eV); nitrogen: N 1s (~400 eV); carbon: C 1s (~285 eV); iron: Fe 2p (~710 eV). The photoelectron lines of Al, which is part of the cathode, are not observed due to the low photoionization cross section for the Al 2p level when using exciting radiation with an energy of 1486.6 eV, as well as its low concentration in the coatings. The presence of an iron peak Fe 2p can be associated both with the partial evaporation of steel structural elements NNV-6.6, and with ionic mixing of the substrate and coating materials.

As follows from the results of the analysis, the composition of the coatings in a thin surface layer differs from the average coating thickness. The increase in carbon concentration is observed, and a decrease in the concentration of nitrogen in a thin layer near the surface with an increase in the time of coating formation. A high concentration of oxygen and carbon suggests the presence of oxy nitrides, carbonitrides, oxy carbonitrides and titanium oxides in the coating composition.

A detailed analysis of the spectra of Ti 2p coatings showed the absence of titanium in the metallic state. Thus, the formation of a droplet phase of titanium in coatings at the indicated production parameters can be completely eliminated.

To study the changes in the chemical state of the elements in depth, we used a sample with a coating formed at a minimum time (15 min).

Fig. 3. presents the results of layer-by-layer XPS analysis. As expected, a gradual increase in the Fe concentration with distance from the surface is observed.

The increase in concentration until the affecting time of the order of 1100 min occurs slowly, and with further affecting much faster. Starting from the affecting time of ~700 min, Mn is present in the spectra, which is the main alloying element of and Hadfield austenitic steel 110G13L.

With the exception of a thin surface layer, in the process of ion exposure there is a tendency to a simultaneous decrease in the concentration of N and C, while the concentration of O increases. The difference in the surface layer is apparently associated with the adsorption of carbon and oxygen on the heated surface of the sample from the residual atmosphere of the vacuum chamber with the formation of chemical bonds after completion of the formation process.

Table 1 shows the micro hardness values measured by the Vickers method at indenter loads of 0.2, 0.5, and 1.0 N for the initial substrate of Hadfield austenitic steel 110G13L and samples with different
coating times. As follows from the table, the penetration depth of the indenter \( h_{cp} \) in the initial substrate for average microhardness was in the range from 1.29 to 3.06 \( \mu m \). The scatter of microhardness values in the initial steel sample 110G13L is related to the difference in the hardness of austenite grains (lower hardness) and intergranular layer, which includes excess manganese and iron carbides (Fe, Mn)_3C and has a higher hardness. For samples with coatings, the smallest average penetration depth \( h_{cp} \) corresponded to the lowest indenter load for the coating with the longest formation time (50 min), and the highest \( h_{cp} \) was observed in the initial sample with an indenter load of 1 N. This is due to the fact that in the case of coating with the maximum formation time when the indenter load is 0.2 N, the hardness of the coating is changing, since the indenter penetration depth does not exceed the estimated value of its thickness. In this case, the steel substrate does not significantly affect the hardness value. However, in the case of coatings obtained at 15 and 35 min, the indenter penetration depth is comparable to or exceeds their estimated thickness. In this case, the microhardness value for these coatings increases in comparison with the initial steel sample for all used indenter loads. It is known that titanium carbonitrides, oxynitrides, and oxycarbonitrides have a higher hardness than titanium nitride [16]. Therefore, high microhardness values for coatings with a formation time of 35 and 50 min can be associated with an increase in the proportion of Ti-C bonds in them, which was recorded by XPS analysis. In addition, the XPS method showed that with increasing depth from the surface, the proportion of oxynitrides increases. It is obvious that a coating with a longer formation time has a longer layer with a high content of titanium oxynitrides and, therefore, has a higher microhardness. A comparison of the microhardness values (Table 1.) shows that the coating formed at 35 min practically does not yield to the coating with a larger thickness (formed at 50 min).

Table 1. Microhardness values of samples of Hadfield austenitic steel 110G13L with different coating times

| Coating time, min | Indenter load 0.2N Microhardness, N/mm² | The average value of microhardness, N/mm² | \( h_{cp} \), \( \mu m \) |
|------------------|----------------------------------------|------------------------------------------|----------------|
| 0 (Initial)      | 4820 4030 4580 4820 4360               | 4522                                     | 1.29           |
| 15               | 5010 7580 7130 6080 5790               | 6318                                     | 1.09           |
| 35               | 8470 7130 8030 7580 9050               | 8052                                     | 0.97           |
| 50               | 8510 9050 8510 9650 7580               | 8660                                     | 0.94           |

