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Formation of titanium carbide in technically pure titanium under the influence of the powerful ion beam

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Using the methods of scanning microscopy and X-ray photoelectron spectroscopy, the effect of exposure to a powerful nanosecond ion beam on the morphology and chemical state of the surface layer of commercially pure titanium was studied. It has been experimentally established that at a current density of 150 A/cm², melting of a surface layer with a thickness of $\sim 1.5 \mu\text{m}$ occurs, which confirms the results of theoretical calculations. The interaction of molten titanium with carbon present on the surface in the form of adsorbed contaminants, as well as implanted into the surface layer, leads to the formation of titanium carbide compounds.

Keywords: titanium, titanium carbide, pulsed ion beam, ion modification.

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Titanium and titanium based alloys are widely used in aircraft and missile engineering due to high specific strength and corrosion-resistance. A challenging group of methods improving the surface properties of titanium and its alloys is their modification by beams of charged particles: ions or electrons [1–3]. As a rule, under such types of modification the most significant changes of chemical composition, morphology and crystal structure of the irradiated materials occur in thin surface layers with thickness from hundreds of nanometers to units of micrometers. At that in case of exposure to nanosecond (~ 10 – 100 ns) powerful ion beams (PIBs) in the surface layer the melting, partial evaporation, further rapid solidification of melt and changes in chemical and phase state of surface layer can occur [4,5]. The traditional methods of materials study, which include X-ray diffraction and energy-dispersive analysis, exclude complete study of changes in the chemical composition of the surface layer occurring during materials treatment by beams of charged particles. In present paper the change in morphology and chemical state of the surface of commercially pure titanium grade VT1-0 treated by the powerful ion beam of nanosecond duration was studied using method of X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM).

The technically pure titanium grade VT1-0 was irradiated at ion accelerator „TEMP“ (Dostoevsky OmsSU). The beam composition is 30% H⁺ + 70% C⁺. Average energy of particles was ~ 250 keV, irradiation pulse width was ~ 60 ns, current density of ion beam was ~ 150 A/cm². Prior to irradiation the samples were polished to high lustre followed by ultrasound washing in ethyl alcohol. The chemical state of the initial and irradiated samples was analyzed by XPS method using nonmonochromatic AlK _{α} -radiation.

XPS-spectra were obtained under conditions of ultra high vacuum ($\sim 10^{-7}$ Pa). Energy resolution during spectra registration was 0.2 eV. The surface contamination before the spectra measurement was removed using the argon ion beam with energy of 3 keV under mode of ion beam scanning over the sample surface for 10 min. The morphology and thickness of the melted layer of the modified samples were analyzed in scanning-electron microscope JEOL JSM 6610 LV at accelerating voltage of 20 kV. For the obtained experiment data interpretation the linear energy losses of ion beams, temperature fields distribution and carbon spatial distribution in titanium under PIB effect were simulated. For this thermal conductivity equation and kinetic diffusion equation were used [6].

Fig. 1 shows XPS-spectra of C 1s and Ti 2p of initial and PIB modified alloy VT1-0. Spectrum of C 1s of initial sample (curve 1 in Fig. 1, a) is approximated by three components. High-energy components (bond energies ~ 287.3 and ~ 289.0 eV) correspond to carbon chemically bonded with oxygen in single (C–O) and double (C=O) bonds, respectively [7,8]. The basic maximum at the bond energy ~ 285.0 eV corresponds to states of carbon in bonds C–C/C=C. High intensity of this component is due to, most probable, incomplete removal of surface contamination during the ion cleaning. The spectrum of the irradiated sample (curve 2 in Fig. 1, a) contains an additional maximum at the bond energy ~ 281.7 eV, it corresponds to the carbon compounds chemically bonded with titanium (C–Ti) [9]. Relative integral intensity of this component is 11.4%, which allows us to talk about the formation of rather large number of carbide compounds. At that the fluence of the powerful ion beam is $\sim 10^{13}$ cm⁻² per one impulse. It is obvious that formation of the carbide compounds is

