

# Laser purification of ultradispersed diamond in aqueous solution

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**Abstract.** The effect of pulsed radiation from a 2.92- $\mu\text{m}$ , 130-ns  $\text{Cr}^{3+} : \text{Yb}^{3+} : \text{Ho}^{3+} : \text{YSGG}$  holmium laser and a 510-nm, 20-ns copper vapour laser on an aqueous suspension of ultradispersed diamond is studied. X-ray photoelectron spectroscopy and electron energy loss spectroscopy revealed that exposure of the suspension to holmium laser radiation reduces the concentration of nondiamond carbon impurity in it. This is due to the dissolution of carbon impurity in supercritical aqueous solution, caused by radiation absorption. Dissolution of the nondiamond fraction may serve as an indicator of the solution being in the supercritical state as a result of laser irradiation of liquids. This process can be used for efficient purification of ultradispersed diamonds.

**Keywords:** ultradispersed diamond, holmium laser, supercritical aqueous solution.

## 1. Introduction

Water and aqueous solutions in the supercritical state have special physicochemical properties. For example, they dissolve substances that are insoluble under normal conditions [1]. This property is used for growing single crystals from aqueous solutions in autoclaves [1, 2]. In recent years, the interest in such dissolution processes has increased considerably due to the problem of utilisation of radioactive wastes. Dissolution in supercritical solutions can be used conveniently for cleaning of substances in the form of suspensions because of their high surface area per unit volume.

One of the most important conversion problems considered in recent years is the purification of ultradispersed diamonds (UDDs) obtained by explosion synthesis [3]. UDDs are nanoparticles of crystalline diamond covered by carbon in a nondiamond phase, as well as by other substances deposited on them during synthesis. The pres-

ence of a shell around diamond nanoparticles makes it difficult to fully use the potentialities of this material for a number of possible applications, for example, for obtaining diamond ceramics with an extremely high thermal conductivity. Moreover, a clean surface of UDDs is necessary for their metallisation in the development of electrochemical electrodes [4]. In this connection, the cleaning of UDDs is an important applied problem.

Liquid-phase oxidation at high temperatures and pressures in autoclaves is the most widely used method of chemical purification. Most of the known materials are soluble in water and aqueous solutions of electrolytes at elevated temperatures and pressures. Diamond and Teflon are the only exceptions; hence, the use of autoclave cleaning of UDDs is a quite natural solution to this problem. Nondiamond carbon constituting about 10% of the mass obtained by exploding the diamond charge may be soluble in water, while diamond nanoparticles are not. However, the pressures and temperatures attained in autoclaves are relatively low in view of finite mechanical strength of structural materials and their low corrosion resistance. On the other hand, high temperatures and pressures can be attained in a liquid exposed to laser radiation at a wavelength falling in the absorption band of the liquid [5, 6]. The pressures and temperatures attained in this case may considerably exceed the critical values.

If a sufficiently high energy is imparted to a liquid, its heating occurs against the background of formation of an expanding vapour–gas cavity in it [7–9] accompanied by the development of instability in the plane evaporation front [10]. Obviously, such a process is essentially unsteady since the temperature and pressure in the cavity remain high only for a short time determined by the duration of the laser pulse and the experimental geometry. Direct measurements in this region are complicated in view of complexity of the method for measuring temperature and pressure with a high spatial and temporal resolution. It can be stated, however, that the amplitude of the pressure pulse in a liquid lies in the range of kilobars while the temperature is in excess of the critical value.

Despite the fact that the critical point for aqueous solutions is displaced towards higher pressures and temperatures as compared to the corresponding values for water ( $T_{\text{cr}} = 647 \text{ K}$ ,  $p_{\text{cr}} = 22 \text{ MPa}$  [11]), laser radiation makes it possible to obtain supercritical parameters of aqueous solutions for the entire vessel being at nearly room temperature, which considerably simplifies the experiment. The part of the UDD situated in the vapour–gas cavity at the instant of the pulse can be cleaned efficiently from impurities

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as they are dissolved in supercritical water. On completion of the laser pulse, the temperature and pressure in the liquid rapidly relax to their initial values and the dissolved contaminations appear in the form of suspension depending on their solubility at room temperature, or are converted into gaseous phase. Before the onset of the next pulse, the solution is replaced due to convective motion of the liquid caused by its nonuniform heating.

