Surface processing of titanium in the medium of n-hexane by ultrashort laser pulses

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Abstract In this paper we conducted research of the surface processed by femtosecond laser radiation in the medium of n-hexane at various scanning speeds. The obtained samples were studied using a scanning electron microscope; a description of the observed effects was presented. It has been demonstrated that depending on the mode of exposure to laser radiation, it is possible to obtain microgranules and surface structuring.

1. Introduction
When exposed to ultrashort laser pulses with a sufficiently high intensity $10^{12}$-$10^{14}$ W/cm$^2$ on the surface of the processed metal located under a layer of liquid, sputtering and partial ionization of ablation products occurs in the area exposed to laser radiation, photoemission and plasma plume formation occur (laser-induced plasma). The main mechanisms responsible for plasma formation are the same for processing not only in liquid, but also in air [1]. The laser energy is transmitted to the material being processed through the excitation of the bound electron shells of the sample atoms. The prerequisites for intense electron emission are high electron temperature maintained during the exposure to an ultrashort laser pulse on metal surfaces, which contributes to the thermal and photo-induced process of N-photon electron emission [2-4]. In [5-6], it was found that for titanium, the emission of electrons from the surface, when the intensity of the effect is below the plasma formation threshold, occurs almost linearly. When the plasma formation threshold is exceeded, the emission of charges of both signs is nonlinear, with an exponent for titanium equals two. In this case, it is characteristic the minimal removal ablation material at the surface layer of the order of several nanometers [5].

In our case, it is advisable to use the laser exposure in the modes that ensure the formation of plasma. It is not advisable to disperse the material in the mode of cold ablation because of the low productivity of the process. Also, this processing mode is characterized by «chipped» particles of the ablation material, hence the name of the mode is «chipped laser ablation». It should be noted that the mode of cold laser ablation is achievable for metals in a very narrow range of processing modes in view of the presence of a large number of free electrons. A mode of cold laser ablation is more characteristic of non-conductive materials.

2. Experimental work
In the experimental scheme (figure 1) the laser beam (2) scanning was carried out along two axes using a galvano scanner system (4) equipped with a flat-plane lens with a focal length of 200 mm
using pulsed femtosecond laser radiation. The source of laser radiation was Ti:Sapphire laser system (1) (wavelength 800 nm, pulse repetition rate of 1 kHz, pulse width 50 fs, average pulse energy 0.8 mJ). Continuous monitoring of the laser power was carried out by diverting the power had been using the plate beamsplitter to the head of the photodetector (10). For position adjustment and moving of the sample (7) on the vertical axis into the focal plane of the focusing system motorized linear translation stage (8) was used. The internal volume of the cuvette was filled with liquid medium (6) [7].

![Figure 1. Scheme of the experimental setup: 1 – Ti:Sapphire laser system; 2 – laser beam; 3 – plate beamsplitter; 4 – galvano scanner system; 5 – cuvette; 6 – liquid media; 7 – sample; 8 – linear translator; 9 – personal computer; 10 – photodetector.](image)

The sample was located under the layer of liquid hydrocarbon (hexane – C₆H₁₄). Laser beam scanning was carried out by means of the galvano scanner system with a speed of 0.1–200 mm/s.

The depth of immersion of the sample was chosen so that the liquid layer covered the surface of the sample being processed, but did not make a tangible contribution to the process of absorption of laser radiation. The effect of the liquid layer thickness at the laser processing of surface sample to be influences a number of parameters, such as the rate of expansion of the ablation products, the cooling rate of the formed particles, the distribution of the laser radiation energy on the immediate surface of the sample being processed. With a large thickness of the liquid layer (of the order of several mm), a significant deterioration of the parameters of the laser beam occurs. At the same time, there is no effective transfer of laser radiation energy, including due to the interaction of laser radiation directly with a liquid medium, since after exposure to laser radiation a vapor-gas channel is formed and intense boiling of the liquid occurs. The resulting hydrodynamic flows in the area of laser irradiation have a greater inertia compared to the laser pulse repetition rate (units of kHz), which negatively affects the efficiency of the energy exchange of the system «laser radiation – treated surface». An additional negative factor significantly worsening the characteristics of the beam/intensity distribution of the laser radiation is the presence of gas bubbles in the liquid.

When processing the surface of titanium in hexane by femtosecond laser radiation with a scanning speed of 200 mm/sec, the formation of a polymeric substance, presumably polyethylene is observed (figure 2a). In this mode of processing overlap areas of laser radiation exposure does not occur. It is possible the formation of polyethylene as a result of the destruction of n-hexane molecules into the early members of the homologous series. In figure 2, white circles indicate the places of formation of the polymer substance.
This phenomenon occurs as a result of the interaction of a liquid medium with laser radiation passing through it, temperature exposure at the contact of ablation products.

