High Intensity Implantation of Aluminium Ions into Titanium[1]

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Abstract – Phase composition, structural state and mechanical properties of the ion-alloyed surface layer of titanium target implanted with Al ions have been investigated. Ion implantation of the Al ions into titanium was carried out using the vacuum-arc, ion-beam and plasma-flow source «Raduga-5». The implantation at the high intensity mode allowed to obtain the ion-alloyed layer with thickness equal to 2600 nm. By the transmission electron microscopy it was established that the fine dispersed equilibrium intermetallic phases Ti_3Al, TiAl and the solid solution of aluminium in titanium were formed in the surface alloyed titanium layer. Additionally, the formation of $TiAl_3$ phase was monitored by means of X-ray diffraction. It was established that the average size of precipitates of the formed phases was equal to 70 nm. Moreover, the agglomeration of the intermetallic particles up to size of 584 nm took place. It was established that the ion-alloyed Ti layer consisting the intermetallic phases was thermostable. The base phase composition remained the same after annealing at 473 K for 1 h. It was found out, that the mechanical properties of the implanted titanium were higher than of the unimplanted material. The microhardness of the implanted titanium sample was in 1.5–3 times higher than the microhardness of the unimplanted Ti. The wear of the implanted Ti was not changed in the temperature range 300–700 K.

1. Introduction

Titanium and titanium alloys are used as the constructional materials in many branches of an industry because of beneficial bulk properties as ductility, tensile and fatigue strength, modulus of elasticity as well as corrosion resistance in aggressive mediums [1, 2]. However, wear behavior and corrosion resistance need to be improved. One of the most promising approaches to this goal is the modification of surface properties by ion implantation without impairing important mechanical bulk properties. The improving of the physical-chemistry surface properties are achieved due to formation of the high concentration solid solutions, interstitial phases and non-equilibrium phases, nanoscale intermetallic compounds and etc. in target surface layer.

In this respect, the alloys on the base of the titanium aluminides having the special mechanical and physical properties have the greatest interest. Titanium aluminides have major hardness at high temperatures which can be compared to hardness of the nickel super alloys. However, the density of titanium aluminides is less than of the nickel alloys. Intermetallic compounds, such as Ti_3Al and TiAl [3], exhibit the excellent high temperature mechanical properties. The strain strength of Ti_3Al and TiAl increases several times at increasing temperature.

The vacuum-arc ion-beam and plasma-flow source «Raduga-5» [4] developed in Nuclear Physics Institute at TPU is perspective one for the intermetallic phase formation in surface layers. Major advantages of this source are the high dose rate of the implanted metal ions, plasma-assisted deposition, heating-up of a target by an ion beam up to necessary temperature and an opportunity of forming the modified ion beam surface layers the thickness of which runs up to several micrometers.

The aim of the present paper was to investigation of the phase composition, structural state, thermalstability and mechanical properties of the titanium target surface layer formed by high intensity implantation of the Al ions using the vacuum-arc ion-beam and plasma-flow source "Raduga-5".

2. Experimental

Pure titanium (VT 1-0) was used as a target for the ion implantation. The implantation of the Al ions into titanium sample was carried out on the ion source «Raduga-5». The implantation conditions of the ion source «Raduga-5» were following: a pulse repetition rate was 170 pulses per second; a duration pulse was 400 μc; a pulsed beam current density was 1.2 mA/cm^2; an accelerating voltage was 20 kV, an average ion energy was ~ 40 keV. The main parameters of the ion implantation are presented in Table 1.

