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INVESTIGATION SURFACE MORPHOLOGY OF CP TI AND TI6AL4V ALLOY TREATED WITH PICOSECONDLASER

Tsanka Dikova*[1,2], Sergei A. Kulinich[2], Satoru Iwamori[2], Kazuyoku Tei[2], Shigeru Yamaguchi[2]

[1]*Medical University of Varna, Varna, Bulgaria*
[2]*Tokai University, 4-1-1 Kitakaname, Hiratsuka-shi, Kanagawa 259-1292, Japan*

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ABSTRACT

The aim of the present paper is to investigate the morphology of titanium surfaces treated with picosecond laser. Round samples of cpTi Gr-2 and Ti6Al4V alloy were treated by a commercial picosecond laser. Two variables were used: average power (1W, 0.5W, 0.2W) and pulse number (1,000-20,000). The samples were investigated by OM, SEM, EDX and non-contact 3D surface profilometer. It was found that the topography of the laser-treated surfaces of both cpTi Gr-2 and Ti6Al4V alloy was similar. It is characterized with micron-scale periodical structures in radial direction, appearance of cavities, submicron-scale periodical structures in the former grains along the periphery of ablated craters (in low energy regimes) and splashed material and debris along the boundaries of the cavities (in higher energy regimes). The depth of the cavities in cpTi Gr-2 treated with the lowest regime parameters was lower than that of Ti6Al4V alloy (0.4 and 5.5 µm, respectively). In cpTi Gr-2, the cavity depth increased mostly with increase in the pulse number while for Ti6Al4V alloy it increased with increasein laser power. The surface of the zone of laser influence and walls of the cavities were covered with layers of different titanium oxides in cp Ti-Gr-2 and with mixed oxides of Ti and Al in the case of Ti6Al4V alloy. The oxides along the cavities walls were characterized with layered morphology, which is finer in Ti6Al4V alloy. The results of this study can be used when applying picosecond pulsed lasers for texturing titanium surfaces to improve their medico-biological properties.

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INTRODUCTION

Implants are artificial structures whose primary purpose is to replace or stabilize damaged body functions. They are of different types - hip and knee implants, spinal implants, dental implants, stents and more. Medical implants have to possess biomechanical properties comparable to those of autogenous tissues without generating side effects [1-4]. The main requirements for all medical implants are high corrosion resistance, biocompatibility, bio-adhesion, bio-functionality and workability. High biocompatibility of implants can be achieved if they are made from biocompatible materials or if their surface is properly modified.

Titanium and its alloys are the main materials for implant manufacturing [1-5], because mechanical properties and elastic modulus of pure titanium are close to that of the bone tissues. Pure titanium possesses high biocompatibility, high corrosion resistance and very good osteointegration. Good corrosion resistance of titanium depends upon the formation of a solid oxide layer (TiO2) to a depth of 10 nm. The geometry, roughness and other properties of the implant surface have a great influence on the interaction with the tissues. The surface of the implants can be modified in various ways, e.g., mechanically, chemically and electro-chemically.

For the last two decades, great attention was paid to laser applicabilityaiming to modify titanium surfaces, as this approach has certain advantages, being contactless, fast, clean and automated process. Lasers give opportunities for treatment of details with complex shape and modification of their surfaces from macro- to nano-level [6-8]. Different types of pulsed lasers are used for this purpose: nanosecond, picosecond and femtosecond [9-11]. However, for surface modification at the micro-/nano-level, ultrashort pulse lasers are preferred, such as femtosecond and picosecond types as they can provide higher precision and low or no heat affected zone (HAZ) in the treated area [12,13].

The research of Grabowski et al. [14] showed that treatment of Ti6Al4V alloy with nanosecond laser leads to melting and further splashing of the melted material. Using picosecond laser, successful texturing can be done with repeated and overlapped pulses, which increases corrosion resistance. In study of the surface morphology of titanium implant, treated by Nd:YAG picosecond laser, Trtica et al. [15] established intensive damage of the central zone of the irradiated area, appearance of hydrodynamic feature at the

* Corresponding author. E-mail: tsanka_dikova@abv.bg

periphery and re-solidified material droplets in irradiated zone, as well as oxidation of the processed surfaces. Surface damage threshold for laser with the wavelength of 1064 nm was estimated to be 0.9 J/cm^2 [16]. It was established that grooves with sizes of 11 μm width and 10 μm depth were more favorable for cell orientation and cell adhesion [17]. The laser-induced linear and dimple geometries on the surface of Ti6Al4V lead to increasing the surface area and wettability of the textured surfaces, which could improve the cell attachment, cell differentiation and growth [18].

