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Evaporation and Condensation of Uranium Dioxide in an Electromagnetic Field[1]

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New physical phenomena related to the interaction of laser radiation with high evaporation materials, in particular with uranium dioxide, have been experimentally revealed by a subsecond heating technique. The first phenomenon, interpreted as an absorption flash, was observed in laser heating the sample and was manifested as a sharp drop in temperature on the heating curve. The second phenomenon, interpreted as a threshold condensation of vapor on the sample, was revealed during the cooling stage of the sample initially heated by laser radiation. This was manifested as an exothermal condensation peak on the cooling curve. The study of these phenomena has shown that there was a stable vapor zone above a sample in the field of laser radiation. The size and shape of the small particles produced due to laser evaporation and mainly formed in this vapor zone depended on the power of the laser radiation and the pressure of the inert gas. A change in the parameters of the vapor zone by changing the power of the laser radiation and the pressure of the inert gas gives the potential to produce nanoparticles of targeted sizes. Thus, the study of physical processes and mechanisms of forming nanoparticles of refractory materials at high temperatures motivates further development of the method of laser evaporation for producing nano-dimensional powders of targeted sizes and properties.

KEY WORDS: cooling; evaporation; high temperatures; laser heating; nanoparticles; thermal radiation properties; uranium dioxide; vapor condensation.

1. INTRODUCTION

Among the methods of obtaining nanopowders, the method of laser evaporation with subsequent condensation occupies a special place. This

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method provides nanopowders of complex chemical composition, which are characterized by a narrow distribution of particles in sizes. But its rather poor productivity hindered the widespread development of the method. However, the intensive development of nanotechnology has recently increased considerably its competitive position. For example, laser technology for producing nanopowders of oxide materials with a particle size of 10 nm and a productivity of 60 g per hour at a mean power of laser radiation of 650 W (pulsed periodical regime with peak power of the radiation of 11.2 kW, pulse duration of 144 μs, and pulse frequency of 435 Hz) was developed [1, 2]. This demonstrates the high potential and prospects of this method.

At the same time, despite the intensive development of the technology for obtaining nano-dimensional powders, it should be noted that there are practically no studies of the physical processes and mechanisms of forming nanoparticles of refractory materials at high temperatures.

The present paper is dedicated to the description of new physical phenomena connected with the interaction of laser radiation with high evaporation materials, in particular, with uranium dioxide, and discovered by a subsecond heating technique. This investigation provides the possibility to have a new look at the mechanism of formation of small particles in a field of laser radiation. These phenomena are as follows: (a) an absorption flash experimentally detected as a shock effect of laser radiation on uranium dioxide and (b) a threshold condensation of uranium dioxide vapor observed in switching off the laser. The study of these phenomena has shown that there was a stable vapor zone above a sample in a field of laser radiation. The sizes and shapes of the produced small particles due to laser evaporation were mainly determined in this vapor zone. Therefore, the study of the processes of forming small particles in an electromagnetic field of laser radiation is of great interest for producing nano-dimensional powders of targeted sizes and properties.

2. EXPERIMENTAL METHOD

The above mentioned phenomena we have studied in our experimental setup are described in detail elsewhere [3–5]. The setup consists of four main parts: a powerful CO_2 laser with 1000 W power working in a continuous regime for sample heating, a working chamber made as an integrating sphere for measuring thermal radiation properties of the materials, a high-speed pyrometer for temperature and reflectivity measurements, and a fast data recording and acquisition system. The method allows simultaneous measurements of thermal radiation properties and radiance temperatures of the sample investigated during the laser heating or cooling

stage. The major feature of the method is the possibility to measure the spectral reflectivity and emissivity of the materials during heating, cooling, and in the neighborhood of the high-temperature phase transition in which the sharp change of the sample surface reflection distribution takes place (other high temperatures methods for reflectivity measurements with laser heating techniques use the assumption that a sample surface is fixed in time and has specular or diffuse reflection distribution). This advantage is very important in measuring thermal radiation properties of high evaporation materials in which the sample surface texture is continuously changing under powerful laser irradiation. Therefore, this method has been applied to study thermal radiation properties of uranium dioxide (which is a high evaporation material at high temperatures) and its interaction with a powerful laser irradiation.

