THERMAL EMISSION OF CARBON MICROPARTICLES IN POLYMER MATRICES UNDER PULSED LASER EXCITATION

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Laser-induced incandescence (LII) of carbon microparticle suspensions in high-viscosity media under powerful excitation with a Q-switched neodymium laser has been investigated. The effect of LII buildup was detected, when suspensions of synthetic resins and polymers were irradiated with a sequence of laser pulses. The experimental data testify to an increase of the effective size of emission centers under the action of the laser radiation.

1. Introduction

A lot of publications during the last two decades have been devoted to studying the interaction between carbon microparticles and a powerful pulsed laser radiation (see, e.g., works [1–5]). The lion's share of those works dealt with the researches of carbon suspensions (mainly, aqueous) and soot microparticles in air which are formed as a result of organic fuel combustion.

The interest of researchers in the interaction between soot microparticles in air and a powerful laser radiation follows, to a great extent, from industrial needs for reliable methods for the express control over the processes of burning in thermal engines. The main physical effect, when soot microparticles in air are subjected to the action of the laser radiation, is their warming up to temperatures of about 4000 K. Thermal radiation of microparticles warmed up by a laser beam was coined as laser-induced incandescence (LII), and now this term is standard. An optical LII signal allows the amount of soot in an exhaust or a combustion chamber to be evaluated, which gives valuable information for the operative control over an engine.

The optical properties of aqueous suspensions of carbon microparticles subjected to the pulsed laser excitation were studied in works [6–14]. In aqueous suspensions, a powerful laser radiation is responsible not only for LII but also for the effect of self-induced relaxation of the laser radiation, which was called "optical limiting". Optical limiting is observed experimentally as a substantial reduction of the optical transmittance of a cuvette filled with a suspension, when the laser radiation intensity increases. The main mechanism of the optical limiting in aqueous suspensions is the stimulated scattering. In particular, the laser radiation warms microparticles up to several thousand kelvins, which results in the formation of vapor-filled microbubbles around particles, which intensively scatter the laser light. The main application of the optical limiting effect in suspensions is the protection of optical devices (e.g., photodetectors) from an accidental excess of the laser radiation power above an admissible level within nanoseconds.

Among other effects which accompany the optical restriction and LII in aqueous carbon suspensions, it is worth mentioning the processes of microparticle substance (carbon) evaporation, which results in a reduction of particle dimensions, when the suspension is being subjected to laser irradiation [14].

A special place among the researches of the interaction between a powerful laser radiation with light-absorbing microparticles is occupied by objects, in which microparticles are embedded into solid transparent matrices. Only a few such objects have been discovered to date (for instance, borate glass [15]). In contrast to suspensions, the optical limiting is absent in solid matrices, although LII is observed with confidence and, moreover, without destruction of glass specimens.

In this work, the optical properties of carbon microparticles in condensed media with a large viscosity – such as synthetic resins (epoxy resin), polymer solutions (polystyrene), and water-soluble gels (technical gelatin, agar) – are studied. The high viscosity of the medium substantially reduces the influence of convectional flows on the processes in microparticles under investigation and in their nearest environment, which allows the properties of suspensions to be studied against the laser irradiation dose. In addition, prospects to control the variations of optical properties in such media by means of the laser irradiation become open. At last, the researches of suspensions in matrices with a high viscosity create a bridge for a gradual transition from liquids to solid transparent matrices activated by light-absorbing microparticles which have been investigated extremely weakly to date.

2. Experimental Technique

In this work, carbon microparticles with an average dimension of about 200 nm, which are contained in aqueous suspensions of carbon (ink, gouache), were used for the specimen fabrication. In addition, suspensions were prepared making use of the method of carbon laser ablation under the liquid surface. Ablation was carried out by using a Q-switched neodymium laser. Namely, a piece of a carbon electrode intended for the spectral analysis was embedded into distilled water or epoxy resin, where it was irradiated with a focused laser beam. As a result, a carbon suspension was obtained with the average particle dimension of about 150 nm.