Water and aqueous solutions can be transferred to supercritical state under the action of laser radiation through a proper choice of the laser wavelength and pulse duration. Water and other hydroxyl-group-containing liquids strongly absorb IR radiation in the wavelength range  $\sim 3 \mu\text{m}$  where they have an absorption coefficient  $\sim 10^4 \text{ cm}^{-1}$  [12]. Several laser radiation sources are available in this range, e.g., erbium- or holmium-doped garnet lasers. Lasing in such devices is possible in the  $Q$ -switched mode as well as in free-running mode. The necessary condition for attaining supercritical parameters of the solutions is a short ( $\sim 100 \text{ ns}$ ) laser pulse, since supercritical parameters are not attained in the free-running mode (pulse duration 150–200 ms). This is indicated by the results of investigations of laser ablation of sapphire at its interface with aqueous solutions for various values of the laser pulse duration [13].

In this work, we study the effect of the holmium laser pulses on aqueous suspensions of UDD. It is shown by the results of electron spectroscopic measurements that the fraction of nondiamond carbon is reduced in the irradiated suspension, which is attributed to the attainment of supercritical parameters of the suspension in the laser beam. These results are compared with the data on the exposure of the same UDD suspension to copper vapour pulsed laser radiation in the water transparency region and the purification of UDD in an autoclave.

## 2. Experimental

The starting material in our experiments was an aqueous suspension of UDD, obtained by the explosion synthesis, with a concentration of about 1 g of solid matter in 10 mL of water. The nanoparticles had a characteristic size of about 4 nm. Nitric acid ( $\sim 1 \text{ mL}$  per 10 mL of the solution) was added to the solution before irradiation, and did not have any chemical effect on the charge under normal conditions. Irradiation was carried out in a cell with a fluorite window through which the laser beam was focused on the liquid. A 2.92- $\mu\text{m}$  yttrium-scandium-gallium-garnet holmium  $\text{Cr}^{3+} : \text{Yb}^{3+} : \text{Ho}^{3+} : \text{YSGG}$  laser was used in the experiments.  $Q$ -switching was produced using a  $\text{LiNbO}_3$  crystal [14]. The pulse energy was 10 mJ, the pulse duration was  $\tau \sim 130 \text{ ns}$ , and the pulse repetition rate was  $f = 1 \text{ Hz}$ . The energy density at the beam focus amounted to  $10 \text{ J cm}^{-2}$ . The suspension was irradiated by 30000 laser pulses.

A 510-nm, 20-ns copper-vapour laser with a pulse repetition rate of 10 kHz was also used for irradiation of the suspension. The energy density in this case was  $2\text{--}3 \text{ J cm}^{-2}$  and the number of laser pulses was  $\sim 300000$ . After irradiation, the suspension was settled until a sediment appeared. The liquid was then decanted and the residue was washed again in distilled water. After multiple cleaning cycles and final decantation of the liquid, the residue was dried.

It is well known that the treatment of UDDs in aqueous solutions of nitric acid at critical temperatures and pressures is the most widely used method for practical applications [3]. For this reason, UDD powder cleaned in dilute nitric acid in an autoclave at  $300^\circ\text{C}$  was used as a reference sample.

Before and after processing, the samples were subjected to X-ray electron spectroscopy, the spectroscopy of characteristic electron energy loss, Raman spectroscopy ( $\text{Ar}^+$  laser  $\lambda = 514 \text{ nm}$ ), as well as X-ray diffraction analysis. The electronic structure of samples was determined by processing spectra by the technique described in [15].

## 3. Experimental results

In the absence of irradiation, no changes were observed in the UDD composition in dilute nitric acid under normal conditions. After irradiation by holmium laser or processing in an autoclave, UDD powder changed its colour from dark-grey to light-grey. The irradiation of the suspension by a copper-vapour laser did not cause any change in colour.

Figure 1 shows a typical X-ray diffraction pattern of the initial UDD. Three characteristic diffraction maxima at  $2\theta = 44^\circ$ ,  $75^\circ$ , and  $91.5^\circ$  corresponding to reflections (111), (220), and (311) from a diamond-type lattice are observed against the diffuse background. After irradiation by a Ho laser and processing in an autoclave, the diffuse background decreased insignificantly as compared to that for the initial sample. Raman spectra of the initial sample as well as the processed material displayed a broad luminescence background against which the UDD lines ( $1320\text{--}1332 \text{ cm}^{-1}$ ) were indistinguishable.

