Investigation of the mechanism of polymorphic transformation in titanium under femtosecond laser pulse exposure

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The change of structural-phase state of near-surface layers of technically pure α-titanium (alloy BT1-0) under the influence of shock waves arising at femtosecond laser irradiation has been investigated. The formation of the near-surface layer hardened by finely dispersed particles of titanium carbides has been established. The elongated particles with FCC -lattice (δ-phase) have a certain orientation ratio with the α-titanium HPC matrix: $\langle 2\bar{1}\bar{1}0 \rangle \alpha(\mathrm{HCP}) \parallel \langle 011 \rangle \delta(\mathrm{FCC})$ and $\{0001\} \alpha(\mathrm{HCP}) \parallel \{111\} \delta(\mathrm{FCC})$. The mechanism of this transformation is discussed, which is related to the segregation of carbon atoms on the defects of the crystal structure induced by shock-wave action.

Keywords: titanium, titanium carbide, shock-wave impact, phase, structure defects, molecular dynamics.

Titanium and its alloys feature high strength and corrosion resistance and good biocompatibility, which makes them indispensable in various technical and medical applications. The titanium crystal lattice has two allotropic modifications: α-phase with a hexagonal close-packed (HCP) lattice and β-phase with a body-centered cubic lattice. When titanium and its alloys are subjected to rolling or pulsed laser processing, the observed significant increase in strength and fatigue resistance [1] may be associated, depending on the parameters of external influence, with refinement of the grain structure (down to nanostructuring) [2] and the formation of a high-pressure ω-phase [3] or a face-centered cubic (FCC) phase [4]. Recent studies have revealed that the allotropic HCP–FCC lattice transformation may be attributed to lowering of the energy barrier to the formation of FCC-phase nuclei in the HCP matrix with a change in local concentration of interstitial impurities (carbon, nitrogen, and oxygen) [5,6].

The present study is focused on examining the changes in the structural and phase state of near-surface layers of technically pure α-titanium (VT1-0 alloy) under the influence of shock waves generated by femtosecond laser irradiation. A comprehensive experimental approach combined with computer modeling was used to elucidate the mechanism of the shock-wave laser-induced HCP−FCC phase transformation in the studied alloy.

Technically pure α-titanium (VT1-0 alloy) with an HCP crystal lattice was used in the studies. This titanium-based alloy has the following elemental composition (mass%): Al — 0.01, Fe — 0.12, Si — 0.002, O — 0.143, C — 0.004, N — 0.003, and H — 0.0008 (in at.%: Al — 0.018, Fe — 0.103, Si — 0.003, O — 0.426, C — 0.016, N — 0.010,

Comparison of known interplanar distances of titanium carbide TiC (FCC lattice, $a = 4.327\,\text{Å}$) and titanium hydride $\mathrm{TiH_2}$ (FCC lattice, $a = 4.44\,\text{Å}$) with the obtained experimental data ($a = 4.334\,\text{Å}$)

(hkl)	d, Å		
	Experiment	TiC	$\mathrm{TiH_2}$
(111)	2.54	2.5	2.56
(200)	2.18	2.16	2.22
(220)	1.50	1.53	1.56
(311)	1.23	1.30	1.339

and H — 0.038), which complies with GOST 19807−91 requirements. Samples were made from rods 8 mm in diameter formed by the method of cross-helical rolling, which ensured the formation of a submicrocrystalline structure. The samples were then recrystallized by annealing at 1123 K for one hour to form a polycrystalline structure with an average grain size of $35 \pm 3\,\mu$m. A femtosecond chromium-forsterite laser system (pulse duration, 110 fs; wavelength, 1240 nm; energy density, 13.7 J/cm^2) was used for laser processing. The laser processing procedure was detailed in [2].

Structural studies were performed with a Tecnai Osiris transmission electron microscope at an accelerating voltage of 200 kV. Thin foils were prepared by ion thinning in a FEI Scios column.