The size of particles in suspensions was monitored by nephelometric measurements. For this purpose, a helium-neon laser with a lasing wavelength of 0.6328 μm was used. The average particle dimension was evaluated by analyzing the asymmetry of the scattering indicatrix and carrying out calculations in the framework of the Mie scattering theory. Additionally, the dimensions of particles were evaluated on the basis of scanning data obtained on a Ntegra Prima Basic atomic-force microscope. Specimens to be scanned were fabricated by evaporating a drop of the aqueous suspension on the surface of chemically polished silicon.

In this work, carbon suspensions were prepared in matrices which can be conditionally divided into two groups. Substances, which contained a significant amount of water, were classed to the first group; these were aqueous solutions of technical gelatin and agar. The second group included epoxy resin and the solution of polystyrene in toluene. All the matrices used were practically transparent in the visible spectral range and had a viscosity high enough that the convection effects in the studied suspensions could be neglected during the period of measurements. Suspensions were stirred at their preparation making use of an ultrasonic device.

Suspensions were irradiated making use of a Q-switched YAG:Nd^{3+} laser (the wavelength was 1.064 μm, the pulse duration was about 25 ns). Simultaneously, the measurements of the suspension glowing intensity were carried out. The power density of laser radiation was about 50 MW/cm^2. The repetition period of laser pulses was varied from 0.5 to 2 s. All measurements were carried out on an automated laser spectrometer, at room temperature, and in glass cuvettes. Suspension incandescence was measured under the conditions of optically thin layer, when the optical density was much less than 1.

In our experiment, the thermal radiation of microparticles consisted of pulses of about 20–30 ns in duration. We experimentally registered the area of those pulses at a fixed wavelength (through a monochromator and making use of a photomultiplier). Oscillographic researches of the shape of nanosecond LII pulses were carried out with the help of a 14ELU-FS photomultiplier (through an optical filter SS-15) and a 6LOR-04 oscillographic recorder with a nanosecond resolution in the single-pulse mode. To initiate the recorder scanning, nanosecond pulses generated by an auxiliary high-speed photocell illuminated with laser radiation were used.

3. Results and Their Discussion

The dependences of the LII intensity at a wavelength of 500 nm on the laser irradiation dose for carbon suspensions in various matrices are shown in Fig. 1. A suspension was irradiated with a sequence of identical laser pulses, and every pulse was followed by the registration of the LII intensity. The laser pulse number N is reckoned along the horizontal axis, and the corresponding LII intensity along the vertical one.

From Fig. 1,*a*, one can see that the first laser pulse excites the most intensive LII in aqueous suspensions with gelatin, and the irradiation by following laser pulses leads to a reduction of the LII intensity. In particular, already after five first pulses of laser irradiation, the incandescence intensity becomes approximately five times lower (Fig. 1,*a*).

A qualitatively different character is observed for the dependence of the LII intensity on the irradiation dose for carbon suspensions in epoxy resin (Fig. 1,*b*) and in a polystyrene solution (Fig. 1,*c*). For instance, in the small-dose section (up to 10 pulses), the LII intensities grow and, when the irradiation dose increases further, fall down. In some suspension specimens, the LII intensity during the second pulse of laser excitation was more than an order of magnitude larger than the LII intensity during the first pulse. To our knowledge, the effect of LII buildup for carbon microparticles in synthetic resins and polymers has been registered by us for the first time.

The effect of LII burning out, which was observed in aqueous suspensions with gelatin (Fig. 1,*a*), completely agrees with the results of works [14, 16]. It can be explained by the evaporation of carbon microparticles warmed up by laser radiation. Due to the evaporation, the dimensions of carbon particles decrease and, respectively, the LII intensity also decreases. In work [14], the carbon evaporation from surfaces of microparticles in aqueous suspensions manifested itself as follows. First, the absorption spectra of irradiated and non-irradiated suspensions were different owing to the absorption by evaporation products. Second, the average size of particles in irradiated suspensions turned out smaller than that in non-irradiated ones. In our work, in contrast to work [14], the introduction of gelatin into the matrix made convection impossible, which allowed us to study the dose dependence of the LII intensity (Fig. 1,*a*) and obtain results, which agree with the model proposed in works [14, 16].

