Interaction of femtosecond laser radiation with titanium in a liquid hydrocarbon medium

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Abstract. A method for the synthesis of microspheres coated with titanium carbide is described. The processes occurring in the region of the action of laser radiation are considered. The formation of microspheres was carried out by the action of femtosecond laser radiation on the surface of titanium located in the reaction medium - the ultimate hydrocarbon. The hydrocarbon source was the medium in which the treatment was carried out. The obtained microspheres have an average size of 1-3 μm and can be used in applications of additive engineering, powder metallurgy as the main raw material, or as an alloying additive.

1. Introduction
Metal powders serve as the primary raw materials in the technologies of additive engineering. Products made on the basis of titanium alloys have high corrosion resistance, chemical inertness, heat resistance, low specific gravity and high strength. Powder materials have found their application in the technologies of aircraft building, in medicine in the manufacture of implants for dentistry and orthopedics.

At present, there are many ways and approaches for obtaining powders of various materials: by mechanical grinding, chemical precipitation, and magnetron sputtering. Each of these methods has its advantages and disadvantages, which determine the field of application of the obtained powder material. In spite of the very limited distribution of laser technological installations, the method of laser synthesis of powder material is of high interest due to the exceptional properties of laser radiation, unattainable by other sources of concentrated energy. Thus, it is possible to obtain powders from virtually any material. By selecting the processing mode it is possible to synthesize granules of different fractional and chemical composition. The peculiarities of laser action make it possible to achieve a change in the structural and phase states, to control the introduction of foreign impurities into it, which makes it possible to obtain pure powder materials in comparison with other synthesis methods. When introducing the necessary impurities, it is possible to obtain complex alloys, composites, and cold solutions in the required aggregate state.

In the field of obtaining powdered materials, the process of material destruction due to the action of laser radiation is of great interest, in particular, it is required to obtain not a melt, not steam, but directly "sprays", which in the process of rapid cooling acquire a spherical shape. By creating certain conditions it is possible to obtain particles with a narrow particle size distribution. For such purposes,
Pulsed laser systems capable of effectively transferring laser radiation energy for the development of the laser ablation process are used. The use of additional means, such as processing media, various sources of physical impact, can influence the dynamics and result of this synthesis process. In recent years, the processes that occur during laser ablation in a liquid have been extensively studied [1-4]. Laser ablation in a liquid medium allows rapid cooling of ablation products, which promotes the formation of a "highly spherical" surface. The liquid medium used can exhibit both inert properties during processing and reaction.

2. Equipment and samples
In experiments we used a Ti:Sapphire laser system with the following parameters: pulse duration 50 fs, average power 450 mV, wavelength 800 nm, repetition rate 1 kHz. A laser beam with a diameter of 30 μm was focused on the surface of a titanium sample located in the reaction medium. A titanium plate of grade VT1-0 was used as a sample. Figure 1 shows the scheme of the experiment. The cuvette was a container isolated from atmospheric air, having a point of attachment of a sample, a transparent window for introducing laser radiation. The sample was located under a layer of liquid hydrocarbon. The laser radiation power was controlled by removing a part of the radiation from the beam splitter plate. Scanning with a laser beam was carried out with the galvanometer scanner with a speed of 0.1-200 mm/s.

Figure 1. Scheme of the experiment. 1 - femtosecond laser system; 2 - light-emitting plate; 3 - laser radiation; 4 - optical head with galvanometer scanner (X-Y); 5 - vessel isolated from the atmosphere with laser input window; 6 - reaction medium; 7 – sample; 8 - optical powermeter; 9 - a plasma torch; 10 - an aerosol of a liquid medium; 11 - a powder granule.

3. Conducting an experiment and discussing the results
A titanium sample of the brand VT1-0 was placed in a cuvette with the reaction liquid with the limiting hydrocarbon-hexane. The depth of immersion of the sample was from 2 to 4 mm. Laser radiation with an optical system focused on the sample, resulting in the formation of a vapor-gas cloud together with the ejection of material particles.

When laser radiation interacts with the sample surface located in a liquid medium, the laser radiation passes through the liquid layer, is absorbed by the surface of the sample. With a small energy contribution, the morphology of the surface changes, including the formation of surface periodic structures. The use of various media can lead to changes in the chemical composition of the treated surface, conditions for the interaction of titanium with the liquid medium are formed, unattainable when processing in gases in view of the greater density of the liquid medium. A schematic representation of the ongoing processes is shown in Figure 2a, the characteristic surface formed as a result of the processing is shown in Figure 2b.
Figure 2. (a) 1 - liquid medium; 2 - steam and gas area; 3 - near-surface layer; 4 - formed micro-bodies; 5 - a sample; 6 - the area of heat removal into the volume of the material; 7 - subsurface overheating region; 8 - front of spreading / rising pressure; 9 - front of temperature propagation due to thermal conductivity; 10 - gas; 11 - the direction of dispersion of the material of the surface layer; (b) the surface formed as a result of the treatment.

