Formation of microspheres under the action of femtosecond laser radiation on titanium samples in hydrocarbons

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Abstract. This work describes the original method of laser synthesis of microspheres which contain titanium carbide. The formation of microspheres is carried out by the action of femtosecond laser radiation on the surface of titanium in the reaction medium – the ultimate hydrocarbon. The resulting microspheres have a high surface smoothness, a narrow particle size distribution, an average size of 1-3 μm. They can be used in applications of additive engineering, powder metallurgy as the main raw material, or as an alloying additive.

1. Introduction

Nowadays, in the technology of materials manufacturing, one of the topical and promising trends is the synthesis of metallic microspheres. The development of technologies in this field led to the searching of efficient methods of obtaining such type of particles. Currently, there are many ways and approaches for obtaining powders of various materials: by mechanical grinding, chemical precipitation, magnetron sputtering, high-temperature sputtering (gas-plasma spraying, electric arc, and rarely powders are produced by laser-induced methods). Each of the proposed methods has advantages and disadvantages, which are determine the field of application of the obtained powder material. Despite the very limited prevalence of laser technological complexes, the method of laser synthesis of powder material has a high interest due to the exceptional properties of laser radiation, unattainable by other sources of concentrated energy.

The method of laser synthesis of powder materials finds its application when it is necessary to get small batches of products. One of the features of laser synthesis of powders is the possibility of getting microgranules from a wide range of materials, the process also has a high spatial localization, which largely determines the low dispersion of particle sizes. The peculiarities of laser action make it possible to achieve a change in the structural and phase states of a material without adding impurities to it (provided that they are absent in the region of laser radiation). This feature makes it possible to get pure powder materials in comparison with other synthesis methods. When introducing the necessary impurities, it is possible to get complex alloys, composites, 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 primary interest, in particular, it is required to obtain not a melt, not steam, but directly "splashes" of the processed material, which have a spherical shape and a close granulometric composition. Pulse laser systems which are able to efficiently transmit the energy of laser radiation for the development of the laser ablation process are suitable for such purposes. Using
In recent years, the processes that occur during laser ablation in a liquid are being intensively studied. Significant progress has been made in this area due to various technological means developed for the study of physical and chemical processes in the laser ablation of solids in liquid media [1-4]. Laser ablation in the liquid has a number of unique properties over the other methods. As for the synthesis of powder materials, the rapid cooling of ablation products promotes the formation of a "highly spherical" surface. The used during the processing liquid medium can have both an inert and reactionary properties. Metallic microspheres obtained by this method can be used in various applications: additive engineering, powder metallurgy, where application is possible both as the main material and as the alloying additive.

2. Equipment and samples
In the experiments was 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 (Fig. 1). A titanium plate of grade titanium (VT1-0) was used as a sample. The cuvette represented a container isolated from atmospheric air, having a point of attachment of a sample and a transparent window for introducing laser radiation. The sample was located under a layer of liquid hydrocarbon. 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](image)

3. Description of the experiment
The depth of immersion of the sample was selected in such a way that the liquid layer would cover the surface of the sample being treated, but did not make a tangible contribution to the absorption of laser radiation. This results in a dynamic ejection of both the liquid and the sample material from the processing area. During the processing in volume of the cuvette has forming a thick enough "fog". Consider in more detail the process of sorption of carbon by titanium. In [5,6], at the study the interaction of laser radiation with the solid-liquid interface was found that the characteristic boiling time of the liquid occurs at subnanosecond times, since the velocity of the liquid flight is practically independent of the laser radiation power [7,8]. The rate of expansion of the laser-induced plasma is of the order of $10^3 [9, 10] - 10^7$ m/s [11, 12]. The speed of motion of the plasma plume strongly depends on the energy of the applied to the impact area and the density of the environment. The rate of expansion of the laser-induced plasma is comparable with the rate of the boiling point of the liquid and...
also with the rate of liquid expansion. In this way, it is impossible to neglect the interaction of the "reactive flux" directly with hexane molecules, in the liquid or gaseous aggregate state, their dissociation and as a consequence of saturation of the ablation products with carbon.