The model that has just been mentioned is capable of explaining practically all regularities of LII and optical limiting in aqueous suspensions. However, it failed in explaining the regularities of the interaction between a powerful laser radiation and the suspensions on the basis of synthetic resins and polymers. For the explanation of the results of experiments depicted in Figs. 1,*b* and *c*, the following speculations are proposed.

In aqueous suspensions, high local temperatures in the vicinity of microparticles mainly result in the evaporation of surrounding water. At the same time, in suspensions with synthetic resins, the crucial role can be played by the thermal decomposition of oligomers in a layer adjacent to a microparticle. It is known that pyrolysis of epoxy resins produces gases (CO_2, CO, H_2, CH_4, and so forth) and nonvolatile carbonized remnants which consist mainly of carbon and, under certain conditions, form porous structures [17–19]. The composition and physical properties of pyrolysis products depend on a lot of conditions, including the heating rate and the maximal temperature. It is logical to suppose that, when being heated by nanosecond laser pulses, the gaseous products of decomposition form small gas-filled blisters, and the condensed products of decomposition can form a porous shell around the microparticle, which is capable of absorbing the laser light and, in its turn, emitting LII. Therefore, it seems probable that the heated suspension particles become absorption centers, each consisting of a carbon nucleus and a light-absorbing shell which is formed from products of the matrix substance decomposition. As the laser irradiation dose grows, the effective dimension of absorption centers, as well as the corresponding buildup of their glowing, increases.

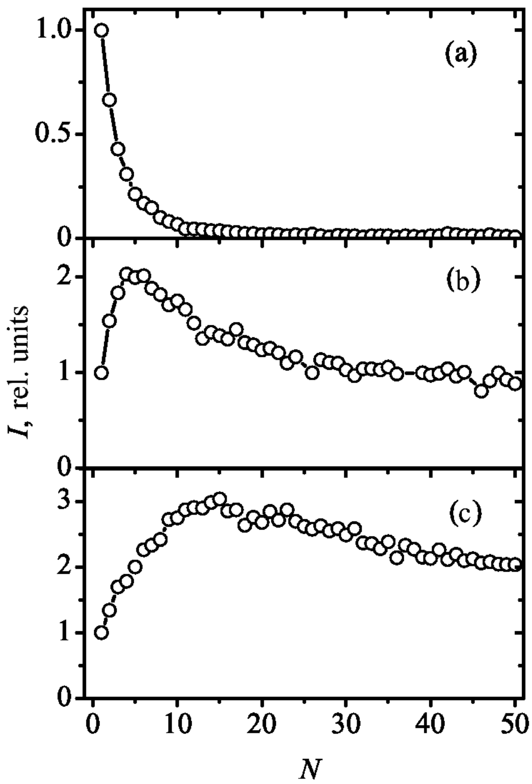

Fig. 1. Dependences of the LII intensity, I, at a wavelength of 500 nm on the laser irradiation dose (i.e. the number of laser pulses in the pulse sequence) for carbon suspensions in the following matrices: (*a*) the aqueous solution of technical gelatin, (*b*) epoxy resin, and (*c*) the solution of polystyrene in toluene

In the case of a monodisperse suspension, the LII intensity measured at a wavelength λ can be presented by the approximate expression

$$I(\lambda) = \text{const} \cdot b(\lambda) \int i_\lambda(T(t))\, dt \Delta\lambda 4\pi R^2 n. \quad (1)$$

Here, the function $i_\lambda(T(t))$ is the spectral density of the incandescence intensity depending on the temperature which, in its turn, varies in the course of time; $\Delta\lambda$ is the spectral interval, where LII signals were registered; n is the number of particles in the volume under consideration; $b(\lambda)$ is the surface emittance of glowing centers at the wavelength λ; and R is the effective radius of a glowing center. Then, it follows that an increase of the LII intensity, which is observed experimentally (Figs. 1,*b* and *c*), can occur owing to an increase of the radius R. Concerning a possible increase of the coefficient b due to laser irradiation, it is worth not-

