VI Serbian-Belarusian Symp. on Phys. and Diagn. of Lab. &
Astrophys. Plasma, Belgrade, Serbia, 22 - 25 August 2006
eds. M. Ćuk, M.S. Dimitrijević, J. Purić, N. Milovanović
Publ. Astron. Obs. Belgrade No. 82 (2007), 45-55 *Invited lecture*

THE LASER METHOD OF METAL NANOPARTICLE FORMATION WITH THE HELP OF SPATIAL SEPARATION

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Abstract. The water nickel nanoparticle suspension was formed by the method of laser erosion using the spatial separation. Nickel nanoparticles diameter and their concentration in water medium were measured with an employment of the laser probing method. The analysis of obtained nanosize particles suspension was carried out by the atomic-power spectroscopy and electron spectroscopy.

1. INTRODUCTION

The nanotechnologies have a wide distribution at the present time. These technologies deal with formation and implementation of the matter particles with nanometer sizes [1]. The physical and chemical matter properties at that range of sizes differ both from single atoms, ions and from massive solids. This fact allows to weaken or to strengthen the known metal properties and to create absolutely new metal or contain-metal materials with unusual and inaccessible before properties. The application of nanoparticles is of great interest of such spheres as medicine, electronics, chemical industry, optics etc.

At the present work, the new method of water nanoparticle suspensions formation is offered. The formation method is based on the penetration of the metallic target erosion products in water medium during the laser action on metallic target.

2. METHODS OF THE METAL NANOPARTICLE SUSPENSION GETTING

Nowadays several methods of nanoparticle suspensions formation are known: electrical discharge in liquids and laser erosion in liquids.

The metal electrodes (Ni, W, steel) placed in liquid medium (water, ethanol) are used for the metal nanoparticle suspension production by the electrical discharge method. The electrodes destroy and great amount of micro- and nanoparticles form during the electric discharge (ark [2] or spark [3]). They consist of every possible sorts and kinds of chemical compounds of electrode and liquid medium materials. The applying of spark discharge [3] provides more effective electrode material entry to discharge zone in compare with ark discharge. The employment of alternating current discharge is governed by the necessity to have uniform erosion of both electrodes. The WC nanoparticles with the diameter from 2.5 to 35 nm were obtained [3]. The possibility of metal (Ag, Au, Ti, Cu and their alloys) nanoparticle production by the laser erosion is under recognition at the work [4]. It was showed that during laser erosion of metal target placed in liquid medium the significant quantity of nanosize objects (with dimensions of 10-100 nm) is formed. The second harmonic of Nd:YAG laser (λ=532 nm) or irradiation of copper vapor laser (λ=510nm) were applied for the laser acting.

Both of these methods possess significant disadvantage: the chemical purity of obtained suspensions seems to be very questionable. The chemical composition of given nanosize objects includes all chemical spectrum (and every possible sorts and kinds of their combinations) both the target (electrode) material and liquid medium substance as the processes of particle formation pass in liquid medium

3. THE SPATIAL AND TIME DISTRIBUTIONS OF THE DROP-LIQUID PHASE OF METAL EROSION LASER JET (WHEN ACTING WITH RECTILINEAR QUASI-STATIONARY LASER PULSE)

The erosion laser jet forms by the action of the moderate laser irradiation intensity (10^5 -10^6 W/cm^2) on the metallic target surface. It consists of a vapor, plasma and drop-liquid phase particles. The particles move to laser jet formed by two mechanisms: the bulk vapor [5,6] (small particles (10-100 nm)) at the beginning of laser action and hydrodynamic mechanism [7,8] (1-100 μm) to the end of the laser action. A highly disperse liquid-drop phase with a plasma moves perpendicularly to the surface target when the depth of crater less than its diameter. More large particles move in the form of cone under small angle to the target surface over border effects on a crater, forming so-called dynamic crown. Since the highlight with laser or plasma irradiation is absent at that moment, the particles are invisible to experimenters. To investigate the dynamic of those particles it's advisable to use the irradiation of subsidiary laser. That probing irradiation must satisfy the next basic requirements: the irradiation wavelength must correspond to

the spectral sensitivity of recording equipment and duration of the laser pulse must be significantly less than duration of the typical dynamic processes in erosion laser jet (10^{-6} s).

