Surface Modification of Titanium by Pulsed Laser Radiation of Femtosecond Duration

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Abstract—The effect of an infrared pulse laser with femtosecond radiation ($\lambda = 744$ nm, $\tau \approx 120$ fs, $E \leq 8$ mJ) on the surface of Ti of commercially purity in the submicrocrystalline state is investigated using scanning electron microscopy (SEM). Laser irradiation leads to the formation of a surface nanorelief consisting of alternating projections (bars) and hollows (grooves). After surface treatment under a water layer, cube-shaped particles are formed on Ti surface; they are composed of many tightly contiguous rectangular plates.

Keywords: titanium, surface, femtosecond laser pulse radiation.

INTRODUCTION

The contactless treatment of solids by pulsed laser radiation can alter the mechanical, electrical, and physicochemical properties of both their surfaces and all of the material as a whole. One of the effective ways to improve the mechanical characteristics of metals and alloys is the formation in them of a submicrocrystalline (SMC) and/or nanostructured (NS) state by plastic deformation [1–4]. However, such a state is generally metastable, and material properties deteriorate to the typical level for materials with coarse-grained structures as a result of the recovery and recrystallization that occur at certain temperatures. It seems urgent in connection with this to develop low-temperature processing methods for SMC and NS materials. These methods include femtosecond processing with pulses of a high-intensity laser together with the cooling medium being transparent to laser light, during which an initial material remains "cold" under treatment. Furthermore, we know that, as a result of such treatment, an ordered relief can be formed on the surface of the material, but the structure of the surface layer in this case may consist of elements with features much smaller than 1 μm [5, 6].

This paper presents experimental results on titanium surface topography after treatment with laser pulses of femtosecond duration.

EXPERIMENTAL

As an object of investigation, we chose SMC titanium of VT1-0 grade, manufactured by Nanostructured Materials and Nanotechnologies, Research-Educational and Innovative Center of Belgorod State University. The SMC structure with an average grain size of 0.25 μm was formed through a plastic deformation combining radial-shear, longitudinal, and helical rolling. Our choice of titanium was due to its wide application both in industry as a structural material and in medicine as an implant. We used samples in the form of a cylindrical target with diameter of 8 mm and with thickness of 4 mm, whose surfaces to be processed by the impulses underwent mechanical polishing with a LaboPol-5 (Struers) unit.

The irradiation was carried out with an infrared titanium-sapphire laser (wavelength of 744 nm, laser action band ~10 nm in width at half-height, pulse duration of ~100 fs at half-height, energy per impulse of up to 8 mJ), whose radiation was focused on the treated surface into a spot with a diameter of 0.5 mm. The surface of the target was irradiated during the scanning mode at low radiation energies (<0.5 mJ, peak power $W < 4$ GW) to avoid noticeable degradation of the energy density distribution along the target surface related to optical-beam self-trapping in air (critical self-focusing power $W_{\mathrm{cr}} \approx 3$ GW) and to eliminate its attendant effects—chromatic emission, filamentation, and laser beam scattering by plasma. When scanning, a movable holder with fixed titanium target passed at a rate of 0.6 to 20 μm/s with passing controlled by the program.

The target was irradiated in air and through a 1.5 mm thick layer of distilled water.

Surface structure analysis after irradiation was performed using a Quanta 600 FEG scanning electron microscope with field electron emission.

RESULTS AND DISCUSSION

The irradiation of the Ti in air with low energy densities ($F \approx 17$ mJ/cm^2, the number of pulses is $N \approx 500$) results in shaping quasiperiodic (average period of ~0.4 μm), pronounced, narrow ($\Delta \leq 0.1$ μm) grooves (Fig. 1a) on its flat surface within the laser spot. At higher energy densities (up to $F \approx 25$ mJ/cm^2) and the same number of pulses N, there is formed a structure in the form of a nanolattice on the target surface, on which “flakes” of white color are visible (Fig. 1b), being most likely oxidized products during titanium ablation. Also, there are fragments in the form of droplets, which are located on the surface of the grooves. The formation of the fragments indicates an increase in temperature of the metal surface during laser pulse bombarding up to values that provide a supercritical thermal mechanism of ablation, rather than a subcritical spallation one [7]. The cooling rate of spheres crystallized on the surface of the grooves is more than 10^8 K/s. Elements (bars) of the nanolattice are almost parallel to each other on the entire irradiated surface of Ti (Fig. 1c).