Molecular dynamics simulations were performed in the LAMMPS package with the modified embedded-atom method interatomic potentials [7]. The model sample
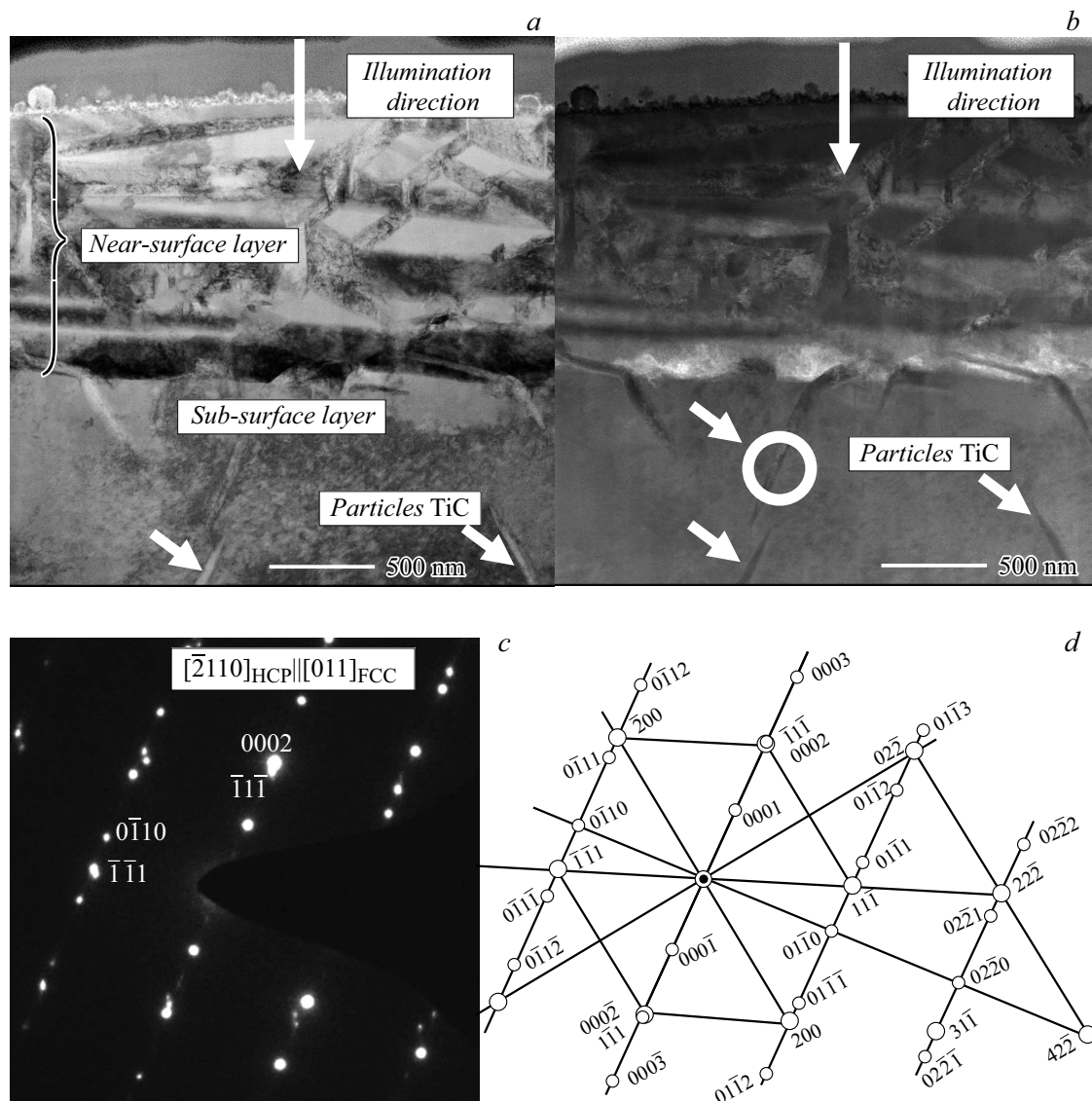
Figure 1. Magnified image of a section of foil with FCC microcarbide particles nucleated by femtosecond laser irradiation. *a* — Bright-field contrast; *b* — dark-field contrast (the circle indicates the region of capture of the microcarbide and the matrix by the field diaphragm); *c* — microdiffraction with an FCC particle captured by the field diaphragm; and *d* — microdiffraction interpretation that illustrates the HCP−FCC orientation ratio. Directions $[\bar{2}110]_{HCP} \parallel [011]_{FCC}$, planes $(000\bar{1})_{HCP} \parallel (1\bar{1}1)_{FCC}$. Transmission scanning microscopy.

contained $4.9 \cdot 10^6$ titanium atoms and 1972 carbon atoms (0.04 at.%). Its dimensions along axes $x-y-z$ were $88-92-10\,708\,\text{Å}$ respectively. The simulation step was 0.2 fs, the total time was 400 ps. The characteristics of a shock wave were specified according to [2] (through the time dependence of velocity of one of the sample faces along the z axis that is perpendicular to the irradiated surface). Although the concentrations of oxygen and iron in the alloy are higher, the interaction of titanium with carbon only was taken into account in modeling. This is attributable to the fact that, according to the results of earlier studies [6], carbon atoms are the ones most efficient in lowering the energy barrier of the HCP−FCC transformation, while the influence of oxygen and iron is focused on other aspects of phase transformations in titanium.

It was found that the near-surface layer modified by laser processing ($\sim 1\,\mu$m in thickness) has a non-uniform nanocrystalline platelet structure with the width and thickness of platelets varying from ~ 5 to ~ 200 nm and their length ranging from ~ 100 nm to several micrometers (Figs. 1, *a*, *b*). Nanoscale platelets are oriented differently relative to the surface: perpendicular to it, at an angle of $45°$, or parallel to the surface. Platelets oriented parallel to the surface and bordering on the matrix, which is the original material with the density of deformation defects increased after shock-wave exposure, are also found in the sub-surface layer. The physical mechanisms of formation of such a microstructure were analyzed in [2].