As there is a great variety of laser equipment with different modes of operations, the data about surface treatment with commercial picosecond lasers are relatively scarce. The aim of the present paper is to investigate the surface morphology of cpTi Gr-2 and Ti6Al4V alloy processed by a commercial picosecond pulsed laser with repeated pulses.

MATERIALS AND METHODS

Round-shaped samples of cpTi Gr-2 and Ti6Al4V alloy with dimensions 24 mm x 3 mm (diameter x thickness) were used in the experiment. Their surfaces were preliminary ground and polished. Before laser-treatment, they were ultrasonically cleaned consequently in acetone, ethanol, distilled water (15 min in each medium), and dried with compressed air.

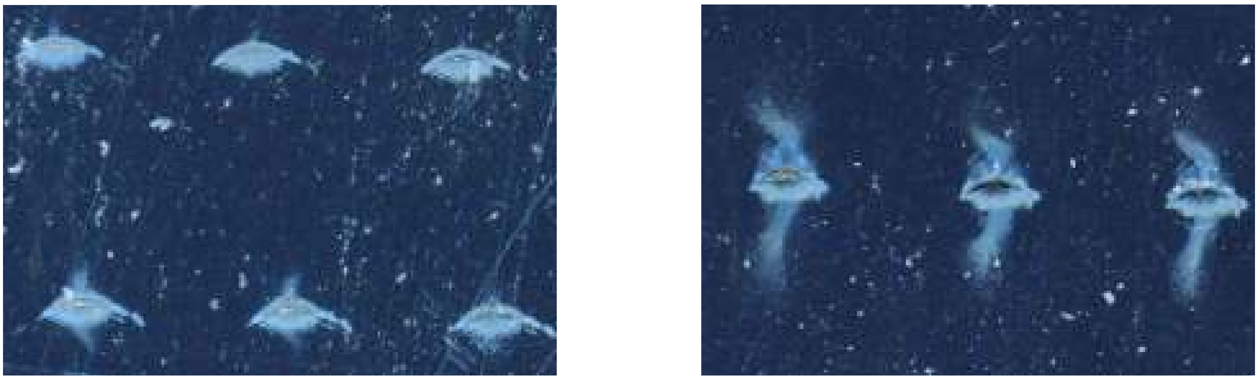
The surfaces of the samples were treated in air environment by a commercial laser Japanese Microchip Laser(from Hamamatsu Photonics K.K). The laser was operated in a stationary (multiple pulses, repeated in the same location) picosecond mode with 1064 nm wavelength, 100 Hz frequency and 500 ps pulse width. The laser beam was focused on the surface with 10 μm spot in diameter. Two regime parameters were varied during the experiment, i.e., the average laser power and the pulse number. The average power was changed from 0.2W to 0.5W and to 1W, which defined the pulse energy of 2 mJ, 5 mJ, and 10 mJ and the laser energy density (fluence) of 2.54 J/cm^2, 6.35 J/cm^2 and 12.7 J/cm^2, respectively. Five different pulse numbers were used: 1000, 2000, 5000, 10 000, 20000.

The surface morphology of the samples was studied by optical microscopy (Sato Tech), field emission scanning electron microscopy FE-SEM(JSM-7100F from JEOL) and super high vertical resolution non-contact 3D surface profiler BW-S500/BW-D500 (from Nikon). The chemical composition was investigated by EDX analysis.

RESULTS OBTAINED

The zones of laser influence (ZLI) on the surface of cpTi and Ti6Al4V alloy are shown in Fig. 1 and Fig. 2. It is clearly seen that the samples' surface is changed even after treatment with the lowest energy density. The heat affected zone is more clearly pronounced on the Ti6Al4V alloy samples than on cpTi. Surface roughness in the zones of influence increases, as it is characterized with wavy surface features and presence of cavities at higher fluence values (Fig. 2 and Fig. 3). The period of the radial waves for all samples is about 20 μm. An excessive amount of splashed material and debris can be seen along the boundaries of the cavities, which additionally affects the surface roughness.

More detailed observation of the ZLI revealed that laser treatment with the lowest laser power/fluence (0.2 W/2.54 J/cm2) changes only the surface roughness of the cpTi Gr-2 (Fig. 4).



a *b*

Fig. 1. Zones of laser influence on the surface of cp Ti – a) and Ti6Al4V alloy – b) (OM images, magnification x50)

The surface of the treated zones is covered with small white formations with nearly round shape and sizes of 1-2 μm. Increasing the laser power and pulse numbers leads to formation of cavities on the surface. Their depth is the lowest (0.4 μm) after treatment with the lowest parameters. It increases mostly with increasing pulse number, reaching 15.7 μm after treatment with 1 W and 5000 pulses. After treatment with 1000 pulses and higher power (0.5 and 1 W), periodic columnar structures of 1 μm width (period of about 1000 nm) are observed in the former titanium grains. The surface inside the cavities, obtained with pulse number higher than 1000 and power of 0.5 W and 1 W, is characterized with layered morphology with layers thickness about 0.5 μm.