Melting of the surface of a groove and formation of relief on it seems to take place a few picoseconds after stopping the action of the femtosecond laser pulse. Therefore, at a sufficiently powerful laser treatment ($F \approx 350$ mJ/cm^2, $N \approx 500$), the apexes of grooves on the titanium surface acquire steplike forms and almost all edges of the steps have a rounded shape (Fig. 2a). As a result of melting and cooling of liquid titanium, bridges of cylindrical shape form (marked by arrows in Fig. 2b), which are randomly located between the grooves. The size of the cross section of bridges is 20–50 nm. In some bridges, there are “built” frozen drops (sometimes, two or three drops) of titanium that may be located anywhere on the bridges. It is noteworthy that, for all employed modes of laser irradiation in air, we did not find particles of more than several nanometers in size, the formation of which could be associated with the processes of ablation in the area of laser treatment (i.e., on the surface of the grooves). They might be located in the hollows between the grooves.

At the radiation power $F \geq 350$ mJ/cm^2 and the number of pulses $N \approx 500$, the average energy density in the surface layer is sufficient to initiate recrystallization in the SMC structure of titanium (Fig. 3).

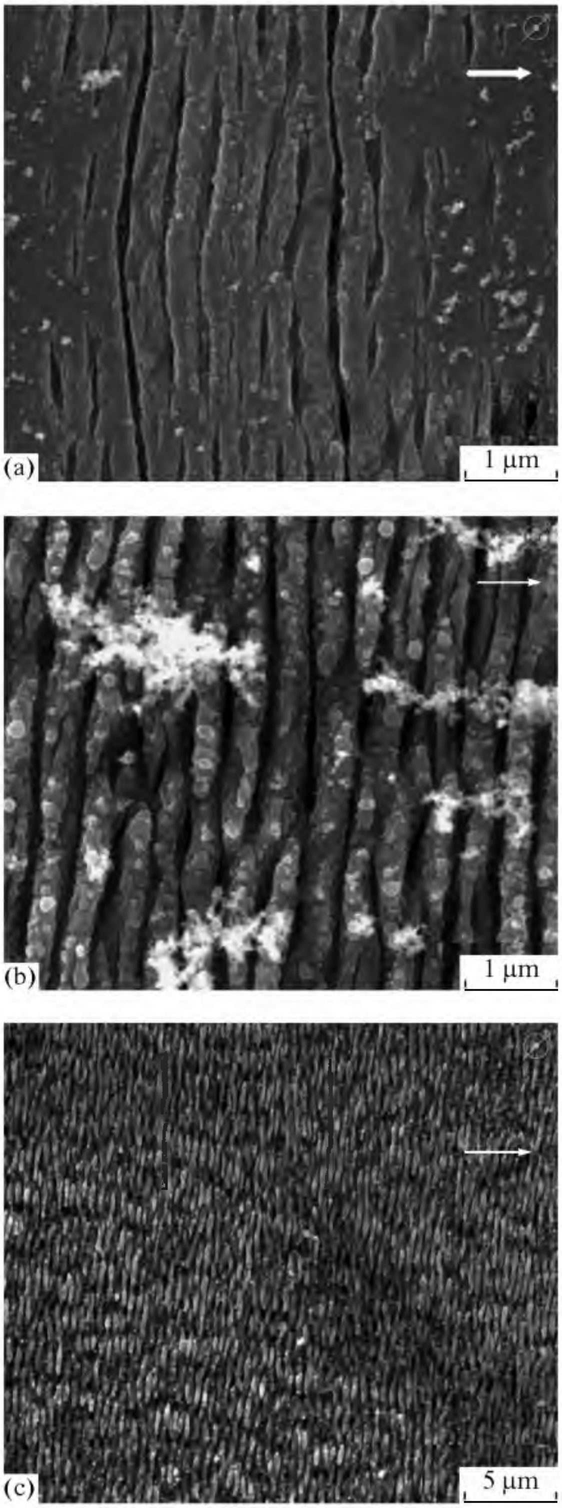

Fig. 1. Surface structure of Ti after irradiation with laser fluence of (a) ~17 mJ/cm^2 and (b, c) ~25 mJ/cm^2. The number of pulses are $N \approx 500$; the direction of laser beam passes and its polarization are shown with the arrow in the upper right corner.

