Physico-mechanical properties of VT6 titanium alloy after combined treatment

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Abstract. One of the directions in the technology is the use of thermal plasma for the production of new materials, as well as the modification of the surface of materials based on a titanium alloy using the action of a plasma jet. The use of pulsed high-speed jets today is one of the promising methods for producing new composite, high-alloy materials on the surface of products from structural materials. An analysis of the results shows that the most optimal is surface modification by high-intensity ion-beam treatment after plasma treatment with microfusion. This work was carried out as part of the state task of the Ministry of Science and Higher Education of the Russian Federation «The influence of magnetic fields and ion implantation on the structure, chemical composition and properties of titanium, aluminum alloys and elementary semiconductors».

1. Introduction

The use of concentrated energy flows to obtain wear-resistant coatings or their synthesis in the surface layer of the workpiece is one of the fundamental directions of modern metal physics [1-4].

In [5, 6], it was shown that double implantation in titanium Cu – Ni alloys; Fe – Zr leads to a change in microhardness, which is primarily associated with hardening of the surface layers due to the formation of martensitic phases and finely dispersed carbides.

Therefore, it is of interest to study the effect of high-dose and intensive implantation of Cu – Pb, Cu – Fe ions on the change in physicochemical properties and operational characteristics of the VT6 titanium alloy.

A large reserve for improving the operational properties of parts working under friction conditions is to combine several types of processing during the formation of a modified layer on the surface of the part. One of these types of processing is ion implantation [7]. Therefore, it is very important to determine the sequence of using various methods in the complex technology of processing the surface layer of the VT6 titanium alloy, including plasma, laser, and ion processing.

Processing materials with concentrated energy flows allows a wide range of changes in the physicochemical properties of the surface. During ion processing, in particular, ion implantation, the surface properties of materials are modified as a result of the introduction of high-energy ions, causing a change in the elemental composition (alloying) and the structural phase state of the surface layers. Using ion implantation, it is possible to directionally change such properties of materials as microhardness, wear resistance, corrosion resistance, heat resistance, as well as frictional, optical, magnetic, emission properties, etc.
2. Materials and methods
The object of the study were samples of VT6 titanium alloy.

Laser processing was performed on a serial laser thermal hardening machine based on a fiber laser with a laser radiation power density at which the surface microgeometry was preserved and its melting on the order of \(2 \times 10^5\) W/cm\(^2\) did not occur.

The surface modification of the VT6 titanium alloy was also carried out by plasma surface treatment in the variant without surface melting and with micromelting. Then, the samples were implanted using cathodes of Cu – Pb and Fe – Cu alloys. Some of the samples after implantation were subjected to surface treatment with a plasma jet without melting the surface.

All obtained samples were tested for wear under dry sliding friction according to the disk – finger pattern with a base value of the friction path of 500 m. The finger pressing force during the tests was 50 N.

The elemental composition of the implanted layer was determined using Rutherford backscattering spectrometry of a 2 MeV helium ion beam obtained using an electrostatic accelerator using a technique similar to that in [8, 9].

Vickers microhardness was measured on a LEITZ universal METAL-PLAN measuring complex with indenter loads of 50 to 100 g. Hardness H and elastic modulus E of the implanted samples were determined by the Oliver and Fahr method.

3. Results
An analysis of the Rutherford ion scattering spectra (POP) of helium ions with an energy of 2.035 MeV obtained on VT6 samples after implantation of Cu and Pb ions with a dose of \(2.5 \cdot 10^{17}\) cm\(^{-2}\) and \(5 \cdot 10^{17}\) cm\(^{-2}\) showed that a wide range was found after implantation a set of elements: C, O, Al, Ti, V, Fe, Mo, W. Processing of the spectra allowed us to obtain the distribution of the concentration of elements over the depth of the surface layer of the samples.

The maximum concentration of Pb ions is about 11 at.% in a layer near the surface at a depth of about 5–8 nm, and the concentration of Cu is 32–38 at.%, And its maximum is located at a depth of 25–28 nm at an implantation dose of \(5 \cdot 10^{17}\) cm\(^{-2}\).