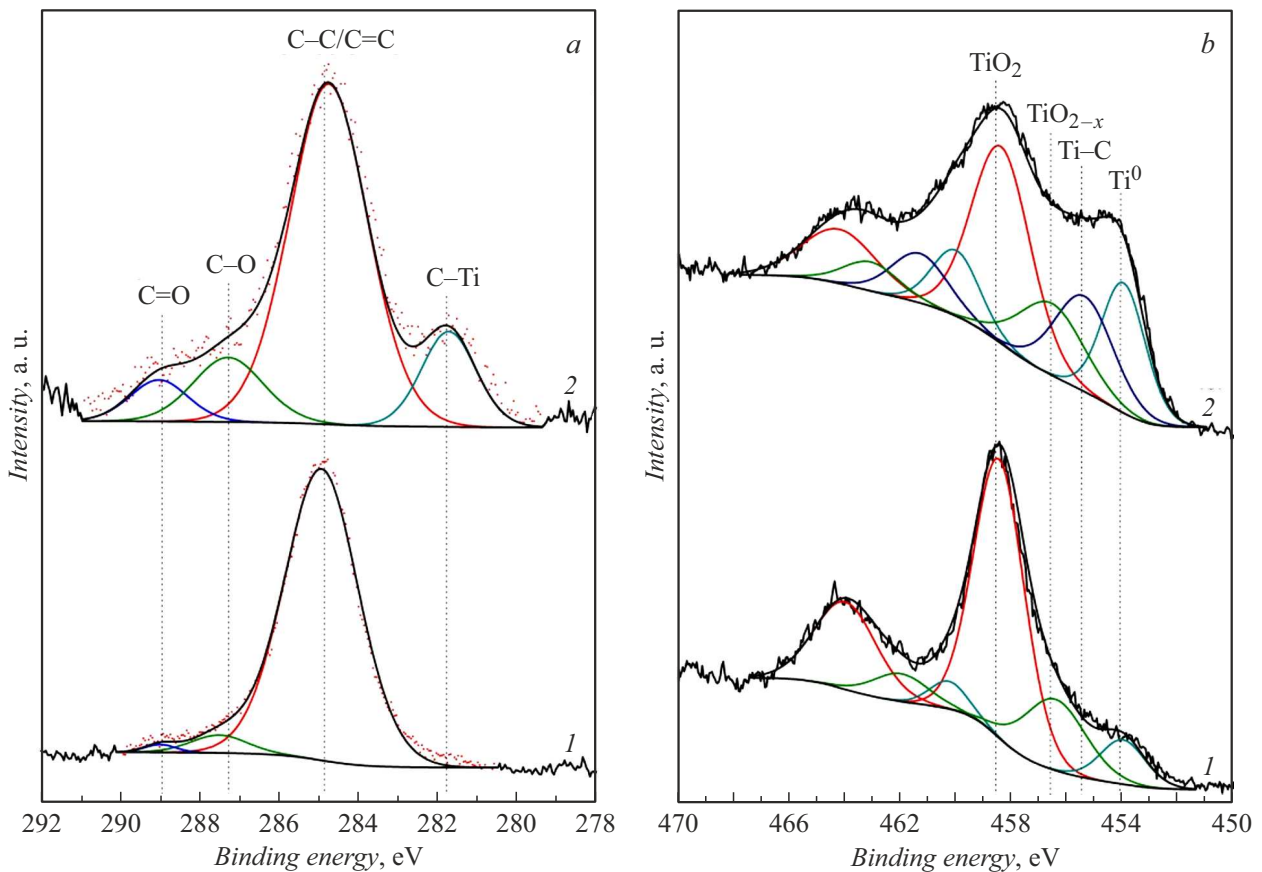


Figure 1. XPS-spectra of initial (1) and irradiated PIB (2) of technically pure titanium grade VT1-0. *a* — C 1s, *b* — Ti 2p.

ensured not only by carbon being part of the beam but also, -apparently, is implemented with participation of carbon existing on the sample surface in form of hydrocarbons that are adsorbed during the samples storage in atmosphere, and also in ion accelerator chamber during its evacuation using the steam-oil pump.

Spectrum of Ti 2p of initial sample (curve 1 in Fig. 1, *b*) shows that titanium is in three chemically nonequivalent states. The doublet component with maximum values at the bond energy ~ 458.6 and 464.0 eV corresponds to titanium dioxide TiO_2 [10], it is formed during samples storage. Low-energy component (bond energy ~ 454.1 and ~ 460.0 eV) corresponds to titanium in metal state Ti^0 [11]. Besides, there is also the component which maxima are localized at the bond energies ~ 456.5 and 462.0 eV, which corresponds to TiO_{2-x} suboxide. Spectrum form of the PIB irradiated sample (curve 2 in Fig. 1, *b*) significantly differs from spectrum form of the initial sample. Noticeable increase in the spectrum intensity in high-energy region is observed, which indicates the decrease in relative amount of titanium oxides on the surface of the irradiated sample. The decomposition results show that the spectrum of the irradiated sample contains an additional component with maxima 455.1 and 461.0 eV, according to literature data [12], and results of decomposition of C 1s spectra this component

corresponds to the states of titanium chemically bonded with carbon.