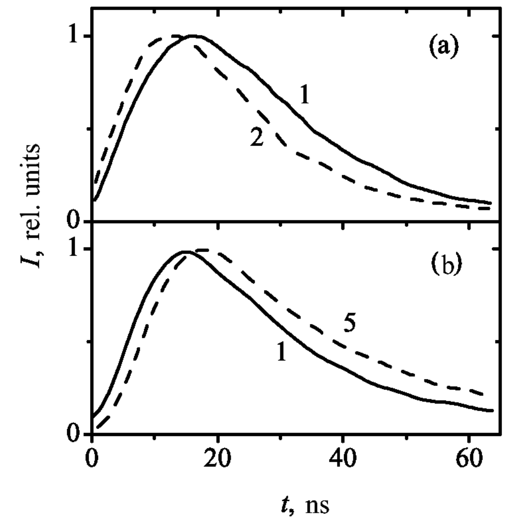

Fig. 2. Oscillograms of LII pulses for carbon suspensions in an aqueous solution of technical gelatin (*a*) and in epoxy resin (*b*). The number near a curve corresponds to the number of a pulse in the pulse sequence

ing that this coefficient cannot exceed 1 (for carbon, it is equal to $0.8 - 0.9$ [20]), which does not enable one to explain the manifold growth of the LII intensity under laser irradiation, which is observed in experiment.

An important factor that affects the LII signal is the temperature of microparticles heated up by laser radiation. It is very difficult to calculate the dependence of the microparticle temperature at pulsed laser excitation on the particle dimension with a sufficient accuracy, because the energy balance for a particle in a laser field is governed by several physical processes which are difficult for simulation. The energy inflow into the particle can be evaluated in the first approximation by calculating the cross-section of light absorption following the Mie theory. At the same time, the processes associated with the energy losses by the particle practically cannot be calculated exactly. For instance, the heat emission from a particle into its environment cannot be calculated correctly owing to the lack of knowledge concerning the scenario of phase and chemical transformations in the particle vicinity. Hence, to analyze possible variations of the temperature of a particle subjected to the action of laser radiation due to the growth of its dimensions, we took advantage of the following semiquantitative reasoning. At rather a low intensity of laser radiation, when the mechanism of particle substance evaporation does not yet dominate in particle energy losses, the simplified equation of energy balance can be expressed in the following form (similarly to what was done in work [16]):

$$\sigma F \tau_{\mathrm{i}} = C(T - T_0) + \mathrm{const}(T - T_0)R^2, \qquad (2)$$

where σ is the cross-section of laser light absorption, F is the laser radiation intensity, τ_i is the laser pulse duration, C is the heat capacity of a microparticle (the absorption center), and T and T_0 are the temperatures of a microparticle and the environment, respectively. In Eq. (2), the left-hand side corresponds to the absorption of laser radiation by a microparticle. The first term corresponds to the growth of the particle internal energy, and the second describes the process of heat emission into the environment through the particle surface. Since the absorption cross-section σ is approximately proportional to the square of the particle radius, R^2, and its heat capacity to R^3, it follows from Eq. (2) that, at fixed F, particles with larger radii would be heated up to lower temperatures.

To confirm this conclusion, we measured the initial section of the dependence depicted in Fig. 1,*b* simultaneously at three fixed wavelengths of LII emission: 400, 500, and 600 nm. The experiments showed that, in the course of the laser irradiation dose accumulation in the section of the LII buildup, the relative contribution of the long-wave part of the glowing spectrum appreciably grows in comparison with that made by its short-wave part, which evidences for a reduction of the particle temperature, driven by an increase of the particle dimension. Therefore, two factors which affect the amplitude of an LII signal registered in experiment can be distinguished. The first factor is the effective dimension of particles, whose growth results in the increase of the LII intensity. The second factor is the particle temperature which decreases to a certain extent owing to the action of the first factor. Due to a competition between those two factors, the initial growth of the LII intensity transforms into its reduction as the laser irradiation dose increases (Figs. 1,*b* and *c*).