Consequently, the formation and sorption of carbon occurs before the boiling of the liquid (hexane). During boiling, intense vapor-gas formation occurs, thereby sharply reducing the density of the carbon-containing medium, the probability of sorption of the formed carbon also decreases. During the movement of the ablation products by volume of chamber filled with a "fog" hydrocarbon, the energy of the ejected substance decreases, begins the self-localization into a spatial form with the smallest surface area, which corresponds shape of a sphere. The rapid cooling of the surface of microgranules, in contact with droplets of "fog", reduces the activity of their surface, so they cannot stick together, deform as a result of strikes. The method of synthesis of spherical particles in a liquid medium contributing to rapid cooling is described in [13]. The release of microspheres directly depends on the efficiency of the energy contribution to the formation and ejection of the liquid phase of the material.

4. Results
The studies were carried out using scanning electron microscopy (SEM) and Raman spectroscopy. As a result of treatment, the surface becomes covered with craters formed under the influence of laser radiation. The structure of the surface is not typical for the mode of processing by ultrashort laser pulses (Fig. 2). There are traces of fusion and ejection of the liquid phase of the material on the surface, consequently, the source of the thermal action was the laser-induced plasma, the lifetime of which is much longer than the laser pulse duration and depends from both the applied energy and the pulse repetition rate. During the processing, the lifetime of the laser-induced plasma was longer than the time interval between the laser pulses, which led to a pronounced increase in the plasma energy, as a consequence, the strong thermal action.

Figure 3 illustrates the SEM-image of the sphere surface on a silicon substrate. The microsphere surface has a high smoothness and sphericity. About 80% of the microspheres fit within a range of sizes of 1-3 μm. Granules collected from the surface of the sample have pronounced defects, pores, cracks, irregularities on the surface, probably formed as a result of repeated exposure to a source of laser radiation or as a result of contact with high-energy laser ablation products. The microspheres collected from the bottom of the cuvette have an almost perfect surface without pronounced defects. This feature of the method is expressed in high localization by the action of the energy source.
The obtained spectra indicate the presence of "polycrystallites" of titanium carbide (wherein, low-intensity spectral lines are quite broad, Fig. 4). To compare the results of the study, were obtained spectra of the surface of a titanium carbide crystal synthesized in an industrial way (135, 249, 431, 601 cm$^{-1}$), the spectrum is shown in Fig. 5, the positions of the obtained lines coincide. The technology of industrial synthesis of titanium carbide involves the sintering of titanium chips with soot under high temperature conditions and mechanical compaction of this mixture, followed by prolonged homogenization in vacuum at high temperature [14]. In our case, as a result of the release of matter from the region of influence into the volume of the reaction medium, the ejected substance is titanium saturated with carbon atoms of the hexane formed as a result of dissociation. Titanium is a fairly active chemical element, in this system the reaction of formation of titanium carbide is the only possible one. Thus, occurs the formation of a chemical titanium-carbon bond. In view of the sharp drop in temperature, the microsphere material cools, the conditions for homogenization of titanium carbide are not met, which means that decrease in phase inhomogeneity due to the growth of grains of titanium carbide by the drift of nuclei occurring during high-temperature homogenization of the material does not occur.
Figure 5. Raman spectra of industrially synthesized titanium carbide, white arrows denote peaks corresponding to titanium carbide

5. Conclusion
The results obtained in this paper can be useful for applications related to additive technologies due to a small range of sizes obtained microspheres: 1-3 μm, high sphericity and smoothness of the formed surface. The carbon deficit, the absence of the expressed grains of titanium carbide (the presence of only their nucleus, crystallization points) will greatly increase the wettability of the components of the composition, for example in NiTi forms [15, 16].

In laser welding there is the problem of burn-out of low-melting alloying additives as a result of laser radiation influence, which is due to the different melting point-evaporation of the components of the composition and different absorption coefficients. The problem of intensive gassing is also widely common; it leads to an increase in porosity of the formed material. The presence of crystallites of titanium carbide at the nuclei stage will significantly reduce the fusion temperature of this composition, which in turn is useful for alloying aluminum, zinc matrices to improve their characteristics (mechanical, strength, operational).

This method is also can be used to introduce carbon into various metallic compositions. The tendency of carbon to the formation of grains of graphite in the structure of metals makes it difficult to distribute it uniformly in the volume of the resulting material. The uses of such alloying add open up new possibilities for the directions of powder metallurgy. Synthesis of powder materials by this approach makes it possible to obtain various powder compositions, because with selecting the processing medium and the intensity of the impact, it is possible to trigger certain processes that contribute structural, phase and chemical changes of processed and synthesized materials [17].

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