Investigation of the effect of the treatment of the surface of VT6 alloy on the penetration depth of implantable ions

V V Ovchinnikov1, E V Luk’yanenko1, I A Kurbatova1,* and S V Yakutina1
Moscow Polytechnic University, B. Semenovskaya st., 38 Moscow, 107023, Russian Federation

*uchevatkina@yandex.ru

Abstract. The article presents studies on the combined treatment of VT6 titanium alloy, including preimplantation treatment of the titanium alloy surface with a laser or plasma and subsequent modification with highly efficient energy flows using a copper and iron cathode. The beneficial effect of preliminary surface laser and plasma treatments of VT6 alloy parts as an operation of preparing the surface for implantation on the mechanical and tribological properties, as well as the penetration depth of the implanted ions in the surface of the VT6 titanium alloy, is shown. 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
Titanium (α+β) alloys are widely used in modern aircraft and mechanical engineering products due to high strength and anticorrosion properties, as well as good weldability. They are used in large-size welded structures of aircraft [1].

However, due to the high tendency to set and push during sliding friction operation, their use for manufacturing movable parts of machines and mechanisms is limited [2].

The improvement of the technology of making coatings on the surface of structural materials, including titanium alloys, has led to the emergence of methods of selective laser melting and direct laser application of materials and ion implantation, which have gained popularity in recent years [3-5].

The properties of the samples of the ion implanted titanium alloy BT6 are largely characterized by the hardness and thickness of the surface strengthened layer. The value of hardness after treatment is in turn related to the initial hardness of the modified surface, the grade of implanted ions and the depth of their penetration into the matrix, the isolation of secondary intermetallic phases in the implanted layer, etc.

A significant drawback of ion implantation is the formation of a modified layer with a length of not more than 1 μm, which is often insufficient to provide wear resistance to the surface.

In connection with the above, it is considered to be advantageous to use an ion implantation station for the treatment of titanium alloy parts BT6, after preliminary surface hardening, for example laser or plasma treatment.
The use of plasma and laser surface effects to form a ВТ6 reinforced layer of the required depth on the titanium alloy, which can then be subjected to ion implantation, will increase the depth of the strengthened layer and preserve the advantages of ion implantation.

The purpose of the present work was to study the microstructure and hardness of the surface layers of the titanium (α + β) alloy of ВТ6 grade subjected to plasma and laser treatment and subsequent implantation with copper and iron ions.

2. Materials and methods
The object of the study was samples of titanium α + β-alloy VT6, the chemical composition of which is as follows, wt.%: 86.485–91.2 Ti; 5.3–6.8 Al; 3.5–5.3 V; up to 0.1 C; up to 0.3 Fe; up to 0.15 Si; up to 0.3 Zr; up to 0.2 O; up to 0.05 N; up to 0.015 H.

In the initial state, VT6 had a lamellar β-transformed structure (Figure 1). The thickness of the plates of the α phase is \( b = 3–5 \mu m \), the size of the colonies is \( d = 140–160 \mu m \), and the width of the layers of the β phase does not exceed 0.2–0.3 \( \mu m \).

![Figure 1. The initial microstructure of VT6 titanium alloy.](image)

Laser hardening was carried out using a fiber laser with a wavelength of 1064 nm, a power of up to 2 kW and various laser beam velocities.

An inverter rectifier of the brand “Forsage – 315” was used as a power source for the plasma torch arc.

Ion implantation of VT6 titanium alloy samples was performed on a plant for implantation with metal and gas ions using copper and iron ions as implantable ions, which irradiated the treated surfaces in the following mode: implantation energy \( E = 35 \text{ keV} \), current density \( I = 40 \ldots 60 \mu A / \text{cm}^2 \), radiation dose (fluence) \( D = (1 \ldots 5) \cdot 10^{17} \text{ ion} / \text{cm}^2 \).