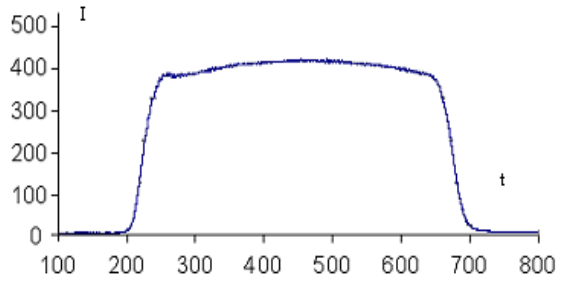


Fig. 1. The time shape of rectilinear quasi-stationary laser pulse.

At present work, the erosion laser jets are investigated. They was obtained during the action of rectilinear laser irradiation pulse (of Nd: glass laser) on surface of metal target made from aluminum alloy D16T. The pulse had duration 500 μs (see fig.1). Diameter of irradiated spot on target surface was equal up to 10 mm, Nd laser irradiation power density at the irradiated spot - $1.4 \cdot 10^6$ W/ cm^2. The crater depth after the laser acting was ~ 0.3 mm.

At the fig.2 were shown frames observed by implementation of highlighting mono-pulse (duration ~50 ns) of ruby laser. As reference of the time (0 s) the beginning of Nd laser irradiation recession (rectilinear pulse) was accepted.

As it is shown at fig. 2 liquid drops formed due to hydrodynamic mechanism appear only when some time passing after the beginning of acting laser irradiation recession. Moreover, as it can be seen from frame-by-frame photography the laser jet enlarges. It's necessary to note that target erosion products (drop-liquid phase) fly under not great angle to target surface. In such way, they form cone-shaped three-dimensional figure and the cone-opening angle (~ 155º) is unchangeable with the time passing. It proves the fact that during all registration time the shape of solid crater borders and it (crater) depth are unchangeable too. This is means that all liquid layer of metal forced by the recoil momentum of acting laser irradiation recession, start to move from the centre of crater to its borders and run out. The run out angle depends on deepness of the crater and form of its borders.

To define the dynamic of liquid phase from the erosive crater (with commensurable diameter and depth) the focusing of acting laser irradiation was changed (reduced). So far the spot with diameter 5 mm was irradiated by the same laser on the target surface. At that case Nd laser irradiation power density at the irradiated spot reached up to $1.7 \cdot 10^7$ W/ cm^2. The crater depth after the laser acting was ~ 0.6 mm.

At such levels of laser pulse power density the intensity of vaporization is significantly higher than in case of acting laser irradiation focusing in spot with diameter of 10 mm. Due to this fact the erosion crater has the greater deepness with

the passing of time. Therefore, liquid drops formed by the hydrodynamic mechanism must start flying under the greater angle to the target surface.

The results of this experiment are given at the fig. 3. As it can be seen from the fig. 3,a at the moment of the beginning of acting Nd laser irradiation recession the "large" particles not appear yet. But passing some time (see fig. 3,b) it can be seen that in the erosion laser jet the liquid drops start to penetrate. In which connection the angle between the direction of their dispersion and target surface is greater than at the previous experiment. That says about the greater influence of the solid crater borders at liquid drops trajectory at present experiment.