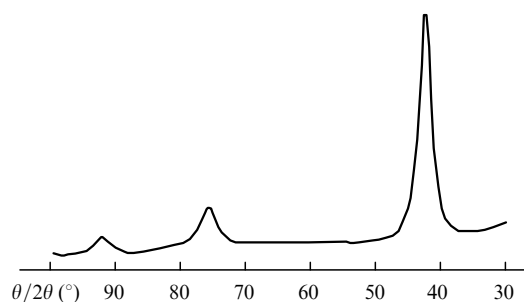
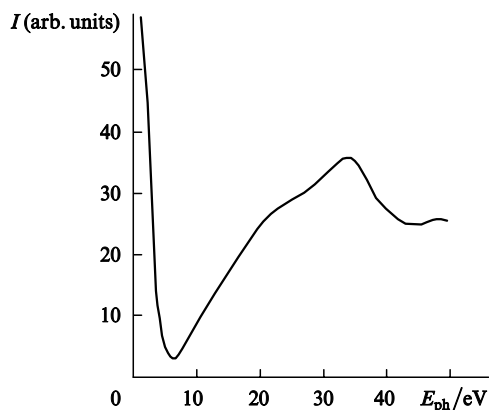


Figure 1. Diffraction pattern of UDD.

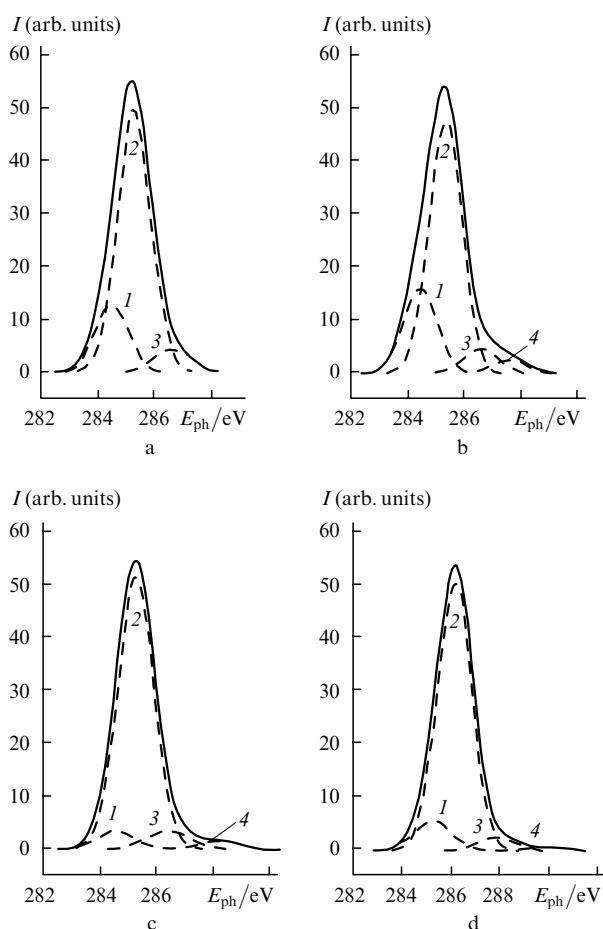
The electron-spectroscopy methods of analysis reveal a typical composition of the initial powder in which the diamond fraction of carbon prevails. The spectrum of characteristic electron energy losses in the samples did not change as a result of laser irradiation and remained the same as the characteristic spectrum for diamond (Fig. 2).

Figure 3 shows the spectra of UDD X-ray photoelectrons before and after laser irradiation and treatment in an autoclave, which are decomposed into the binding energy components. It can be seen from Fig. 3b that irradiation of UDD by a copper vapour laser leads to an increase in the peak height corresponding to graphite-like phase ( $sp^2$  bonding), while other components remain unchanged. After irradiation by the Ho laser (Fig. 3c), the height of the peaks whose intensity is determined by the amount of nondiamond carbon decreases. This is manifested most strongly for the



**Figure 2.** Spectrum of photoelectron energy losses  $E_{ph}$  in a UDD after laser irradiation of its suspension.

peak of the graphite-like phase, while the peak associated with the phase with carbon-oxygen bonds is lowered only slightly. Such a spectrum was observed after processing of UDD in an autoclave (Fig. 3d). The intensity of the peak



