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Formation of periodic structures upon laser ablation of metal targets in liquids

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***Abstract*. Experimental data on the formation of ordered microstructures produced upon ablation of metal targets in liquids irradiated by a copper vapour laser or a pulsed Nd : YAG laser are presented. The structures were obtained on brass, bronze, copper, and tungsten substrates immersed in distilled water or ethanol. As a result of multiple-pulse laser ablation by a scanning beam, ordered microcones with pointed vertexes are formed on the target surface. The structures are separated by deep narrow channels. The structure period was experimentally shown to increase linearly with diameter of the laser spot on the target surface.**

Keywords: *laser ablation, periodic structures.*

1. Introduction

Laser ablation of solids in liquids enables producing microstructures free from the sputtered target material. This is due to a high pressure of the vapour of a surrounding liquid, which removes the laser-modified target material from the target surface [1 – 8]. Furthermore, the laser ablation in a liquid is a method of producing nanoparticles [9 – 19]. Upon ablation of solids immersed in a liquid, the molten target layer borders directly on the vapour of the ambient liquid. Under these conditions, the viscous interaction of the vapour with the molten target layer may be responsible for several instabilities like the Kelvin–Helmholtz or Rayleigh – Taylor instabilities [20].

The periodic structures produced due to the development of these instabilities are easily observable in the case of laser ablation of solids in vacuum or in diluted gases [21 – 25]. Upon ablation of targets of Si, W, Cu, bronze, etc., the vapour pressure of the target material above its surface is low and the structure growth is determined primarily by thermocapillary forces. They appear due to the existence of a temperature gradient along the melt surface caused by the variation of the target reflectance in a periodic relief. During the growth of this instability, three-dimensional periodic structures emerge on the target surface, which protrude above it by tens of micrometers, with a period close to the period of capillary waves [26 – 32]. Also, one of the reasons responsible for the nonuniformity of the melt surface is the defect-deformation instability [33]. The regular structures developing in the field of mechanical deformations under nonuniform laser heating may have a period of the order of laser beam dimension [34], because this is precisely the dimension which determines the characteristic scale of the nonuniform surface deformation.

Upon laser ablation of a solid in a liquid, its vapour pressure, as a rule, significantly exceeds the vapour pressure of the target material. Therefore, it is precisely the ambient liquid vapour that determines the ablation rate. When laser pulses are short enough, the lateral dimension of the molten layer is close to the laser beam diameter, and therefore the structure period would be expected to correlate with the dimension of the focal spot on the surface. The formation of regular structures on the surface under its laser ablation in a liquid may result in changes in the properties of the nanoparticles produced in the process, in particular in a change in the nanoparticle size distribution function. Furthermore, the investigation of these structures is of significance from the standpoint of the practical use of laser in-liquid ablation for the decontamination of radiation-polluted surfaces.

The aim of this work is to investigate the periodic structures produced on a solid target (copper, brass, tungsten, bronze) under its laser ablation in a liquid (water, ethanol) as well as their dependence on the experiment parameters. We show that the morphology and properties of these structures differ from the characteristics of the structures produced by ablation in diluted gases.

2. Experimental

The formation of periodic structures on metal targets upon laser in-liquid ablation was investigated employing the same experimental setup as in the production of copper and brass nanoparticles in Ref. [19]. A detailed description of the experimental technique used to produce nanoparticles by laser in-liquid ablation of solids was given in earlier papers [14, 15, 17]. The metal targets were made of electrolytic copper, brass (40 % Zn, 60 % Cu), bronze (8 % Sn, 92 % Cu), and tungsten (single crystal). The target ablation was produced in distilled water and in 95-% ethanol. The surface morphology was investigated with an optical microscope and a scanning electron microscope.

Two types of laser sources were employed in the experiment. The first one was a pulsed Nd : YAG laser

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emitting 1.06-μm, 130-ns pulses. The pulse repetition rate could be varied from 1 to 5 kHz, the average output power depended on the repetition rate and the pump current and amounted to 5 W. The radiation was focused onto the surface of a metal target to a spot ranging from 10 to 60 μm in diameter, the energy density at the target was 20–50 J cm^{-2} (depending on the lens selected). The second radiation source was a 0.511-μm copper vapour laser emitting 20-ns pulses with a pulse repetition rate of 7.5 kHz and an average output power up to 3 W. In this case, the energy density at the target surface was about 30 J cm^{-2} and the focal spot diameter was from 10 to 60 μm. The laser radiation was focused on the 1–2 mm thick metal target immersed under a layer of selected liquid. In this case, the liquid-containing cell was placed on a computer-controlled translation stage which displaced the target under the laser beam. The target scanning velocity and the beam overlap in successive displacements determined the total number of laser pulses absorbed by the target. To reduce the optical thickness of the colloidal solution formed above the target, ablation was produced in several cases in the flow of a thin liquid layer above the target, the typical liquid flow rate being equal to several centimetres per second.