Thermal annealing of VT6 alloy samples after implantation for 2 hours at a temperature of 540–550°C contributed to an increase in the ion penetration depth by about 1.5–1.7 times.

Additionally, V (\(\sim 3.91\) at.%), Ti (37 – 87.57 at.%), Al (7.15 – 9.52 at.%) Were found. The peak of oxygen (16 at.%) Is at a depth of about 23.5 nm, and carbon (42.53 at.%) At a depth of 7 nm. With a decrease in dose to \(2.5 \cdot 10^{17}\) cm\(^{-2}\), the concentration of Pb at a maximum reaches 4.44 at.%, And the concentration of Cu drops to 11.65 at.%.

The phase composition of the implanted VT6 sample includes \(\alpha\)-Ti, \(\beta\)-Ti, Al\(_3\)Ti, and Al\(_2\)Ti. After annealing the implanted samples, the main changes are associated with the Al\(_3\)Ti phase. In particular, a separate 111 Al\(_3\)Ti peak appears in the diffraction pattern. Shooting in the moving geometry (angle 0.5°) shows that in the region between the 001 and 100 \(\alpha\)-Ti reflections, an increase in the radiation intensity is observed, which is due to the appearance of an additional 111 Al\(_3\)Ti line.

The results of determining the hardness and elastic modulus at imprint depths of 50, 100, and 150 nm for VT6 alloy are shown in Figure 1.

The results of wear tests are shown in Figure 2.

The surface of the VT6 alloy was treated at the laser installation before and after ion implantation using a cathode made of Cu-Pb alloy. The surface microhardness measurement results are presented in Figure 3.

In the framework of the studies, we evaluated the effect of the material composition of the cathode of the implant during implantation using cathodes of Cu – Pb and Fe – Cu alloys with a dose of \(5 \cdot 10^{17}\) ion / cm\(^2\) on mass wear during friction with varying friction paths. The obtained experimental results are summarized in accordance with table 1.
Figure 1. Dependence of microhardness of titanium alloys on depth during double implantation of Pb and Cu: VT6 alloy (1 - initial sample after plasma surface treatment; 2 - after plasma surface treatment and implantation; 3 - after isothermal annealing of the sample in state 2).

Figure 2. Dependence of the mass wear of samples of VT6 alloy for various surface treatments with a friction path of 500 m: K, K + I - the initial sample without and with subsequent implantation; 1, 4 - plasma treatment without fusion and subsequent ion implantation; 2, 5 - plasma treatment with microfusion without and with subsequent ion implantation; 3, 6 - plasma treatment with macromelting without and with subsequent ion implantation. Implantation dose $5 \cdot 10^{17}$ ion / cm$^2$, cathode material Cu – Pb alloy.
Figure 3. The effect of ion implantation and laser treatment on the microhardness of the surface of VT6 titanium alloy: K - control sample without treatment; II - ion implantation; LH - laser hardening; LH + II - laser hardening and subsequent ion implantation; II + LH - ion implantation and subsequent laser processing.

### Table 1. Mass wear of samples of VT6 alloy subjected to plasma treatment with micromelting and ion implantation, depending on the friction path.

| Cathode material | Dose of implantation, ion / cm$^2$ | Mass wear $\Delta m$, mg |
|------------------|------------------------------------|--------------------------|
|                  |                                    | Friction path, m         |
|                  | 0 100 200 300 400 500 600 700      |                          |
| Cu–Pb            | $5 \times 10^{17}$                 | 0 8,2 17,3 28,5 41,6 52,3 68,8 81,4 |
| Fe–Cu            | $5 \times 10^{17}$                 | 0 3,1 8,4 13,2 22,7 31,7 44,5 51,3 |

4. Discussion of the results

The POP spectra indicate that the implantation of Pb and Cu ions in the VT6 titanium alloy leads to the formation of individual peaks of the implanted elements. Isothermal annealing is accompanied by smearing of peaks, which is explained by the diffusion of implanted ions.