Figure 1 shows a schematic diagram of the complete measurement facility. A flat sample is placed on the water cooling holder in the center of an integrating sphere. One side of the sample is heated to high temperatures with a focused laser beam of 1000 W power. Optical probing of the heated sample surface for reflectivity measurements is performed by flash lamps located just below the sample inside an integrating sphere. The light of the flash lamp optimally placed inside the sphere produces an almost perfectly diffuse irradiation of the sample surface after multiple reflections in the sphere. This method of sample surface irradiation enables one to make high temperature reflectivity measurements independent of the sample surface texture. Also, pyroreflectometry for simultaneous measurements of thermal radiation properties and the radiance temperature has been used in this study. A fast micropyrometer working at 0.644 μm has been applied as a pyroreflectometric measurement device. The calibration procedure of the pyrometer and its application for simultaneous reflectivity and temperature measurements with an estimation of their uncertainties was described in earlier publications [3–5].

3. RESULTS

The samples of uranium dioxide were obtained from the Institute for Transuranium Elements, Karlsruhe, Germany in the form of sintered pellets of 97% theoretical density. A disk of 9 mm diameter and 2 mm thickness was located in the center of an integrating sphere of 180 mm diameter and was heated by a powerful laser beam through the upper hole of the sphere. To reduce sample evaporation during the measurements, the excess pressure of a pure inert gas was maintained in the sphere. The heated sample surface area was 1 mm. The viewing spot of the pyrometer on the sample surface was 0.2 mm.

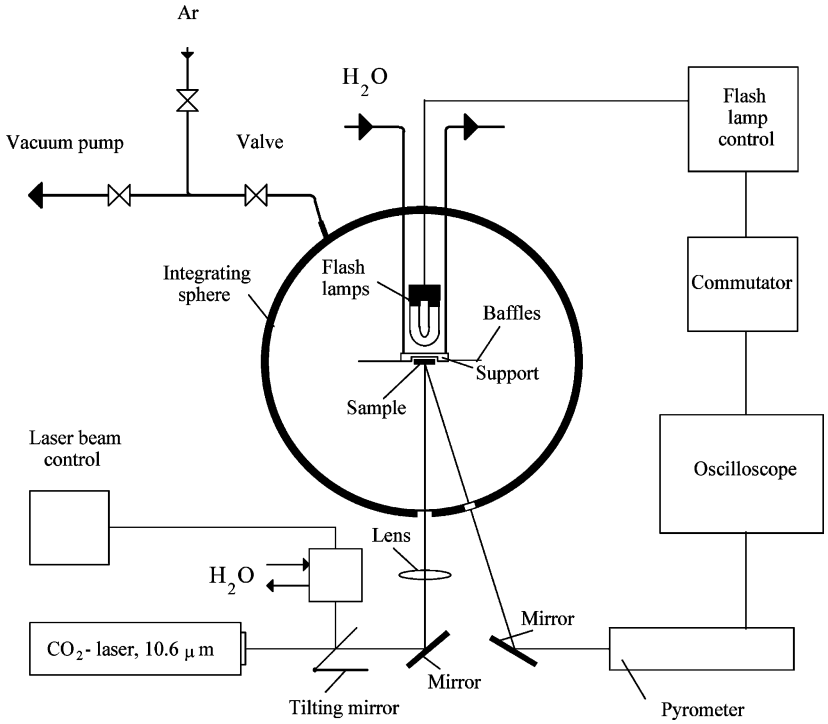

Fig. 1. Experimental setup.

An absorption flash observed in intensive laser heating of the sample has been experimentally discovered. The absorption flash was manifested as a sharp drop in temperature on the heating curve. The energy of the observed absorption exceeds the energy level of solid phase transitions. Also, an exothermal peak on a cooling curve has been found after switching off the laser. This peak was identified as threshold condensation of the vapor during the sample cooling stage.

