Elastic recovery of nanostructured surface layer of Ti-6Al-4V titanium alloy after scratch-test

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Abstract. Surface nanostructuring of Ti-6Al-4V titanium alloy samples in the process of electron-beam treatment and ultrasonic impact treatment have been studied using the methods of transmission electron microscopy and X-ray structural analysis. The effect of nanostructured surface layer of the Ti-6Al-4V titanium alloy on elastic recovery during scratch test, and, therefore, their wear resistance was demonstrated.

1. Introduction
The Ti-6Al-4V titanium alloy is widely used in the fields of automobile manufacturing, aerospace, ships and chemical industry due to its characteristics of high specific strength, low density and so on [1,2]. But this alloy has poor tribological behavior, which is clear from its high friction coefficient, and poor abrasive wear resistance [3, 4].

The formation of a nanocrystalline microstructure in the surface layer of the titanium alloy is one of the most promising ways to enhance its wear resistance. The presence of metastable martensite phase in surface layer can also increase in mechanical and tribological properties by reversible local structural-phase transformations in the material.

In present paper ultrasonic impact treatment and electron-beam irradiation were used to produce nanostructure in surface layer of Ti-6Al-4V titanium alloy samples. Since scratch test is a powerful technique that offers relatively easy and quick comparison of different materials on abrasive wear [5, 6] it was applied to reveal effect of nanostructured surface layer on wear resistance of Ti-6Al-4V titanium alloy samples.

2. Experimental details
Samples of the Ti-6Al-4V titanium alloy (Al-6.00, V-4.00, O-0.17, Fe-0.16, Si-0.01, C-0.14, Ti-balance, wt.%) were investigated. One part of the samples was treated by three pulses of 50 µs using SOLO electron beam irradiation system (IHCE SB RAS, Tomsk). The beam energy density was 25 J/cm², and the pulse frequency was equal to 0.3 Hz. Irradiation was performed in argon atmosphere with a residual pressure of 0.02 Pa. The second part was treated by ultrasonic impact treatment with speed by axis x=1.7 mm/s, y=4.4 mm/s, frequency 22 kHz.
A JEM-2100 transmission electron microscope (TEM) was used to investigate the defective substructure and phase composition of the samples. X-ray diffraction analysis was performed using a Shimadzu XRD-6000 diffractometer with Cu Kα-radiation.

Nano-hardness tests were used to assess mechanical properties of the treated surfaces, and performed on a NanoTest system (Micro Materials Ltd.). The indentation measurements were performed in a load controlled mode with a Berkovich diamond tip at a maximum load of 100 mN, with the adjacent indents being separated by 30 µm. The loading and unloading times were set to be 20 s. The dwell time at the maximum load was 30 s. The Vickers hardness of the samples was measured at the lateral surface using 50 g loads. In order to obtain relevant statistics, the hardness value indicated corresponds to the measurement of 8 different hardness tests.

The scratch tests were performed using a conical diamond with a tip radius of 25 µm. A scratching track of 600 μm was applied to all samples. In the experiment, an initial surface profile (Step 1) of the tested samples was obtained by pre-scanning with a very low load of 5 μN (no wear occurs at this load). During scratching (Step 2), the surface profile could be sensed and recorded by the depth sensing system. After scratching, the surface profile of the samples was again scanned by the indenter to record the deformation recovery (Step 3). In the second (scratch) step, the applied load was constant at 5 mN between 0 and 200 µm; then, at 200 to 400 µm the normal load of the indenter was linearly, ramped to the maximum load to 300 mN, and at the end of the scan (400-600 µm) the applied load was constant at 300 mN. A total of 7 scratches were performed for statistical purposes.