3. Results

Target ablation in a liquid by a stationary laser beam produces a deep crater. Periodic structures appear only when the laser beam scans the target. Laser ablation of a metal sample under a thin liquid layer results in a significant change in its absorption spectrum. This is indication that the substrate material in the form of nanoparticles is dispersed into the ambient liquid [9–19]. The irradiation region becomes substantially darker than the initial surface and is located beneath it for a high energy density. The typical appearance of an area of a brass target ablated in water by radiation of the copper vapour laser is shown in Fig. 1. One can see that periodic structures are located on the bottom of the modified region. Note that the structures may protrude over the initial target surface when the beam energy density is high enough for the onset of melting.

Periodic structures are observed for all the samples investigated, independently of their crystallographic structure. The typical view of irradiated surfaces is shown in Fig. 2. The structures on brass, bronze, and tungsten substrates are roughly similar to each other. They are densely arranged cones with a small sharpening at the tip. The structures on the copper substrate are different: they may have several sharpenings of this kind (Fig. 2d).

An examination of the microcone array section perpendicular to the surface plane reveals a deep fusion penetration into the substrate material (Fig. 3). One can see that the cones which make up the microstructure are separated by deep narrow channels.

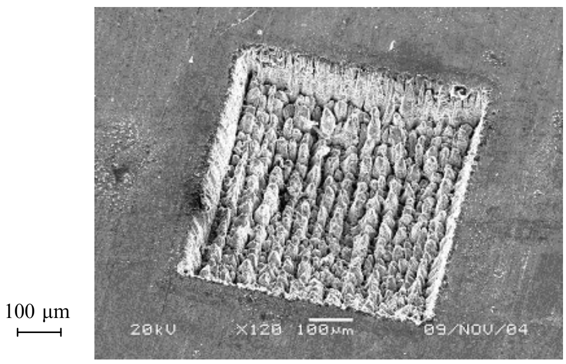

Figure 1. View of the ablated surface formed upon ablation of brass targets under a water layer by a copper vapour laser. The energy density was 4 J cm^{-2}.

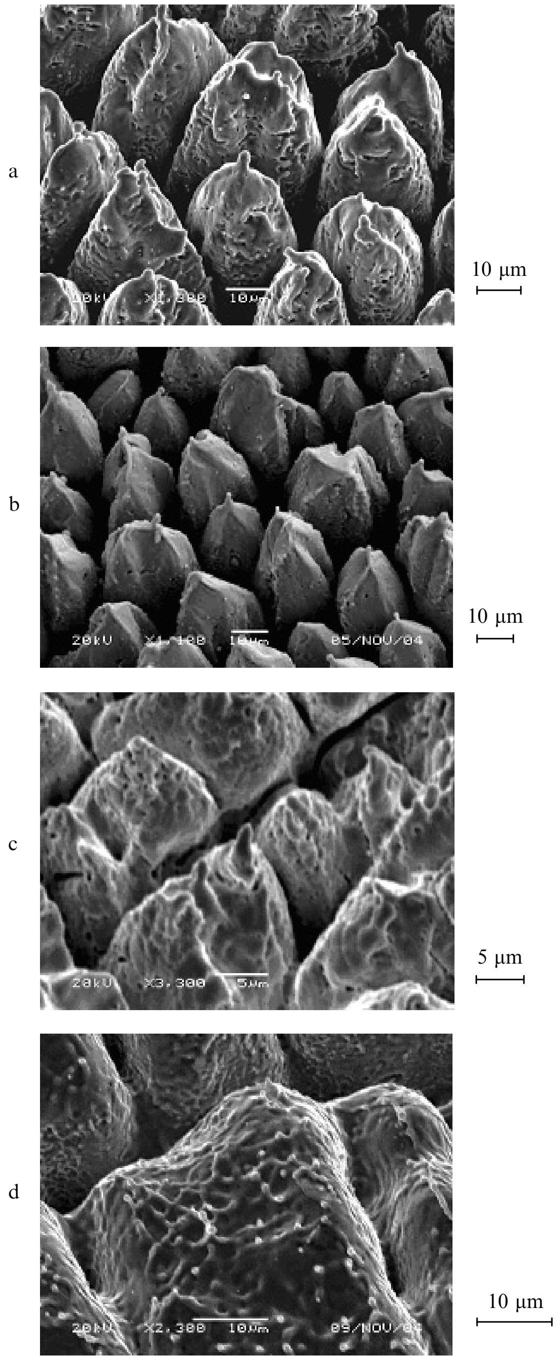

Figure 2. View of periodic structures produced upon ablation of metal targets under a liquid layer by a copper vapour laser. A bronze substrate in ethanol (a), a brass substrate in water (b), a tungsten substrate in ethanol (c), and a copper substrate in ethanol (d) were used.