Figure 2 shows the typical heating and cooling curves of uranium dioxide in an argon environment at different laser power densities. It can be seen that the sharp temperature decrease is observed on the laser heating curve at a certain radiant flux. It is a very strange experimental observation since at such laser power densities the plasma state of vapor above the sample is not formed.

Under a power density of $5\,\mathrm{kW}\cdot\mathrm{cm}^{-2}$, a certain decrease in the heating rate is observed on the heating curve. The decrease is probably related to the beginning of intense evaporation. But a very interesting

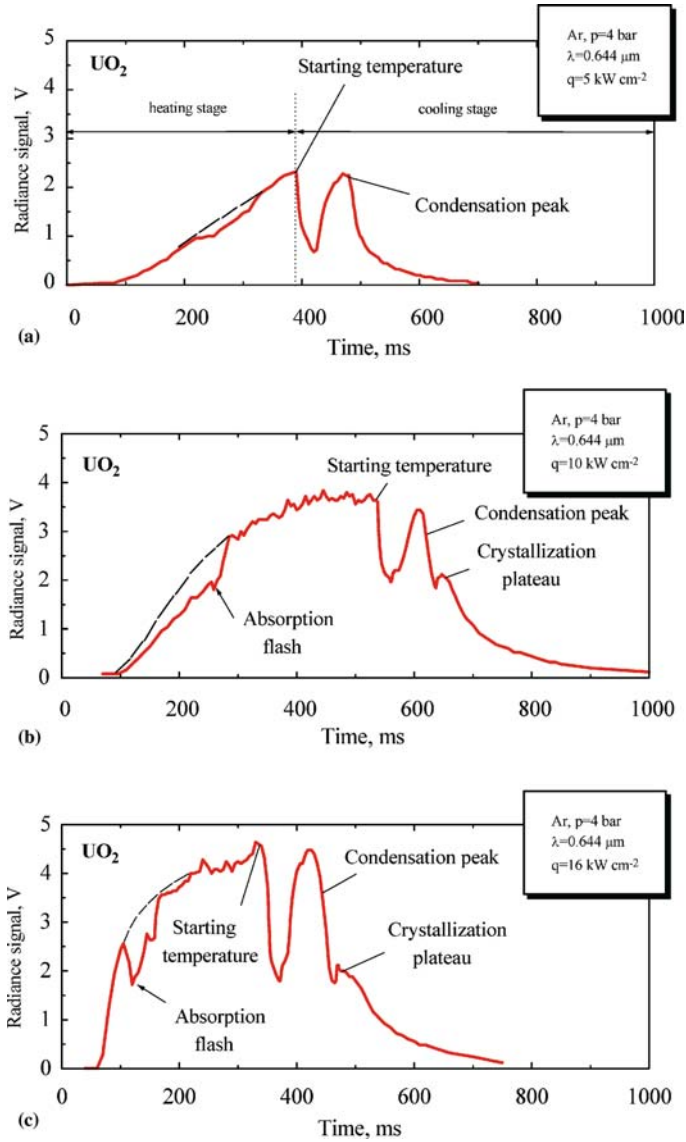

Fig. 2. Thermograms of heating and subsequent cooling for the samples of uranium dioxide recorded at various power densities of laser radiation. The procedure of recording the thermograms is as follows. The sample is heated by continuous laser radiation up to the maximum temperature at a given laser radiation power. Then the laser beam is isolated by the shutter, and the sample is cooled. The starting temperature is the maximum temperature achieved when the laser is switched off. The heating and cooling stages of the thermograms are recorded by a high speed radiance pyrometer.

phenomenon was observed during the sample cooling stage after switching off the laser (Fig. 2a). A peak for threshold condensation on the cooling curve can be seen. The form of the peak presents a "cog" with the front line typical for the classical heating curve of a solid. The back line of the "cog" looks like a classic exponential cooling curve of a solid. So we can reach a conclusion that the vapor zone is kept above the sample even after switching off the laser. The peak shows a release of energy during threshold condensation of a stable vapor structure on the sample surface during the cooling stage. It is of interest to note that the vapor zone resulted from laser heating the sample, and the energy of the laser radiation absorbed by the vapor phase was enough to heat the sample surface up to the starting temperature (temperature at the moment of switching off the laser) for threshold condensation of vapor on the sample surface for the cooling stage.