The hardness of the implanted layer is slightly higher than that obtained after surface plasma treatment, especially at a depth of 50 nm. Annealing after implantation leads to a significant increase in the hardness of the surface layer, moreover, as a result of the influence of the underlying unreinforced material, the decrease in hardness with depth occurs more intensively compared to the initial sample in the state after surface plasma treatment.

An increase in the concentration of radiation defects, as well as the introduction of Fe$^+$ and Cu$^+$ ions, leads to an almost twofold increase in hardness in the surface layer. The formation of Fe$^+$ and Cu$^+$ ions during implantation in the surface layers of titanium alloys of oxycarbides can also affect the reduction of the friction coefficient during tests for hardness and wear.

The polyionic joint implantation of Fe – Cu and Cu – Pb ions into a titanium alloy leads to the formation of concentration profiles of elements with a high maximum content. So, a dose of $2.5 \times 10^{17}$ cm$^2$ leads to the formation of a Cu profile with a maximum Cu concentration of about 15 at.%, And Pb about 6 at.%. At the same time, as a result of the combined polyionic implantation of Cu$^+$ and Pb$^+$ ions with a dose of $5 \times 10^{17}$ cm$^2$, the maximum concentration of Cu increases to 35 at.%, And Pb about 13 at.%. Thermal annealing of the samples after implantation leads to a decrease in the peak concentration of Cu and Pb and a smearing of the element profiles [10, 11].

Studies show that the maximum change in nanohardness is observed at a depth of about 50 nm, and at a depth of about 150 nm, its increase is much smaller. After thermal annealing, the elastic recovery
of the imprint depth during unloading is somewhat larger than for the initial sample, which indicates that the hardness of VT6 samples increases more intensively than the elastic modulus.

An increase in the implantation dose of \( \text{Cu}^+ \) and \( \text{Pb}^+ \) ions from \( 2.5 \cdot 10^{17} \text{ cm}^{-2} \) to \( 5 \cdot 10^{17} \text{ cm}^{-2} \) leads to an increase in hardness by almost 100% at a depth of 50 nm and up to 45% at a depth of 150 nm. The modulus of elasticity of the samples after implantation also increases at shallow (50 nm) depths to 50% and decreases with increasing indentation depth.

The study of endurance showed that during friction of VT6 titanium at stages with a high wear rate, the material of the samples is transferred to the surface of the counterbody, as a result of which a layer of transferred material forms on the surface of the counterbody. However, at stages with a low wear rate, this layer is not observed, and secondary structures in the form of islands are present on the friction surface of the samples.

X-ray microanalysis of the surface of islet structures revealed that in addition to titanium, oxygen (up to 55 at.%), Carbon and iron (up to 4 at.%) Are present in them. Analysis of the main friction surface showed that the above elements are not present in its composition. Apparently, the presence of carbon is explained by the processes of interaction of the test sample with the counterbody.

A comparison of the ratios of oxygen concentration and titanium concentration favors the very likely presence of titanium dioxide islands \( \text{TiO}_2 \) in the material structure.

Taking into account the morphology of island structures and their chemical composition, it can be suggested that the material of such structures contributes to an increase in hardness values while maintaining a fairly high level of ductility. The presence of a titanium dioxide film \( \text{TiO}_2 \) serves as a barrier to the development of the process of intense adhesive interaction of these islands and the counterbody.

An analysis of the results shown in Figure 2 shows that the most optimal is the modification of the friction surface by high-intensity ion-beam treatment after plasma treatment with microfusion of the surface along the projections of its roughness.

An analysis of the data presented in Table 1 indicates that the use of a cathode made of Fe – Cu alloy is more efficient, especially in the region of large values Fe–Cu of the friction path.

In the future, it seems appropriate to study the effect of the implantation dose on the mass wear of VT6 alloy samples when using Cu – Pb and Fe – Cu alloys as implant cathodes.