With an increase in the energy of exposure (the number of pulses in the impact area), changes in the surface structure of the material being processed are observed (figure 2b); so-called laser-induced periodic surface structures are formed (LIPS). The formation of LIPS is characteristic of exposure to ultrashort laser pulses with a small energy contribution, which does not lead to pronounced ablation of the material from the exposure area of laser radiation [8]. Polymer components are also present on the processed surface, but in smaller quantities. On the processed surface which shown in figure 2b, the amount of overlap of the areas of exposure to laser radiation was about 50%. The increase in the energy of exposure to the sample surface, achieved by reducing the laser beam scanning speed of the surface, leads to a change in the morphology of the LIPS formed.

Figure 3 shows the results of surface processing with different speeds.

On the processed surface is not observed the presence of polymer components. The surface structure formed, shown in figure 2b and figure 3a, is practically the same, with the exception of the formation of randomly shaped polymer granules [9]. With an increase in the number of laser pulses per unit of surface area, and, consequently, an increase in the energy of exposure, leads to a further change in the surface morphology. The surface acquires a pronounced scaly structure (figure 3b).
Also, it is worth noting the increase in the depth of the relief presented in figure 3b relative to the microrelief shown in figure 3a.

A further increase in the number of laser pulses in the area of exposure leads to the destruction of the formed structure, localization of the relief maxima, increased roughness, local melting of the relief surface, the formation of ablation products on the processed surface (figure 4a). The form of ablation products is random, the surface contains inclusions from micro- and nanoobjects of spherical shape, one way or another, it is impossible to relate the bodies to the form of simple geometric bodies. On some parts of the formed surface there are hardened titanium splashes of spherical shape close to the shape of a drop. This fact indicates the beginning of the formation of the liquid phase of the metal after exposure to laser radiation, the point of release of the liquid phase in figure 4b is indicated by circles. The white arrows in figure 4a indicate the areas of the formed polymeric substance, the dotted line indicates the region with the formed microgranules in the polymer bond.

![Figure 4](image)

**Figure 4.** Processed surface of titanium under the layer of hexane with laser beam scanning speed: a – 20 mm/sec, b – 10 mm/sec.

Thus, with increasing energy in the area of exposure, the processed mode acquires a thermal character despite the physics of the interaction of ultrashort laser radiation with materials. The energy of laser radiation (about 500 μJ) absorbed by the material being processed cannot be completely distributed due to the mechanism of heat conduction into the volume of the material, into the volume of the liquid medium. By the time of arrival of the next pulse, the residual heating of the region exposed to laser radiation remains at the time of arrival of the next pulse. This type of processing corresponds to the heat accumulation model proposed in [10-11]. With a further decrease in speed up to 10 mm/sec, not only the liquid phase emissions are present on the processed surface, but also the presence of microspheres caused by the separation of a certain volume of melted material with subsequent reprecipitation on the processed surface. The surface obtained as a result of processing has a rounded shape of the microrelief structure, which also indicates a significant temperature effect on the material induced by a combination of thermal energy accumulation processes and the «feed» of the heated treated area with an additional portion of energy from the next laser pulse.

Figure 5 shows the image of the processed surface of titanium under the layer of hexane with laser beam scanning speed of 0.1 mm/sec.
This processing mode is characterized by the effect of heat accumulation, contributing to the dynamic erosion of the surface of the material being processed [12], with abundant release of the liquid phase. The presence of abundant release of the liquid phase is a kind of indicator of this process. This phenomenon to some extent contributes to an increase in the rate of formation of the hole channel [10-11, 13], and as a result, an increase in the dynamics of laser ablation of the material. In this mode, a residual heating of the material must be ensured, which is achieved either when the pulse repetition frequency exceeds a certain level or by increasing the energy in the area affected by laser radiation. One way or another, the phenomenon is of a threshold nature and cannot occur before certain values of the energy in an impulse.

An SEM image of the surface of microsphere exiting the area of impact is shown in figure 6a. The surface of the microsphere has a high smoothness and sphericity. About 80% of microspheres are placed in a size range of 1-3 microns. Microspheres located on the sample surface (figure 6b) have pronounced defects, pores, cracks, shape disturbances probably caused by repeated exposure to the heat source (laser-induced plasma plume, laser radiation), or by contact with high-energy laser ablation products. Microspheres collected from the bottom of the cuvette have a nearly perfect surface without pronounced external defects. This feature is characteristic of laser methods for obtaining spherical microgranules due to the high power density and localization of the impact of the energy source. Formed spheres leave the processing area, without being exposed to a prolonged exposure to the energy source, as is the case with electric arc and gas-plasma methods for the synthesis of microgranules.
3. Conclusion
The results of titanium surface processing under the layer of hexane by femtosecond laser radiation with different beam scanning speeds are presented. Research suggests that as the scanning speed decreases, heat accumulates in the area of exposure, which contributes to the dynamic erosion of the material. Thus, by changing the laser beam scanning speed, it is possible to carry out various processing modes: at low speeds, ablated synthesis of spherical microgranules is possible; as the scanning speed increases, the surface is structured. The relief and period of the obtained microstructures also depend on the speed of scanning by laser radiation.

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