Investigation of the laser treated surfaces of Ti6Al4V alloy showed similar results (Fig. 5). For instance, the cavity with 5.5 μm depth is obtained still during processing with the lowest regime parameters (0.2 W and 1000 pulses). There is no clear dependence between the pulse number increase and the depth of the cavities. The cavities with larger depth (9.8 μm after treatment with 1W and 20 000 pulses) were obtained rather by increasing the power than by increasing the number of pulses. Similar to the cpTi Gr-2, during processing with 1000 pulses, periodic columnar structures with the same sizes are observed in the former grains along the periphery of the cavity. The layered morphology in depth of the cavities has appeared in treatment with technological parameters higher than 0.2 W/5000 pulses and 0.5 W/1000 pulses. As it can be seen, the layered morphology of the Ti6Al4V alloy is finer than the cpTi Gr-2.

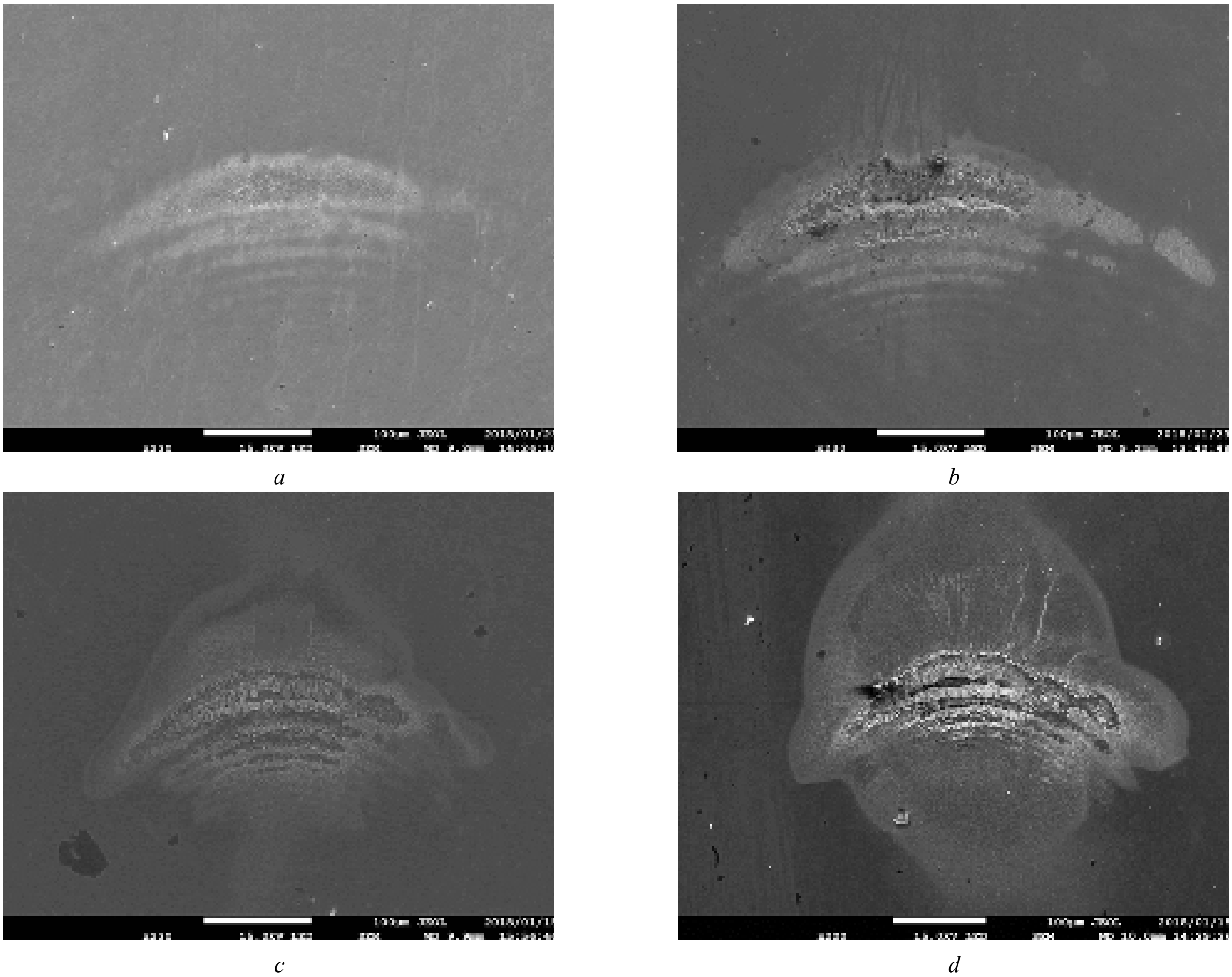


Fig. 2. Zones of laser influence on the surface of cp Ti (0.2 W, 1000 pulses – a) and 1 W, 5000 pulses – b) and Ti6Al4V alloy (0.2 W, 1000 pulses – c and 1 W, 1000 pulses – d) (SEM images)