Figure 2b shows the considerable deviation of the recorded heating curve from the classic heating curve when the power density is increased to $10\,\mathrm{kW\cdot cm^{-2}}$; however, the monotonic character of the curve is maintained in this case. For the cooling stage the peak of threshold condensation can be clearly seen. For the given experimental conditions, it was observed at the moment of the sample crystallization.

A further increase of the power density up to $16\,\mathrm{kW\cdot cm^{-2}}$ allowed detection of a new phenomenon manifested as a sharp drop in temperature on a heating curve. Also, the most powerful peak of threshold condensation was recorded on the cooling curve. Here the maximum temperature of threshold condensation achieved the sample temperature at the moment of switching off the laser.

4. DISCUSSION

Information obtained in the framework of this paper is sufficient to form a certain viewpoint on the mechanism of interactions of moderate dense laser radiation with oxide materials and to apply the results obtained for producing nanopowders of these materials. Let us consider our interpretation of the discovered phenomena.

4.1. Mechanism of Forming a Stable Vapor Zone Near an Irradiated Sample

At the power density sufficient for achieving the regime of developed evaporation, a vapor flow directed from the sample towards the radius is formed. Adiabatic expansion of the vapor leads to a sharp drop in temperature and pressure, and vapor condensation will take place. The drop in

temperature results in oversaturation of the expanding vapor with respect to density fluctuations leading to the rapid growth of nuclei. Equilibrium in the system of vapor–condensate particles shifts towards condensation. Thus, intensive vapor condensation starts at a certain distance from the irradiated sample.

The given picture of evaporation of the target does not take into account the interaction of the laser radiation with vapor and condensate particles. Evaporation and condensation processes in the field of electromagnetic laser radiation were considered in detail in Refs. 6–8. The authors showed that equilibrium between oversaturated vapor and condensate particles in the field of laser radiation was established. In the absence of the field, only equilibrium of unsaturated vapor with condensate droplets was possible. Oversaturated vapor cannot be in equilibrium with the condensate droplets according to the classical model of condensation. In this case the nuclei reach the critical size, grow freely, turning into large droplets of liquid. With availability of the external field, the condensate droplets cannot grow freely. Their sizes are limited by a certain radius, which enables the vapor layer to be transparent for the heating radiation. The equilibrium of oversaturated vapor and condensate particles is maintained due to partial absorption of the heating laser radiation by the liquid droplets. If the droplet sizes start to grow for any reason, this leads to an increase in radiation absorbed by the droplet. As a result, in the power balance of the droplet, the evaporation–condensation equilibrium shifts towards the evaporation process predominance and the droplet size reduces to optimal levels.

We suggest that the above mentioned processes of homogeneous vapor condensation and formation of condensate droplets in the field of laser radiation occur into the zone near a sample irradiated by a powerful laser. In this case the sizes and other physical parameters of the vapor zone are obviously influenced by the pressure of the surrounding inert gas, the molecules of which reduce the free mean path of vapor particles and cool them noticeably. The regions of the stationary vapor zone formed in the field of laser radiation is shown in Fig. 3.

4.2. Absorption Flashes in Laser Heating

As mentioned above, it has been experimentally discovered that an absorption flash manifested as a sharp drop in temperature of the sample surface on the heating curve was observed in laser heating uranium dioxide with a Co_2 laser with a wavelength of $10.6\,\mu m$ under certain experimental conditions. We suggest the following mechanism of appearance of the absorption flash. The sample surface temperature and the evaporation