According to Planck's formula for thermal radiation emission, the glowing intensity at a fixed wavelength strongly depends on the body temperature. At temperatures of the order of a few thousand kelvins, this dependence can be approximated by a power-law function with the exponent ranging from 2 to 5 [10]. Hence, even an insignificant reduction of the microparticle temperature can produce an appreciable quenching of LII. In addition, the reduction of the LII intensity observable in experiments at high doses (Figs. 1,*b* and *c*, $N > 20$) can also be caused by a reduction of the laser excitation intensity owing to the scattering by transformed absorption centers.

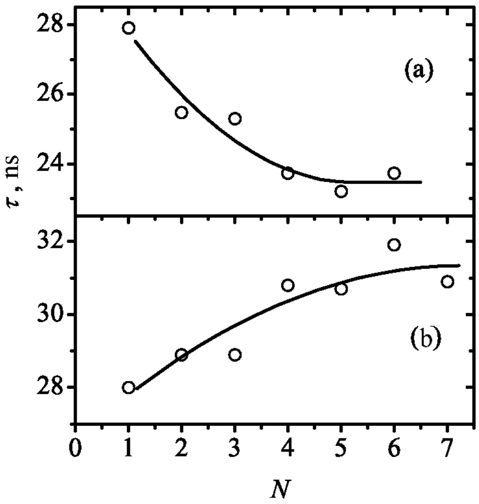

Fig. 3. Dependences of the LII pulse duration τ on the laser irradiation dose for carbon suspensions in an aqueous solution of technical gelatin (a) and in epoxy resin (b)

An additional argument that testifies to the increase of the effective dimension of LII centers under laser irradiation is presented by the results of studies of the influence of laser radiation on the LII pulse duration. Figure 2 demonstrates the typical oscillograms of LII pulses, and Fig. 3 shows the dependences of the pulse duration of LII (at a level of 0.5) on the laser irradiation dose. From the figures, one can see that the laser radiation brings about an appreciable reduction of the glowing pulse duration in the case of aqueous suspensions with gelatin (Figs. 2,a and 3,a), which is explained by a reduction of the microparticle dimension in suspension as a result of the evaporation of particles. On the contrary, in the suspensions on the basis of synthetic resins, a 10%-growth of τ is observed already after several laser pulses, which is explained by the growth of the effective dimensions of glowing centers. Moreover, together with an increase of the pulse duration τ, a shift of the leading edge of the glowing pulse is observed (Fig. 2,b), which testifies to a delay in the heating of microparticles at the increase of their dimensions.

4. Conclusions

In this work, the regularities in the laser-induced incandescence of carbon microparticles embedded into transparent liquid matrices with a high viscosity have been analyzed. Substantial differences between the behavior of water-containing suspensions and suspensions on the basis of polymeric resins have been revealed. The phenomenon of LII buildup in the course of the laser irradiation dose accumulation in suspensions on the basis of polymeric resins has been observed for the first time. The experimental results can be explained by an increase of the effective sizes of glowing centers subjected to the action of laser radiation.

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ТЕПЛОВЕ ВИПРОМІНЮВАННЯ ВУГЛЕЦЕВИХ МІКРОЧАСТИНОК У ПОЛІМЕРНИХ МАТРИЦЯХ ПРИ ІМПУЛЬСНОМУ ЛАЗЕРНОМУ ЗБУДЖЕННІ

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Р е з ю м е

Досліджено теплове випромінювання в'язких суспензій вуглецевих мікрочастинок під час опромінення потужним випромінюванням неодимового лазера з модуляцією добротності. При опроміненні послідовністю лазерних імпульсів зареєстровано розгоряння теплового випромінювання в суспензіях на основі синтетичних смол та полімерів. Отримані експериментальні дані свідчать про зростання ефективного розміру центрів світіння при лазерному опроміненні.