Laser ablation of titanium in the medium of n-hexane by femtosecond laser pulses at various pressures

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Abstract The paper presents the results of studies on the synthesis of spherical titanium nanopowders in the medium of n-hexane depending on the pressure of the buffer gas. The dependence of the size dispersion of the obtaining nanopowders on pressure is considered. SEM images of the obtained nanopowders are shown. It has been demonstrated that adjusting the value of the external pressure, it is possible to control the size of the ablation products of laser processing.

1. Introduction
Currently, the ablation of materials under the action of ultrashort laser pulses in various media was great practical interest. With the help of such type of processing it is possible not only to obtain various structures on the surface of the material, which can have a significant difference from the original surface and have improved physical and mechanical properties but also to synthesize the difference granules, that may constitute a powder material of different shapes and sizes. Nanomaterials obtained by laser radiation are widely used in various fields: they can be used as a micro-tool for soldering chips or cutters for metal processing, as a sintering additive to improve physical and mechanical properties, as a filler [1-3]. The laser method of obtaining powder materials is the most modern, due to the appearance of powerful sources of laser radiation. This method has such advantages such as uniformity of the sizes of the received particles, reception of particles with the set properties, high purity of the received powders, high sphericity. All these properties together generate great interest in this method.

In this time, the search for the most effective schemes for this synthesis is being actively conducted. The paper [4] describes a method for producing nanopowders by high-power radiation of ytterbium-doped fiber laser. In addition, as an example, a patent [5], which described the invention relating to the manufacture of metal powders. This method involves heating the metal material to its melting point by laser radiation, forming droplets from the melt; cooling them in free flight in a neutral gas environment to a temperature below the melting point of the metal material and picking powder particles.

2. Experimental work
In this work, the effect of femtosecond laser pulses on titanium samples in a liquid hydrocarbon medium (n-hexane) at various pressures and ablation processes were studied. The source of laser radiation was femtosecond Yb:KGW-laser system (wavelength 1030 nm, pulse width 280 fs, pulse
repetition rate of 10 kHz, pulse energy 150 μJ). As the focusing optics a galvano scanner system equipped with a flat-plane lens was used (focal length of 200 mm). Laser pulse energy was measured using a highly sensitive photodetector. N-hexane had been used as the liquid medium. The internal volume of the reaction chamber was filled with argon through a leak valve, the pressure control was carried out through a pressure regulator connected to the gas vessel. During the experiment, the value of the external pressure was changed by means of a buffer gas – argon, the value varied from 6.3 mbar to 22 Bar. Schematic drawing of the experimental setup presented in figure 1.

![Figure 1. Schematic drawing of the experimental setup: 1 – Yb:KGW laser system; 2 – laser beam; 3 – plate beamsplitter; 4 – galvano scanner system; 5 – reaction chamber; 6 – pressure regulator; 7 – gas vessel with argon; 8 – liquid media; 9 – sample; 10 – linear translator; 11 – personal computer; 12 – photodetector.](image)

After the experiments, ablation products were investigated. The solution from the test tube was deposited on a silicon substrate, causing the liquid to evaporate, and the ablation products remained on the substrate. Some substrates were examined using a scanning electron microscope. Figure 2 shows the SEM images of sample № 1 processed at a pressure of 6.3 mbar.

![Figure 2. SEM images of precipitated titanium ablation products for sample № 1, that processed at a pressure of 6.3 mbar.](image)

In figure 2, it is possible to observe the formation of granules of ablation products having a spherical shape. The adhesion of the particles to each other can be explained by the use of hydrocarbon as a liquid medium, which was converted into a polymer. Figure 3 shows the SEM images of sample № 2 processed at a pressure of 10 Bar.
Figure 3. SEM images of precipitated titanium ablation products for sample № 2 that processed at a pressure of 10 bar.

Figure 3 also shows the formation of granules. However, when comparing figure 3 and figure 2, a decrease in the particle size, while preserving their shape can be observed.

Figure 4 shows the SEM images of sample № 3 processed at a pressure of 20 bar. There are can notice the formation of spherical granules. Sample № 3 was examined using a scanning electron microscope, but the material was re-precipitated onto the surface of two thin carbon films that were on a copper grid.

Using the obtained images, the sizes of the formed granules were determined. So, the graph of the distribution of particle size of sample № 1, that processed at a pressure of 6.3 mbar is presented in figure 5.
Figure 5. Graph of the distribution of particle size of sample № 1, that processed at a pressure of 6.3 mbar.

In figure 5, based on the graph, it can be seen that the sizes of particles mainly varies from 35-75 nm. For sample № 1, the average particles size was 82 nm. In addition, a graph of particle size distribution was constructed for sample № 2, that processed at a pressure of 10 bar (figure 6).

Figure 6. Graph of the distribution of particle size of sample № 2, that processed at a pressure of 10 bar.

Figure 6 shows the narrowing of the graph lines. After this processing, particles with an average size of 74 nm were obtained, which indicates a decrease in the particle size spread.

The graph of the distribution of particle size of sample № 3, that processed at a pressure of 20 bar is presented in figure 7.
Figure 7. Graph of the distribution of particle size of sample № 3, that processed at a pressure of 20 bar.

For sample № 3, the average particles size was 47 nm. Based on the graphs presented in Figures 5, 6, 7 we can conclude that the average particle size decreased with increasing pressure in the reaction chamber. In [6, 7], it was found that external pressure directly affects the behavior of material destruction in the reaction chamber. Due to the change in the density of the liquid medium, owing external pressure, the plasma plume becomes limited for further expansion. Due to this limitation, there is a concentration of a large amount of energy in this area, as a result of which it is possible to observe the synthesis of nano-sized particles. However, the area of distribution of ablation products decreases, respectively, and its effectiveness decreases. In this case, this can be explained by the use of a liquid medium during laser processing. The focus of the laser spot shifts due to such processes as: effective boiling of the liquid, absorption of a part of the radiation by the liquid medium, and defocusing of the laser spot [8-10]. As a result, a graph which shows a comparison of the distribution of particle sizes depending on pressure was constructed (figure 8).

Figure 8. Graph of the distribution particle sizes depending on pressure.
The results obtained in this work confirm the data from literary sources. Thus, the greater the pressure value during the processing of the titanium target, the more the average particle size decreased. Based on this, changing the external pressure, it is possible to synthesize powder materials with the required size, depending on the task.

3. Conclusion
Thus, in the course of the experiments, titanium particles having spherical shape were obtained. The size of these particles varied depending on the value of the external pressure during processing. Thus, for a pressure value of 6.3 mbar, the average particle size was 82 nm, for 10 bar – 74 nm, for 20 bar – 47 nm. It was found that the average particle size decreased with increasing pressure in the reaction chamber. Accordingly, by adjusting the value of the external pressure during processing, it is possible to control the size of the ablation products.

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