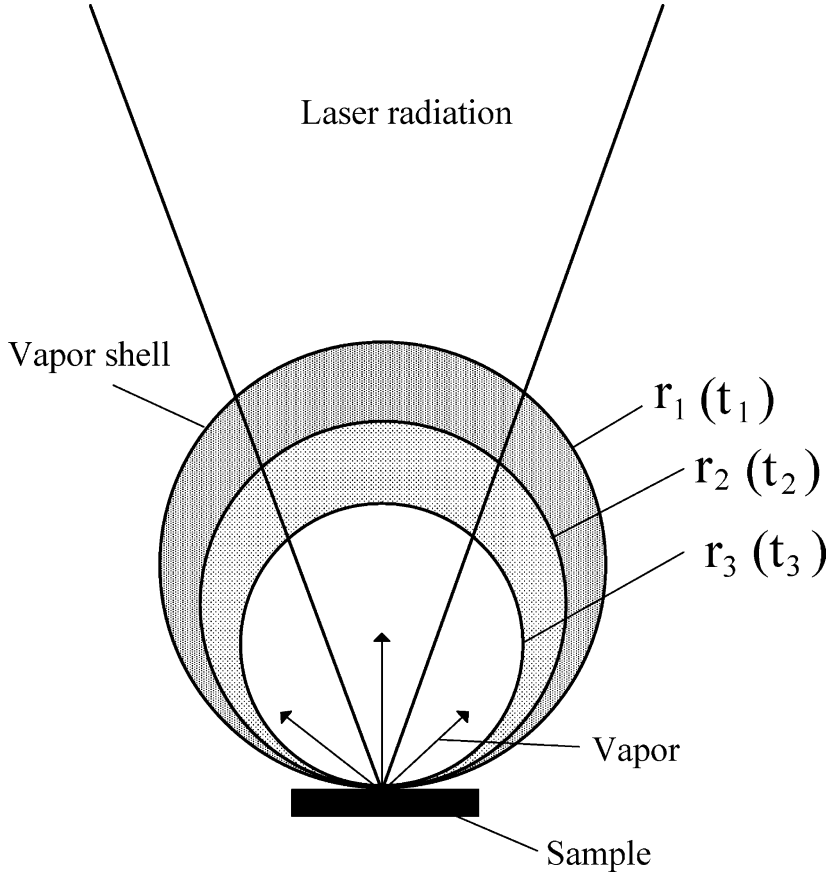

Fig. 3. Schematic diagram of the vapor zone above the sample irradiated by a powerful laser.

rate are rapidly increasing under the effect of the powerful laser radiation. The particle emission speed increases (Fig. 3) while the vapor zone radius, at the border of which the conditions for condensation of the oversaturated vapor have arisen, decreases. As a result, at a sufficiently high rate of temperature increase, the rapid reduction of the initial radius of the vapor zone ($r_1 > r_2 > r_3$) (Fig. 3.) takes place as well as almost simultaneous achievement of oversaturation of vapor in the zone volume $r_1 > r > r_3$. The evaporation processes initially prevail in the vapor zone at a high rate of heating; therefore, only insignificant monotonic absorption is observed for some period of time. The shift of the balance in the vapor–condensate particles system towards evaporation takes place due to the partial

absorption of the laser radiation. However, as soon as nucleation starts at the external border of the $r = r_1$ zone, condensation becomes an avalanche process in the whole volume of $r_1 > r > r_3$ zone. In this case, the condensate droplets irradiated above the sample absorb the incident laser radiation. This leads to the sharp decrease of the sample surface temperature, and an absorption flash takes place. The absorption flash can be multistage and repeated up to coming to the point of reaching the stationary regime. The absorption flash takes the modulation form of the heating radiation, related to the fluctuations of vapor zone density at the stationary regime.

4.3. Phenomenon of Vapor Threshold Condensation in the Cooling Stage

The phenomenon of threshold vapor condensation in cooling the sample was discovered for the first time for uranium dioxide in our earlier publications [4, 5]. This phenomenon was manifested as a large exothermal peak on a cooling curve of a sample initially heated by a laser up to high temperatures and then switching off the Co_2 laser. In this paper it is asserted that this phenomenon can be explained on the basis of the model presented if we assume that the appearance of the condensation peak on the cooling curve is the result of destruction of the stationary vapor zone formed above the sample in laser heating. The following scheme of this process can be suggested.

