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The Formation of Oxide Layers on a Titanium Surface by Irradiation with Femtosecond Laser Pulses

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Abstract—By subjecting technical grade titanium to irradiation with femtosecond laser pulses with high energy density, we create a microporous nanocrystalline oxide layer with a thickness of ~50 μm on its surface. The structure and phase composition of the modified surface layers are studied using X-ray diffraction and high-resolution scanning and transmission electron microscopies.

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Owing to their unique electric physical, optical, and chemical properties, thin films of different polymorphs of titanium oxides attract great interest in view their use in modern science-based technologies [1]. Recent research has established that titanium dioxide coatings can improve antithrombotic properties of coronary and vascular stents [2], suppress cancer cell proliferation [3], and exhibit antibacterial and antiviral properties [4]. Photocatalytic processes occurring at the titanium dioxide surface enable oxidative destruction of many organic contaminants to smallest molecular products already at room temperature. This opens great possibilities for application of titanium oxide-based photocatalysts to air and water purification [5, 6]. In view of the broad perspectives for practical applications of titanium dioxide in technology and medicine, the development of new methods for preparing this material and fabricating respective oxide coatings is a topical problem.

Technologies for fabricating titanium oxide thin films extensively rely on various chemical methods (e.g., vapor phase deposition, bath deposition, sol–gel technique) and physical methods (e.g., magnetron sputtering using composite targets). As for the chemical methods, these include a number of stages to produce a product of desired size and shape, and additionally require special treatment of production wastes. For magnetron sputtering, titanium dioxide must be synthesized and prepared in the form of a sizable cathode, e.g., by using hot-pressing [7].

Irradiation with short (nanosecond) and ultrashort (femtosecond) laser pulses in the presence of oxygen (in air) is one promising physical method for obtaining oxide films and coatings. Our survey of literature on the subject showed that in many studies oxide layers at titanium surface were obtained using nanosecond laser pulses [8–13]. Correlations between the structure and phase composition of the prepared oxide films and applied accumulated laser fluence (F) were investigated in [8], and a possibility for fabricating oxide films 3–10 μm thick using $F > 294$ J/cm^2 was demonstrated. There is considerable interest in studying the formation of thin titanium dioxide films prepared by irradiation with femtosecond laser pulses. It was shown earlier that titanium surface can be oxidized using a femtosecond laser; however, due to very low accumulated laser fluence used (below the ablation threshold for titanium, which is $F_{frag} \sim 0.5$ J/cm^2), the prepared oxide coating was not sufficiently thick [14].

The aim of this study is to create oxide layer at titanium surface under controlled conditions using irradiation with femtosecond laser pulses and to characterize the phase composition and structure of the prepared oxide layers.

For our experiments, in which a femtosecond laser was used to create an oxide coating, we used technical grade titanium VT1-0 in its initial, submicrocrystalline state that was prepared using mechanothermal treatment [15]. Before subjecting samples to laser irradiation, these were pretreated by sanding and polish-

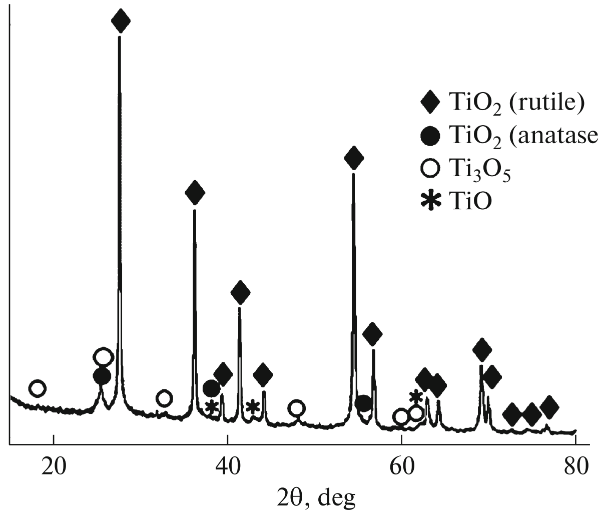

Fig. 1. XRD pattern of type VT1-0 titanium alloy subjected to irradiation with a femtosecond laser (full exposure, $F \sim 1600$ J/cm^2).

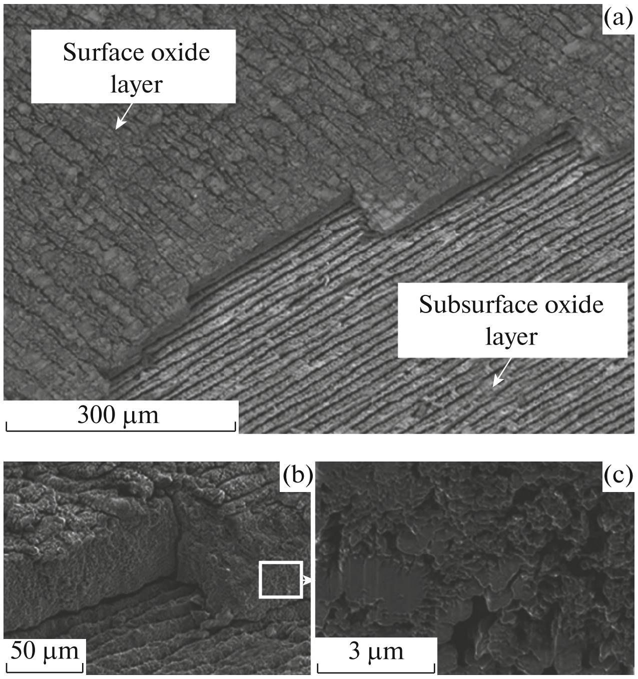

Fig. 2. SEM images (view angle, 30°) of the surface of type VT1-0 titanium alloy subjected to irradiation with a femtosecond laser (full exposure, $F \sim 1600$ J/cm^2).

ing on a LaboPol-5 machine (Struers) using sandpaper and dedicated liquid suspensions.

