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POSSIBILITIES OF OBTAINING NICKEL NANOPARTICLES IN AN AQUEOUS MEDIUM USING LASER ACTION

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An aqueous suspension of nickel nanoparticles has been obtained by the laser-erosion method. The diameters and concentrations of nickel nanoparticles in the aqueous medium have been measured using the laser-probing method. The obtained suspension of nanosize particles has been analyzed with the use of atomic-force and electron microscopy.

Introduction. Methods of obtaining nanosize objects and of monitoring their characteristics have gone through rapid development. According to the most popular classification, one recognizes clusters (particles 1–10 nm in size) and nanoparticles proper (10 to 100 nm in size). The physical and chemical properties of matter in this range of sizes differ from the properties of both individual atoms and ions and a massive substance. For example, mechanical, electrical, magnetic, optical, and chemical properties significantly change for many metals on passing to the nanostate. This enables one to enhance or weaken the existing properties of metals and to create new metallic or metal-containing materials. It is of great interest to use nanoparticles in such fields as medicine, precision chemicals, electronics, etc.

Several techniques for obtaining nanoparticle suspensions have been developed at present: electric discharge in liquids [1] and laser erosion in liquids [2, 3].

In this work, we propose a new method of obtaining suspensions of metal nanoparticles and a method of monitoring the parameters of nanoparticles in optically transparent media (particle size and concentration).

Laser-Erosion Method. In the process of action of laser radiation on a target in a plasma torch, particles of the dropping-liquid (liquid-droplet) phase of the target material appear; they can absorb and scatter the incident radiation. Initially the erosion torch consists of the transparent luminous vapor of the target material; thereafter, with a certain time delay, small liquid droplets (~50 nm) arrive at the erosion laser torch due to the volume vaporization [4].

The mechanism of action is as follows: the surface metal layer is heated to temperatures higher than the boiling point in the process of action of laser radiation of moderate power density, and the vapor-gas bubbles formed, which burst, supply liquid-phase particles to the erosion torch of the metal. According to the theoretical evaluations for microdefect-free media and for media not containing gases, the process of volume vaporization is essential for power densities higher than 10^8 W/cm^2 [5]. Under actual conditions, the process of volume vaporization begins at much lower power densities [6]. By the end of the acting laser pulse, larger particles (~1–100 μm) begin to arrive at the torch by the hydromechanical mechanism [7].

Particles of the condensed phase resulting from both mechanisms are present in the torch for a time, and thereafter only large particles formed by the hydrodynamic mechanism are predominantly left in the surface zone [4].

An analysis of the configuration of the scattering of large particles has been made in the process of studying the characteristics of erosion metal torches. It was established that these particles predominantly move at a small angle to the target surface, making up a peculiar dynamic corona. Thus, smaller and larger particles have different preferred directions of scattering (smaller particles are directed perpendicularly to the target surface, whereas larger ones are directed at a small angle to it).

This effect makes it possible to use spatial separation of particles by diaphragming the particle "beam" in a solid angle, eliminating the zone of scattering of large particles, which can significantly hinder their arrival at the sus-

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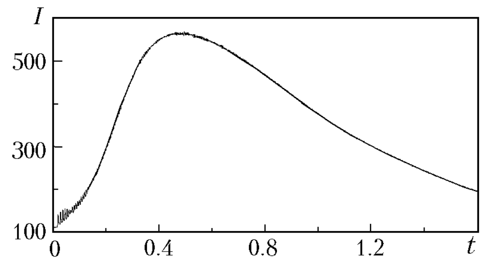

Fig. 1. Time shape of the quasistationary acting pulse of a neodymium laser. t, msec.

pension (despite the fact that it is precisely the particles formed by the hydrodynamic mechanism that are the bulk of the substance removed from the target). The angular characteristics of this zone can be determined by an analysis of the configuration of the scattering of large particles. Small particles of the diaphragmed beam settle into the aqueous medium, thus forming an aqueous suspension of nanoparticles.

Laser-Probing Method. This method has been proposed in [8, 9] for investigating of the parameters of the dropping-liquid phase of the erosion laser torch of metallic targets. Its essence as applied to this work is as follows. Probing laser radiation is fed to the investigated sample placed at the center of an integrating sphere. The radiation scattered by the sample is uniformly distributed over the interior mat surface of the sphere. An optical sensor is placed into one orifice of the sphere to determine the scattered-radiation intensity. The other two optical sensors record the intensities of the probing radiation and of that transmitted by the sample. Part of the radiation, absorbed by the sample, is found from the energy balance of the probing radiation. Thus, for spherical particles whose size is much smaller than the probing-radiation wavelength ($d << \lambda$), the relation [8]

$$\frac{Q_{\mathrm{sc}}}{Q_{\mathrm{abs}}}=\frac{\pi^3}{9}\left(\frac{d}{\lambda}\right)^3\frac{(n^2-\chi^2-1)^2+4n^2\chi^2}{n\chi} \tag{1}$$

is true with account for $n = n_{\mathrm{h}}/n_{\mathrm{med}}$ and $\chi = \chi_{\mathrm{h}}/\chi_{\mathrm{med}}$.