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Table 1. The conditions of the Al ions implantation into titanium target

Accelerating voltage, kV	20
Sample temperature, K	1173
Distance between samples and ion source, m	0.40
Period of implantation treatment, min	125
Ion dose, ion/cm^2	$2.2 \cdot 10^{18}$

The elemental composition of the ion-alloyed surface layer was analyzed by Auger electron spectroscopy (AES) using a spectrometer «Shuna-2». The phase composition and structural state were investigated by transmission electron microscopy (TEM). Measurement of the grain size of the formed phases was carried out on the dark field images by the «secant method». The phase analysis was carried out by identification of the microdiffraction patterns. Additionally, the phase composition was studied by X-Ray diffraction (XRD) method. XRD spectra over the 2θ interval 16–150° were recorded on a difractometer «DRON-3» using FeKα radiation.

The mechanical and tribological properties of the implanted sample were studied in Tomsk Investigated centre at Nuclear Physics Institute TPU. Depth depenent changes of the hardness due to the implantation were studied by measuring the dynamic microhardness with the microhardness tester «Nano Hardness Tester NHT-S-AX-000X» of the Swiss firm «CSEM». A Vickers nanoindentor was used for the investigation of the microhardness. The indenter load was in the range of 15–280 mN. The tribological properties were investigated by «High Temperature Tribometer THT-S-AX000» of the Swiss firm «CSEM». Wear studies were carried out by means of a method «ball-on-disc» using a SiC ball (1.5 mm diameter). The experiments were carried out at 298, 473, 673 K temperatures at an air atmosphere.

In order to investigate the thermalstability of the intermetallic phases formed at high intensity implantation the ion-alloyed sample was annealed at 473 K for 1 h at Ar atmosphere. The phase structure of the annealed sample was studied by TEM.

3. Results and Discussion

The AES depth profiles in the Ti sample implanted with the Al ions are presented in Fig. 1. According to AES profiles (Fig. 1) the thickness of the titanium ion-alloyed surface layer formed at high intensity implantation is equal to 2600 nm. Besides for Al and Ti elements the oxygen and carbon impurities are observed in the implanted surface layer from the residual atmosphere of the vacuum system (Fig. 1). They were absorbed on the substrate surface during ion implantation and then were mixed with the ion beam.

The Al concentration profile has two maximums. The first maximum (~40 at.% Al) is located on the implanted sample surface, another one (~60 at.% Al) at the depth 1000–1100 nm from the irradiated surface. The O, C concentration maximums are located at depth 400 nm from the irradiated surface. It has to be noted, that at depth range 0–400 nm the Ti concentration does not exceed to 0.25 at.% (Fig. 1).

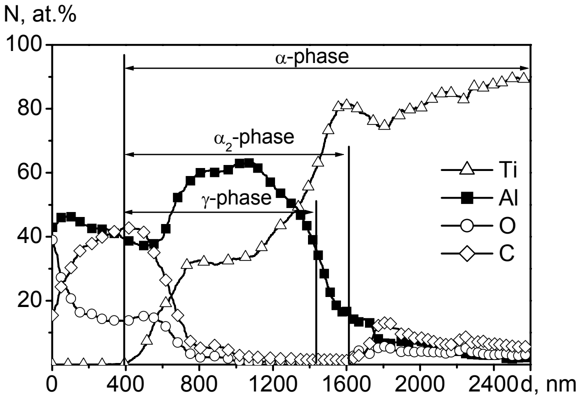


Fig. 1. AES depth profiles for the titanium sample implanted with Al ions

In Fig. 2 the bright field and microdiffraction patterns of implanted titanium are presented. The TEM investigations showed the α_2-Ti_3Al ($D0_{19}$, Ni_3Sn type) and γ-TiAl ($L1_0$, CuAu type) phases formation in the implanted surface layer (Table 2). The formation of these phases in titanium target corresponds to the phase diagram of Ti-Al system [5].