Previously TiC formation was observed during multiple (≥ 100 pulses) titanium radiation by PIBs [13]. As per authors' opinion, TiC is formed as result of interaction of melted titanium and surface carbon containing contaminants. But hydrodynamic agitation of surface layer melt occurring under multiple irradiation, as well as method of X-ray diffraction analysis used herein provide only data averaged through the titanium thickness comparable with thickness of layer of half attenuation of X-ray radiation ($\sim 8 \mu\text{m}$), this by many times exceeds the ion travel depth under PIB action. Use for analysis of such surface-sensitive method as XPS provides data on chemical state of the titanium in travel zone of the ion beam during single irradiation.

The carbide compounds on surface of the irradiated samples can be formed in different ways. For example, when thin layer of natural titanium oxide interacts with carbon being part of the beam, and with carbon contaminants adsorbed on the sample surface as per reaction $\text{TiO}_2 + 3\text{C} \rightarrow \text{TiC} + 2\text{CO}$ [14]. Temperature of this reaction is ~ 1473 K and decreases if titanium oxide stoichiometry changes (towards oxygen content decreasing). Achievement of these temperatures under PIB action is confirmed by the

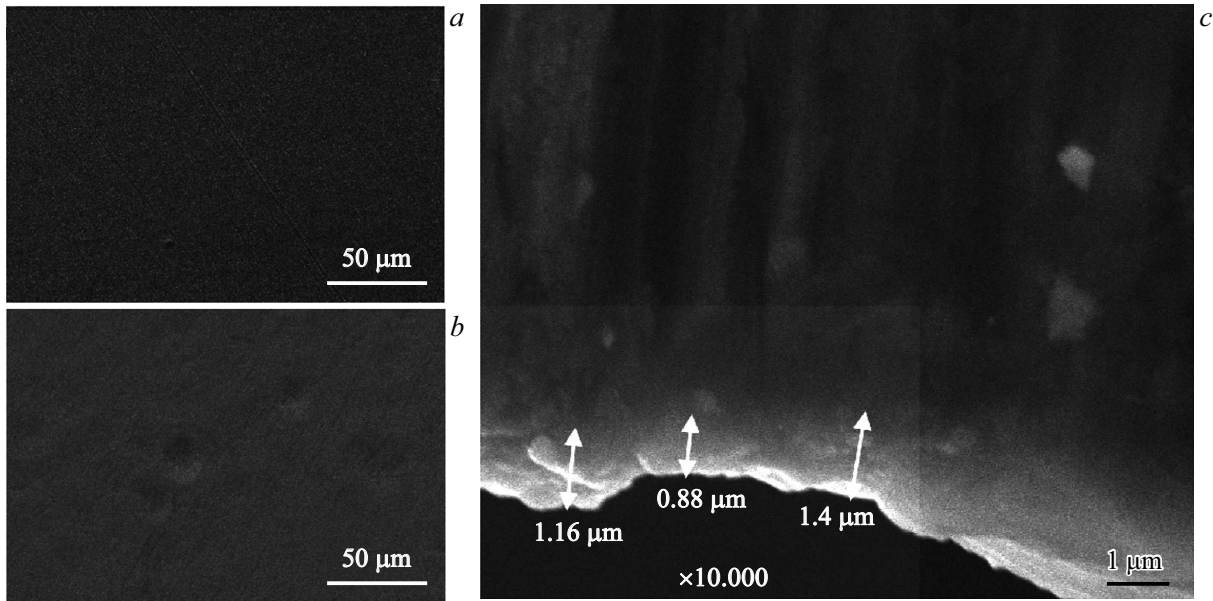


Figure 2. SEM-images of surface of titanium VT1-0. *a* — initial surface; *b*, *c* — surface and end face chip of PIB irradiated sample, respectively.

