Improving the performance properties of titanium alloy VT6 after ion implantation with copper and aluminum ions

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Abstract. The objective of this work was to study the processes occurring on the surface of VT6 titanium alloy samples when implanting with copper and aluminum ions. Elemental composition, structural-phase state, mechanical and tribological properties of VT6 titanium alloy surface layers modified by aluminum and copper ions was being researched. As can be seen from the undertaken studies, the mode of high-intensity ion-implantation process makes it possible to obtain ion doped surface layers of VT6 alloy containing finely dispersed intermetallic phases and a solid solution of aluminum and copper in titanium of a composition varying in depth. The thickness of the ion-doped layer, the average grain size of the intermetallic phases and their conglomerates increases with the increase in implantation dose while aluminum implantation is in progress. It has been shown that the implantation of aluminum and copper ions into VT6 alloy leads to a considerable increase in its microhardness and wearability. Based on the research results, a conclusion on the positive effect of a structural-phase state of ion-doped titanium layers on their mechanical and tribological properties of VT6 titanium alloy has been drawn.

High specific strength and corrosion resistance of titanium and its alloys have caused their widespread application in engineering and medicine. However, the use of titanium alloys in friction joints is restrained by their low resistance to wear. A fair amount of attention has been paid to research of titanium alloys wearability [1, 2].

Ion-implantation process is one of the promising methods for controlling the strength properties of metals and alloys surface layers. Ion-implantation process is an effective method of modifying the microstructure and elemental composition of structural and tool materials surface layers due to formation of high-density solid solutions, interstitial phases or intermetallic compounds [3, 4].

In this regard, the objective of this work was to study the processes occurring on the surface of VT6 titanium alloy samples when implanted with copper and aluminum ions. VT6 alloy samples having the form of a parallelepiped with dimensions of 5×5×30 mm were used as a study material. Irradiation of VT6 alloy samples was carried out at an accelerating voltage of 30 kV. The distance from the samples to an ion source was 0.35 m. The treatment was being begun at room temperature.

The structural study of samples was performed via scanning (Carl Zeiss EVO 50 instrument) and transmission diffraction (EM-125K) electron microscopy.

Research of tribological characteristics of ion-doped titanium layers was performed in the air according to the ‘disk-finger’ scheme at a sliding speed of 3m/s and at a load of 25 N [5].
counterbody was made of 11X15 hardened steel. Measurements of samples mass losses during the wear test were carried out by means of weighing them on the analytical scales.

The research of structural-phase state, elemental composition and mechanical properties of VT6 titanium alloy surface layers modified by ion-implantation method with aluminum ions in a high-intensity mode showed that the modified layers with a thickness from 420 nm to 2,100 nm were obtained (Table 1). The maximum concentration of embedded aluminum reached 50-55 at. %.

Certain regularity is observed during formation of surface layers on the alloys based on titanium when implanting VT6 titanium alloy with aluminum ions. The layout of phase layers being formed during ion-implantation process is shown in Figure 1.

Two regions smoothly passing into each other can be distinguished from the irradiated surface of the sample deep into the implanted layer. The first region is an oxide-carbide film containing aluminum, oxygen and carbon (zone IV). A region consisting of intermetallic phases and a solid solution of aluminum in titanium is formed from the oxide-carbide film existence boundary.

Table 1. Basic characteristics of VT6 titanium alloy surface layers implanted with aluminium and copper ions.