Study of the chemical element distribution in the ZLI on the surface of both materials showed increase of the oxygen and decrease of titanium and alloying elements quantity (Fig. 6 and Fig. 7). In the cpTi Gr-2, increasing the laser power leads to an increase of oxygen amount. Therefore, the oxide layers in the zone of influenceconsist not only of TiO2, but also of a mixture of titanium oxides. While the layers on the treated surface of Ti6Al4V alloy consist of mixed oxides of Ti and Al. In that case, increase of the oxygen and decrease of Ti and alloying elements quantity is observed rather with increasing the pulses numbers than the laser power.

DISCUSSION

Our previous investigations [19-21] showed that the microstructure of the cpTi Gr-2 consists of equiaxed grains of α-Ti with sizes of 8-15 μm. The grains dimensions of Ti6Al4V alloy are nearly the same, but the microstructure is two-phase - α-Tiis situated in the matrix of β-Ti.

The topography of the laser treated surfaces of cpTi Gr-2 and Ti6Al4V alloy is similar. It characterizes with micron-scale periodical structures in radial direction, appearance of cavities, submicron-scale periodical structures in the former grains along the periphery of the craters in low energy regimes and splashed material and debris along the boundaries of the cavities in higher energy regimes.

The surface morphology of laser treated sample is defined by the microstructure and thermal-physical properties of the material, peculiarities of the equipment used and the parameters of technological regimes, such as energy density (depending on the laser power and laser beam spot diameter), peak power density, pulse duration and number of accumulated pulses [5,10,11,16,22].

In case of laser treatment with multiple pulses which are repeated in the same location, the total energy per unit area is higher than in case of a single pulse, resulting in heat cumulative effect and creating of unique structures on the surface [12,14]. Depending on the laser energy density processes as melting, vaporization of molten metals, dissociation, ionization of the vaporized material and plasma formation can be run on the samples surface [5,10]. During the interaction of laser beam with the metal, the energy is absorbed by the free electrons that transport it to the lattice in characteristic for each material internal relaxation time [5,14-16]. This parameter for titanium is 3-5 ps. If the duration of the laser pulse is much longer than the internal relaxation time (nanosecond pulses), the melting and ablation processes run with domination of melting.

In our experiments, the pulse duration was 500 ps, which is much longer than the internal relaxation time of Ti but still shorter than pulses generated by nanosecond lasers. Therefore, the ablation process could prevail and partial melting of the phases with low melting temperatures such as grain boundaries could occur, which was observed in our experiments with the lowest energy parameters (Fig. 4 and Fig. 5).