For implantation of the VT6 titanium alloy after plasma and laser treatment, copper and iron ions were chosen. For the manufacture of the implant cathodes, an alloy with an iron and copper content of 50: 50% was used. Samples were implanted with a fluence (implantation dose) of \( 5 \cdot 10^{17} \text{ ion} / \text{cm}^2 \).

Surface preparation of the sample included grinding, coarse and fine polishing. Chemical etching of microsections was carried out in a prepared reagent of composition, cm³: HF– 15, HNO₃– 35, H₂O– 200, glycerin –100.

Studies of implanted samples were performed by secondary mass spectrometry on a Physical Electronics PHI-6600 SIMS System.

The surface structure of metallographic samples was analyzed using the Axiovert – 200M universal inverted microscope. An electron microscopic image of the surface of the samples was obtained at the Aurig Cross Beam workstation.

Microhardness was measured on a PMT-3 device at loads of 0.19, 0.49 and 0.98 N according to GOST 9450-84 on transverse sections.
To determine the penetration depth of copper and iron ions during implantation, methods of secondary ion mass spectroscopy and Auger electron spectrometry were used.

The mechanical properties under static tension were determined on cylindrical and flat samples according to GOST 1497–84 [6].

The residual stresses generated in the surface layers of flat samples as a result of plasma treatment were determined by stepwise cutting with measurements of relative deformation at each stage in two places: on the treated surface at a distance of 2-3 mm from the edge of the slot and against the slot on the opposite side of the sample.

The deformation was measured by KF-5-P1-3-100 strain gages and the R-3500 strain gauge (USA). An incision was made with a diamond wheel 1 mm thick.

Comparative tribological testing of the samples was carried out on a friction machine 2070СМТ – 1 according to the “disk – finger” scheme in sliding mode at a speed of 1 m / s at a normal load of 50 ... 200 N.

To study the wear resistance of the samples, a mass estimation method was used. Mass characteristics were determined on optical laboratory scales of the ADV model.

3. Results
An important indicator of the effectiveness of hardening the surface of metallic materials during plasma treatment is an increase in microhardness. By varying the plasma treatment regimes, it is possible to adjust the depth of the hardened surface layer and the degree of hardening based on the technical requirements for the parts used in specific operating conditions. A similar result can be achieved by increasing the duration of the plasma arc exposure on the surface of the metal being treated during reflow processing. Thus, changing the plasma treatment regimens (depth of the hardened layer), a batch of samples of VT6 alloy was obtained with a different ratio of the depth of the hardened layer and the working thickness of the sample [7].

The decrease in the plastic characteristics of materials after plasma treatment is associated with the localization of the plastic flow near the mouth of the main crack that nucleates near the surface.

With a small hardening depth, the decrease in ductility is insignificant. For a sample with surface plasma hardening, the presence of a crack-type defect in the surface layer can be considered as a variant of brittle fracture passing through the entire hardened layer. Thus, the presence of a layer in a first approximation is equivalent to the presence of a crack nucleus with a length equal to the layer thickness.

Thus, the presence of a layer in a first approximation is equivalent to the presence of a crack nucleus with a length equal to the layer thickness. It should be noted that such an approximation is simplified and corresponds to the most “hard” case, since the hardened layer can exhibit some plastic properties and detect an increase in the yield strength, which should affect the mechanical properties of the material [8].

From the obtained results it follows that the plasma treatment of the VT6 alloy across the axis of the sample leads to brittle fracture, but with a longitudinal arrangement of tracks with an overlap of 0.6, an elongation of up to 12% can be obtained. In this case, the yield strength increases by 15–20%. Plasma treatment of two opposite faces of the sample reduces the temporary resistance in comparison with the processing of one plane [9].

The research results showed that, despite the influence of several factors, the ratio of the depth of the hardened metal layer to the working thickness of the part can be considered the determining technological parameter of the workability of a part with surface plasma hardening.