| Implantation dose, ion/cm² | Ion-doped layer thickness, nm | Phase composition | Oxides and carbides |
|---------------------------|------------------------------|------------------|---------------------|
| Average size, nm          |                              |                  |                     |
|                           |                             | Intermetallic (phase localization areas) |
| Ti-Al                     |                              |                  |                     |
| 2×10¹⁷                    | 420                          | γ-TiAl (95–110 nm); α₂-Ti₃Al (45–195 nm); α-solid solution (50–420 nm) | TiO (monocl.), TiO₂ (hex.), TiC (cub.), Al₂O₃ (hex.) |
| 7.2×10¹⁷                  | 680                          | γ-TiAl (75–310 nm); α₂-Ti₃Al (90–395 nm); α-solid solution (90–680 nm) | TiO₂ (hex.), TiC (cub.), γ-Al₂O₃ |
| 5.2×10¹⁸                  | 1550                         | γ-TiAl (125–610 nm); α₂-Ti₃Al (125–700 nm); α-solid solution (125–1550 nm) | TiO₂ (hex.), γ-Al₂O₃ |
| 1.2×10¹⁹                  | 2100                         | γ-TiAl (225–800 nm); α₂-Ti₃Al (300–1700 nm); α-solid solution (300–2100 nm) | TiO (monocl.), TiO₂ (hex.), γ-Al₂O₃; γ′-Al₂O₃ |
|                           |                              |                  |                     |
| Ti-Cu                     |                              |                  |                     |
| 2×10¹⁷                    | 320                          | Ti₃Cu (30–70 nm); α-solid solution (70–320 nm) | TiO (monocl.), TiO₂ (hex.) |
| 7.2×10¹⁷                  | 460                          | Ti₂Cu (10–30 nm); Ti₃Cu (30–110 nm); α-solid solution (110–460 nm) | TiO₂ (hex.) |
| 5.2×10¹⁸                  | 680                          | TiCu + Ti₂Cu (10–70 nm); Ti₃Cu (70–180 nm); α-solid solution (180–680 nm) | TiO₂ (hex.) |
| 1.2×10¹⁹                  | 860                          | TiCu (10–30 nm); TiCu + Ti₂Cu (40–120 nm); Ti₃Cu (120–280 nm); α-solid solution (280–860 nm) | TiO₂ (hex.) |
Three zones can also be distinguished in this region: the first zone contains three phases: α₂-Ti₃Al, γ-TiAl and α-solid solution; the second zone consists of two phases: α₂-Ti₃Al and α-solid solution; there is only a solid solution of aluminum in titanium in the third zone.

A regular increase in the thickness of implanted layer and oxide-carbide film is observed with the increase in the dose of VT6 titanium alloy specimen irradiation with aluminum ions.

The increase in the average grain size of intermetallic phases and their conglomerates is observed at the same time. Formation of conglomerates has been detected at irradiation doses of 7.2·10¹⁷ ion/cm² and more. Grains of intermetallic phases being formed on all four implantation modes of aluminum ions are nanoscale ones according to the classification. Conglomerates can reach the sizes of up to 280 nm at the same time.

The study of a structural-phase state, elemental composition and mechanical properties of VT6 titanium alloy surface layers modified by the ion-implantation method with copper ions showed that modified layers with a thickness of 320 nm to 860 nm were obtained. At the same time, the maximum concentration of embedded copper reached 20-25 at. %.

A layer-by-layer phase analysis showed that the intermetallics determining the surface layers hardening propagate to deep depths, which is a qualitative characteristic for improving the mechanical-and-physical properties of the surface layer when alloying with copper.

The thickness of the entire implanted layer during copper implantation with consideration for the oxide-carbide film is determined in the same way as in the case of aluminum implantation, i.e. by the implantation conditions. A titanium sample made of VT6 alloy irradiated with copper ions with a dose of 2·10¹⁷ ion/cm² has an ion-doped layer thickness of 320 nm. The increase in the thickness of ion-doped layers is observed with the increase in the irradiation dose and is 860 nm in case of a mode with aluminum ions irradiation dose of 1.2·10¹⁹ ion/cm².

The research of concentration profiles made it possible to find out the localization spots of formed intermetallic phases. The aluminum concentration according to Ti—Cu diagram corresponds to Ti₃Cu phase homogeneity range for an implantation dose of 2·10¹⁷ ion/cm² starting from the boundary of the surface oxide-carbide film and down to a depth of 70 nm. The displacement of Ti₃Cu phase existence lower boundary to deep depths is observed with the increase in the irradiation dose and reaches 280 nm in case of implantation dose of 1.2·10¹⁹ ion/cm².
An intermetallic of Ti$_3$Cu compound can be formed at lesser copper concentrations according to Ti-Cu system state diagram. The region of its existence extends to deep depths in comparison with TiCu phase accordingly.