Table 2. Characteristics of Al ion-alloyed layer in Ti target

Thickness of ion-alloyed layer, nm		2600
Phase composition	TEM	Ti_3Al, TiAl, TiO (cub.), TiO_2 (anatase, orthoromb.), γ-Al_2O_3 (cub.), γ '-Al_2O_3 (cub.)
	XRD	Ti_3Al, TiAl, $TiAl_3$, Ti_2O (hexag.), TiO (monocl.), TiO_2 (rutile, orthoromb.), Al_2O_3 (corundum, hexag.)
Average size of phases and conglomerates (*), nm		70 584*

The grain zone axes of the Ti_3Al phase (021, $\bar{1}52, 17.6.\bar{8}, 2.1.\bar{2}$) were established by the microdiffraction pattern analysis (Fig. 2,b). The sizes of the phase grains were measured on the electron microscopy dark field images. The average size of precipitates of the formed intermetallic phases is equal to 70 nm (Table 2). Moreover, the formation of the intermetallic phase conglomerates was found out. The average size of the conglomerates is achieved to 584 nm (Table 2). Besides, it was established the formation of the oxide TiO (cub., zone axis (221)); TiO_2 (anatase., zone axis $(\bar{7}.1.1)$); TiO_2 (orthoromb., zone axis $(1.7.\bar{3})$) and aluminium oxides – γ-Al_2O_3 (cub., zone axis $(\bar{3}.\bar{6}.7)$); γ′-Al_2O_3 (cub., zone axis (310)). The zone axes of Al and Ti oxides are presented in Fig. 2,b,c.

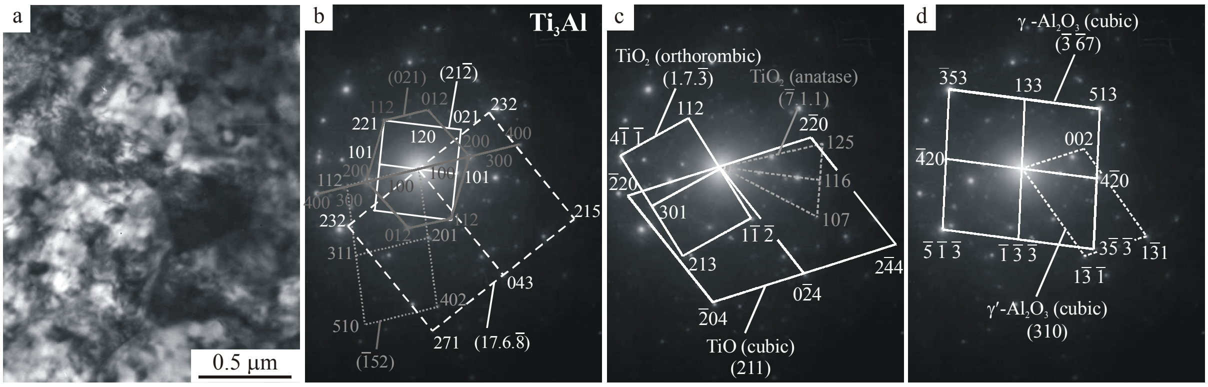


Fig. 2. TEM images of Ti surface layer implanted with Al ions. Bright field image (a); SAD pattern with zone axes of Ti_3Al phase (b); SAD pattern with zone axes of titanium oxides (b); SAD pattern with zone axes of aluminium oxides (c)

The results obtained by XRD confirmed the TEM investigation of the implanted titanium sample. On the X-ray diffraction patterns there are the Ti_3Al and TiAl peaks (Fig. 3,a, Table 2). In addition to intermetallic phases, it was established the $TiAl_3$ compound formation (Fig. 3,a, Table 2). Probably, the $TiAl_3$ phase was formed locally at the depth ~1000 nm from irradiated surface. The titanium target peaks of high intensity are visible on the X-ray diffraction patterns (Fig. 3,a). The lattice parameters of α-titanium ($a = 0.2948$ nm and $c = 0.4680$ nm) were not changed significant after the ion implantation. The formation of the titanium and aluminium oxides was found out by XRD (Table 2). The phase composition of the implanted surface layer is following: Ti – 69.5 wt.%, $TiAl_3$ – 21 wt. %, Ti_3Al – 4 wt.%, TiAl – 4 wt.% and Al_2O_3 – 1.5 wt.%.