In the process of laser hardening without fusion, two zones can be observed. The first (A) is a highly dispersed martensite, formed as a result of high-speed heating and subsequent cooling, located near the substrate or structure of the base metal (O) of VT6 titanium alloy. The second region (B) is a thin oxide film that appears on the surface itself as a result of the interaction of titanium with the atmosphere of air. This zone has increased values VT6 of hardness, and its thickness does not exceed 2 μm [10].

As you move deeper into the metal, the size of the martensitic plates increases.
In the case of laser hardening with fusion, three characteristic zones can be distinguished in the surface layer in which the microstructure is different from the base material (O). The first zone (A) is characterized by the martensitic microstructure $\alpha'$. Just as in the case of hardening without reflow, here there is an increase in hardness relative to the original by about 1.5 times.

Further, this region is transformed into an intermediate zone B with a dendritic structure. Zone B, lying close to the surface, contains well-developed dendrites directed from the base metal to the surface. However, the increased hardness of this dendritic layer located in the surface layers is achieved by oxidation in air.

A study was made of the influence of the depth of penetration of copper and iron ions into the implanted target surface of a VT6 alloy with a plasma pretreated surface. Plasma treatment was performed in two versions: without fusion and with fusion of the target surface. Laser hardening was carried out by two mechanisms with surface melting and without melting due to polymorphic transformation. Fragments of the structures of VT6 titanium alloy after laser hardening are shown in Figure 2.

![Figure 2. Fragments of the microstructure of VT6 titanium alloy after laser hardening: a– with surface reflow, b– without reflow.](image)

The results of studies of the distribution of implanted ions in the surface layer of VT6 titanium alloy after treatment with a plasma arc showed that the presence of a molten layer during reflow processing significantly changes the character of ion penetration into the target (Fig. 3-5).
**Figure 3.** Distribution of copper and iron ions in the surface layer processed by a plasma arc without fusion.

**Figure 4.** Distribution of copper and iron ions in a surface layer processed by a plasma arc with fusion.
4. Discussion of the results

Comparison of the distribution profiles of implanted ions upon irradiation of samples with preliminary plasma treatment (Figure 3, a, b) showed that if 50% Cu – 50% Fe alloy is used as the cathode material, they are identical. The penetration depth of ions is 0.20 ... 0.25 microns for copper, and 0.25 ... 0.28 microns for iron ions during plasma surface treatment without reflow.

Melting the surface of the sample with a plasma arc before ion implantation is accompanied by a sharp increase in the depth of penetration of iron ions (up to 0.45–0.48 μm) compared with the option of surface treatment without fusion. Moreover, in the case of surface fusion, the concentration of iron in the implanted layer will exceed the concentration of copper ions. In the case of plasma treatment prior to implantation without melting the surface, the opposite picture is observed.

Table 1 shows the values of the concentration peak and its position for copper and iron ions, depending on the variant of preliminary processing of the sample surface with a plasma arc and the magnitude of the implantation dose.

| Dose of implantation, ion / cm² | Processing by a plasma arc without melting the surface | Treatment with a plasma arc melting surface |
|---------------------------------|--------------------------------------------------------|--------------------------------------------|
|                                 | Cu          | Fe          | Cu          | Fe          | Cu          | Fe          |
|                                 | h, мкм     | C, ат. %    | h, мкм     | C, ат. %    | h, мкм     | C, ат. %    | h, мкм     | C, ат. %    |
| 10^{17}                         | 0,12       | 6,2         | 0,15       | 5,9         | 0,18       | 8,6         | 0,45       | 10,1        |
| 5·10^{17}                       | 0,22       | 7,8         | 0,25       | 7,2         | 0,38       | 10,4        | 0,77       | 15,4        |
| 10^{18}                         | 0,35       | 8,8         | 0,41       | 8,3         | 0,54       | 13,2        | 0,99       | 19,7        |

An analysis of the results allows us to conclude that with an increase in the implantation dose with preliminary plasma surface treatment without melting, an increase in the peak in the concentration of copper and iron is observed with a shift of this peak deeper into the surface of the sample. Moreover,
the concentration of copper ions in the entire range of implantation dose values exceeds the concentration of iron ions.