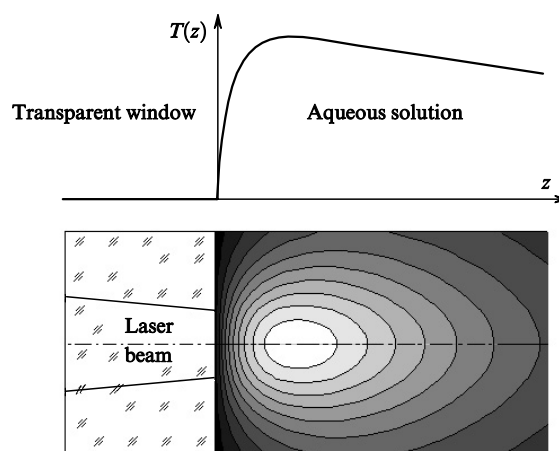
**Figure 3.** Binding energy distribution of C 1s photoelectrons in UDD in the initial sample (a), after irradiation by copper vapour laser (b), and by holmium laser (c), as well as after its processing in an autoclave (d). The main peak (solid curve) is decomposed into components (dashed curves) corresponding to the graphite-like (1) and diamond (2) phases, as well as to the phase with the carbon-oxygen bond (3), and a satellite peak associated with the spectrum asymmetry (4).

associated with the diamond phase ( $sp^3$  bonding) remained virtually unchanged in all cases. The lowering of the peaks can be attributed to cleaning of the diamond nanoparticle surface from the impurity phase. The increase in the height of the peak corresponding to graphite-like phase as a result of irradiation by copper-vapour laser may be due to laser-induced graphitisation of diamond [16]. The fact that UDD does not exhibit graphitisation under the given conditions is primarily associated with a small diamond absorption coefficient at laser wavelength of  $2.92 \mu\text{m}$ . It should be noted that, within the sensitivity limits of measurements, traces of nitrogen are absent in UDD subjected to laser irradiation.

#### 4. Discussion of results

The idea of cleaning of nanodispersed diamond from carbon impurity in a supercritical liquid is based on a considerable difference in their solubilities in such liquids. The supercritical state appears in the experiments in the region of laser heating of a strongly absorbing liquid like the aqueous suspension of UDD for laser radiation with  $\lambda \approx 3 \mu\text{m}$ . Laser heating of the transparent window-absorbing liquid interface is characterized by a highly nonsymmetric temperature distribution relative to the interface. Such a distribution is caused by a difference in the thermal conductivities of the media (about two orders of magnitude) [17]; namely, the suspension is heated to high temperatures, while the transparent window remains virtually cold.

Figure 4 shows the temperature distribution at the interface between the media in the case of pulsed laser heating. This distribution is obtained by solving the thermal conductivity equation [18]. The heated region can be treated as a microscopic-size autoclave formed in the suspension during the action of the laser pulse. The microscopic autoclave, situated near the window through which radiation is introduced, is not in thermal contact with the cold substrate, and cold layers of the surrounding liquid serve as its walls. During the action of the laser pulse, intense



**Figure 4.** Characteristic temperature distribution emerging in the liquid subjected to pulsed laser irradiation of the transparent window-liquid suspension of UDD interface. The solid lines in the aqueous solutions are isotherms. The darkening gradient conventionally represents the temperature distribution (lighter regions correspond to higher temperatures).

dissolution of carbon impurity phases takes place in this autoclave in the supercritical aqueous solution. It is well known that the solubility in supercritical aqueous solutions increases considerably when electrolytes are added to them. In our experiments, we used nitric acid as the solvent which dissolves and oxidises the carbon impurity.

Let us estimate the temperature and pressure attained in such an autoclave under the action of a 10-mJ Ho laser pulse. The radiation absorption coefficient of the aqueous solution is  $\alpha \sim 10^4 \text{ cm}^{-1}$  and radiation is almost completely absorbed in a liquid layer of thickness 1  $\mu\text{m}$ . The characteristic transverse size of the irradiation region ('microautoclave') is  $\sim 100 \mu\text{m}$ . However, the longitudinal size of the supercritical region cannot be taken equal to the radiation absorption depth  $\alpha^{-1}$ . A liquid layer of such a thickness remains superheated only for a time period required by the pressure wave to pass through this layer. In the conditions of our experiment, this period is several orders of magnitude smaller than the laser pulse duration. After the termination of the pulse, the water temperature remains high as before (tens of times higher than the boiling point of water under normal pressure), while the pressure remains close to atmospheric. This leads to the formation of a vapour cavity in the liquid. Since the laser pulse is still active at this stage, evaporation will take place from the interface between the cavity and the liquid.