| Coating time, min | Indenter load 0.5N Microhardness, N/mm² | The average value of microhardness, N/mm² | \( h_{cp} \), \( \mu m \) |
|------------------|----------------------------------------|------------------------------------------|----------------|
| (Initial)        | 4730 4230 4480 4730 4230               | 4480                                     | 2.05           |
| 15               | 5480 7410 6430 5480 7660               | 6492                                     | 1.71           |
| 35               | 6430 9270 6260 8580 7410               | 7590                                     | 1.58           |
| 50               | 7660 7410 6010 7410 7130               | 7124                                     | 1.63           |

| Coating time, min | Indenter load 1.0N Microhardness, N/mm² | The average value of microhardness, N/mm² | \( h_{cp} \), \( \mu m \) |
|------------------|----------------------------------------|------------------------------------------|----------------|
| 0 (Initial)      | 4200 3830 4130 3900 4130               | 4038                                     | 3.06           |
| 15               | 5720 5850 5140 6260 6570               | 590.8                                    | 2.53           |
| 35               | 8470 7820 7240 8030 6890               | 7690                                     | 2.22           |
| 50               | 8020 7240 8020 7240 8700               | 7844                                     | 2.2            |

The effectiveness of changing the micro- and mesostructure after the surface modification of the cutters of road mills made of Hadfield austenitic steel 110G13L was tested using tribological bench tests.
The results of resistant tests are shown in Fig. 4. Option 1: cutters made of Hadfield austenitic steel 110G13L identical in geometry to W6 / 20X. Option 2: cutters made of Hadfield austenitic steel 110G13L identical in geometry to W6 / 20X subjected to high-energy ion-plasma modification of TiN. The comparison was made with the W6 / 20X cutters, manufactured by the Wirtgen Group.

The calculation of functions and the construction of graphs were performed using the freeware Graph 4.4.2 program [17]. The obtained dependencies for the results of comparative bench tests are characterized by the following functions.

For cutters made of Hadfield austenitic steel 110G13L:

\[ F(x) = -0.0003x^2 + 0.1086x - 0.0127; \quad R^2 = 0.9938. \]

For cutters made of modified Hadfield austenitic steel 110G13L:

\[ F(x) = -0.0007x^2 + 0.0758x + 0.0103; \quad R^2 = 0.9964. \]

For cutters W6/20X:

\[ F(x) = 0.0001x^2 + 0.0595x + 0.0009; \quad R^2 = 0.9989. \]

In the obtained regression equations, the wear value is taken as the response function \( F(x) \), \( x \) is the friction path, \( R^2 \) is the coefficient of determination.

An analysis of the regression equations demonstrates that for cutters made of Hadfield steel, the wear rate increases with an increase of the friction path; for modified cutters made of the same steel, with an increase of the friction path, the amount of wear increases with lower intensity; for standard cutters W6/20X, with an increase in the friction path, the amount of wear increases with the same level of intensity as modified cutters from Hadfield steel.

The kinetic curves of the cutter wear are shown in Fig. 4.

![Figure 4](image_url)

**Figure 4.** Example of kinetic wear curves for initial and modified cutters made of Hadfield austenitic steel 110G13L in comparison with cutters W6/20X

5. Conclusion

1. A comprehensive study of changes in the structural state of materials at all hierarchical levels and properties of materials with coatings helps to solve practical problems of achieving a degree of hardening at which the coating provides increased wear resistance. The results obtained allow us to talk about the effectiveness of the proposed integrated method of
research and testing, as well as the possibility of obtaining with its help both new knowledge about the structure and properties of the material, and new technological solutions to production problems.

2. It was found that coatings with different formation times have a fairly similar chemical composition. The largest amount of titanium is in the composition of nitride and oxynitride. The presence of Ti-C bonds suggests the presence of more complex compounds (titanium oxyxycarbides and titanium oxycarbonitrides). It was found that with an increase in the formation time, and, consequently, the thickness of the coatings, an increase in the relative content of Ti-C bonds is observed. It is shown that for all variants of coating formation, titanium in the metallic state is absent. Consequently, with the used parameters for the production of coatings, the formation of droplet microfraction of titanium metal does not occur. Conducted layer-by-layer XPS analysis showed that the coatings have a heterogeneous composition in depth. It was found that with increasing distance from the surface in the coatings, the content of oxynitrides and titanium oxides increases.

3. It was found that the microhardness increases significantly during coating. One of the reasons for the increase in microhardness values on coated samples is the formation of TiN, C, O compounds with higher hardness than TiN. Coatings formed at 35 and 50 min contain more of these compounds and have maximum microhardness values. The microhardness value for coatings at 35 and 50 min formation differs insignificantly. Therefore, a sufficient time for the formation of coatings to increase the hardness of products from Hadfield austenitic steel (110G13L - GOST 977-88) is 35 min.

4. The example of steel road cutter cutters 110G13L show that the lowest wear intensity is provided by TiN-based coatings.

6. References

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