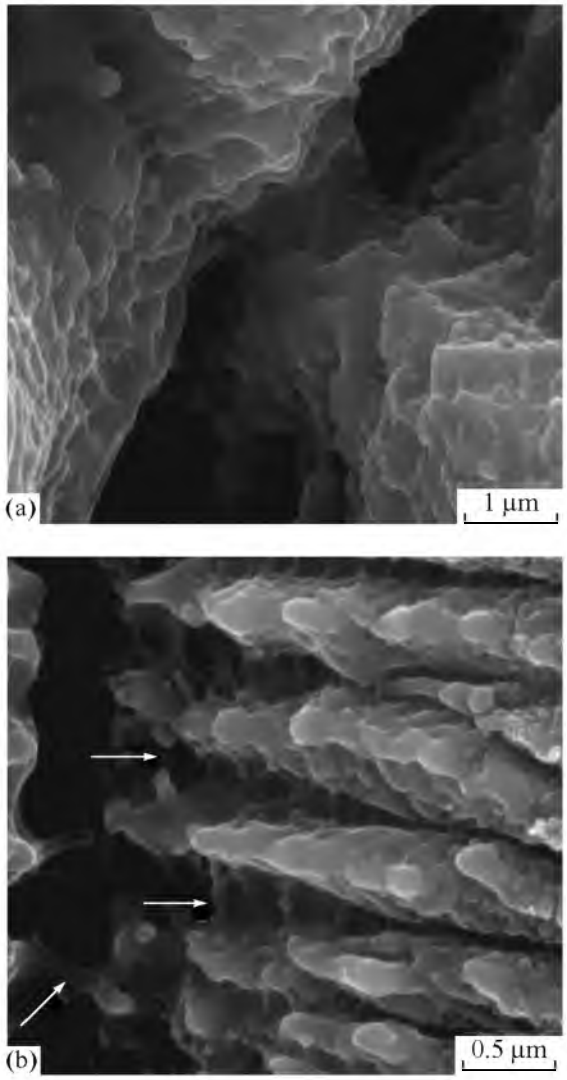

Fig. 2. Structure of the grooves (bars) on the surface of Ti resulting from high-power ($F \geq 350$ mJ/cm^2, $N \approx 500$) laser irradiation: (a) steplike structure of the groove vertices, (b) bridges between the grooves.

The surface of grooves formed after irradiation is smooth and there are no visible fragments of relief on it with roller coasters of height even at magnification of ×250 000; the microphotographs do not show either a grain structure, which seemingly should have been formed at cooling of the liquid phase, or effects of growth. Thus, we can assume that the size of grains on the surface of projections and cavities in the relief formed by laser irradiation does not exceed a few nanometers. More accurate data on the structure of the titanium surface layer irradiated can be obtained by a detailed study of a precision-treated cross section of the target using transmission electron microscopy.

One should also take into account that the processing of titanium by ultrashort laser pulses for which the rate of heating and cooling of the target surface layer will reach extremely high values will inevitably lead to the formation of a significant number of structural defects, which might be distributed throughout the height of the grooves quite nonuniformly.

It is interesting to note that, in some cases, there were detected particles of cubic shape on the titanium surface irradiated with laser pulses through a layer of water. Each of the particles consists of ten or more rectangular plates, tightly adjacent to each other (Fig. 4). However, the very small amount of these particles is insufficient to determine the type of their crystal structure and elemental composition.

CONCLUSIONS

Scanning electron microscopy analysis of the structure of the titanium surface after irradiation with femtosecond laser pulses has shown the formation of ordered relief on it composed of a set of parallel grooves and hollows that form nanolattices.

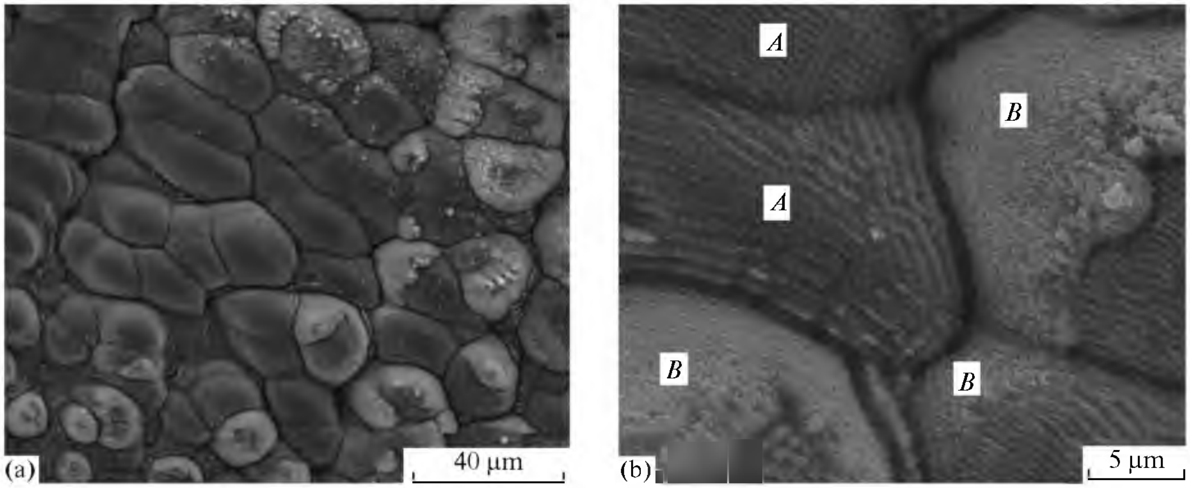

Fig. 3. Surface of Ti after high-intensity laser irradiation ($F \geq 350$ mJ/cm^2, $N \approx 500$). The micrographs (a, b) were obtained at different magnifications.