The equality $K_{\mathrm{sc}}/K_{\mathrm{abs}} = Q_{\mathrm{sc}}/Q_{\mathrm{abs}}$ holds for single scattering (the average scattering mean free path must be larger than the dimension of the probed object). Thus, a comparison of the ratio $K_{\mathrm{sc}}/K_{\mathrm{abs}}$ measured experimentally and the ratio $Q_{\mathrm{sc}}/Q_{\mathrm{abs}}$ calculated theoretically from formula (1) enables us to determine the effective particle diameter.

A formula for calculation of the concentration of particles can be obtained in the following manner. The cross section of radiation loss on one particle is $S^1_{\mathrm{loss}} = Q_{\mathrm{ex}}\pi r^2$ [10]. The number of particles in the sample's probe volume is $N_{\mathrm{v}} = NSl$. Then the radiation-loss cross section on all particles of the probed volume is $S_{\mathrm{loss}} = S^1_{\mathrm{loss}}N_{\mathrm{v}} = Q_{\mathrm{ex}}\pi r^2 NSl$. For single scattering, the ratio of the radiation-loss cross section on particles of the probed volume to the cross section of the probing beam is equal to the relative loss coefficient $K_{\mathrm{abs}} = K_{\mathrm{sc}} + K_{\mathrm{abs}}$, i.e., $\frac{S_{\mathrm{loss}}}{S} = K_{\mathrm{loss}} = K_{\mathrm{sc}} + K_{\mathrm{abs}} = Q_{\mathrm{ex}}\pi r^2 Nl$, whence we can determine the concentration

$$N=\frac{K_{\mathrm{sc}}+K_{\mathrm{abs}}}{\pi r^2 Q_{\mathrm{ex}} l}\,. \tag{2}$$

Consequently, experimentally measuring K_{sc}, K_{abs}, and l and theoretically calculating Q_{ex} (the procedure of calculation of Q_{ex} according to the Mie theory has been presented in [8] in detail), we can establish the averaged concentration of particles in an optically transparent medium.

Experimental. The action was realized on a nickel target in air. The erosion of the metallic target was carried out by a quasistationary neodymium-laser pulse (λ = 1.06 μm). Laser radiation was focused onto the target using the lens and the reversing prism. The pulse duration was ~1500 μsec, the total energy was ~1 kJ, and the irradiation-spot diameter was 7 mm. A tenfold repetition of the pulse acting on the target recovered nickel particles in the aqueous

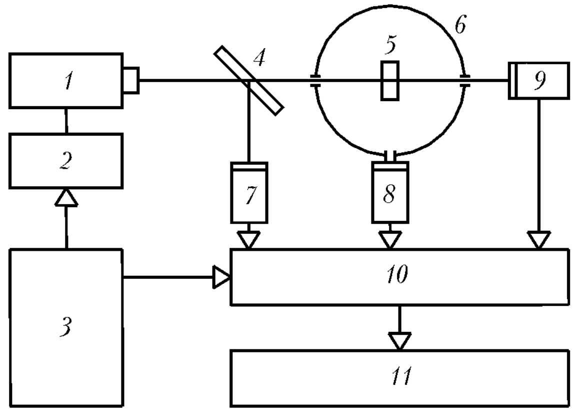

Fig. 2. Experimental setup for investigation of the size and concentration of nanoparticles in an optically transparent medium: 1) ruby laser; 2) supply unit of a ruby laser; 3) synchronizing system; 4) separating plate; 5) sample under study; 6) integrating sphere; 7, 8, and 9) sensors for recording the intensity of probing, scattered, and transmitted radiation respectively; 10) ADC; 11) computer.