For sample irradiation, we used a Satsuma fiber laser operating at a wavelength of 1030 nm with a pulse duration at half maximum of ~300 fs, energy up to 6 μJ, and a repetition rate of 250 kHz. The laser beam was focused on a target sample to a spot with a 1/*e*-diameter of ~15 μm. Samples were attached to a motorized computer-controlled 3D platform. With the energy density per pulse of ~3.4 J/cm^2, the total energy delivered to a sample in the pulsed irradiation mode (full exposure) over one complete scan of the sample surface was ~1600 J/cm^2.

The modified surface of processed samples was examined on a FEI Helios 660 focused ion beam scanning electron microscope and an FEI Quanta 600 field emission electron microscope equipped with an energy dispersive spectrometer (EDS; resolution, 127.1 eV for MnK_α line; picks up elements starting from Be). X-ray diffraction (XRD) analyses were performed on a Rigaku SmartLab diffractometer in the Bragg–Brentano focusing geometry using CuK_α radiation.

The structure and phase composition of the modified subsurface layer were studied by transmission electron microscopy (TEM) on a Tecnai G2 F20 field emission instrument. Foil samples for TEM characterization were prepared by focused ion beam using an FEI Helios 660 microscope [16].

Following treatment with the femtosecond laser, a fairly homogeneous white coating with a high oxygen content (50–65 at %, EDS microanalysis) was observed on the processed titanium samples. The main phase component of the coating was the rutile polymorph of titanium dioxide (TiO_2), as established by XRD analysis (Fig. 1). In addition, the coating contained small amounts of the other titanium dioxide polymorphs (anatase), as well as the lower oxide Ti_3O_5 and monoxide TiO.

Using scanning electron microscopy (SEM), we identified that the oxide film consisted of two layers: the surface (upper) and subsurface (lower) layers, as shown in Fig. 2a. The black-colored subsurface layer has a quasi-periodic structure with a period of ~15 μm, a characteristic feature of a titanium surface subjected to irradiation with a femtosecond laser performed in a raster scan mode with a line spacing of 15 μm. The white-colored surface layer was ~50 μm thick (Fig. 2b). SEM images of a cross section of this layer, shown in Fig. 2c, reveal its microporous structure (pore size, 0.5–5 μm).

By examining cross-section foils of the surface oxide layer in the TEM, we found that the applied femtosecond laser treatment produced the layer consisting of large particles (up to a few microns) of the rutile polymorph of titanium dioxide in the (Figs. 3a, 3b) and nanoparticles of the anatase polymorph with an average size of ~20 μm (Fig. 3b).

The photocatalytic properties of titanium dioxide are well known to be significantly affected by its phase composition and morphology. Photoactivity is thought to be higher in anatase than in rutile; however, by adjusting the ratio between the two polymorphs (i.e., the anatase-to-rutile ratio), it is possible to create a composite material with a synergetic effect; i.e., its

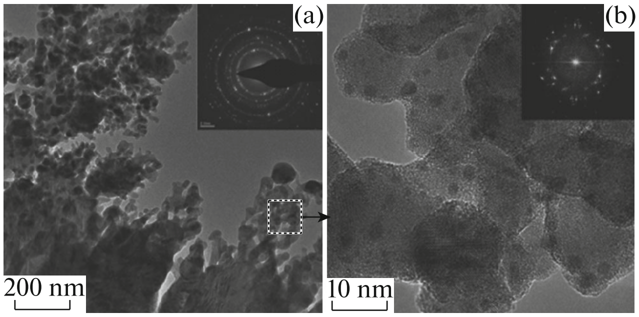

Fig. 3. TEM images of cross sections of the surface oxide layer formed on type VT1-0 titanium alloy subjected to irradiation with a femtosecond laser (full exposure, $F \sim 1600$ J/cm^2). The inset in panel (a) shows an electron diffraction pattern, and that in panel (b) shows a Fourier transform of corresponding regions.

photocatalytic activity will be considerably higher than that of the individual phases. In addition, if the material has spherical nanoparticles with a developed surface in its structure, it will exhibit faster rates of degradation of organic compounds [17]. Broadly, activity of a titanium dioxide-based photocatalyst is considerably enhanced if it has a developed surface; consequently, it is highly desirable to create TiO_2-based catalysts with multimodal (micro-, nano-, meso-) structures [18].

In summary, by taking titanium as an example, we demonstrated that irradiation with femtosecond laser pulses can be used to create microporous nanocrystalline oxide layers with thicknesses of ~50 μm. This result inspires further research into the photocatalytic properties of such coatings, as well as the mechanisms and features of formation of oxide films at surfaces of titanium and other metals due to irradiation with ultrashort laser pulses.

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