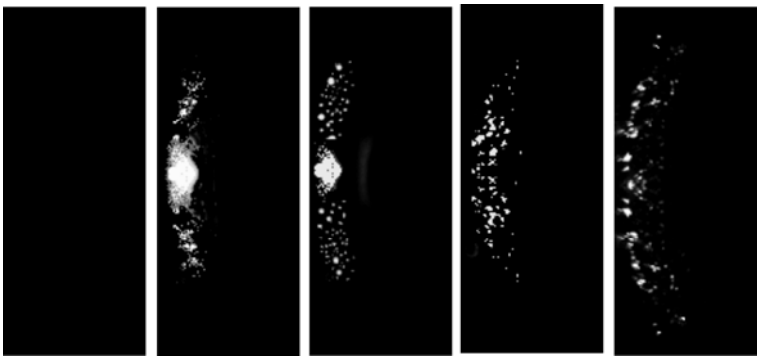


Fig. 2. The frame of drop-liquid phase erosion laser jet (diameter of irradiated spot 10 mm) passing time interval Δt after the beginning of acting laser irradiation recession: a) Δt= 0 μs, b) Δt= 170 μs, c) Δt=260 μs, d) Δt=350 μs, e) Δt=450 μs.

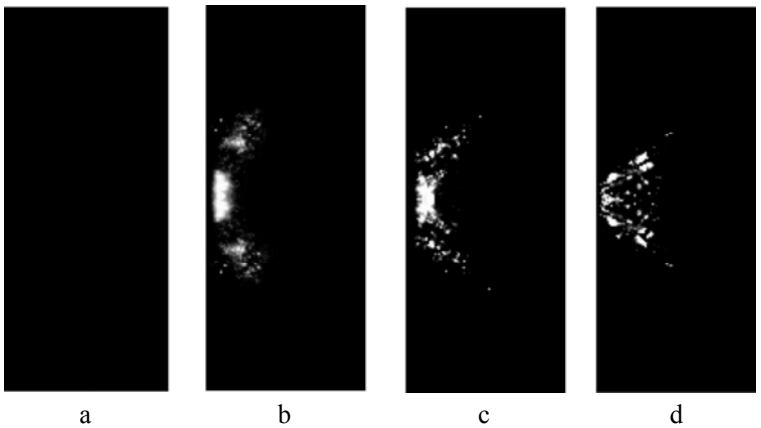


Fig. 3. The frame of drop-liquid phase erosion laser jet (diameter of irradiated spot 5 mm) passing time interval Δt after the beginning of acting laser irradiation recession: a) Δt= 0 μs, b) Δt= 30 μs, c) Δt=250 μs, d) Δt=450 μs.

During the action of laser pulse with bell-shaped form (when the fronts of laser intensivity increasing and decreasing are commensureable to pulse duration) at the matal liquid drops formed due to hydrodynamic mechanism penetrate into laser jet significately earlie (even at the time of laser pulse intensivity resession). This fact is determined by the distinctions in process of condenced phase formation. In this case drop-liqiud phase forms both due to bulk vapore mechanism and due to hydrodynamic mechanism, which are passing simultaneously [9]. At this work, it was established that the time and spatial distribution of erosion laser jet drop-liquid phase had the common features for the wider circrle of metals.

4. FORMATION THE WATER NANOPARTICLE SUSPENSIONS

Therefore, the "small" and "big" particles possess the different directions of dispersion. This effect allows to separate particles spatially by a diaphragm placing (see fig.4). Thus, small particles mainly move in the cavity with water after diaphragm. This is the objects of the present work.

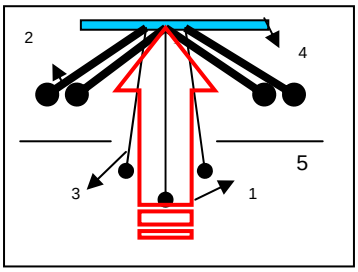


Fig. 4. Scheme of the laser erosion mechanism. 1) Acting laser irradiation, 2) The particles formed by hydrodynamic mechanism, 3) The particles formed by the bulk vapor mechanism, 4) Sample, 5) Mask.

