Stressed State of the Surface Layer of VT6 Titanium Alloy after Copper and Lead Ion Implantation

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Abstract

Background/Objectives: The article describes the results of the experimental measurement of the level of residual stresses in the surface layer of VT6 titanium alloy after ion implantation using polyion beams. Methods/Statistical analysis: To study the effect of ion implantation on the residual stresses in the surface layer of VT6 titanium alloy, flat sheet samples of 1 mm thick and 10 mm wide were used. Before implantation the samples were annealed in a vacuum furnace to relieve stresses which arose during sheet rolling. The annealing temperature was 750 °C. Cathodes of copper, Cu-Pb monotectic alloy, and monotectic alloy with additional contact doping with tin were used. Findings: As a result of ion implantation in the studied range of doses of irradiation of VT6 titanium alloy, microstructure of its surface layer substantially hardens due to breakage of the particle size and the increase in the dislocation density. After implantation, it was managed to achieve the thickness of the modified layer comprising the actual implanted layer and the layer with changed dislocation structure of about 60...100 microns with an average size of nanoparticles near the surface of 50...100 nm. The dislocation density as a result of plastic deformation reached the values of ρD ≈ (2,7…9,8)•1012 (cm-2) at the initial value ρDinit ≈ 5•1011 (cm-2). The regularity of the increase in the residual compressive stresses at the increase in the implantation dose to 5•1017 ion/cm2, and then with a further increase of the implantation dose, the residual stresses decrease. In general, the depth of occurrence of the residual stresses slightly exceeds the depth of the implanted layer. Applications/Improvements: It is shown that by using beams with two and more ion kinds, residual stresses in the surface layer of VT6 titanium alloy increase.

Keywords: Ion Implantation, Mechanical Stresses, Multi-Element Ion Beams, Surface Layer, Titanium Alloys

1. Introduction

In the course of ion implantation, various defects of crystal lattice form and interact in the target, implanted atoms accumulate, new phases form and scatter. The aggregate of these effects gives rise to internal stresses in the target.

Because both stationary (defects, impurities, phases) and dynamic phenomena which relax at the end of implantation (relaxation and annealing of radiation defects, formation and dissociation of new phases, target sputtering) occur in the implanted layer, the internal stresses can also be conditionally divided into dynamic or time-space (existing during implantation) and static or residual (remaining after implantation).

After gaining extra energy during implantation, the atoms displace and due to their high mobility, form a region rich in vacancies. The presence of these disordered regions leads to mechanical stresses within each region and between them. In case of amorphization, disordered regions overlap resulting in relaxation of mechanical stresses between them.

Defects propagation (both ballistic and diffusive) causes the target atoms to move. Atomic flows in the alloy, associated with the flow of interstitial atoms will selectively transfer certain alloy elements, unless interstitial flow involves the atoms of all elements in the process of transfer in a ratio corresponding to their atomic concentration.

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It should be noted that even a slight predominant participation of one or more alloying elements in the interstitial flow may cause disproportionate resulting flows of atoms of these elements. Similar considerations apply to the transfer of atoms and vacancy flows but with a significant difference: in this case, the flow of atoms is distributed in the direction opposite to the flow of vacancies.

Furthermore, predominant participation of any alloying element in migration of vacancies leads to a disproportionate transfer of this alloying element by the flow of vacancies.

Both implantation and the above processes lead to formation of the regions in the target enriched by the atoms of impurities leading to concentration gradients and, as a consequence, a change in the mechanical stress field. Furthermore, new phases (chemical compounds) may form accompanied by a change in specific volume which also leads to stresses.

Since the elemental and phase compositions of such areas differ, they may have different coefficients of thermal expansion and upon heating of the target during implantation it may cause thermal stresses with the sign and magnitude determined by the ratio between the coefficients of thermal expansion. Such thermo elastic stresses should be attributed to the dynamic stresses.

Elastic stress of the target during implantation may also vary due to sputtering, and this effect is particularly noticeable in case of implantation of heavy ions.

Thus, it can be believed that the following processes contribute to formation of a strained layer (region) in implantation: defect formation, relaxation and annealing of defects, accumulation and segregation of impurities, diffusion (thermal and radiation-induced), pore formation (in case of gas ion implantation) and sputtering.

Stress distribution across the depth of the sample is such that the doped layer is strongly compressed along the surface, and all components of the stress (and deformation) tensor underneath change sign and decrease in absolute value.