Ti$_3$Cu exists at the depths from 30 to 70 nm for an implantation dose of $2 \cdot 10^{17}$ ion/cm$^2$ and it exists at the depths from 120 to 280 nm even when implanted with a dose of $1.2 \cdot 10^{19}$ ion/cm$^2$. A solid solution of copper in titanium is formed over the entire thickness of the ion-doped layer, excluding the oxide-carbide film.

A certain regular pattern is observed in the formation of surface layers on titanium-base alloys when implanting VT6 titanium alloy with copper ions. The layout of phase layers formed during ion-implantation process is shown in Figure 2.

Two areas smoothly passing into each other are located from the sample irradiated surface deep into the layer implanted via copper atoms. The first area is an oxide-carbide film containing copper, oxygen and carbon in its composition. An area consisting of intermetallic phases and a solid solution of copper in titanium is formed from the boundary of the oxide-carbide film position.

The following zones can also be distinguished in this area: the outer zone contains the following phases: TiCu$_3$ and $\alpha$-solid solution; the second zone consists of three phases: TiCu + Ti$_2$Cu and $\alpha$-solid solution; there is only a solid solution of copper in titanium in the third zone.

The increase of the implanted layer and oxide-carbide film thickness is observed with the increase in the irradiation dose of VT6 titanium alloy samples via copper ions as in the case of implantation with aluminum ions.

The increase in the average grain size of intermetallic phases is observed at the same time. Formation of conglomerates has not been established during implantation with copper ions. Grains of intermetallic phases being formed based on the entire modes of copper ions implantation are nano-scale ones regarding sizes.

The microhardness at the depths of up to 1.8-2 microns exceeds the microhardness at the relevant depth for VT6 initial titanium alloy for the entire implanted samples.

The increase in microhardness of 1.4-2.9 times is observed in the near-surface region in the thickness of ~ 0.9-1 μm for a sample of VT6 alloy implanted with aluminum ions with a dose of $1.2 \cdot 10^{19}$ ion/cm$^2$.

The diagram of VT6 alloy samples wear rate change (Figure. 3) as a function of temperature has shown that there is no significant difference in the wear rate for ion-doped and initial alloy at room temperature.
Figure 3. Wear of VT6 titanium alloy samples at various test temperatures:

1 – without implantation; 2 – implantation of aluminum ions; 3 – implantation of copper ions. The implantation dose is $1.2 \times 10^{19}$ ion/cm².

However, there is a marked increase in the wear of VT6 initial alloy with the temperature increase in contrast to doped alloy, which wear does not change in the researched temperature range. Thus, as the temperature rises up to 200°C, the wear level of VT6 initial alloy has increased by a factor of 2.3, while the wear level of implanted alloy has remained almost unchanged.

The average friction factor of test samples has been monitored during performance of tribological tests. The friction factor of VT6 alloy implanted layer is much lower at the elevated temperatures than for initial state. The average friction factor of VT6 alloy being in the initial state was increasing with the rise of sample temperature while it almost was not changing for the ion doped alloy.

It should be noted that the implantation of aluminum ions into VT6 titanium alloy is more effective as compared with implantation of copper ions from the standpoint of increasing its wearability at an elevated temperature.

Thus, the formation of multilayer ion-doped layers containing intermetallic phases during implantation of VT6 alloy with aluminum and copper makes it possible to significantly increase the alloy mechanical properties. The formation of ion-doped layers consisting of several regions different from each other in phase composition and base of an alloy is important for practical purposes.

The estimation of the residual stresses value in VT6 alloy samples surface layer after implantation with metal ions with a high implantation dose has been performed within the framework of this work.