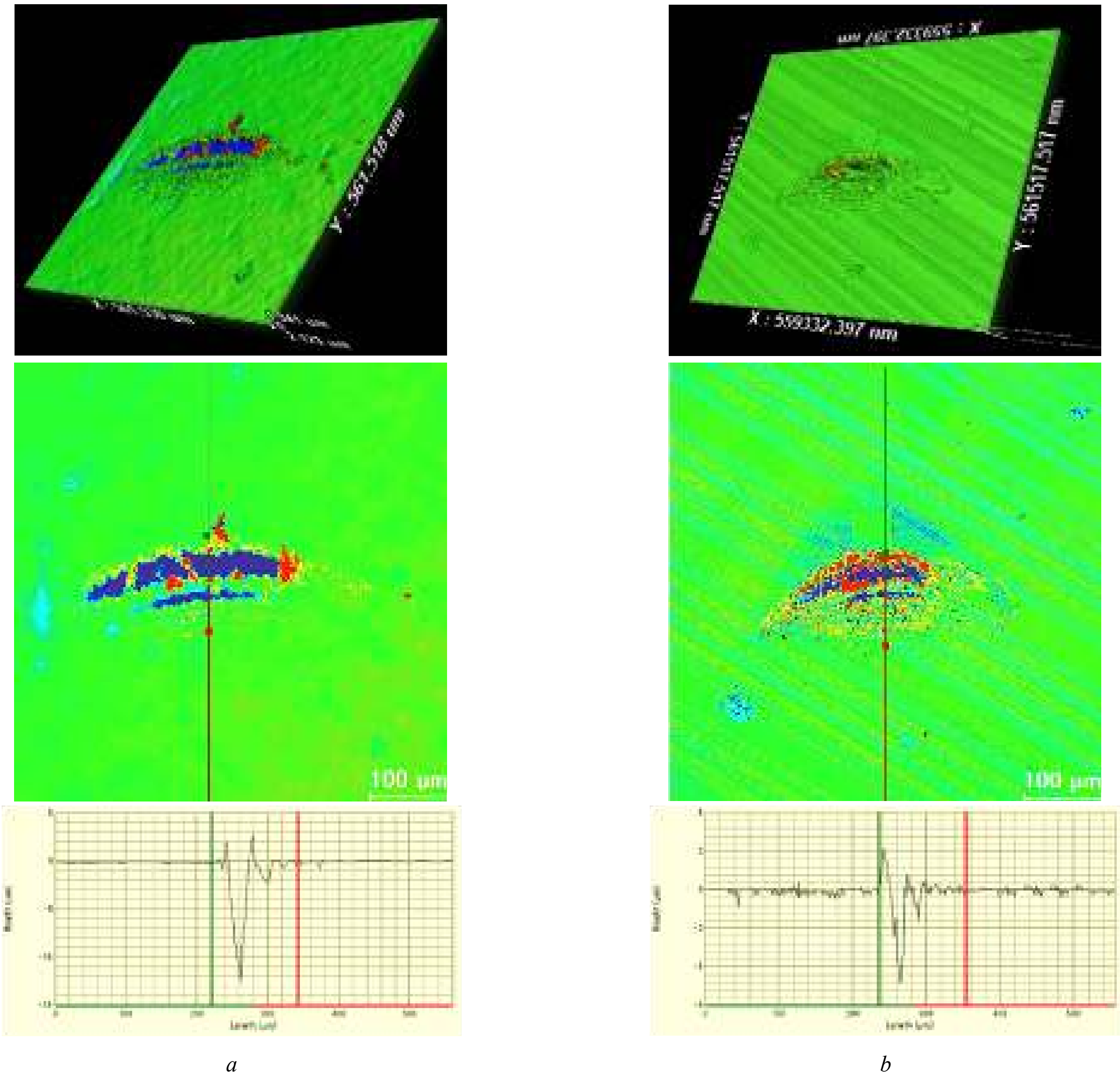


Fig. 3. 3D view, 2D view and cross section of the surface profile of cp Ti – a) and Ti6Al4V alloy – b), treated by picosecond laser (0.5 W and 20 000 pulses for cp Ti and 0.2 W and 1000 pulses for Ti6Al4V alloy.)

It was established that the damage threshold of the interaction between the picosecond Nd:YAG laser and titanium is about 0.9 J/cm^2, while that of nanosecond Nd:YAG laser and titanium is about 1.5 J/cm^2[15]. The energy density in our experiments varies between 2.54 J/cm^{2}and 12.7 J/cm^2, which is higher than the damage threshold. This defines the changes of the surface roughness and presence of cavities in treatment with higher regime parameters. But due to the nearly 2.5 lower thermal conductivity of Ti6Al4V alloy compared to the cpTi Gr-2 [2], the cavities are obtained on its surface still in processing with the lowest regime parameters.

At higher laser energy densities and taking into account the heat cumulative effect of the multiple pulses, the surface temperature in the spot of interaction can increase above the boiling temperature and vaporization starts. The pressure, generated by vaporization, exerts a force on the metal surface and can cause splashing effect by pushing the liquid out of the melted pool [12,14], which is observed in treatment with high fluences and number of pulses in Fig. 2 and Fig. 3.

Depending on the regimes used during treatment with picosecond laser, the surface roughness can be changed by melting, ablation or by induced corrugation on the surface [16]. The laser induced periodical surface structures (LIPSS) are typical in processing with pico- and femtosecond lasers [10,16,22]. The micron-scale LIPSS in radial direction are result of melting and subsequent corrugation due to the kinetic pressure [16].The submicron-size LIPSS are formed by laser beams with low intensity [12]. That is why they are observed along the boundaries of the cavities, created in treatment with the lowest number of pulses – 1000 (Fig. 4 and Fig. 5). LIPSS represent parallel “ripples” which are positioned perpendicularly to the laser polarization direction [8,11,12,15]. The “ripples” periodicity is about 1000 nm that is in accordance with the laser beam wavelength 1064 nm. They are result of the interference of the incident laser beam with scattered electromagnetic waves, created at the surface irregularities. [5,10,11,16,22].