Monograph1 details the technique and experimental results of the diagnostic of implanted layers in the course of implantation by the method of surface acoustic waves. To calculate the stresses and strains induced in the crystal by ion implantation, the authors used temperature method, substituting temperature term αΤ in the relevant equations of thermo elasticity by βC, where β is a coefficient of volume expansion of the lattice per one implanted ion. The rationale for this substitution is the experimental fact that in the range of low implantation doses, volumetric expansion of the lattice is directly proportional to the concentration of implanted ions.

In2, as part of the continuum theory of elasticity, an assessment of residual stresses in high speed steel after high-intensity ion implantation of nitrogen is given. Due to the low (1 keV) ion energy, their penetration depth is not more than a few interatomic distances (the case of “ballistic profile” is considered). It is found that at the surface, stress level reaches the yield strength of the material being processed.

Residual stresses arising according to structural mechanism can be either tensile or compressive. It is believed that in most cases implantation effect leads to compression stresses2,3. Stress diagram with small doses of doping is virtually the same as the distribution of the implanted impurity, but the stress growth is limited by tensile strength of the material.

Further increase in the dose above a certain threshold (critical dose) should lead to stress relaxation due to plastic flow of the material or brittle failure of the surface layer. It is believed that the spatial distribution of stresses is plateau-like with a maximum gradually reaching the surface3.

As already mentioned, in allocation of new phases accompanied by a change in specific volume, the sign of stresses will depend on the ratio of specific volume of the resulting phases to specific volume of the matrix. Therefore, these stresses can be either tensile or compressive.

In2, the values of these stresses are assessed for high-speed steel after high-intensity ion implantation of nitrogen. Calculations show that in this case, the elastic limit (yield point) of the material processed is already achieved at about 5% content of new phases. A further increase in their concentration causes stress relief.

In2, it is noted that the calculations of the stressed-deformed state of the ion-doped layers using the representations of the continuum theory of elasticity by the analytical methods are not quite correct to evaluate the stresses in the plastic region. In such cases, finite element method (FEM) is acceptable which allows to take into account the features of elastic-plastic behavior of the material (ideally rigid, rigid-plastic).

This calculation for VT6 titanium alloy implanted with copper showed that compressive residual stresses occur in the surface layer of the material with a thickness...
of 90 to 250 microns. The magnitude of these stresses in the center of the implanted plate is more than at the edge. This difference increases with increasing concentration of implanted atoms and radiation dose, and the depth of occurrence of the residual stress in the center of the plate is equal to the depth of the implanted layer, and decreases at the edge. It is noted that taking into account plastic deformation leads to a decrease of the stresses in the surface layers compared with a solution for purely elastic material.

In3, X-ray diffraction studies were conducted of the relative change in the lattice spacing of martensite depending on the glancing angle of X-ray beam determining penetration depth. It is found that at a depth of about 0.3 micrometers, the relative change in the lattice spacing changes sign. This may be due to the fact that at the boundary of the doped layer and nitrogen containing sublayer of the target located deeper, stresses change sign: compressive stresses inherent in the surface layer become tensile in the underlayer.

In3, it was attempted to determine the dynamic stresses in samples of steel of type 18-10 during high-intensity ion implantation of nitrogen. Sample deformation was measured by a capacitive method. Rapid of the growth stresses during the initial period of implantation was found. After the first 100 seconds of implantation, compressive stresses reach up to 1.5 GPa. During this time, a in small \(4.7 \times 10^{15} \text{ cm}^{-2}\) dose of nitrogen ions accumulate in the target. In the subsequent period of exposure (30 minutes), their number is slightly increasing.

It is noted that the main reason for such behavior of stresses is an increase in the lattice deformation caused by high levels of generated defects (mainly stacking faults). Upon reaching the level of stress of 1.8 GPa, plastic flow of the material begins.

To explain the absolute values of the stresses, two mechanisms are proposed. The first is based on slow diffusion that does not comply with Fick’s law. The second (more likely according to the authors) is associated with simultaneous contribution of sputtering and diffusion constants independent of time.

However, the most interesting result was obtained after the end of treatment. When turning off the beam (63 min of the process), a surge of the stresses was found. Subsequently (within 15...30 min), these stresses are relaxed by about 50% according to an exponential law. It is noted that such a behavior of the stresses can not be explained by diffusion processes.

Apparently, the reduction in stress values below the limit of plasticity is sufficient to maintain the material in the stressed-deformed state. This state of the surface layers accumulating impurity-defect and structural-phase components of the process of high-intensity ion implantation, largely determines physical, mechanical and, ultimately, functional (operational) properties of tool materials.