3. Results and discussion

X-ray analysis of as-received Ti-6Al-4V titanium alloy reveals peaks of hcp α-phase with lattice parameters a=0.29345 nm and c=0.46741 nm and bcc β-phase with lattice parameter a=0.32218 nm. The fraction of β-phase is 8 %. (figure 1, curve 1). The electron beam treatment of the titanium alloy samples causes a change in the intensity of the α-phase peaks, which indicates the occurrence of recrystallization processes in the melted surface layer. Along with a change in the intensity, broadening of the α-phase peaks is observed which can be caused both by strong distortion and by α'-phase formation in the melted surface layer as a result of electron beam treatment (figure 1, curves 1, 2). Moreover, there are no peaks of β-phase on the diffraction pattern (figure 1, curve 2), and splitting of 100 and 002 α-phase peaks into doublets (111+021), and (112+022) is observed, which indicates α′-phase formation. Grazing incidence X-ray diffraction shows that distribution of α′-phase over the depth of the modified surface layer is non-uniform. So, analysis of X-ray diffraction pattern taken at 3° shows that the phase fraction is 45% at the depth of 2 μm and gradually decreases as the angle of incidence increases. The distribution of α″-phase over the depth of the melted surface layer is also gradient and correlates with the distribution of macro-stresses therein. So, the maximum volume fraction of α″-phase is in the upper melted surface layer where the residual tensile stresses reach 2.6 GPa. At the same time, there is no α″-phase at the depth of 1 μm where the tensile stresses do not exceed 1 GPa.

Figure 1. X-ray diffraction pattern of as-received Ti-6Al-4V titanium alloy (1) after electron beam (2) and ultrasonic impact treatment (3).
After ultrasonic impact treatment (figure 1, curve 3) the intensity of the $\alpha$-phase peaks is considerably lower than in as-received Ti-6Al-4V titanium alloy, and significant broadening of the peaks is also observed. It is indicative of high residual compressive stresses (1.5 GPa) and significant refinement of crystallites. In addition, redistribution of individual $\alpha$-phase peak intensities appears to take place along with changes in the preferred crystallographic orientation (101) and formation of structure with equiprobable orientations (002) and (101). There are also no peaks of $\beta$-phase on the diffraction pattern (figure 1, curve 3).

TEM studies reveal the initial structure of the Ti-6Al-4V titanium alloy consisting of $\alpha$-phase grains with an average size of 2 $\mu$m and $\beta$-phase grains of 500 nm in size which are located in the triple junctions of the $\alpha$-phase grains or along their boundaries (figure 2). The microstructure of the melted layer is represented by primary $\beta$-phase grains with lamellar morphology (figure 3a). The transverse dimension of the martensitic $\alpha'$-phase plates is 80 nm; inside the plates $\alpha^{''}$-martensite with transverse dimensions of 5 nm is observed (figure 3b). The heat affected zone is characterized by the presence of large (5-10 $\mu$m) grains of the primary $\alpha$-phase, also having lamellar morphology, and $\beta$-phase grains with an average size of ~1 $\mu$m.

Ultrasonic impact treatment results in grain refinement and formation of a fragmented dislocation band substructure in the surface layer. The width of the bands varies from 20 to 150 nm (figure 3ab). The fragments within the bands have a non-uniform shape and are elongated in the direction of the microbands. The average fragment size is 50 nm (figure 3d). As the depth of the treated layer increases, the width of the bands and the size of the fragments gradually increase and at a depth of 70 $\mu$m they reach 1 $\mu$m and 500 nm, respectively. At the depth over 80 $\mu$m, the initial structure of the Ti-6Al-4V titanium alloy is preserved.

Nanoindentation technique was used to measure hardness of Ti-6Al-4V titanium alloy samples at the maximum load of 50 mN which corresponds to the maximum indentation depth of 1 mm. It was found that there were no changes in the mechanical properties of the 1 $\mu$m thick surface layers after electron beam treatment, irrespective of the energy density of the beam. On the other hand, analysis of the micro-hardness distribution along the lateral surface showed that the hardness of surface layer increased to 5.2 GPa (table 1). The latter is due to the fact that 40% of soft $\alpha^{''}$-phase is present in the thin surface layer along with hard $\alpha'$-phase, and high tensile stresses also develop. At the same time, at a depth of 2-3 $\mu$m from the surface, where no $\alpha^{''}$-phases are observed and the stresses decrease to zero, micro-hardness increases. In the case of ultrasonic impact treatment, when $\alpha$ nanocrystalline structure of $\alpha$-phase is formed in the surface layers, the increase in micro-hardness is much greater (6 GPa) (table 1). The measurement of the micro-hardness distribution along the lateral surface of the Ti-6Al-4V titanium alloy samples showed that the depth of the hardened layer was 80 $\mu$m which correlates well with the TEM investigations.