In the case of a plasma surface treatment with surface melting, there is a tendency to a substantial increase in the concentration of intercalated ions, as well as a shift in the location of the concentration peak inland from the surface of the sample. In this case, the concentrations of the implantable elements and the location of the concentration peak relative to the surface being treated are twice as high as those indicated for the plasma treatment variant without surface melting. A more intense penetration of iron ions both in concentration and in depth compared with copper ions is also observed over the entire range of implantation dose values.

Analysis of the distribution curves of implantable ions along the depth of the surface layer is almost identical to that considered for the case of using a plasma jet for heating.

At high laser radiation power, the surface of the titanium alloy melts and a developed dendritic structure forms at the coating – substrate interface. In this case, the hardness of the titanium alloy increases due to the formation of a martensitic structure in the surface layers and their alloying with elements that make up the surfacing coating.

In laser micromelting of the surface of a titanium alloy sample to a depth of 35–45 μm, the formation of amorphous sublayers in the structure of the surface layer is noted. Ion implantation of such layers further enhances the wear resistance of the material.

5. Conclusion
The beneficial effect of preliminary surface laser and plasma treatments of parts made of VT6 alloy is shown as a preparatory stage for the matrix surface for ion implantation. Combined processing improves mechanical and tribological properties.

The increase in microhardness of VT6 titanium alloy under combined ion-laser irradiation is associated with the influence of radiation defects formed by ions and an incorporated impurity 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.

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

References
[1] Boyer R R 1996 An overview on the use of titanium in the aerospace industry Mater. Sci. Eng. A. Vol. 213.P. 103—114.
[2] Santecchia E Hamouda A M S Musharavati F Zalnezhad E Cabibbo M Spigarelli S 2015 Wear resistance investigation of titanium nitride-based coatings. Ceram.Int Vol 41 Iss 9 Pt A P 10349-10379.
[3] Hemmati I Ocelik V De Hosson J Th M 2013 Effects of the alloy composition on phase constitution and properties of laser deposited Ni — Cr — B — Si coatings Phys. Procedia Vol 41 P 302-311.
[4] Karg M Ahuja B Kuryntsev S Gorunov A Schmidt 2014 Processability of high strength aluminum-copper alloys AW-2022 and 2024 by laser beam melting in powder bed. 25th Ann. Int. Solid FreeForm Fabrication Symp. (Austin, Texas, USA) P 420-436.
[5] Amend P Hentschel O Scheitler K Gorunov A I Schmidt M 2015 Effect of additive manufactured metallic structures on laser-based thermal joining of thermoplastic metal hybrids. KeyEng.Mater Vol 651-653 P 777-782.
[6] Margolin B 3 Experimental-calculation method for determining residual stresses 1991 Shipbuilding industry. Welding. Ser. Material Science: Welding No 11 P.17-23.
[7] Semendeeva O V Uchevatkina N V Ovchinnikov V V 2013 Hardening of the surface layer of parts from titanium alloy VT6 by laser surface treatment Technology of metals No 1 S. 30-35.
[8] Kondratiev SYu 2011 Optimization of surface hardened layer parameters during laser hardening
of parts *Welding production* Number 3 P 11-15.

[9] Ovchinnikov V V Uchevatkina N V Kurbatova I A Lukyanenko E V Yakutina S V 2019 VT6 Titanium alloy wearability increase via implantation of copper and aluminum ions *Periodico Tche Quimica* Volume 16 No. 32 P 2179 - 0302.

[10] Pogrebnyak A D Erdybaeva N K Bratushka S N et al. 2008 Effect of high-dose implantation of metal and gas ions on the physicomechanical properties of titanium alloys *Questions of atomic science and technology* No 1 P 81-92