The existence of the condensation peak in sample cooling supports the existence of the vapor zone formed above the sample in laser heating. We can follow further this path. At the moment of switching off the laser radiation, the disappearance of two zones of the vapor shell takes place: the zone of unsaturated vapor and the zone containing the mixture of condensate droplets and the vapor phase. The first zone undergoes adiabatic compression, and the vapor becomes oversaturated. The second zone is dispersed because of its weak bonds with the sample. This statement is supported by the fact that the spectral reflectivity of the sample before and after the condensation peak do not differ significantly. Otherwise, there would be a temperature jump on the cooling curve. This means that, at the moment of switching off the heating laser, a transparent purely vapor zone without condensate particles is maintained above the sample surface. But, in spite of oversaturation of this vapor, threshold condensation occurs not at once after switching off the laser but only at a certain moment of the cooling stage. This interesting experimental effect supports that the different processes occur in the vapor zone volume for sample cooling but it requires futher research.

The influence of the initial heating (starting temperature) on the temperature at the start of the condensation can be explained simply. The difference in the temperatures between the vapor zone and the sample surface is the main condition for the start of condensation. This difference slightly changes with an increase in temperature. Therefore, for a significant increase in the vapor temperature, condensation starts earlier.

4.4. Mechanism of Forming Small Particles in a Field of Laser Radiation

Let's consider the mechanism of formation of condensate droplets near the sample surface in laser evaporation. The theory of homogeneous condensation of oversaturated vapor in an electromagnetic field has been developed [6–8]. It has been shown that, in contrast with the classical theory of condensation, there were two typical sizes of droplets in the electromagnetic field:

$$y_1 \cong 1 + \frac{D}{4D^*}, \quad y_2 \cong \frac{4D^*}{D}, \tag{1}$$

Here, $D \sim W_\lambda$ and W_λ is the volume density of the electromagnetic field energy (in particular, laser radiation). The parameter D^* is determined from

$$D^* = \frac{1}{4} \frac{\ln^2 S}{q_o - \ln S} \tag{2}$$

where S is the degree of vapor oversaturation which is equal to the ratio of the vapor pressure p to the saturation pressure above the plane surface p_s;

$$S = \frac{p}{p_s(T)}, \tag{3}$$

and $q_o = \frac{q}{\mathrm{k}T}$ where q is the evaporation energy of one molecule.

It was established that the first size of droplets y_1 corresponds to the critical radius of nuclei of the classical theory of condensation, but it is somewhat shifted to the side of greater sizes due to heating nuclei by laser radiation. The second critical size of nuclei is a new value characteristic for homogeneous condensation in a field of electromagnetic radiation. It has been found [6] that in this case there are three regimes: at $y < y_1$ evaporation predominates over condensation; at $y_1 < y < y_2$ condensation predominates over evaporation; and at $y > y_2$ evaporation again predominates over condensation. It can be seen from Eq. (1) that with an increase in the electromagnetic field of the laser radiation, the first critical size y_1 achieves the second critical size y_2, and at $D = D^*$, $y = y_1 = y_2$.

The equality of critical sizes means disappearance of the area in which condensation predominates over evaporation despite the presence of oversaturated vapor. This is a new result which principally differs from the outcome obtained within the framework of the classical theory of condensation.

According to the classical theory of condensation, the oversaturated vapor cannot be in equilibrium with droplets of the condensate; in this case, the equilibrium state of unsaturated vapor with droplets is only possible. The nuclei, which have reached a critical size, penetrate the area of predominance of condensation and unrestrictedly grow, turning into drops of liquid.

A completely different situation arises at the presence of laser radiation. According to the approach offered in Ref. 6, the growth of droplets is possible only up to the size y_2, the droplets with sizes $y > y_2$ penetrate the area of predominance of evaporation that restricts their further growth. In other words, laser radiation supports equilibrium of droplets of condensate with oversaturated vapor above a sample, reducing further growth of the condensate droplets by laser evaporation.