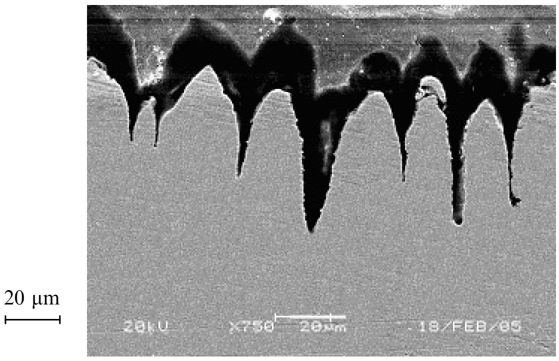

Figure 3. Substrate cross section with an array of microcones produced upon ablation of a brass target under a layer of ethanol. The radiation energy density of the copper vapour laser was equal to 16 J cm^{-2}. The image was obtained with a scanning electron microscope.

The dependence of the structure period on the laser beam diameter was determined in the following way. An optical microscope was used to determine the distances between the summits of neighbouring cones produced for a fixed diameter of the laser beam on the target surface. The peak of the hystogram was taken as the characteristic period of the microstructures produced for a given diameter of the laser beam. The dependence of the structure period on the laser beam diameter is shown in Fig. 4; one can see that it is linear in the $1-50$ μm range.

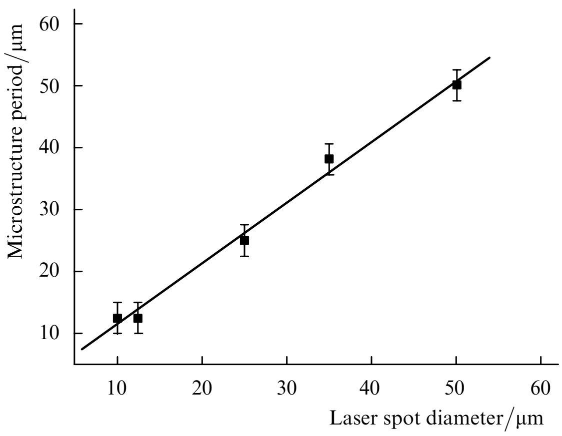

Figure 4. Period of microstructures produced by laser ablation of a brass substrate in water as a function of the diameter of the laser spot on the target surface. The radiation energy density is about 25 J cm^{-2}.

Interestingly, periodic structures are not produced upon ablation of a brass target in vacuum, unlike other metals [21–25]. The ablation surface and the neighbouring regions are covered with a white metal film-like deposit, zinc in all likelihood.

4. Discussion

In the production of periodic structures by laser ablation, a material is removed from the surface of a sample, and therefore the depth at which the microcone array is located relative to the substrate depends on the energy density. Deep, or so-called dagger-like melting is caused by the displacement of the sample melt by the recoil pressure of the material vapour [35]. The melt is removed along the cone surfaces, which results in the formation of sharp tips of the structures. However, in the case of a copper substrate, numerous tips are observed at the structure summits, because the structures terminate in rather flat areas (see Fig. 2d).

For a fixed target, the interaction of laser radiation with the substrate material results in crater formation. One of the crucial prerequisites to the formation of the structures is the scanning of the area intended for structure growth. The scanning velocity required for the formation of periodic structures determines the number of laser pulses absorbed by the surface and depends directly on the material properties and on the radiation energy density. For a fixed radiation energy density, the reduction of the scanning velocity leads to a greater removal of the material into the ambient liquid and therefore to an increase of the depth of ablated target region in which the structures are located.

The dependence of structure period on the diameter of the laser beam on the target surface is a distinctive feature of ablation in liquids. For instance, the period of three-dimensional periodic structures produced upon ablation of solids in vacuum or in gases is determined by the material constants of the target, like the coefficient of surface tension of the melt etc. [$21-25$].

