Particles synthesis in erosive laser plasma in a high pressure atmosphere

A.G. Gnedovets a,*, E.B. Kul’batskii a, I. Smurov b, G. Flamant c

a Baikov Institute of Metallurgy, Russian Academy of Sciences, Leninsky Prospekt 49, 117911 Moscow, Russian Federation
b Ecole Nationale d’Ingénieurs de Saint-Étienne, 58 rue Jean Parot, F-42023 Saint-Étienne Cedex 2, France
c Institut de Science et de Génie des Matériaux et Procédés, CNRS, BP 5, F-66125 Font-Romeu Cedex, France

Received 22 May 1995

Abstract

Synthesis of ultrafine particles as a result of condensation in an erosive jet at laser vaporization of materials (metals, metal oxides, carbon) in gases (hydrogen, oxygen, helium, argon, xenon and air) at high pressures is investigated. The granulometric, phase, and chemical composition of the condensate particles is analyzed in relation to the elaboration conditions. It is found that the mean dimensions of the condensate particles increase with increasing the ambient gas pressure. A particle nucleation and growth theory is used to describe the formation of the dispersed condensate in the erosive plasma. It is shown that the resulting particle size distribution is determined by the cooling rate dependence of the vapor–gas mixture on the pressure of the surrounding gas.

1. Introduction

Various methods have been developed for producing ultrafine powders of materials by means of homogeneous nucleation in the vapor phase. A detailed survey of the existing techniques, such as vaporization of material in vacuum chamber, magnetron sputtering, chemical vapor deposition, laser ablation, arc and RF plasma methods, etc., can be found in Refs. [1–4], for example. These processes are connected with supersaturation in the vapor, which is usually achieved by cooling of the vapor during its rapid expansion [5–7] and/or by interaction with “cold” ambient gas atmosphere [2].

This paper concerns with the synthesis of ultrafine particles based on the condensation of vapors at laser irradiation of materials (metals, metal oxides and carbon) in an atmosphere of gases (hydrogen, oxygen, helium, argon, xenon and air) at high pressures.

2. Experimental conditions and methods of analysis

The experiments were conducted in air and in a 40 cm³ reaction chamber filled with gas (hydrogen, oxygen, helium, argon, xenon) at a pressure (1–20) ×10⁵ Pa. To vaporize material and create a vapor phase, the radiation of pulsed, pulsed-periodic (free generation mode, energy per pulse $E = 5–30$ J, pulse duration $\tau = 1–5$ ms) and continuous Nd:YAG lasers

* Corresponding author.
A laser beam incidence to the target was varied from normal to 45°. The energy flux of the incident radiation on the surface of the target was in the range $q_s \approx 10^4 - 10^7 \text{ W cm}^{-2}$. The formation of the erosive jet was recorded with the use of integral and high-speed photography and laser interferometry. The targets were pressed tablets of powdered materials (metal oxides, carbon) with irregularly shaped particles in the 5–150 $\mu$m range, or metallic and graphite samples. The ejection of material from the target surface was determined by weighting and measurement of the crater size. The erosion products were deposited on salt or glass substrates placed at different distances from the target. The morphology and granulometric composition of the condensate particles were studied with a JEM-1000 transmission electron microscope.

### 3. Results and discussion

#### 3.1. Laser-plasma synthesis of ultrafine particles

##### 3.1.1. Metal particles

One of the methods to produce ultrafine particles of metals is laser evaporation of their oxides (WO$_3$, MoO$_3$) in the ambient atmosphere of reductive gas (H$_2$). The use of an oxide with a low heat of vaporization which efficiently absorbs laser radiation allows to remove a substantial amount of material from the target and to form a jet of vapor from its surface. Vapors are ionized in a field of laser radiation and a plasma jet is formed. Gaseous chemical reactions take place at high rates inside this jet.

The pulsed irradiation regime with $q_s = 3 \times 10^5 \text{ W cm}^{-2}$ and focusing of the laser beam in the depth of the target to provide for flow of a vapor–gas mixture in the form of submerged jet, was chosen as the basis for the analysis of condensation products. The deposited erosion products consist of finely dispersed metallic particles of a condensational nature with a size $< 0.1 \mu$m (Fig. 1).