On the basis of this theory, our experimental results, and our interpretation of them, we can draw a conclusion that the formation of droplet sizes in the field of laser radiation occurs in the vapor zone above the sample in laser evaporation. Therefore, by changing the parameters of the vapor zone, we can obtain nanoparticles of targeted sizes and properties. This conclusion is very important from an applied point of view since the conception of the vapor zone gives the possibility to manage technological processes for producing nanopowders with unique properties by the method of laser evaporation.

4.5. Analysis of the Powder Settled on the Chamber Wall

Since, according to our conclusion, the formation of condensate droplets in laser evaporation occurs in the vapor zone near the sample, their sizes and shape must be maintained out of the vapor zone. Therefore, we have made an analysis of the droplets settled on the wall of the experimental chamber. It has allowed us to detect the dependence of the dispersion of the powder settled on the chamber wall at the pressure of the inert gas. Unfortunately, available technical capabilities have not allowed us to perform the analysis of particle size distributions at the level of 10–20 nm. However, preliminary analysis of settling obtained at various pressure levels of the inert gas has shown a notable decrease in particle size with an increase in the pressure level of the inert gas. Figure 4(a) and (b) shows the particle distribution in sizes obtained at pressure levels of (a) 1 bar

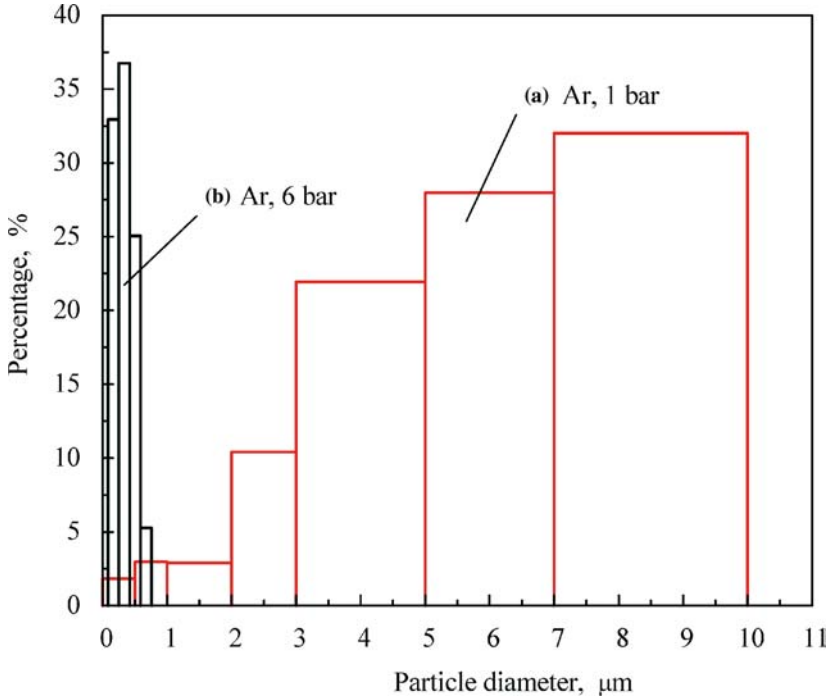

Fig. 4. Size distribution of the uranium dioxide particles settled on the chamber wall at an inert gas pressure of 1 or 6 bar: (a) sedimentation method (argon,1 bar) and (b) photographic method (argon, 6 bar).

and (b) 6 bar, respectively. The estimation of the distribution of particles in size was obtained by a sedimentation method in isopropanol. Figure 5 shows the shape of the particles of uranium dioxide at a pressure level of 6 bar of inert gas obtained by electron scanning microscopy. It can be seen that most particles are spherical. These experimental results are in accordance with the proposed model of forming small particles in laser evaporation of refractory materials, but additional investigations are required to get experimental data for nano-dimensional particles formed in the field of laser radiation.