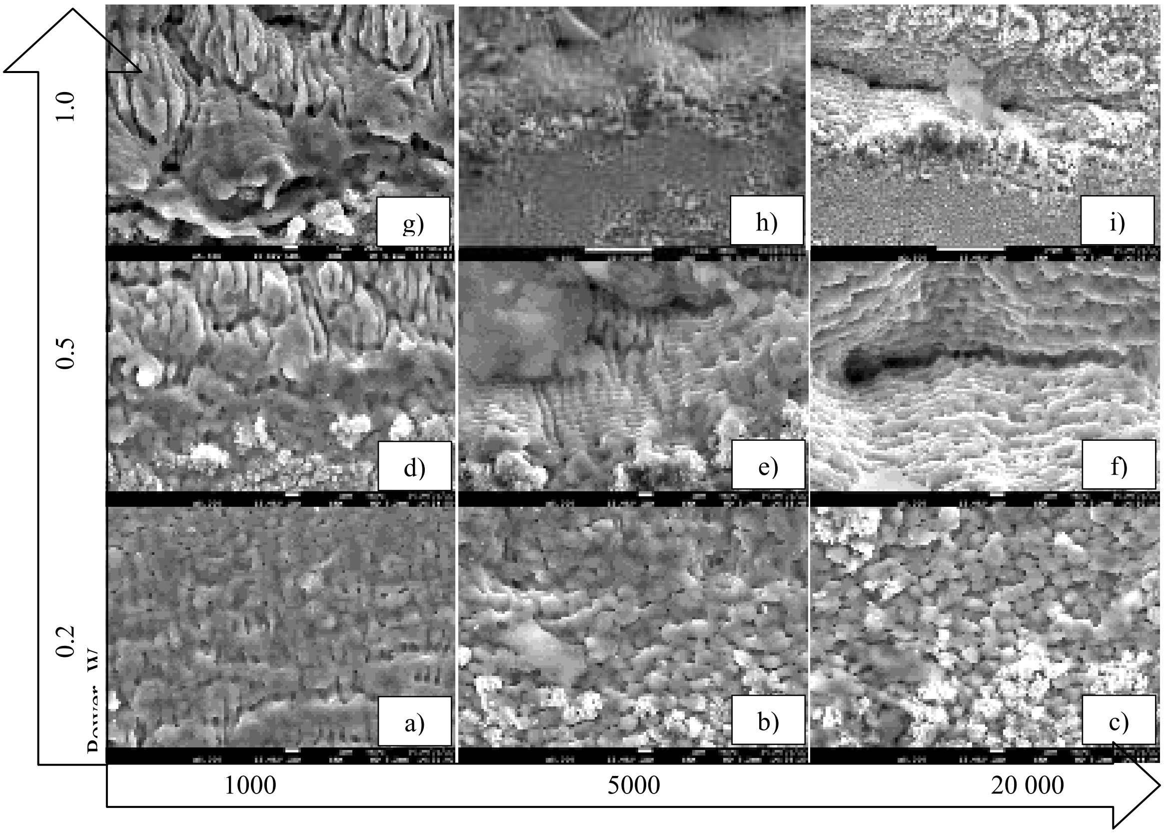


Fig. 4. Surface morphology of cpTi after treatment with different regimes of picosecond laser (SEM images)