Flattened sheet specimens of 1 mm in thickness and 10 mm width were used to research the ion implantation effect on residual stresses in VT6 titanium alloy surface layer. Samples were exposed to annealing in a vacuum furnace before implantation in order to relieve the stresses that arose during rolling of the sheets. The annealing temperature was 750 °C.

The implantation dose was being varied within the range of $5 \cdot 10^{16} - 5 \cdot 10^{19}$ ion/cm² in addition to varying the implanter cathode material during experiments. An experimental plant was being used to measure the level of residual stresses in VT6 alloy samples surface layer after implantation. The plant operation principle is based on measuring the sample surface displacement during metal stripping via electrochemical method and automatic recalculation of sample surface displacements into residual stresses by means of a special program to be measured via a laser displacement controller.
The measurement results of residual stresses are shown in Figure 4. These data were obtained at an implantation dose of $5 \cdot 10^{17}$ ion/cm$^2$. It follows from the obtained results that the residual stresses at a level of 85 MPa are present in the initial sample without implantation.

![Figure 4](image.png)

**Figure 4.** Distribution curve of the residual macrostresses magnitude $\sigma_{\text{res}}$ (MPa) of VT6 titanium alloy surface layer over the depth $h$ (μm) as a result of layer-by-layer analysis:

1 – initial state; 2 – implantation with aluminum; 3 – implantation with copper; 4 – successive implantation with aluminum and copper.

Implantation with aluminum ions contributes to the appearance of compressive stresses of the order of 540–550 MPa in the surface layer, which relax within a layer of 56-60 μm in thickness.

Further growth of residual stresses of up to 670–685 MPa is observed during implantation with copper in case of stress distribution area of approximately 100 μm in depth from the sample surface.

The highest residual stresses were being observed with successive implantation with aluminum and copper. They have amounted to approximately 850 MPa at a depth of the compressive stress distribution range of 160–180 μm.

Thus, it can be said that the complication of implantation (successive implantation) contributes to increase in the level of residual compressive stresses in the irradiated sample and in the depth of their propagation. It may be concluded while analyzing the presented graphical dependences of changing residual compressive stresses in the surface layer depth on the processing mode within the indicated process range that the absolute value of residual stresses increases and then drastically decreases while increasing an implantation dose both with aluminum and copper.

The effect of reducing residual stresses in the implantation dose range $(1–5) \cdot 10^{18}$ ion/cm$^2$ may be related to the formation of new phases in the implanted layer.

It is important to note that the presence of residual stresses of the second kind, i.e. microstresses was identified during measurement of residual stresses, which indicates the availability of a high dislocation density in them.

It may be concluded based on the experimental studies that the residual compressive stresses of the surface layer increase multiple times in comparison with the initial state after VT6 titanium alloy implantation. The regularity of residual compressive stress increase was established with the increase in the implantation dose of up to $5 \cdot 10^{17}$ ion/cm$^2$, following which the decrease of residual stresses is observed with further increase of an implantation dose. Generally, the occurrence depth of residual stresses slightly exceeds the depth of implanted layer.

It may be concluded in studying electron microscopic images of VT6 titanium alloy surface layer obtained via X-raying the thinned films in the thickness of 100 nm at a scale of 500…50 nm
via an electron beam that ion-implantation process makes it possible to obtain a finely nanostructure on the irradiated sample surface (Figure 5).

Figure 5. Nanostructure of the near-surface layer (thickness 100 nm) of VT6 titanium alloy after ion-implantation process using a copper cathode (x235000 on the surface): a – dose of $5 \cdot 10^{17}$ ion/cm$^2$; b – dose of $5 \cdot 10^{18}$ ion/cm$^2$

The particle size was about 30 nm in the initial state in the near-surface layer. The particle size has increased to 40...55 nm as a result of ion implantation using a copper cathode with a dose of $5 \cdot 10^{17}$ ion/cm$^2$ and the particle size has increased to 70...85 nm at an implantation dose of $5 \cdot 10^{19}$ ion/cm$^2$.