The installation base [10] on Nd-glass laser with λ=1.06 μm produce semi-stationary high power pulses with duration ~ 1.2 ms, energy 1 kJ and focusing diameter 10 mm. The water suspension of nanoparticles was produced by the multi action of the laser irradiation on nickel target.

5. THE CONTROL OF METAL NANOPARTICLES CHARACTERISTICS IN WATER SUSPENSIONS

In water medium particle characteristics was controled with the emplamentation of laser probing method [11]. This method was optimized for the probing of nanoobjects in pan fulled with water.

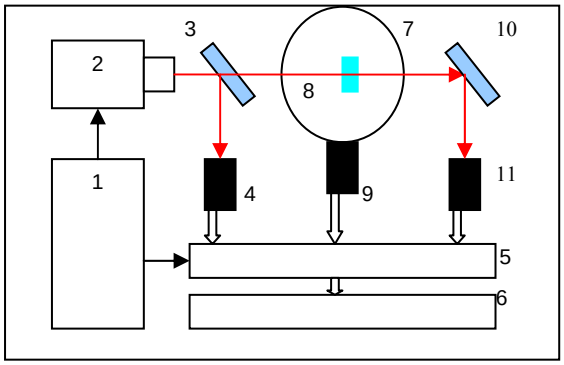


Fig. 5. The scheme of experimental equipment for the laser probing. 1 - System of synchronization, 2 - Ruby laser, 3, 10 - Beam splitter, 4, 9, 11 - Photo detectors, 5 - ADC, 6 - Computer, 7 - Integrating sphere, 8 - Sample

The main point of this method (at the present work) is following – see fig. 5. At the investigated sample 8 placed in the centre of integrating sphere 7 the probing laser irradiation is act. Scattered by the sample irradiation distributes uniformly all along the inside suffused surface of sphere. To define the intensivity of scattered irradiation the photo detector 9 is placed into one of sphere apertures. Two athers photodectors 4,11 registrate the intensivity of probing irradiation and the intensivity of passing throu the sample irradiation correspondinly. The absorbed (by the sample) part of probing irradiation can be determined from the balance of energy.

Therefore, for the spherical particles with size that significantly less than the probing irradiation wavelength ($d << \lambda$) there is known following equation [11]:

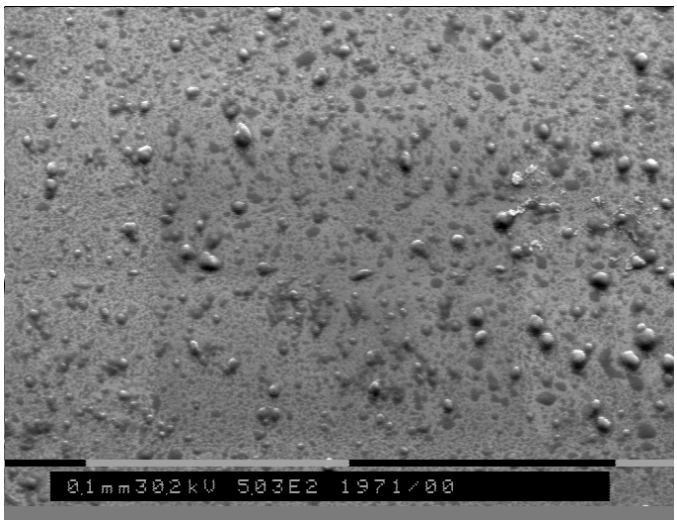
$$\frac{Q_{рас}}{Q_{пог}} = \frac{\pi^3}{9}\left(\frac{d}{\lambda}\right)^3 \frac{(n^2 - \chi^2 - 1)^2 + 4n^2\chi^2}{n\chi}, \quad (1)$$

Taking into account $n = \frac{n_{part}}{n_{med}}$ and $\chi = \frac{\chi_{part}}{n_{med}}$, where d - effective particle diameter; n_{part} - index of medium refraction; $m_{part} = n_{part} - i \cdot \chi_{part}$ - complex index of refraction of particle material; Q_{scat} and Q_{abs} - efficiencies of scattering and absorption (rates of scattering cross-section and absorption cross-section to square of transverse section of particle); λ – probing laser irradiation wavelength.