The condensate deposited after the irradiation of WO$_3$ and MoO$_3$ in hydrogen was subjected to X-ray and electron-diffraction analyses. Metal is condensed in the form of spherical or faceted particles in the size range $\sim 0.001$–$0.1 \mu$m. Both the spherical and faceted particles are single crystals or block crystals of tungsten and molybdenum. In the case of WO$_3$ evaporation, it was found that two phases were present in the condensate: the first phase was identified as W with a bcc lattice (A-2), while the second was $\beta$-W with an A-15 structure.

With an increase in hydrogen pressure, the mean diameters of the metal particles increase from $\sim 12$ nm at $p_{H_2} = 2 \times 10^5$ Pa to $\sim 38$ nm at $p_{H_2} = 1.5 \times 10^6$ Pa for tungsten (Fig. 2) and from $\sim 20$ nm at $p_{H_2} = 2 \times 10^5$ Pa to $\sim 35$ nm at $p_{H_2} = 1 \times 10^6$ Pa for molybdenum (Fig. 3), while the number of faceted particles decreases. Whereas faceted tungsten particles predominate at pressures below $5 \times 10^5$ Pa, their number corresponds to no more than 5% of the total number of particles at $1.5 \times 10^6$ Pa. The shape of microscopic particles with a size exceeding $\sim 15$ nm is nearly ideally spherical. The size distribution of the condensate particles is close to log–normal distribution.

#### 3.1.2. Metal oxides particles

Zirconia (ZrO$_2$) particles have been synthesized under the action of continuous laser radiation ($q_s \approx 5 \times 10^5$–$2 \times 10^7 \text{ W cm}^{-2}$) on Zr, ZrO$_2$, and ZrSiO$_4$ targets in air and oxygen atmosphere.

Evaporated material is condensed as monocrystal (Zr and ZrO$_2$ targets) or amorphous (ZrSiO$_4$ target) particles (Figs. 4 and 5). Amorphization of zirconia is caused, probably, by the presence of silicon in the condensate particles. High-temperature cubical and tetragonal modifications of ZrO$_2$ are stabilized in the condensate after the evaporation both of zirconia and zirconium targets in the oxidizing atmosphere. The sizes of ZrO$_2$ particles do not exceed $\sim 0.1 \mu$m in air and $\sim 1 \mu$m in oxygen. The particle size distribution is log–normal in the case of laser evaporation in air. In the oxygen atmosphere, synthesized powder exhibits bimodal size distribution (Fig. 6).

#### 3.1.3. Carbon particles

Laser deposition of carbon particles have been performed in inert gases (He, Ar, Xe) atmosphere.
The targets both of crystalline graphite and amorphous carbon were used in experiments, which lead to identical results in phase composition and morphology of the dispersed condensate. Pulsed laser radiation with the heat flux density $q_s \approx 10^6$ W cm$^{-2}$ was used for the evaporation of the material.

![Image of tungsten particles deposited at different hydrogen pressures: $p_{H_2} = 5 \times 10^5$ (a), and $1.5 \times 10^6$ Pa (b).]
In argon and xenon at \( p < 5 \times 10^5 \) Pa and in helium in the whole pressure range, only amorphous carbon particles are condensed. With an increase in the gas pressure, the crystalline phase (graphite) appears in the condensate. Amorphous carbon black deposited in Ar and Xe contains large spherical particles with a smooth surface or a surface covered with crystal needles. The crystal phase is represented by cylindrical whiskers and spherulites of graphite. The diameters of whiskers \( \sim 0.1-0.5 \) \( \mu \text{m} \), their lengths are about tens of micrometers; the diameters of spherulites are up to \( \sim 0.5 \) \( \mu \text{m} \). The body of the whisker consists of two concentric parts. One of them, which is close to the axial nappe, is formed by long graphite layers with a thickness \( \sim 0.06 \) \( \mu \text{m} \). The outward part with a thickness up to \( \sim 0.08 \) \( \mu \text{m} \) is formed due to carbon deposition on the inner one. Each of the graphite spherulites consists of a number of crystals growing from a single center.

The mean dimensions of the carbon particles increase with an increase in pressure and molecular weight (from He to Xe) of the ambient gas.