Another characteristic feature of the microstructure is the presence of elongated particles with a length of approxi-
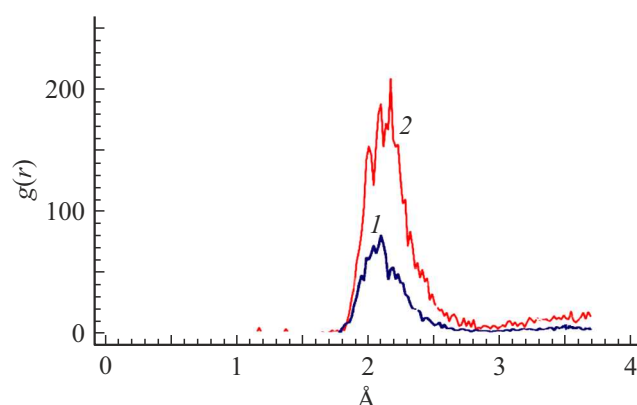
Figure 2. Ti−C partial radial distribution function for the first coordination shell of titanium atoms with a local environment characteristic of dislocations in the HCP structure. *1* — State established immediately after the passage of a shock wave; *2* — result after 400 ps of molecular dynamics simulations.

mately $1\,\mu$m and a thickness close to $50\,$nm oriented at angles of 45, −45, and 0° to the direction perpendicular to the foil surface (marked with arrows in Figs. 1, *a*, *b*). The interpretation of the microdiffraction pattern of these particles revealed that they have an FCC lattice (Figs. 1, *c*, *d*). The splitting of titanium carbide reflections (in particular, the $\bar{2}00$ reflection) is attributable to the complex internal structure of the particle with varying local concentrations of carbon and, consequently, slightly varying parameters of the crystal lattice.

The table presents a comparison of known literature values of interplanar distances for titanium carbide TiC (FCC lattice, $a = 4.327\,$Å, JCPDS 32-1383) and titanium hydride TiH$_2$ (FCC lattice, $a = 4.44\,$Å, JCPDS 07-0370) with the obtained experimental data for the observed phase. This comparison reveals that the studied structure fits the data for both titanium hydride and titanium carbide; however, other experimental and calculated data (see below) support unambiguously the carbide interpretation of these precipitates. Thus, the elongated particles with an FCC lattice marked with arrows in Figs. 1, *a*, *b* are titanium carbides. The data from recently published studies [4–6] also indicate that the interplanar distances and crystallographic lattice ratios of FCC particles precipitating in the process of rolling in the HCP titanium matrix are typical of the titanium carbide TiC phase.

Quantum-mechanical calculations performed in [5] revealed that the allotropic HCP–FCC lattice transformation in technically pure titanium is associated with the loss of stability of the HCP lattice and its rearrangement into the FCC structure induced by segregation of carbon atoms at crystal structure defects (dislocations, subgrain boundaries, etc.). It was demonstrated in [6] that an increase in concentration of interstitial impurities (carbon, nitrogen, and oxygen atoms) leads to lowering of the

energy barrier between the HCP and FCC lattices, thereby facilitating the HCP−FCC transformation. The authors of [8] noted that the detection of the FCC phase in the HCP matrix may be attributed to the formation of titanium hydrides due to contamination of the studied samples with hydrogen. However, the formation of stable FCC-phase particles was later [9] detected at a temperature exceeding significantly the decomposition temperature of TiH$_x$ ($x \geqslant 1$). In this case, the emergence of the FCC phase in the HCP titanium matrix may only be attributed to the influence of interstitial impurities present in the crystal lattice, which, as was already noted, lower the energy barrier of the transformation in question. This proves once again that the FCC phase found after laser irradiation of HCP titanium is indeed titanium carbide.

It should also be noted that no carbide particles were detected on the periphery of the crater or outside the laser exposure area. The latter fact indicates clearly that their formation was initiated by the shock-wave action of a laser pulse. It has already been demonstrated in [1] that titanium microcarbides play a decisive role in stabilizing the grain structure in the poly-, submicro-, and nanocrystalline states of titanium by inhibiting the migration of grain boundaries and hindering the recrystallization processes.

It was established in modeling that the concentration of carbon atoms at defects of the crystal structure (dislocations) increases within $400\,$ps after the passage of a shock wave. This agrees with the results of examination of the partial radial distribution function (PRDF) for Ti−C atoms. The first PRDF peak demonstrates that the number of carbon atoms in the local environment of Ti atoms belonging to dislocations after modeling increases by a factor of more than 3 compared to the initial dislocation structure that arose immediately after the passage of a shock wave. This is consistent with the proposed mechanism of microcarbide formation that includes the diffusion transfer of carbon atoms in dislocation stress fields and the capture of carbon atoms by moving dislocations (Fig. 2).

The present study is the first to report on the formation of a near-surface layer strengthened by finely dispersed carbide particles in technically pure titanium under the examined conditions of shock-wave laser action.

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Conflict of interest

The authors declare that they have no conflict of interest.

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