The increase in dislocation density of approximately 8.9–9.4 times was observed at initial dislocation density $\rho_{Dinit} \approx 5.4 \cdot 10^{11}$ (cm$^{-2}$) as a result of ion-implantation process with a dose of $5 \cdot 10^{17}$ ion/cm$^2$ and the increase in the dislocation density was approximately 19.6 times in case of implantation with a dose of $5 \cdot 10^{18}$ ion/cm$^2$, (Table 2).

| Implantation dose, ion/cm$^2$ | Dislocation density, cm$^{-2}$ |
|-----------------------------|-------------------------------|
|                             | Aluminum implantation         | Copper implantation          |
| Initial state               | $5.4 \cdot 10^{11}$           | $9.6 \cdot 10^{11}$          |
| $5 \cdot 10^{16}$           | $6.6 \cdot 10^{11}$           | $9.6 \cdot 10^{11}$          |
| $1 \cdot 10^{17}$           | $9.7 \cdot 10^{11}$           | $2.7 \cdot 10^{12}$          |
| $5 \cdot 10^{17}$           | $1.7 \cdot 10^{12}$           | $4.7 \cdot 10^{12}$          |
| $1 \cdot 10^{18}$           | $3.8 \cdot 10^{12}$           | $8.8 \cdot 10^{12}$          |
| $5 \cdot 10^{18}$           | $4.3 \cdot 10^{12}$           | $9.8 \cdot 10^{12}$          |

It may be concluded while analyzing the submitted data that the dislocation density increases while increasing an implantation dose.

Conclusion

The high-intensity ion implantation mode makes it possible to obtain the implanted layers which thickness exceeds the projective range amount of aluminum and copper ions by times. The increase in the thickness of implanted layers was found out with the increase in the implantation dose and reaching 2.1 μm in case of aluminum implantation as well as achieving 0.86 μm in case of copper implantation with a maximum irradiation dose ($1.2 \cdot 10^{19}$ ion/cm$^2$).
Nanocrystalline phases of $\alpha_2$-Ti3Al, $\gamma$-TiAl intermetallics and a solid solution of aluminum in variable composition titanium are being formed in the implanted layer during ion implantation of aluminum into VT6 titanium alloy. The growth of formed phase grains is observed in the surface ion-doped layers with the implantation dose increase. Finely divided grains of intermetallic phases are united into conglomerates of irregular geometrical shape at an irradiation dose of $7.2 \times 10^{17}$ ion/cm$^2$ and more. Formation of oxides and carbides (TiO$_2$, TiO, Al$_2$O$_3$, TiC) in various modifications in traces is also possible during aluminum implantation. It has been shown that several polyphase regions are distinguished in the implanted layers of VT6 alloy. A three-phase field containing $\text{Ti}_3\text{Al}$, TiAl and a solid aluminum solution in titanium is most close to the irradiated surface and has the greatest influence on the physical and mechanical properties of implanted samples.

A three-phase field containing $\text{Ti}_3\text{Al}$, TiAl intermetallic phases and a solid solution (in case of aluminum implantation) both TiCu + Ti$_2$Cu and $\alpha$-solid solution (in case of copper implantation) is closest to the surface when implanting VT6 alloy with copper ions. The increase in the thickness of this three-phase field contributes to a significant improvement of mechanical properties. The surface layers of VT6 alloy ion-doped with aluminum and copper have substantially better macroscopic features in comparison with the original target material. A significant increase in microhardness is observed in the surface layer in the thickness of up to 2.1 $\mu$m.

The wearability of VT6 alloy implanted samples almost do not change during testing at room temperature (20–25°C) in comparison with the initial state. The wear level of VT6 initial alloy increased by 2.3 times, while the wear level of the implanted alloy changed little, if at all with the increase in the temperature of samples of up to 200°C. VT6 alloy sample implanted with aluminum ions at an irradiation dose of $1.2 \times 10^{19}$ ion/cm$^2$ is characterized by a maximum thickness of a three-phase intermetallic area of the entire implanted layer (2.1 $\mu$m) as well as enhanced mechanical and tribological properties.

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