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Formation of the oxide coating on the titanium surface by multipulse femtosecond laser irradiation

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Abstract. The effect of the femtosecond laser irradiation on the formation of oxide layers on the surface of a commercially pure titanium VT1-0 was studied. The methods of X-ray analysis, scanning electron and transmission electron microscopies were used to study the structural and phase state of oxide layers. As a result of the femtosecond laser irradiation, the porous multi-phase nanocrystalline oxide coating with a thickness of 50 µm is formed on the titanium surface. The coating consists of titanium oxides: TiO_2 (rutile and anatase), TiO and Ti_3O_5.

1. Introduction

At present, numerous researchers agree to the fact that thin films of titanium oxides with their various modifications have a great future in modern high-end technologies due to their unique electrophysical, optical and chemical properties [1]. Such thin films and coatings have significant prospects of application in the field of ecological catalysis and medicine due to photocatalytic and bactericidal properties [2-4].

Thin films and coatings based on titanium oxides are obtained by various physical and chemical methods. The most commonly used methods for the deposition of thin films and coatings are micro-arc oxidation [5], sol-gel technology [6], plasma spraying [7], magnetron sputtering [8, 9]. The actively developing method of femtosecond laser processing is of particular interest for the synthesis of thin films and coatings based on titanium dioxide. In the most papers devoted to the formation of oxide layers on the surface of titanium alloys under the action of laser irradiation nanosecond pulsed lasers were used [10-14]. However, the literature data on the titanium oxidation by femtosecond laser pulses are disunite and incomplete.

The present paper is aimed at the study of the effect of the femtosecond laser irradiation on the process of formation of the oxide layers on the titanium surface, its phase composition and structure.

2. Experimental setup and characterization techniques

In our experiments commercially pure titanium VT1-0 with submicrocrystalline structure was used. The femtosecond laser irradiation (FSLI) was performed in air using Ti-sapphire laser with a wavelength of 1030 nm and a pulse width of 300 fs at a rate f =250 kHz and maximum pulse energy of 6 μJ. The laser pulses were focused onto the sample surface into a 15 μm spot (1/e – diameter σ), resulting in the peak laser fluence $F \geq 3.4$ J/cm^2 and the number of accumulated laser pulses per spot ≈600. The study of the modified surface of the laser irradiated sample was carried out using a FEI Helios 660 scanning electron-ion microscope and a FEI Quanta 600 scanning electron microscope with field emission. The X-ray diffraction (XRD) studies were performed using a Rigaku SmartLab X-ray diffractometer with the Cu-Kα radiation in a Bragg–Brentano focusing mode. Transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) studies of the subsurface structure of the irradiated sample were carried out by using a field-enhanced emission microscope Tecnai G2 F20.

3. Results and discussion

After FSLI homogeneous light-gray layer with high oxygen content was formed on the surface of commercially pure titanium VT1-0 (figure 1). Figure 1 shows that this layer is characterized by the presence of ridges (asperities) with diameter up to 20 μm, micron and submicron size particles and spherical nanoparticles with average size 75±5 nm.

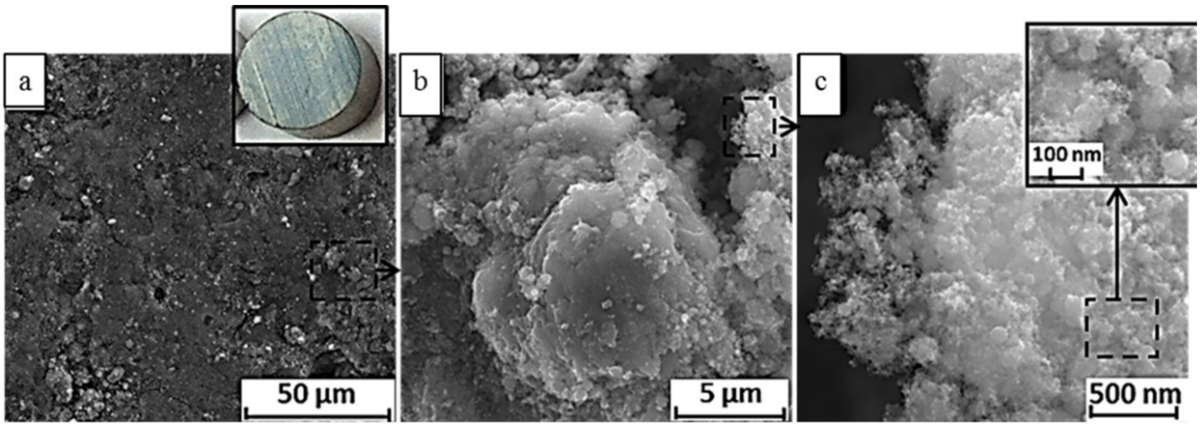

Figure 1. The surface structure of titanium alloy VT1-0 after FSLI.

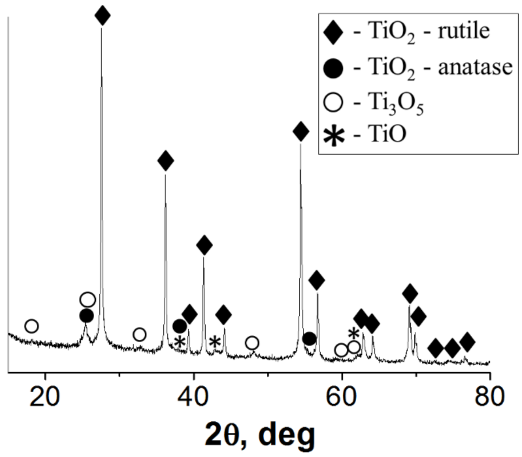

Figure 2. XRD pattern of titanium alloy VT1-0 after FSLI processing.