When using these modes, there is a slight decrease in wear rate. Studies of the morphology of the friction surfaces of these samples did not show significant differences from the morphology of the friction surfaces of the initial VT6 titanium.

An analysis of the results obtained in the study of the wear resistance of VT6 titanium alloy as a result of laser radiation treatment and ion implantation of those given in accordance with Table 2 shows that the most optimal is the modification of the surface of VT6 alloy by high-intensity ion-beam processing followed by laser surface treatment without fusion.

| Sample surface treatment option | Friction path, m |
|--------------------------------|-----------------|
|                                | 0   | 100  | 200 | 300 | 400 | 500 | 600 | 700 |
| The initial state              | 0   | 9,2  | 21,3| 30,5| 47,6| 58,3| 78,8|101,4|
| After ion implantation         | 0   | 4,8  | 9,7 |13,5 |21,8 |30,4 |44,3 |55,6 |
| Laser surface hardening        | 0   | 5,1  |10,3 |14,6 |22,9 |33,1 |47,9 |61,5 |
| Laser surface hardening + ion  | 0   | 3,9  | 7,7 |11,15|17,06|24,83|35,4 |44,9 |
| implantation                   | 0   | 3,12 |6,05 |9,03 |13,77|19,97|28,66|36,98|

Note: Implantation using a Cu – Pb alloy cathode with an implantation dose of \( 5 \cdot 10^{17} \text{ ion/cm}^2 \).
It is noteworthy that the wear resistance of VT6 alloy samples after ion implantation is slightly higher than after laser hardening of the surface. In this case, the microhardness of the surface of the VT6 alloy after laser treatment exceeds the microhardness values VT6 after ion implantation.

With combined exposure in the initial period, a transition from strong to weak wear is observed, and the decrease in friction is due to the formation of oxide and amorphous films on the surface.

Even after testing the samples for 3 hours, the volumetric ablation of the material is about 1287 · 10^3 mm^3, which is 45–50% less than in the initial state. A significantly lower value of ablation during the test for 2.25 hours is associated with a large penetration depth during carbon implantation (up to 2.5–3 μm) from the residual atmosphere of the implant chamber.

A similar effect on wear resistance was also obtained in the case of implantation of iron ions of various doses into samples of VT6 alloy. In this case, it was found that with an increase in the dose of implantation of Fe + ions, the volume of material carried away decreases, which is associated with an increase in the thickness of the modified layer. In addition, an increase in the microhardness measured according to Vickers and a decrease in the friction coefficient due to the formation of an amorphous Fe – Ti – C layer, as well as the release of Ti2Fe particles, were also observed.

5. Conclusion

It was revealed that a significant increase in the microhardness of the surface of the VT6 alloy is observed during ion bombardment by iron and copper ions.

Thermal annealing after implantation of Cu + and Pb + ions with a dose of 5 × 10^{17} cm^{-2} leads to a sharp increase in the hardness of the surface layer, while at depth the hardness decreases more significantly compared to the initial samples after surface plasma treatment.

A sharp increase in the microhardness of VT6 titanium alloy under combined ion-laser irradiation can be explained by the influence of radiation defects formed by ions and introduced impurities on the subsequent formation of a quenching structure during laser thermal hardening, a change in the surface microstructure, and, in particular, an increase in the dispersion of martensite.

The surface roughness of the sample of VT6 alloy after complex treatment decreased compared to the roughness of the alloy after implantation of copper and lead and is on the order of (210–260) nm.

Complex processing led to a decrease in the coefficient of friction from 0.8 (in the initial state) to 0.15 (after complex processing), volumetric wear and fatigue strength by 55%, and an increase in microhardness.

The increase in microhardness in the studied samples after complex processing compared with the initial sample is associated with grain refinement due to the formation of Ti2Cu and Ti2Ni particles in the surface layer, an increase in the dislocation density to 2 · 10^{10} cm^{-2}, and a significant penetration depth of carbon and oxygen (3000 and 2500 nm, respectively) and their transition to the bound state - carbides and oxycarbides.

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