The depth dependence of the formation of intermetallic phases can be deduced from the Ti–Al diagram. Comparison of the AES profiles (Fig. 1), TEM images and the phase diagram [5] allowed determining the intermetallic phase localization regions. The phase localizations are shown in the Fig. 1. The narrowest region (400–1400 nm from irradiated surface) corresponds to phase γ-TiAl. Whereas, the $α_2$-phase (Ti_3Al) localization area is much thicker compare to γ-phase.

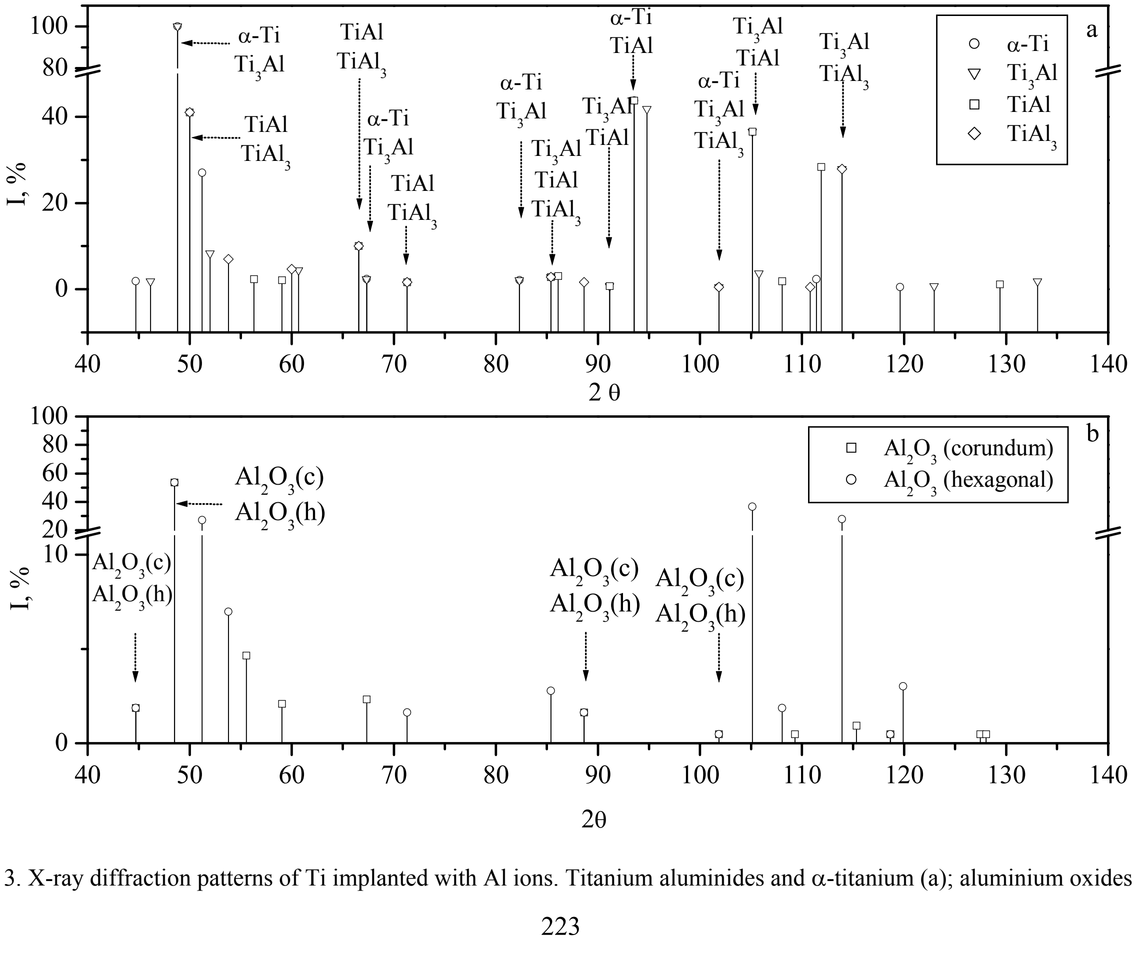
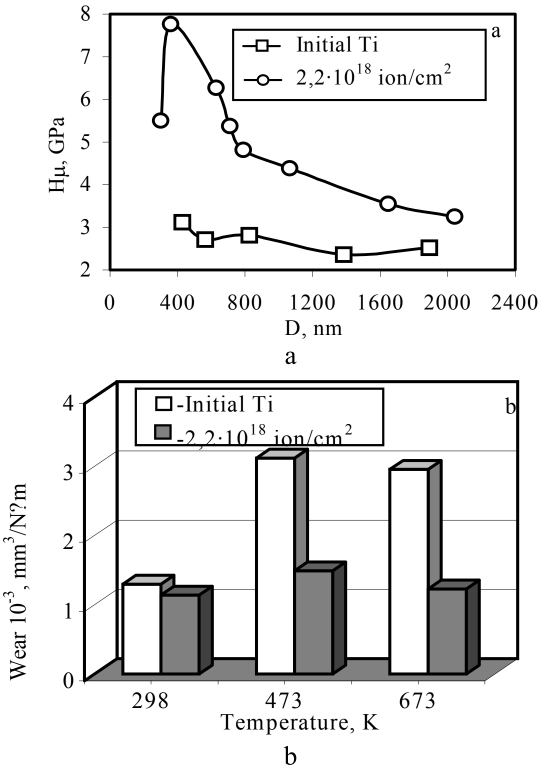