On condition that we have single scattering approximation, (average free path of scattered photon is more than probing sample size) it's known the following equation: $\frac{K_{scat}}{K_{abs}} = \frac{Q_{scat}}{Q_{abs}}$. The effective particle diameter can be determed (using formula (1)) by the comparison of experimentally measured $\frac{K_{scat}}{K_{abs}}$ with the theoretically calculated $\frac{Q_{scat}}{Q_{abs}}$,

Formula for the particle concentration definition can be observed by the following way. The cross-section of irradiation extinction at the one particle is $S_{ext}^1 = Q_{ext}\pi \cdot r^2$ [12]. In probing sample volume the quantity of particles is $N_V = NSl$. Then cross-section of the extinction on all particles in probing volume is $S_{ext} = S_{ext}^1 N_V = Q_{ext}\pi \cdot r^2 NSl$. On condition that we have single scattering approximation, the rate of extinction cross-section (on the particles in probing volume) to transverse section of the probing beam is equal to relative extinction coefficient $K_{ext} = K_{scat} + K_{abs}$, i.e. $\frac{S_{ext}}{S} = K_{ext} = K_{scat} + K_{abs} = Q_{ext}\pi \cdot r^2 Nl$. Then we can determed the concentration

$$N = \frac{K_{\text{scat}} + K_{abs}}{\pi r^2 Q_{ext} l} \tag{2}$$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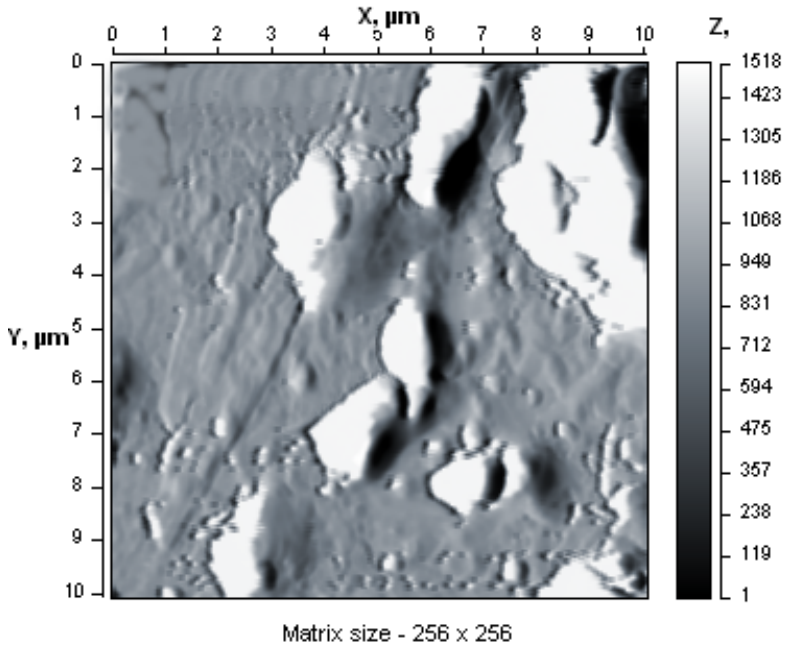
a