An increase in the power of the laser radiation leads to the formation of a near-surface plasma, an intensive expansion of the ablation products into the liquid volume occurs, is schematically shown in Figure 3a. The ablation products rapidly cooled as a result of contact with the liquid and settled on the bottom and walls of the vessel. Rapid cooling of the ablated material promotes the formation of particles with a spatial shape corresponding to the body with the smallest surface area - the sphere.

Figure 3. (a) 1 - liquid medium; 2 - plasma torch; 3 - area of action of laser radiation; 4 - formed microgranules; 5 - a sample; 6 - area of heat removal into the volume of material; 7 - zone-intensive reflow; 8 - front of temperature and pressure; 9 - front of temperature propagation due to thermal conductivity; 10 - particles of material forming a plasma torch; (b) the surface formed as a result of the treatment.

During the interaction of laser radiation with the surface of a titanium sample, dynamic erosion of the material was achieved by moving the laser beam along the processing plane, the SEM image is shown in Figure 3b. With prolonged exposure to laser radiation, a significant decrease in the intensity of the ejection of the processed material occurs over a localized area of the material over time. This effect is observed in view of the significant screening properties of the plasma. Laser radiation is partially absorbed by the plasma, partially reflected, the effect of laser radiation on the surface of the material is practically not realized. The structure of the formed surface is not typical for the treatment regime by ultrashort laser pulses. On the surface there are traces of reflow and ejection of the liquid phase of the material. The dominant role is played by the thermal contribution from the plasma torch, whose lifetime is estimated by hundreds of nanoseconds. The properties of the formed plasma flame largely depend on the pulse repetition frequency, wavelength, and laser radiation intensity. Under the experimental conditions created, the lifetime of the plasma torch was much greater than the gap between the laser pulses, which led to intense melting. The liquid in the processing area, when in contact with ablation products, was intensely sprayed and evaporated, and a fog formed. The formed
fog in the caustic region promoted the formation of a plasma flare due to the absorption of laser radiation.

The treated surface was investigated by Raman spectroscopy. Figure 4a shows the Raman spectrum of the treated titanium surface, as shown in Figure 2a, in Figure 4b, the Raman spectrum of the microgranule surface corresponding to Figure 5 is shown. The pronounced peaks corresponding to the titanium carbide peaks are indicated by white arrows with a black outline at positions 135, 249, 431, 601 cm\(^{-1}\). The detected peaks of titanium carbide both on the treated surface and on the surface of the microspheres are characterized by intensity and width, which can speak of conditions conducive to the growth of crystallites of titanium carbide. The formation of titanium carbide on the sample surface can be formed as a result of the contact of the heated metal with carbon containing media, by sorbing carbon with a metal surface [5]. Thus, due to the dissociation of hydrocarbon molecules, carbon sorption takes place on the surface of the sample to form titanium carbide.

![Figure 4](image4.png)

**Figure 4.** (a) Raman spectra of the treated surface; (b) Raman spectra of the microgranule surface.

As a result of the studies, a direct relationship between the duration of exposure of laser radiation in the treatment area was established. When scanning a surface with a high speed of conditions for dynamic erosion does not occur, the material ejected as a result of laser ablation leaves the area of action. The adhered particles do not feed the plasma torch, which significantly reduces the heat load on the surface being treated, thus creating conditions for the formation of surface periodic structures. Reducing the speed of scanning laser radiation leads to an increase in the thermal contribution to the processing area due to the formation of a plasma flame, which is an intense source of thermal energy. As a result, the sample surface acquires a relief containing reflow zones, liquid phase emissions and grad. This exposure mode can be used in the synthesis of microgranules of powder materials. As a result of the study of ablation products, particles of a spherical shape with a size of the order of 1-3 \(\mu m\) were found with a sufficiently long and intensive action - Figure 5.

![Figure 5](image5.png)

**Figure 5.** SEM image of the obtained microgranules.

4. Conclusion

The results obtained in this paper can be used to produce micro-structured surfaces of titanium alloys, to obtain coatings on the surface of materials using reaction media, as well as to obtain titanium
microgranules of a highly spherical shape, a narrow granulometric composition. The use of this kind of powder materials, for the cultivation of various medical instruments and parts, is a promising and developing direction due to the production of products of high dimensional accuracy. These technologies open up new opportunities for creating new materials with a wide range of properties, in some cases unique, not achievable by other methods. The process of laser processing of materials in a liquid has great potential, both from the point of view of research activity, and from the point of view of technological applications of this kind of processing.

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