Fig. 3. X-ray diffraction patterns of Ti implanted with Al ions. Titanium aluminides and α-titanium (a); aluminium oxides (b)

The formation of Ti-Al solid solution is occurred in all depth implanted layer (Fig. 1). The solid solution composition is variable as function of surface layer depth.

Additionally to the structural investigations, the tests of the tribological and mechanical properties of the implanted titanium were carried out. The significant increasing of microhardness of the implanted sample was observed. The maximum microhardness increases by a factor of approximately 1.5–3 (Fig. 4,a).



a

b

Fig. 4. Mechanical and tribological properties of the implanted and unimplanted titanium. Microhardness in dependence on the penetration depth of the indenter (a); wear diagram in dependence on the temperature (b)

The microhardness of the implanted titanium well correlates with the aluminum concentration in the titanium layer. The wear diagram of Ti samples dependence on temperature is shown in Fig. 4,b. The implanted and unimplanted titanium samples do not show the difference in wear properties at 298 K. However the wear of the unimplanted titanium decreases with temperature rise, whereas no change of the implanted Ti wear is observed. The wear of the unimplanted Ti increased by 2.5 times in the temperature range 400–700 K (Fig. 4,b).

It has to be noted that the ion-alloyed titanium layer formed at high intensity implantation consists the highstable intermetallic phases. The present of the α_2-Ti_3Al и γ-TiAl phases after annealing at 473 K was confirmed by TEM.

4. Conclusion

The Al ion implantation into Ti sample at the high intensity mode using the vacuum-arc ion-beam and plasma-flow source «Raduga-5» allowed to form the ion-alloyed surface layer of thickness equal to 2600 nm. The diffusion processes played important role for the forming the Al concentration profile in the Ti target. It was established that the finely dispersed equilibrium intermetallic phases Ti_3Al, TiAl and $TiAl_3$ were formed in the surface alloyed titanium layer. The formation of these phases occurred in exact accordance with the phase diagram of Ti–Al system. The obtained ion-alloyed titanium surface layer was thermostable. The base phase composition was not changed after annealing at 473 K. The mechanical and tribological properties of the implanted titanium sample were higher then of the unimplanted material. The increased hardening and wear resistance due to formation of intermetallic phases may be favorable for industry applications of this alloy.

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