5. CONCLUSIONS

New phenomena related to the interaction of laser radiation with uranium dioxide have been experimentally observed for the first time: (a) an absorption flash was observed in laser heating the investigated sample; (b)

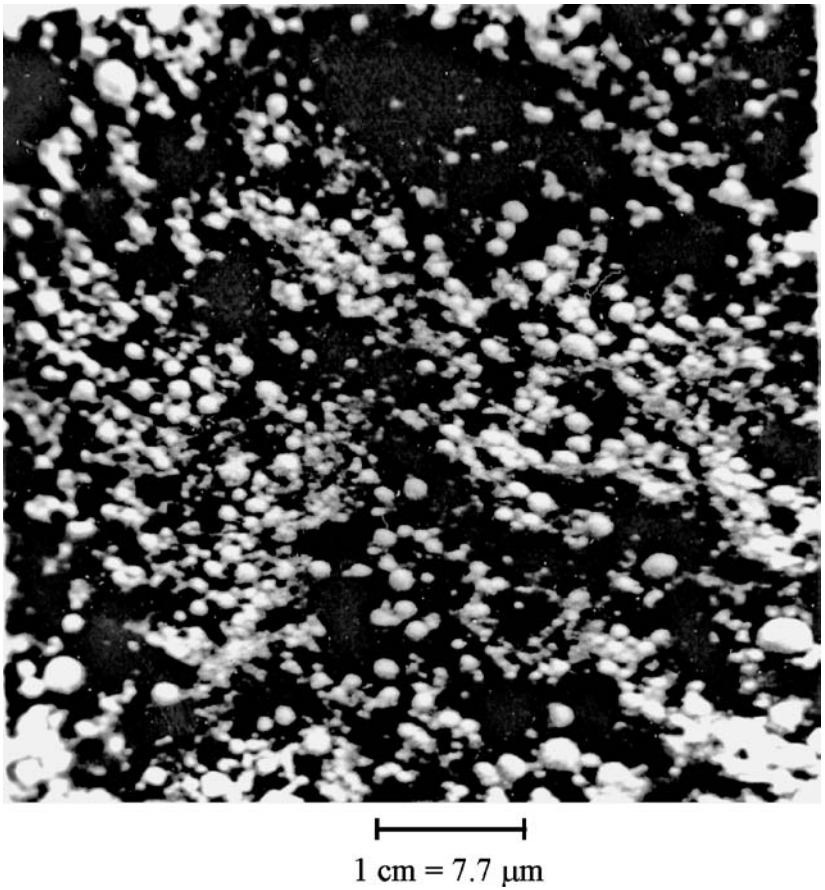

Fig. 5. Microphotograph of the uranium dioxide particles settled on the chamber wall under an inert gas pressure of 6 bar.

a threshold vapor condensation occurred in cooling the sample; and (c) the sample cooling depended on the conditions of laser heating. On the basis of the experimental results, the following observations can be made:

(1) A stationary dynamically stable vapor zone is formed above a sample in the interaction of laser infrared radiation of moderate density ($<10^2$ kW·cm^{-2}) with uranium dioxide.

(2) An absorption flash is observed in laser heating. This phenomenon is manifested as a sharp drop in temperature on a heating curve and related to the process of formation of the dynamically stable vapor zone above the irradiated sample.

(3) A threshold condensation of the vapor on the sample investigated is observed during the cooling stage of the sample initially heated by laser radiation. This phenomenon is manifested as an exothermal condensation peak on a cooling curve.

(4) The discovered phenomena are responsible for formation of nanoparticles of uranium dioxide in an electromagnetic field of laser radiation and provide results with the potential to manage and control technological processes for producing nanopowders of uranium dioxide with high efficiency.

Thus, the obtained experimental results support the formation of a stable vapor zone above a sample using laser heating. This zone actively interacts with incident laser radiation. As a result of this interaction, the condensate droplets of the particular sizes are formed in the vapor zone. The sizes of the droplets depend on the power of laser radiation and the pressure of the inert gas. Therefore, a change in the parameters of the vapor zone by changing the power of laser radiation and the pressure of the inert gas provides the possibility to produce nanoparticles of targeted sizes.

Thus, it can be seen that the experimental capability of subsecond thermophysics has allowed the study of physical processes and mechanisms of forming nanoparticles of refractory materials at high temperatures. This work will motivate futher development of the method of laser evaporation for producing nano-dimensional powders of targeted sizes and properties.

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