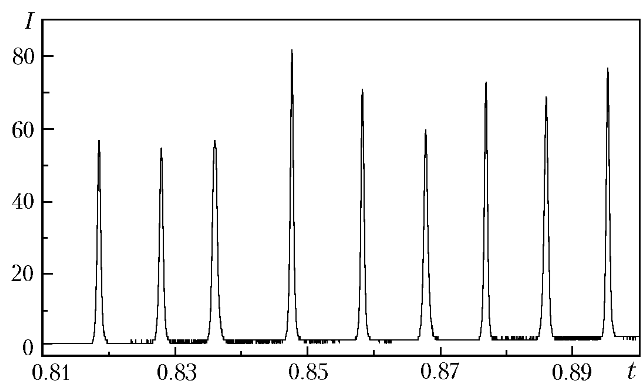

Fig. 3. Time sample of the pulse of probing radiation of a regular-running ruby laser. t, msec.

medium placed in the cell. Two types of aqueous suspension were obtained. In preparing the first type of suspension, we used the procedure of diaphragming of the "beam" of particles of the dropping-liquid phase, i.e., a diaphragm hindering the arrival of larger particles at the suspension was placed on the path of the "beam." In preparing the second type of suspension, we did not use the diaphragming procedure, i.e., all particles of the dropping-liquid phase arrived at the suspension.

The time characteristic of the acting pulse is given in Fig. 1. The size and concentration of nickel particles in the aqueous medium were monitored on the experimental setup whose diagram is shown in Fig. 2.

The investigated suspension in a rectangular plane-parallel cell 5 is placed at the center of the integrating sphere 6. Probing radiation of a regular-running ruby laser 1 is fed via the orifice in the sphere perpendicularly to the face of the rectangular cell. The time sample of duration 80 μsec of the radiation pulse of the regular-running ruby laser is given in Fig. 3. Part of the laser radiation is fed by plate 4 to an optical sensor of recording of the intensity of the radiation probing the object 7. The radiation transmitted by the object and whose intensity is monitored by an optical sensor 9 is removed via the second orifice in the sphere.

A certain part of the radiation scattered on the object arrives at the optical sensor 8 via the third orifice. Analog signals from the sensors for recording the intensities of the radiation incident on the object 7, transmitted by the object 9 and scattered on the object 8, are fed to an analog-to-digital converter (ADC) 10, after which they are processed on computer 11. A synchronizing system 3 is used for timing of the laser and ADC operation. A 4-channel ADC with a sampling time of 25 nsec and a 10-bit capacity was used in the experiments. The ADC structure makes

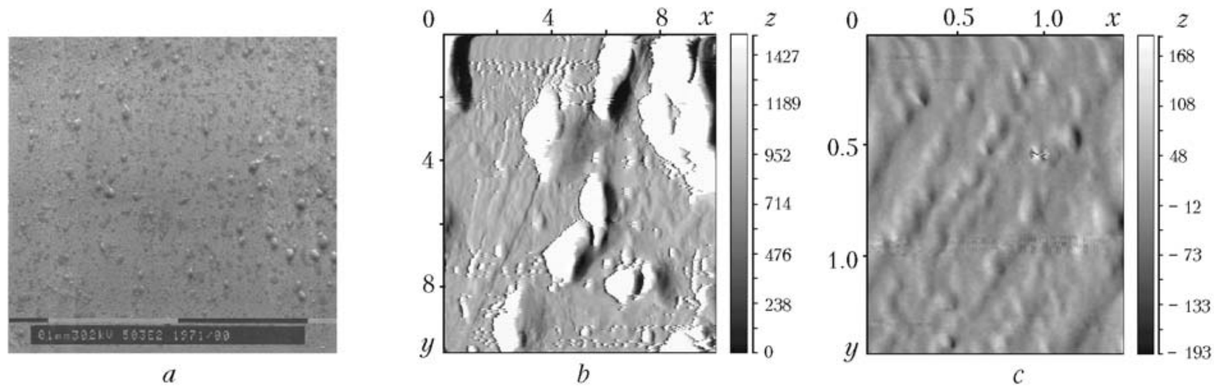

Fig. 4. Picture of the surface relief of a substrate with nickel particles obtained: a) without the procedure of diaphragming after evaporation, the electron microscope; b) the same, the atomic-force microscope; c) with the procedure of diaphragming after evaporation, the atomic-force microscope.

it possible to accumulate 64,000 values of data per channel, which is 1.6 msec in time. Using a special program based on more exact formulas of the Mie theory [10] than expression (1) we calculate the averaged diameters and concentration of nanosize particles. The use of the formulas of the Mie theory enables one to extend the range of applicability of the method, since, unlike formula (1), they allow a more correct result for a wider range of particle sizes.

As has been mentioned above, one condition of adequacy of the method proposed is the singleness of the scattering of probing radiation on the sample. It has been established [11] that scattering can be assumed to be single, when the loss of probing laser radiation in interaction with particles (scattering and absorption) does not exceed 30%. For this requirement to be met, we selected the optical density of the sample.

