Ablative laser processing of titanium surface in n-hexane

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Abstract The work is devoted to the problem of high-spherical powders synthesis by the method of laser ablation processing of refractory metals. An investigation of interaction of ultrashort laser pulses with titanium in an n-hexane medium has been carried out. The dependence of granules size and dispersion of synthesized micro- and nanoparticles on the parameters and processing conditions, namely, laser radiation energy, scanning speed, working medium and pressure is shown.

1. Introduction
The use of laser radiation for synthesis of micro- and nanopowders makes it possible to obtain microgranules of a wide range of materials (metals, dielectrics, semiconductors, ceramic materials) [1-4]. The features of laser impact allow to achieve a change in the aggregate, structural and phase state of a material without introducing undesirable impurities into it (provided they are absent in the area of laser radiation action) [5-8].

The main disadvantages of this method are extremely low productivity of the process and insufficiently small fraction of synthesized particles. Based on the results of previous studies, as well as literature data [9,10], a number of disadvantages of traditional use of laser sources with a sufficiently low laser pulse repetition rate (1 kHz) and high pulse energy (~ 800 mW) for the synthesis of micro- and nanopowders were revealed. The resulting powders have a large granule size (the main fraction is in the range of 1-3 microns), the productivity of operation is rather low, and it is of the order of 0.01 grams per hour (for the above conditions). To eliminate these disadvantages, it is proposed to use a laser radiation source with a higher pulse repetition rate, which will improve the efficiency of material dispersion.

2. Experimental part
The experimental work was carried out using a Yb3+ KGW femtosecond laser setup: pulse duration 300 fs, main wavelength 1030 nm, pulse repetition rate 10 kHz. The sputtered target was a titanium plate placed in a container filled with n-hexane under pressure.

The scanning mode and radiation impact are shown in figure 1: (a, b) – processing was carried out with a change in the scanning speed. In (a) the speed was selected to achieve overlapping of laser radiation impact areas, in (b) the overlap was minimal, and density of the formed tracks was 30 lines per 1 mm.
Figure 1 (c, d) shows a scan mode that does not overlap the affected areas. The efficiency of laser ablation processing was determined by the amount of material removed. The study of this parameter was carried out by weighing the sample before and after processing. Weighing was carried out after washing the sample in an ultrasonic bath in kerosene at a temperature of 40°C, followed by washing in acetone and drying in air. The measurement results are shown in figure 2. The dispersion of sizes obtained as a result of nanoparticles laser ablation processing in an n-hexane medium was studied using a particle size analyzer. The obtained dispersion of nanoparticles depending on buffer gas pressure in vessel is presented in figure 3 (the data correspond to the scanning mode (a) shown in figure 1).

Figure 2. Dependence of titanium ablation speed on pressure in working vessel and processing mode according to given scheme.
Figure 3 shows a pronounced dependence of resulting nanoparticles dispersion on the pressure in working vessel. Increasing the pressure in the vessel contribute to reduce the resulting nanoparticles size dispersion. At low pressures of 0.006-1 bar, a bimodal distribution is observed. A similar character can be caused by repeated falling of nanoparticles under laser beam, therefore the resulting nanoparticles combine into clusters. At a pressure of 10-15 bar, a decrease in dispersion is observed with a tendency to reduce in particle size. At a pressure of 20-25 bar, a pronounced fraction of 60% particles with a diameter of 30 +/- 2 nm is observed (95% of the fraction are particles of 20-40 nm).

The pronounced change in the dynamics of ablation can be associated with the effect of pressure on both the process of direct material ejection and the process of plasma formation. At a pressure of 6 mbar, intense boiling of n-hexane is observed in the laser radiation area (see figure 4 (a)), and ablation occurs not so much in a liquid medium as in a vapor-gas medium. The dynamics of processing at atmospheric pressure is almost the same as processing using the Ti:Sapphire laser system. This corresponds to the literature data [11-14], which describes the modes with an average laser power of ~1W. Thus, the average power has a decisive impact on the productivity of laser ablation processing for a given pressure. With pressure increase in the vessel, a decrease in intensity of boiling is observed, which is shown in figure 4. Gassing during the passage of laser radiation is practically not observed. From the diagram shown in figure 2, it can be concluded that the distortion of transverse profile of laser beam distribution having the most profound impact on productivity of ablation operation.
Fig. 4. The image of processing according to the scheme in figure 1 (a) at pressure:

a – 0.006 bar, b – 1 bar, c – 10 bar, d – 20 bar.

3. Conclusion
The production of nanoparticles in an n-hexane medium at elevated pressure has shown an increase in the productivity of the ablation operation due to a decrease in intensity of vapor-gas formation, leading to a distortion of the laser beam shape. The pressure change in the vessel made it possible to carry out a controlled change in the size and dispersion of resulting titanium nanoparticles. The productivity of this ablation operation is low, but it can find application in the fields of medicine, colloidal chemistry, where it is required to obtain a small number of spherical nanoparticles of a given sizes dispersion.

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