The aim of this study was to investigate the value of residual stresses in the surface layer of samples of VT6 alloy after implantation of metal ions with a high implantation dose.

2. Materials and Methods

To study the effect of ion implantation on the residual stresses in the surface layer of VT6 titanium alloy, flat sheet samples of 1 mm thick and 10 mm wide were used. Before implantation the samples were annealed in a vacuum furnace to relieve stresses which arose during sheet rolling. The annealing temperature was 750 °C.

Cathodes of copper, Cu-Pb monotectic alloy, and monotectic alloy with additional contact doping with tin were used for implantation.

The implantation setup used in this paper is experimental and intended for experiments on implantation of gas and metal ions. Its distinctive feature is the presence of two independent ion sources – metal ion source and gas ion source (so-called two-beam setup). The source of metal ion refers to the type of sources with vacuum arc in metal vapors and represents a new type of source, where vacuum arc in metal vapors is used as the plasma medium where ions are extracted from. The source operates in a pulsed mode, and generates pulsed beams of metal ions.

The distinctive feature of this type of ion sources is that they form polychromatic ion beam, i.e. beam structure includes not only singly, but also multiply charged ions.

In addition to varying the implanter cathode with the material, the implantation dose was changed within \(5 \times 10^{16} - 5 \times 10^{18} \text{ ions/cm}^2\) during the experiment.

To measure the level of residual stresses in the surface layer of the samples of VT6 alloy after implantation, experimental setup shown in Figure 1 was used.

The operating principle of the setup is based on measuring the displacement of the sample surface in the process of metal etching by an electrochemical method, and automatic recalculation into the residual stresses in a special program of the sample surface displacements measured by a laser displacement meter.
3. Results and Discussion

The results of measurement of residual stresses are shown in Figure 2. These data were obtained at the implantation dose of $5 \times 10^{17}$ ion/cm$^2$. The results show that in the original sample without implantation, residual stresses are present at a level of 85 MPa.

Figure 1. The setup for the study of residual stresses in the implanted samples by optical-mechanical method:
1—Bath; 2—Mounting plate; 3—Electrolyte; 4—Mount of the cathode; 5—Cathode; 6—Mount of the anode; 7—Anode (ring or flat sample); 8—Lever; 9—Flat reflective flag; 10—Laser displacement meter; 11—Remote control of laser meter; 12—Computer; 13—Laboratory rectifier.

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

When implanting 64%Cu-36%Pb monotectic alloys, further growth of residual stresses is observed to 670-685 MPa at with a field of their distribution at a depth of about 100 microns from the surface of the sample.

The highest residual stresses were observed during implantation with monotectic alloy with additional contact doping with tin. They were about 850 MPa at a depth of the distribution region of compressive stresses of 160-180 microns.

Thus, we can say that the complication of the cathode material and implantation of polyion beam contribute to an increase in the level of residual compressive stresses in the irradiated sample and the depth of their distribution. This is particularly true with the introduction of the heavy elements of the implanter cathode material.

Analyzing the above dependencies of the changes in the residual compressive stresses by the depth of the surface layer on the mode of treatment in the said range, it can be concluded that at an increase of the implantation dose (cathode material – Cu–Pb–Sn), the absolute value of the residual stresses increases (Figure 3), and then sharply reduces.

Figure 2. Distribution diagram of the residual macrostresses $\sigma_{\text{res}}$ (MPa) of the surface layer of VT6 titanium alloy by depth $h$ (microns) as a result of the by-layer analysis:
1—Initial state; 2—Implantation of copper; 3—Implantation of Cu-Pb monotectic alloy; 4—Implantation of tin-doped Cu-Pb monotectic alloy.

Figure 3. Dependence of the change of residual compressive macrostresses $\sigma_{\text{res}}$ (MPa) of the surface layer of VT6 titanium alloy on the implantation dose (cathode—Cu–Pb–Sn alloy):
1—Implantation dose of $5 \times 10^{16}$ ion/cm$^2$; 2—Implantation dose of $10^{17}$ ion/cm$^2$; 3—Implantation dose of $5 \times 10^{17}$ ion/cm$^2$; 4—Implantation dose of $10^{18}$ ion/cm$^2$; 5—Implantation dose of $5 \times 10^{18}$ ion/cm$^2$. 
The effect of reduction of the residual stresses in the range of the implantation dose of \((1–5)\times10^{18}\) ion/cm\(^2\) can be associated with formation of new phases in the implanted layer.

It should be noted that during the measurement of residual stresses, residual stresses of the second kind were found—microstresses indicating the presence of high density of dislocations in them.