X, µm
0 1 2 3 4 5 6 7 8 9 10
Y, µm
0 1 2 3 4 5 6 7 8 9 10
Z,
1518
1423
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712
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475
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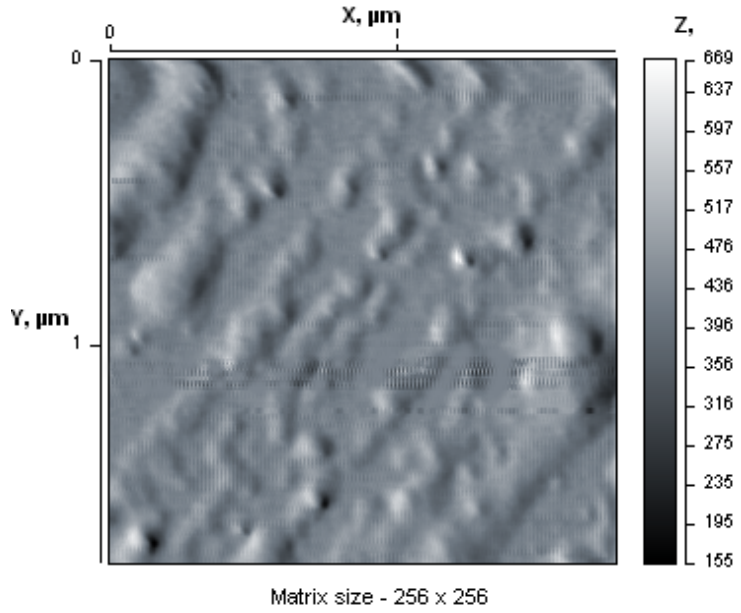

c

Fig 3. Relief surface image of substrate with nickel nanoparticles: a – obtained without diaphragm (electron microscope); b – obtained without diaphragm (image of atomic-power microscope); c – obtained with diaphragm (image of atomic-power microscope).

Consequently, by experimentally measuring K_{scat}, K_{abs} (rates of scattering by the sample irradiation and absorbed irradiation to intensity of probing laser irradiation), l (interacting length of probing laser irradiation with investigated sample) and theoretically calculating Q_{ext} (the method of calculation Q_{ext} is given in proper way at [12]) it's possible to determine average particle concentration in transparent optical medium using formula (2).

At the present work analysis of two examples was made. The first one – water suspension of nickel particles, obtained with an employment of a diaphragm (small particles was in water). The second one – water suspension has nickel particles, obtained without this procedure (i.e. small and large particles flow move in water).

It has been determined parameters by the method laser probing of the sample obtained using diaphragm: the average particles diameter 85 nm, average particles number concentration 1.2×10^{9} cm^{-3}. The probing of the sample obtained without diaphragm shows that the large particles ~ 1 µm are in a water suspense.

The comparative analysis of suspense's (by the atomic-power and electronic microscopy) was made to prove the results, obtained with laser probe method. The water samples were evaporated and drifted on substrate.

Relief surface image of substrate with nickel nanoparticles, obtained without diaphragm is given in Fig.3a. This image was taken with an employment of the electron microscope. Average particles size at the image is 3-5 μm. This fact is in agreement with data obtained with an employment the probing laser method. However we can see at this image that there are a lot of submicron particles with the relatively large particles. They are in the resolution limit of the electron microscope. Submicron particles of this sample have been found with an employment of the atomic-power microscope (Fig.3b). At this image we can clear see the relatively large particles ~2-4 μm and small particles ~40-70 nm.

The investigating results of the particles obtained with an employment of diaphragm are given in Fig.3c. This image has been made with an employment of the atomic-power microscopy. The nickel particles were prepared similar previous case. Even the primary relief surface investigation of the substrate shows a significant reduction of the large particles quantity. Image analysis (Fig.3c) shows that effective particles diameter is 80 nm with dispersion 40% .

Effective particles diameter measured by the laser probe method is in agreement with results obtained with an employment of atomic-power microscopy.

5. CONCLUSION

Thus it's possible to produce nanosize nickel particles with effective diameter ~70-80 nm and their suspense's using mechanism of the metal laser erosion. The main advantage of given method is independence the process of nanoparticles suspense production on the type of penetrating medium and its physical-chemical properties. So it's possible to produce metallic suspense's of nanoparticles in different mediums apart from corrosive mediums to material nanoparticles.

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