It was shown in [7–9] that the action of a laser pulse with  $\lambda \simeq 3 \mu\text{m}$  on water and other liquids with hydroxyl groups is accompanied by the formation of a cavity in the irradiation region, propagating along the laser beam axis. The cavity is formed under the action of the recoil vapour pressure from the evaporated liquid. The rate of cavity formation depends on the laser beam intensity and cannot exceed the velocity of sound in the liquid. The justification of such an assumption is provided by the data presented in [19], where radiation of wavelength  $\lambda \simeq 3 \mu\text{m}$  and  $\tau = 130 \text{ ns}$  passed through a layer of thickness 100  $\mu\text{m}$ . Connecting the pulse transmission with the formation of an extended cavity (channel) in this layer under the action of a laser beam, we can estimate the average velocity of its propagation as  $10^3 \text{ m s}^{-1}$  (i.e., of the order of the velocity of sound in water). Taking the maximum possible velocity (i.e., the velocity of sound  $V_s$  in water) as the velocity of the cavity, we obtain the following estimate for the length of the cavity formed under the action of the laser pulse:  $V_s \tau = 1.5 \times 10^3 \text{ m s}^{-1} \times 1.3 \times 10^{-7} \text{ s} \approx 2 \times 10^{-4} \text{ m}$  (200  $\mu\text{m}$ ). Water in a cavity of characteristic size 100  $\mu\text{m} \times 100 \mu\text{m} \times 200 \mu\text{m}$  is heated by a pulse of energy  $10^{-2} \text{ J}$ . By neglecting the heat of evaporation, we find that the temperature in the cavity  $T = 1500 \text{ K}$ , i.e., twice as high as the critical temperature (the specific heat of water is  $4.2 \text{ J g}^{-1} \times \text{K}^{-1}$  and its density is  $1 \text{ g cm}^{-3}$ ). Obviously, the temperature will be lower if we take into account the losses associated with evaporation of the liquid.

The pressure  $\Delta p$  emerging in the suspension is estimated under the assumption that this pressure is the result of thermal expansion the substance. We use the formula  $\Delta p = \Gamma E/V$  [5], where  $E$  is the energy ( $10^{-2} \text{ J}$ ) supplied to the volume  $V$  ( $100 \mu\text{m} \times 100 \mu\text{m} \times 200 \mu\text{m}$ ) and  $\Gamma$  is the Grüneisen coefficient (equal to  $0.09 \text{ Pa m}^3 \text{ J}^{-1}$  for water). The pressure  $\Delta p$  in the channel attains values up to  $5 \times 10^8 \text{ Pa}$  (5 kbar) and is higher than the critical pressure by more than an order of magnitude. Although the radiation-induced phase transition of the substance is not taken into

account in the estimates of temperature and pressure, these estimates indicate the possibility of attaining the supercritical conditions in the region being heated.

The above estimates are in good agreement with the data on the variation of the UDD composition upon irradiation of its aqueous suspension. Indeed, a considerable change in the carbon peak components C 1s under irradiation of this suspension points toward the predominant dissolution of the nondiamond components of UDD, which may be due precisely to their dissolution in a supercritical aqueous solution. No noticeable variations in the diamond component are observed, which is also characteristic of dissolution in supercritical water. The variation of the UDD composition after irradiation can be treated as an indication that the solution is in the supercritical state. It should be noted that laser cleaning is a highly effective process: formally, the total duration for which the suspension has supercritical parameters (total duration of all laser pulses) is of the order of  $10^{-2} \text{ s}$ .

The fact that irradiation of the UDD suspension by a copper-vapour laser does not cause any changes in UDD indicates that water does not pass to the supercritical state under the action of radiation. Indeed, water itself is transparent in the visible spectral range, while the carbon layer around UDD particles absorbs too little laser energy to heat the surrounding liquid to the critical temperature.

## 5. Conclusions

We have shown experimentally that the graphite fraction in UDDs decreases when their suspension in water and in an aqueous acid solution is exposed to laser radiation whose wavelength lies in the region of valence vibration band of water. This decrease is attributed to the formation of a region in the solution, in which water has supercritical parameters. A realistic estimate of water temperature in the region exposed to a laser beam (about 1500 K) is in good agreement with the preservation of the UDD structure. Previous estimates [14, 19] led to exaggerated values of temperature, at which the UDD structure is completely destroyed. The very fact of cleaning of UDD indicates the attainment of the supercritical state by the liquid. From the point of view of practical applications, laser dissolution has a relatively high cleaning efficiency since laser action leads to supercritical parameters of the substance, which are unattainable under steady-state conditions. The UDD cleaning process may be very efficient at high pulse repetition rates. It can be expected that the process considered in this work will be useful for cleaning that cannot be done by traditional methods.

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