As a rule, several structure periods are observed within the laser beam on a target. The melt dynamics in the case under study is determined by the vapour pressure of the liquid surrounding the target rather than the surface tension gradient along the melt surface. Since the dimension of the vapour cloud above the molten layer depends on its area and hence on the diameter of the laser beam on the target surface, the structure period upon in-liquid ablation is defined precisely by the geometrical radiation parameters. For a laser ablation of easily melted metals (lead, tin), the relief on the melt surface is formed due to recoil pressure of the vapour of the target itself [22, 23]. In our case, all the targets investigated possess a high melting temperature, with the result that the vapour pressure of the target itself is significantly lower than the vapour pressure of the ambient liquid in which the target is immersed.

One can assume that the linear dependence of the period on the laser beam diameter will no longer hold for large diameters due to the development of small-scale instabilities with a short lateral dimension within the laser spot.

The periodic microstructure formation can substantially change the distribution of laser radiation intensity on the target. Unlike the laser irradiation of a plane target surface under a liquid layer, the exposure of a developed surface (the surface with a periodic structure) to laser radiation leads to the localisation of radiation in the structure channels. In a narrow dagger-like melting channel, the light undergoes multiple reflections from the side faces of the structure to be totally absorbed by the wall material and the medium located in the channel. The absorption of the laser beam energy by the channel walls gives rise to high pressure and a temperature above 1000 °C. In the small channel volume, the substance of the liquid can therefore pass to a supercritical state, which may change the properties of the nanoparticles produced upon laser ablation.

The features of the structures observed on a copper substrate are supposedly related to its high thermal conductivity (352 W m^{-1} K^{-1}), which significantly increases with a decrease in the temperature compared to other metals investigated (for brass and tungsten it is equal to 120 and 118 W m^{-1} K^{-1} for 1000 K) [36]. As a result, in the case of a copper substrate a thinner molten layer will form and its recrystallisation time will be shorter than for brass or bronze substrates. That is why in the case of copper one would expect a very narrow dagger-like melting channel.

The dependence of the structure period on the beam diameter in vacuum is different from this dependence in the case of in-liquid ablation. The structure period in the case of in-vacuum ablation is related to the capillary properties of the melt. Upon in-liquid ablation with a low (compared to the ablation rate) scanning velocity, within the laser beam, a channel is produced with steep slopes, which reflect the laser radiation towards its bottom. As a result, the target melting at the slope almost ceases and the laser beam is captured in the hole. A new hole begins to form only when the major part of the scanning beam leaves the previous hole.

The absence of structures on a brass target irradiated in vacuum is possibly explained by the selective removal of zinc, which has a lower specific evaporation heat. Upon ablation under a liquid, zinc is primarily retained in the target due to a high vapour pressure of the ambient liquid.

5. Conclusions

We have shown that the ablation of metal targets under a liquid layer results in the formation of periodic structures. They are microcones with sharpened tips and are separated by long narrow channels directed into the target material. A distinctive feature of the structures is the dependence of their period on the laser beam diameter. The formation of these structures may affect the characteristics of nanoparticles produced in the liquid in this case, which invites additional investigations. The formation of periodic structures should be taken into account when employing in-liquid laser ablation of solids as a method for decontamination of radiation-polluted surfaces.