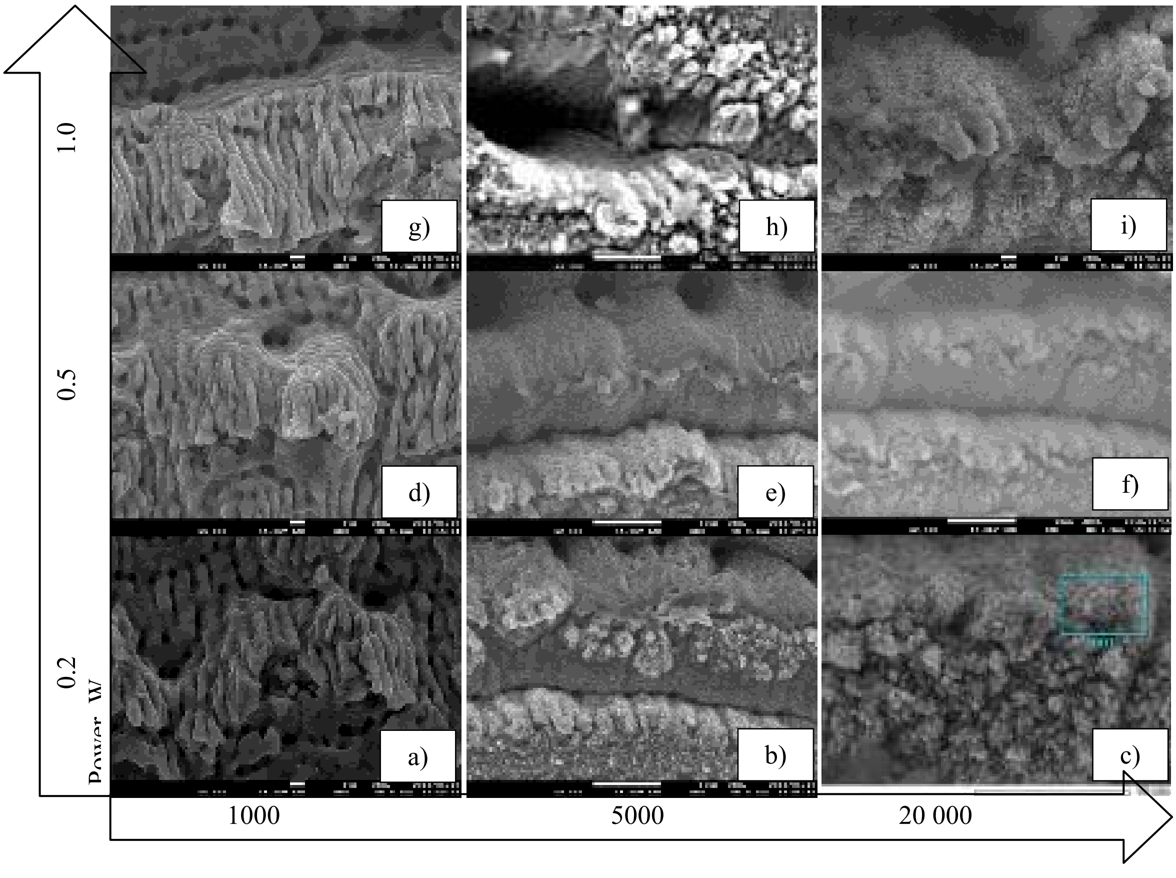


Fig. 5. Surface morphology of Ti6Al4V alloy after treatment with different regimes of picosecond laser (SEM images)

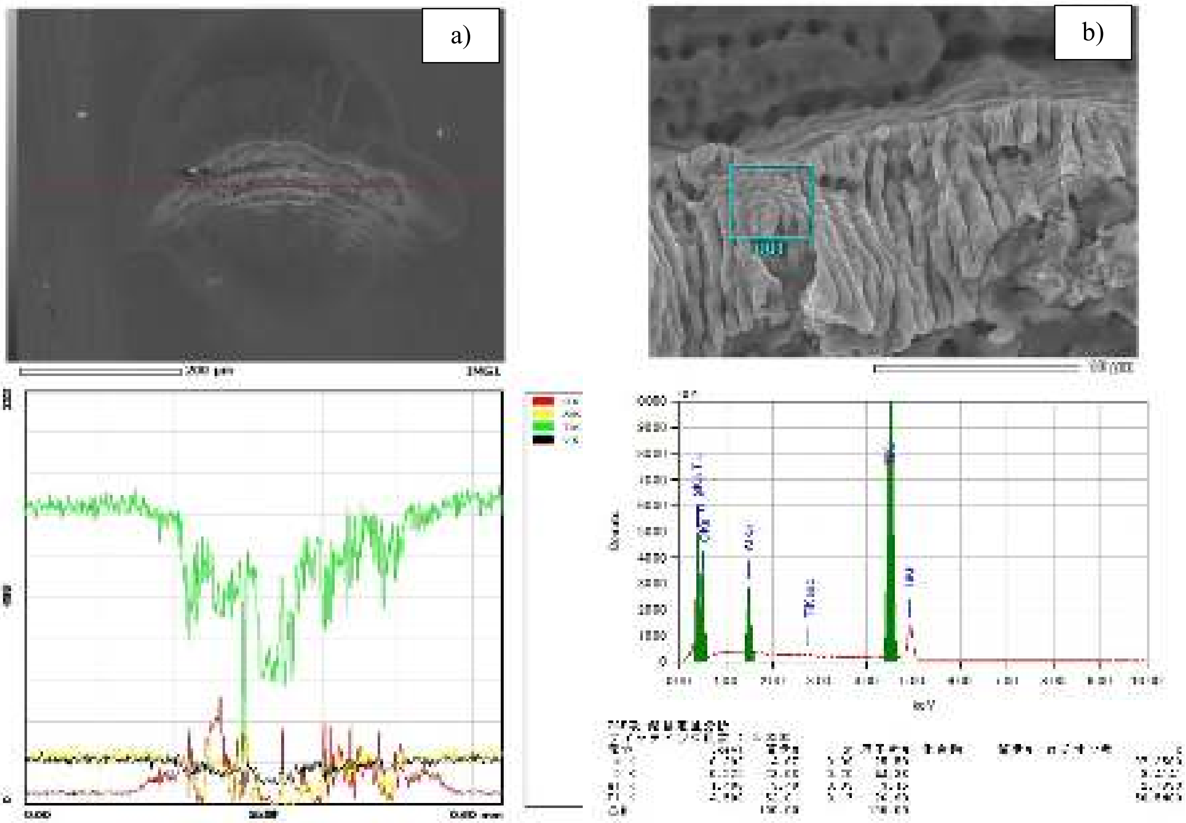


Fig. 6. Chemical elements distribution in the zone of laser influence on the surface of Ti6Al4V alloy, treated with 1 W power and 1000 pulses