Based on the experimental studies conducted, we can conclude that after implantation of VT6 titanium alloy, residual compressive stresses of the surface layer greatly increase compared with the initial state. The regularity of the increase in residual compressive stresses with the increase in the implantation dose up to \(5\times10^{17}\) ion/cm\(^2\) was determined, and then with a further increase of the implantation dose, residual stresses decrease. In general, the depth of occurrence of the residual stresses slightly exceeds the depth of the implanted layer.

In the course of studying the electron-microscopic images of the surface layer of VT6 titanium alloy obtained by radiocopy of the thinned foils with a thickness of 100 nm with a beam of electrons at a scale of 500 . . . 50 nm (×80,000 . . . 1,060,000), it can be concluded that ion implantation allows to obtain an atomized nanostructure on the surface of the irradiated sample (Figure 4).

The particle size was about 200 nm in the initial state in the near-surface layer. As a result of ion implantation using a cathode of Cu-Pb-Sn alloy with a dose of \(10^{17}\) ion/cm\(^2\), a decrease in the particle size to 70 . . . 90 nm was noted, and at the implantation dose of \(5\times10^{17}\) ion/cm\(^2\), particle size reduced to 40 . . . 50 nm.

The dislocation density \(\rho_D\) in the near-surface layer was calculated by the method of sections according to\(^6\):

\[
\rho_D = 2N/L\cdot t \text{ (cm}^{-2}\text{)},
\]

(1)

where \(N\) is the number of points of intersection of arbitrary cross-sections with dislocation lines (pcs.); \(L\) is the total length of the cross-sections (cm); \(t\) is the thickness of the test sample (cm).

At the initial dislocation density of \(\rho_{\text{initial}} = 5\times10^{11}\) (cm\(^{-2}\)) as a result of ion implantation with a dose of \(10^{17}\) ion/cm\(^2\), an increase in the dislocation density of about 8.9-9.4 times was noted, and at the implantation dose of \(5\times10^{17}\) ion/cm\(^2\), an increase of the dislocation density was approximately 19.6 times. Implantation of a dose of \(5\times10^{17}\) ion/cm\(^2\) is accompanied by an increase in the dislocation density of about 18 times compared with the initial state (Table 1).

By analyzing the data given it can be concluded that the dislocation density increases and the particle size decreases with the increase in the implantation dose.

### Table 1. The change in the dislocation density depending on the implantation dose when using a cathode of Cu-Pb-Sn alloy

| Implantation dose, ion/cm\(^2\) | Dislocation density, cm\(^{-2}\) |
|-------------------------------|---------------------------------|
| Initial state                 | \(5\times10^{11}\)              |
| \(5\times10^{16}\)            | \(9.6\times10^{11}\)            |
| \(10^{17}\)                   | \(2.7\times10^{12}\)            |
| \(5\times10^{17}\)            | \(4.7\times10^{12}\)            |
| \(10^{18}\)                   | \(9.8\times10^{12}\)            |
| \(5\times10^{18}\)            | \(8.8\times10^{12}\)            |

By analyzing the data given it can be concluded that the dislocation density increases and the particle size decreases with the increase in the implantation dose.

### 4. Conclusions

1. Based on the experimental studies conducted, it may be concluded that as a result of ion implantation in the studied range of doses of irradiation of VT6 titanium alloy, microstructure of its surface layer substantially hardens due to breakage of the particle size and the increase in the dislocation density.

![Figure 4. Nanostructure of the near-surface layer (thickness—100 nm) of VT6 titanium alloy before and after ion implantation using a cathode of Cu-Pb-Sn alloy (×235,000 on the surface): a—Dose of \(10^{17}\) ion/cm\(^2\); b—Dose of \(5\times10^{17}\) ion/cm\(^2\); c—Initial state.](image-url)
2. After implantation, it was managed to achieve the thickness of the modified layer comprising the actual implanted layer and the layer with changed dislocation structure of about 60...100 microns with an average size of nanoparticles near the surface of 50...100 nm.

3. The dislocation density as a result of plastic deformation reached the values of $\rho_D \approx (2,7...9,8) \times 10^{12}$ (cm$^{-2}$) at the initial value $\rho_{D_{ini}} \approx 5 \times 10^{11}$ (cm$^{-2}$).

4. The regularity of the increase in the residual compressive stresses at the increase in the implantation dose to $5 \times 10^{17}$ ion/cm$^2$, and then with a further increase of the implantation dose, the residual stresses decrease. In general, the depth of occurrence of the residual stresses slightly exceeds the depth of the implanted layer.

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6. References

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