### Table 1. Mechanical properties of Ti-6Al-4V titanium alloy samples.

| Treatment                  | Yield strength ($\sigma_{0.2}$, MPa) | Tensile strength ($\sigma_{B}$, MPa) | Elongation ($\varepsilon_{max}$, %) | Microhardness (H, MPa) |
|----------------------------|--------------------------------------|--------------------------------------|-------------------------------------|------------------------|
| As-received                | 720                                  | 950                                  | 8                                   | 3600                   |
| Electron beam treatment    | 775                                  | 975                                  | 7                                   | 5200                   |
| Ultrasonic impact treatment| 920                                  | 1000                                 | 6                                   | 6000                   |

A higher increase in the hardness of the surface layer of the Ti-6Al-4V titanium alloy samples after ultrasonic impact treatment in comparison with electron-beam treatment is accompanied by a major in their strength characteristics under uniaxial tension. Yield strength of the samples subjected to ultrasonic impact treatment increases from 720 to 920 GPa, and tensile strength from 950 to 1000 MPa. After electron beam treatment, yield and tensile strength are 775 and 975 MPa respectively.
Figure 2. STEM (a) и TEM-images (b,c) of as-received Ti-6Al-4V titanium alloy; a,b – bright-field images, c – dark-field image taken with a (143)βTi reflections (indicated by an arrow).

Figure 3. TEM-images of the melted layer after electron-beam treatment (a, b) and of the upper surface layer after ultrasonic impact treatment (c, d) of Ti-6Al-4V titanium alloy; a, c – bright-field images, b,d – dark-field image taken with a (111)α”-Ti (a) and (101)α-Ti (b) reflection (indicated by an arrow).

In spite of insignificant increase in the surface layer hardness of the Ti-6Al-4V titanium alloy samples subjected to electron beam treatment, their tribological properties be enhanced by formation of metastable martensite phases. Total penetration depth in as-received Ti-6Al-4V titanium alloy samples at the maximum load of 300 mN is 950 nm. After the load is removed, the scratch is partially restored; as a result, the scratch depth is reduced to 550 nm (figure 4a, curve 2 and 3). In the samples subjected to electron beam treatment, scratch depth is still 940 nm, but elastic recovery considerably increases (the scratch depth reduces to 400 nm) (figure 4b, curve 2 and 3). In the samples subjected to ultrasonic impact treatment with surface layer hardness, the total scratch depth does not exceed 700 nm (figure 4c). However, as there are no martensite phases, elastic recovery is inessential.

AFM-analysis has shown that plastic deformation of Ti-6Al-4V titanium alloy surface layer develops through viscous-plastic edging with pile-up formation at the edges of a scratch during scratching (figure 5). Elastic recovery of as-received titanium alloy is clearly demonstrated by the flat bottom of the scratch generated by conical indenter (figure 5, curve 1). Increase in the elastic recovery
as a result of electron-beam treatment is evidenced by the scratch bottom assuming a convex shape, which means that it is characterized by positive curvature (figure 5, curve 2). The scratch depth is smaller in the samples subjected to ultrasonic impact treatment, and the scratch bottom becomes flat again. The latter suggests decrease in the elastic recovery (figure 5, curve 3).

![Figure 4. Scratch profile of as-received Ti-6Al-4V titanium alloy (a), after electron beam treatment (b) and ultrasonic impact treatment (c).](image)

![Figure 5. Cross-sectional profiles of Ti-6Al-4V titanium alloy (1), after electron beam treatment (2) and ultrasonic impact treatment (3).](image)

4. Conclusion
Analysis of nanocrystalline structure formed in the surface layer of Ti-6Al-4V titanium alloy after ultrasonic impact treatment and electron beam treatment was performed. It was shown that ultrasonic impact treatment leads only to α-phase grains refinement up to nanosize, and β-phase grains disappear. During electron beam treatment of martensitic α’-phase plates with transverse dimension 80 nm was formed, and also β-phase grains disappear. Moreover, α’’-martensite is formed as a result of electron beam treatment.

Effect of metastable α-phase formed in surface layer of Ti-6Al-4V titanium alloy on elastic recovery during scratch test, and, therefore, their wear resistance was demonstrated. The elastic recovery is 400 nm, and the scratch has the flat bottom in as-received samples and in one subjected to ultrasonic impact treatment. In case of electron beam treatment elastic recovery increase to 540 nm and the scratch bottom is assuming a convex shape.

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