During laser treatment of titanium in air environment different oxides, such as TiO, TiO_2 and Ti_2O_3, are formed on its surface due to oxidation by air [5,7,8]. Their formation depends on laser parameters used, the latter parameter determining the temperature in the ZLI. Increasing the laser energy density and pulse numbers leads to increased oxidation due to elevated temperature [16]. Consequently, the surface of the ZLI and walls of the cavities are covered with layers of different titanium oxides in cp Ti-Gr2 and mixed oxides of Ti and Al in Ti6Al4V alloy.For the best of our knowledge, layered morphology of the oxides along the cavities walls in treatment of titanium surfaces by picosecond laser is observed for the first time. The most probable reason for such kind of layered morphology is the multiple action of extremely high number of pulses in the same location. In Ti6Al4V alloy, the two-phase structure can contribute to formation of a finer morphology of the oxide layers compared to the cp Ti-Gr2.

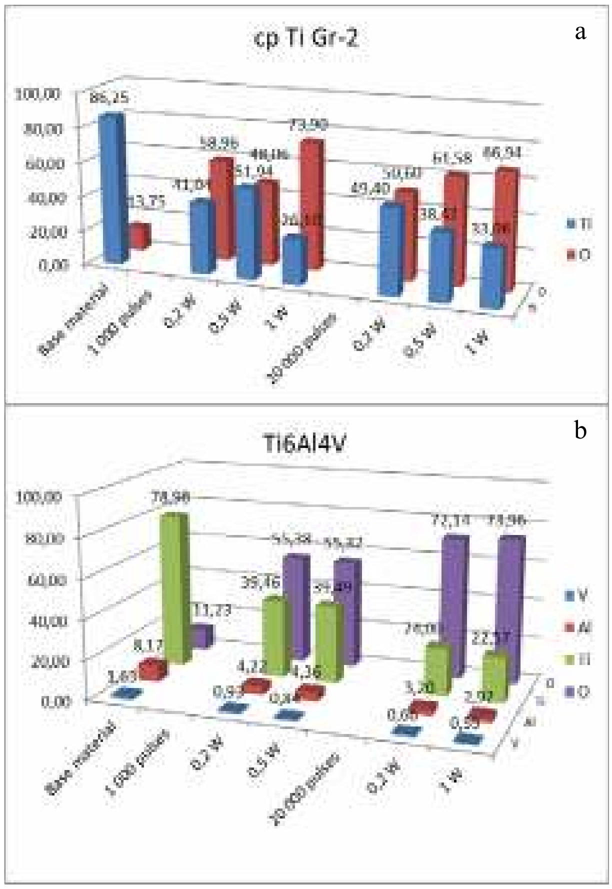


Fig. 7. Chemical elements distribution in the "melted zone" of cp Ti – a) and Ti6Al4V alloy – b), treated by picosecond laser with different regimes

CONCLUSION

Surface morphology of cp Ti-Gr2 and Ti6Al4V alloy, treated with picosecond laser, is investigated in the present paper. During processing of metals and alloys with picosecond laser the surface roughness is changed by melting, ablation or by induced corrugation on the surface.

It is established that the topography of the laser treated surfaces of cpTi Gr-2 and Ti6Al4V alloy is similar. It is characterized with micron-scale periodical structures in radial direction, appearance of cavities, submicron-scale periodical structures in the former grains along the periphery of the craters in low energy regimes and splashed material and debris along the boundaries of the cavities in higher energy regimes.

The depth of the cavities in cpTi Gr-2 in treatment with the lowest regime parameters is lower than that of Ti6Al4V alloy (0.4 and 5.5 µm, respectively). In cpTiGr-2 the cavity depth increases mostly with increasing of the pulse number while for Ti6Al4V alloy it increases with increasing the laser power. The surface of the zone of laser influence and walls of the cavities are covered with layers of different titanium oxides in cp Ti-Gr-2 and mixed oxides of Ti and Al in Ti6Al4V alloy. The oxides along the cavities walls are characterized with layered morphology, which is finer in Ti6Al4V alloy. For the best of our knowledge, layered morphology of the oxides along the cavities walls in treatment of titanium surfaces by picosecond laser is observed for the first time.

The results of present study will be helpful in selection of technological regimes for treatment of titanium surfaces with picosecond pulse lasers for enhancement of their medico-biological properties.

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