The values of the complex refractive index of nickel have been taken from [12] for a wavelength close to that of the radiation of the ruby laser used as the probing one $\lambda = 694.3$ nm.

Analysis of Results. In this work, we have analyzed two samples: an aqueous suspension of nickel particles obtained by diaphragming the particle "beam", and the suspension produced without this procedure. Laser probing of the cell with the aqueous suspension of nickel particles formed with the use of the procedure of diaphragming the particle "beam" yielded the following results: particle size $d \approx 85$ nm and volume concentration $1.2 \cdot 10^9$ cm^{-3}.

Investigation, by the laser-probing method, of the aqueous suspension of nickel particles obtained without the procedure of diaphragming of the particle "beam" has shown that the suspension contains relatively large particles (>1 μm) in an appreciable concentration, but in this range, the method in question has substantial limitations (increase in the error) for this probing-laser wavelength ($\lambda = 694.3$ nm) because of the growth in the diffraction parameter $\pi d/\lambda \approx 40$.

We should note that for our case ($d \approx 85$ nm and $\pi d/\lambda \approx 0.38$) the values of the particle diameters, calculated from the approximate formula (1) and from the formulas of the Mie theory, differ only slightly.

To confirm the results offered by the laser-probing method we analyzed particles obtained after the evaporation of water and applying them to the substrate. We used atomic-force and electron microscopy for the analysis.

The picture of the surface relief of the substrate with nickel particles obtained without diaphragming of the particle "beam" is shown in Fig. 4a. The photograph was obtained with the electron microscope. As is clear from the photograph, the particle size is 3–5 μm, which confirms, at a qualitative level, the results obtained by the laser-probing technique. However, apart from the relatively large particles, there are numerous submicron particles which are at the limit of resolution of this electron microscope. In investigating the same sample with the atomic-force microscope, we can determine the size of submicron particles (see Fig. 4b). Relatively large particles of ~2–4 μm and smaller particles of ~40–70 nm are clearly seen on the photograph.

The results of investigation of particles formed using the procedure of diaphragming of the particle "beam" are given in Fig. 4c. This photograph was obtained using atomic-force microscopy. Nickel particles were prepared analogously to the previous case. The preinvestigation of the substrate's relief already showed a significant reduction in the number of large particles. An analysis of the photograph (Fig. 4c) has shown that the particle diameter is equal to ~80 nm with a standard spread of ±20%.

The values of the particle diameters measured by the laser-probing method are in agreement with the values obtained using atomic-force microscopy.

Conclusions. Using the laser-erosion method we can form nanosize particles and their suspensions. The main advantage of this method is that this process is independent of the type of solvent (in this case it serves as just the "trap" of "ready" particles) and its physicochemical properties, i.e., nanoparticle suspensions can be formed in quite different media, excluding those aggressive to the material of the nanoparticles. The laser-probing method enables one to determine, with a sufficient degree of accuracy, the effective size and concentration of particles in an optically transparent medium in real time. We should note that the method is applicable for monitoring the change in the particle size and concentration in transient processes. An additional advantage of the method proposed is nondestructive monitoring of the sample's characteristics.

NOTATION

d, particle diameter, nm; I, relative intensity of the incident radiation; K_{sc} and K_{abs}, experimentally measured ratios of the intensities of the scattered radiation and that absorbed by the sample to the intensity of the radiation probing the sample; K_{loss}, relative loss factor; l, length of interaction of the probing radiation with the sample under study, cm; $m_{part} = m_{part} - i\chi_{part}$, complex refractive index of the particle material; N, number concentration of particles, cm^{-3}; N_v, number of particles in the probed volume, cm^{-3}; n_{med}, refractive index of the medium; n_{part}, refractive index of the particle material; Q_{sc} and Q_{abs}, scattering and absorption efficiencies (ratios of the scattering and absorption cross section to the cross-sectional area of a particle); Q_{ex}, extinction efficiency (ratio of the cross section of total radiation loss by scattering and absorption to the cross-sectional area of a particle); r, particle radius, cm; S, cross section of the probing laser beam, cm^2; S^1_{loss}, cross section of radiation loss on one particle, cm^2; S_{loss}, cross section of radiation loss on all particles of the probed volume, cm^2; t, time, msec; x and y, coordinates on the sample's surface in scanning by the atomic-force microscope, nm; z, coordinate reflecting the level of the sample's relief in scanning by the atomic-force microscope, μm; λ, probing-radiation wavelength, nm; χ, absorption coefficient of the particle material. Subscripts: sc, scattered; abs, absorbed; loss, loss; v, volume, volumetric; med, medium; part, particle; ex, extinction; 1, single.

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