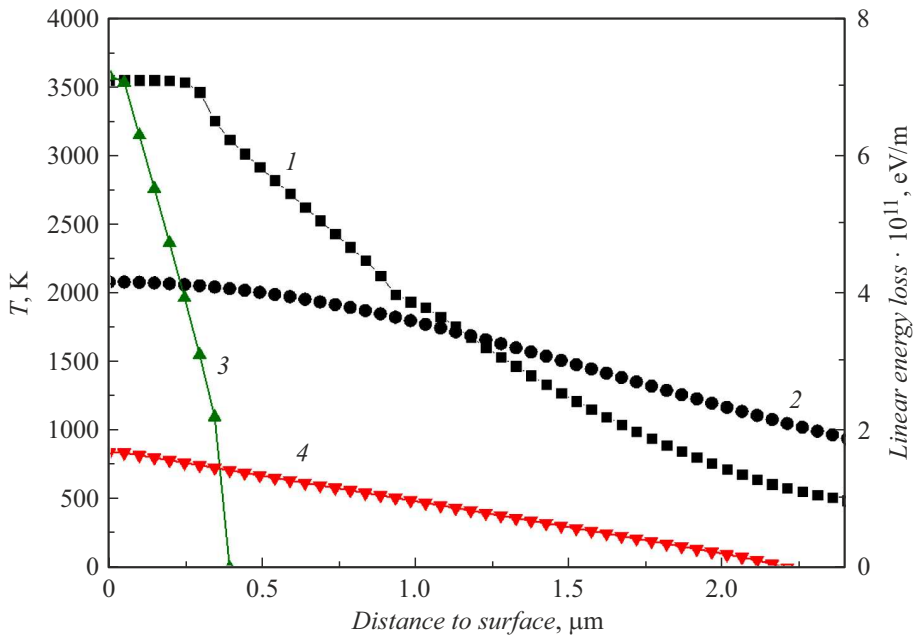


Figure 3. Distribution of temperature (*1* — upon pulse end, *2* — in 10^{-6} s after irradiation) and linear energy losses of ions (*3* — carbon ions, *4* — protons) under single irradiation by PIB with current density ~ 150 A/cm².

titanium surface melting (Fig. 2, *a*, *b*), this is accompanied by edges smoothing and decrease in width of scratches formed at sample preparation stage (titanium melting point is (T_m) ~ 1943 K). SEM-image of end face chip of irradiated sample (Fig. 2, *c*) indicates that thickness of the modified layer reaches $1.4 \mu\text{m}$. Considering melting of sample surface under PIB action, we can suppose that the titanium carbide can be formed under direct interaction of Ti and carbon adsorbed on surface under action of the beam when the

surface temperature reaches ~ 1873 K, i.e. value required for this reaction execution.

To evaluate the temperature distribution in the near-surface region of the titanium under PIB action the temperature distribution was simulated based on the linear energy losses of carbon ions and protons, which contribution to the distribution function of bulk heat sources considered their amount in the ion beam. The obtained distribution of the bulk power of the beam was used in thermal conductivity

equation. The sample room temperature was accepted as initial conditions. Following limit conditions are used: left border (sample surface) — heat removal by radiation, right border — solution for semi-infinite environment. The calculations results are presented in Fig. 3. In calculation the energies of phase transitions were considered: melting and boiling. For solution the implicit finite difference scheme was used. The temperature distribution shows that melting point is reached at depth below $1\ \mu\text{m}$, in this case depth of thermal influence ($\sim 0.5T_m$) is $1.4\ \mu\text{m}$, which is comparable with SEM data (Fig. 2, c).

For analysis of carbon concentration in surface layers we calculated distribution of the implanted carbon (not shown in Figures). Maximum of the implanted carbon is at depth of $0.4\ \mu\text{m}$, and according to the used irradiation mode it complies with $\sim 10^{-3}$ at.%. Such low calculated concentration confirms the assumption that the carbon source to form carbides is mainly the layer of adsorbed carbon contaminants. The obtained results do not contradict the experiment data on carbon concentration on surface of the initial and PIB irradiated titanium.

Studies performed show that as result of single irradiation by PIB with current density $j \sim 150\ \text{A}/\text{cm}^2$ of the technically pure titanium the titanium carbide is formed mainly with participation the carbon contaminants adsorbed on the sample surface. Data of electron microscopy, as well as simulation results of temperature distribution indicate the structure change of the near-surface layer of the material over $1\ \mu\text{m}$ thick, determined also by melting and rapid solidification. It was supposed that the most probable mechanism of the titanium carbide formation is interaction of titanium with carbon at high temperatures occurred in the surface layer.

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Conflict of interest

The authors declare that they have no conflict of interest.

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