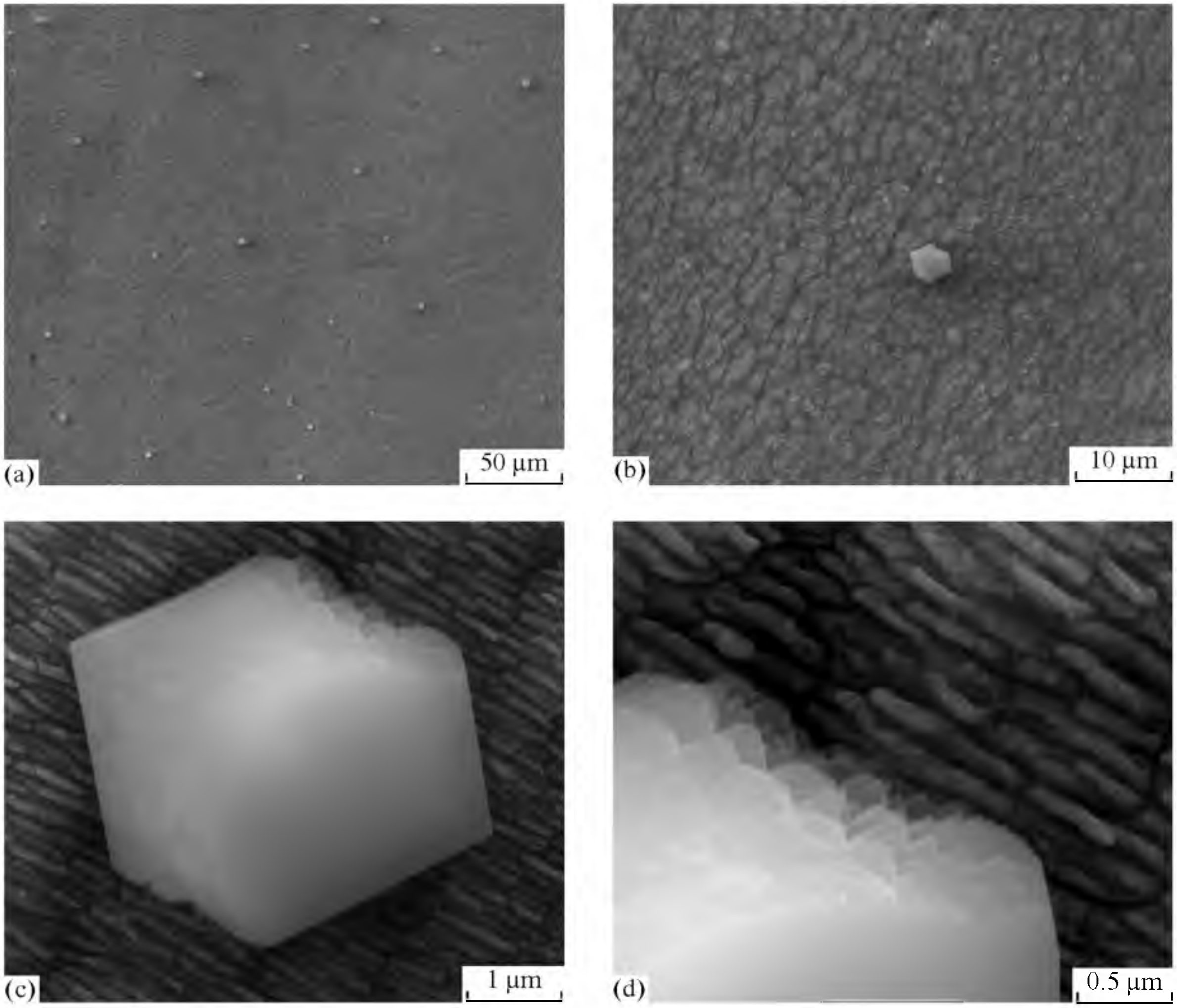

Fig. 4. Cubic particles on the surface of Ti after irradiation with femtosecond laser pulses through a layer of water. The micrographs were obtained at different magnifications.

After irradiation of Ti through a layer of water, particles of cubic shape, consisting of a set of tightly contiguous rectangular plates, have been detected on its surface.

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