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References

1. Shafeev G.A., Simahkin A.V. *Appl. Phys. A*, **54** 311 (1992).
2. Brook M.R., Shafeev G.A. *Appl. Surf. Sci.*, **54**, 336 (1992).
3. Simakin A.V., Shafeev G.A. *Laser Phys.*, No 3, 610 (1994).
4. Simahkin A.V., Shafeev G.A. *Appl. Surf. Sci.*, **86**, 422 (1995).
5. Shafeev G.A., Bellard L., Themlin J.-M., Fauquet-Ben Ammar C., Cros A., Marine W. *Appl. Phys. Lett.*, **68** (6), 773 (1996).
6. Dolgaev S.I., Lyalin A.A., Shafeev G.A., Voronov V.V. *Appl. Phys. A*, **63**, 75 (1996).
7. Dolgaev S.I., Voronov V.V., Shafeev G.A., Fauquet-Ben Ammar C., Themlin J.-M., Cros A., Marine W. *Appl. Surf. Sci.*, **109-110**, 559 (1997).
8. Shafeev G.A., Obraztsova E.D., Pimenov S.M. *Appl. Phys. A*, **65**, 29 (1997).
9. Sibbald M.S., Chumanov G., Cotton T.M. *J. Phys. Chem.*, **100**, 4672 (1996).
10. Yeh M.-S., Yang Y.-S., Lee Y.-P., Lee H.-F., Yeh H.-F., Yeh C.-S. *J. Phys. Chem. B*, **103**, 6851 (1999).
11. Kamat P.V., Flumiani M., Hartland G.V. *J. Phys.Chem. B*, **102**, 3123 (1998).
12. Takami A., Kurita H., Koda S. *J. Phys. Chem. B*, **103**, 1226 (1999).
13. Link S., Burda C., Nikoobakht B., El-Sayed M.A. *J. Phys. Chem. B*, **104**, 6152 (2000).
14. Dolgaev S.I., Simakin A.V., Voronov V.V., Shafeev G.A., Bozon-Verduraz F. *Appl. Surf. Sci.*, **186**, 546 (2002).
15. Simakin A.V., Voronov V.V., Shafeev G.A., Brayner R., Bozon-Verduraz F. *Chem. Phys. Lett.*, **348**, 182 (2001).
16. Anikin K.V., Melnik N.N., Simakin A.V., Shafeev G.A., Vitukhnovsky A.G. *Chem. Phys. Lett.*, **366**, 357 (2002).
17. Bozon-Verduraz F., Brayner R., Voronov V.V., Kirichenko N.A., Simakin A.V., Shafeev G.A. *Kvantovaya Elektron.*, **33** (8), 714 (2003) [*Quantum Electron.*, **33** (8), 714 (2003)].
18. Simakin A.V., Voronov V.V., Kirichenko N.A., Shafeev G.A. *Appl. Phys. A*, **79**, 1127 (2004).
19. Kazakevich P.V., Voronov V.V., Simakin A.V., Shafeev G.A. *Kvantovaya Elektron.*, **34** (10), 951 (2004) [*Quantum Electron.*, **34** (10), 951 (2004)].
20. Landau L.D., Lifshits E.M. *Fluid Mechanics* (Oxford: Pergamon Press, 1987).
21. Brailovskii A.B., Dorofeev I.A., Ezerskii A.B., Ermakov V.A., Luchin V.I., Semenov V.E. *Zh. Tekh. Fiz.*, **61** (31), 129 (1991).
22. Ageev V.P., Gorbunov A.A., Konov V.I. *Kvantovaya Elektron.*, **16** (6), 1214 (1989) [*Sov. J. Quantum Electron.*, **19** (6), 785 (1989)].
23. Ursu I., Mihailescu I.N., Popa Al., Prokhorov A.M., Ageev V.P., Gorbunov A.A., Konov V.I. *J. Appl. Phys.*, **58** (10), 3909 (1985).
24. Golubev V.N., Dorofeev I.A., Libenson M.N., Luchin V.I. *Pis'ma Zh. Tekh. Fiz.*, **17** (24), 67 (1991).
25. Brailovsky A.B., Gaponov S.V., Luchin V.I. *Appl. Phys. A*, **61**, 81 (1995).
26. Sanchez F., Morenza J.L., Aguiar R., Delgado J.C., Varela M. *Appl. Phys. Lett.*, **69** (5), 620 (1996).
27. Her T.-H., Finlay R.F., Wu C., Deliwala S., Mazur E. *Appl. Phys. Lett.*, **73** (12), 1673 (1998).
28. Pedraza A.J., Fowlkes J.D., Lowndes D.H. *Appl. Phys. Lett.*, **74** (16), 2322 (1999).
29. Voronov V.V., Dolgaev S.I., Lavrishchev S.V., Lyalin A.A., Simakin A.V., Shafeev G.A. *Kvantovaya Elektron.*, **30**, 710 (2000) [*Quantum Electron.*, **30**, 710 (2000)].
30. Voronov V.V., Dolgaev S.I., Lavrischev S.V., Lyalin A.A., Simakin A.V., Shafeev G.A. *Phys. Vibrations*, **7** (3), 131 (2000).
31. Voronov V.V., Dolgaev S.I., Lavrischev S.V., Lyalin A.A., Simakin A.V., Shafeev G.A. *Appl. Phys. A*, **73**, 177 (2001).
32. Simakin A.V., Voronov V.V., Shafeev G.A. *Proc. SPIE Int. Soc. Opt. Eng.*, **5121**, 103 (2003).
33. Emel'yanov V.I. *Kvantovaya Elektron.*, **28** (1), 2 (1999) [*Quantum Electron.*, **29** (7), 561 (1999)].
34. Emel'yanov V.I., Karimov I.M. *Pis'ma Zh. Tekh. Fiz.*, **31**, 84 (2005).
35. Bunkin F.V., Tribel'skii M.I. *Usp. Fiz. Nauk*, **130**, 2 (1980).
36. Grigor'ev I.S., Meilikhov E.Z. (Eds) *Fizicheskie velichiny. Spravochnik* (Handbook of Physical Quantities) (Moscow: Energoatomizdat, 1991).