### 3.2. General features of the process

Under high-pressure conditions, the condensate particles are formed as a result of supersaturation caused by cooling of the erosive vapor–gas flow as it interacts with the surrounding gas atmosphere. The process of particles nucleation and growth can occur (a) during the action of the laser pulse within a narrow condensation front at the boundary of the plasma with the cold gas and, (b) after the end of the pulse, throughout the volume of the cooling jet. In the range of sufficiently high pressures \( (p > 10^5 \text{ Pa}) \) and comparatively short radiation pulses \( (\tau \approx 1 \text{ ms}) \), during the period of laser action, only a small part of the metallic vapor is consumed, and the disperse composition of the condensate is determined mainly by processes which take place after the end of the pulse. A key role in these processes is played by the rate of cooling of the erosive jet, which in turn is related to the attainable degree of supersaturation and the rates of homogeneous nucleation and condensational growth of the particles.

The characteristic parameters of the process of a disperse condensate formation can be examined with the help of a qualitative model based on equations expressing the balance of vapor mass, number and mass of particles and describing the evolution of averaged characteristics of the erosive jet during its disintegration after the end of laser pulse:

\[
\frac{d}{dt}M_p = -M_n - M_c - M_D, \\
\frac{d}{dt}N_p = J_n, \\
\frac{d}{dt}M_p = M_n + M_c, \tag{1}
\]
with initial conditions $M_v(t = 0) = M_{v0}$, $N_p(t = 0) = 0$. $M_p(t = 0) = 0$.

Here, $M_v$ and $M_p$ are the masses of the vapor and particles; $N_p$ is the number of condensate particles; $M_n$, $M_c$, and $M_D$ are the mass rates of the substance per unit time due to nucleation, condensational

Fig. 4. Particles deposited after the irradiation of zirconium target in air (a) and oxygen at $p_{O_2} = 3 \times 10^3$ Pa (b).
growth of particles, and diffusional losses, respectively, and $J_n$ is the rate of nucleation [5].

An analysis of the numerical solution of system of
diffusion Eq. (1) allows to sketch the general features of the process. As an example, the results of calculations of tungsten particles formation in hydrogen at pressures...
The reduction in the temperature of the vapor-gas mixture \( T \) due to the removal of heat into the surrounding gas is accompanied by an increase of supersaturation \( s = p_v / p_s' \), which leads to the initiation of nucleation. The rate of nucleation \( M_n \) increases sharply at the initial stage of the process. The subsequent evolution of the system is determined by the competition of two processes: the formation of new particles during homogeneous nucleation, and condensational growth of the particles. Until the number of particles \( N_p \) is not very large, the vapor is consumed almost entirely by nucleation. The consumption of vapor by condensational growth of the particles increases rapidly with their number, and \( M_c \) becomes greater than \( M_n \). The conversion of vapor into condensate leads to depletion of the vapor–gas mixture, supersaturation \( s \) begins to decrease, and the nucleation rate passes through a maximum to zero. Since no more new particles are formed, their number \( N_p \) in the system remains constant. The initial stage of condensate formation occurs within a narrow time interval \( (\sim 10^{-5} - 10^{-4} \text{ s}) \) with a nearly constant temperature \( T \). This stage is followed by the ‘slow’ \( (\sim 10^{-3} - 10^{-2} \text{ s}) \) phase of condensational particles growth in the cooling and diminishing vapor–gas mixture.

The rate of cooling of the vapor–gas mixture proves to have the deciding effect on the nucleation rate and, thus, on the mean dimensions \( \bar{R} \) of the condensate particles. An increase in cooling rate leads to greater degrees of supersaturation and an exponential increase in number of particles formed. Since condensation rate is not so dependent on the degree of supersaturation, then for a given initial vapor concentration, smaller particles are formed in the case of higher cooling rates because the vapor is deposited at a larger number of condensation centers. The mean dimensions of the resulting particles of condensate increase rapidly with an increase in the pressure of the gas atmosphere, since in this case the cooling rate reduces. Thus, the following peculiarities of the process are predicted: with an increase of the ambient gas pressure the number of condensed particles decreases while their mean dimensions increase. These conclusions, obtained in the calculations, are confirmed by the experimental results described above.

4. Conclusions

(1) Ultrafine particles have been synthesized under the laser action on materials (metals, metal oxides, carbon) in a high-pressure atmosphere of chemically active (hydrogen, oxygen, air) and inert (helium, argon, xenon) gases as a result of vapor condensation.

(2) The mean dimensions of the synthesized particles can be varied by changing the ambient gas.
pressure, namely the sizes of condensate particles increase rapidly with an increase in the pressure of the surrounding atmosphere.

References