According to XRD (figure 2) the main phase in a surface layer is rutile (TiO2). In addition, an insignificant value of another modification of titanium dioxide was detected – anatase (TiO2), trititanium pentoxide Ti3O5 and monoxide TiO. All peaks of TiO phase shifted to smaller angles. This indicates that this phase lies below the layer containing all the remaining oxides.

The thickness of the surface oxide layer is about 40–50 µm. It can be seen from the image of the surface layer cleavage (figure 3) that the layer has a microporous structure (pore size is 0.5–5 µm). Formation of the oxide surface layer seems to be associated with the process of deposition of the oxidized products of laser ablation on a substrate (surface of titanium).

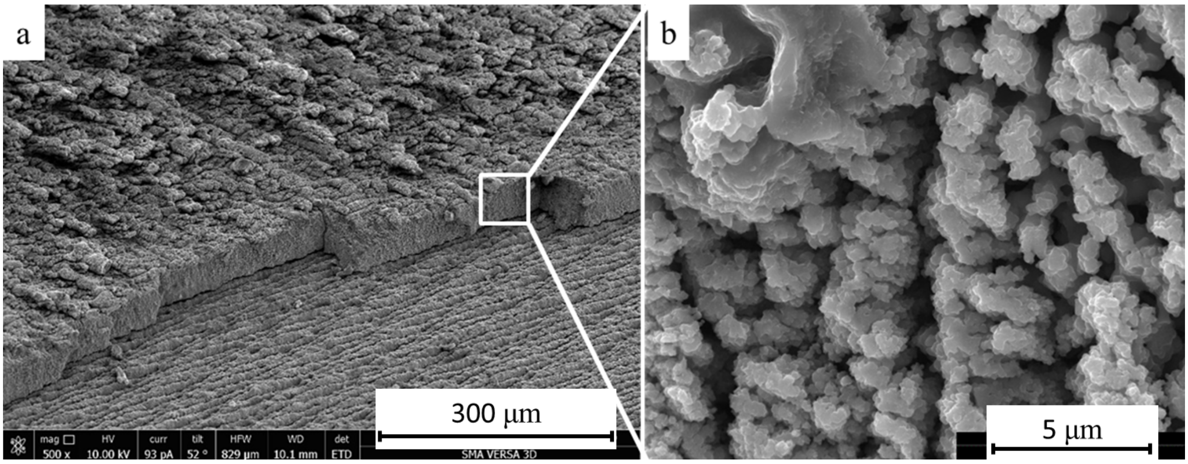

Figure 3. Structure of surface oxide layer formed on titanium alloy VT1-0 by FSLI.

According to TEM investigations the surface layer formed by FSLI has large particles of rutile with the size up to several micrometers and anatase nanoparticles with size 20±3 nm (figure 4). Energy dispersive analysis showed that the ratio of oxygen to titanium in the surface layer corresponds to the stoichiometric composition of titanium dioxide: Ti – 33.33 at.%, O – 66.67 at.%.

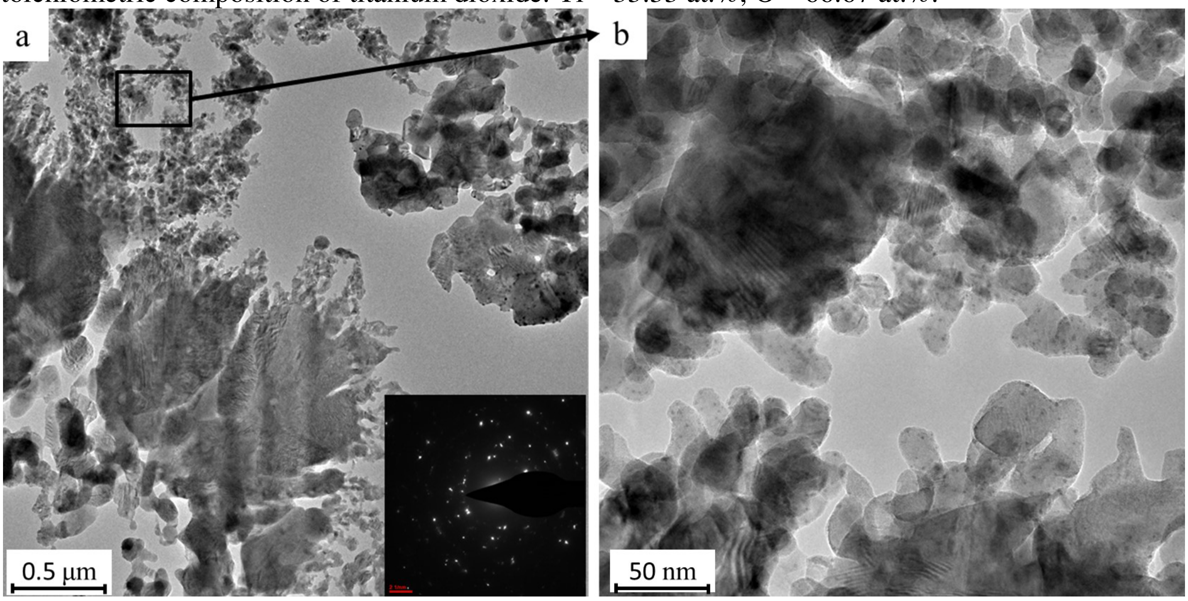

Figure 4. TEM image of cross-section of surface layer formed on titanium alloy VT1-0 by FSLI.

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4. Conclusion

It is found that under femtosecond laser irradiation of the surface of the titanium alloy VT1-0 the microporous nanocrystalline coating with the thickness of ~50 μm is formed. According to X-ray diffraction and transmission electron microscopy, this coating consists of titanium oxides: TiO_2 (rutile and anatase), TiO and Ti_3O_5.

Acknowledgments

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