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Evolution of Laser-Induced Incandescence of Porous Carbon Materials under Irradiation by a Sequence of Laser Pulses

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Abstract

For porous carbon samples made of bio-materials (nutshells) by pyrolysis, laser-induced incandescence is investigated under irradiation by a sequence of pulses of a Q-switched YAG:Nd laser. For the intensity of LII as a function of the laser irradiation dose, two- or three-stage kinetics is observed depending on the incident laser intensity. Physical mechanisms of the observed increase and decrease of LII with the irradiation dose are discussed. The mechanisms include transformations of structure of the irradiated surface layer due to the vaporization of carbon. Besides, the effect of heating of the whole sample on the intensity of LII is also considered.

Keywords: Thermal emission, Laser-induced incandescence, Porous carbon.

1. Introduction

Under irradiation by powerful nanosecond-scale laser pulses, different materials demonstrate transient thermal emission (laser-induced incandescence, LII) in the visible spectral region. For example, LII of aerosol soot particles is a well-known phenomenon, which has promising applications [1–3]. Concerning condensed materials, easily-detectable LII is observed in suspensions of light-absorbing microparticles, including (aqueous) suspensions of carbon black and other pigments (diluted china ink, paints, etc.), natural turbid water with unknown nature of suspended particles, used engine oil, etc [4–7]. Oxide glasses and polymers containing micro-inclusions of carbon (or of other light-absorbing materials) demonstrate LII similar to suspensions [8–10]. Surface layers of various materials with high absorption at a wavelength of laser radiation also can be heated to incandescent temperatures under pulsed laser irradiation [11–15]. In all of the above-mentioned examples, under irradiation by a sequence of powerful laser pulses, the irradiated material becomes transformed with the increase of dose of laser irradiation, and the parameters of LII change from pulse to pulse in the sequence. For example, for aqueous and epoxy carbon suspensions, it was observed [10] that the LII pulse length depends on the number of laser pulses in the irradiating sequence. This fact was interpreted as a consequence of laser-induced change of the average particle size due to the vaporization of carbon (in aqueous suspensions) and due to the pyrolytic decomposition of polymer in the neighbourhood of the particle (in epoxy suspensions). Besides, for surface layers of porous carbon samples, it was revealed that LII pulse length is changing with the increase of dose of laser irradiation due to the complicated processes of transformation of porous structure of the surface layer [14].

In previous works [8, 10, 11], for different materials, the intensity of LII (measured as time-integral of LII pulse) was monitored during the irradiation by a sequence of laser pulses. The experiments [8,10] revealed that some materials demonstrate the decrease of the intensity of LII with the increase of dose of laser irradiation, whereas in other materials LII grows with

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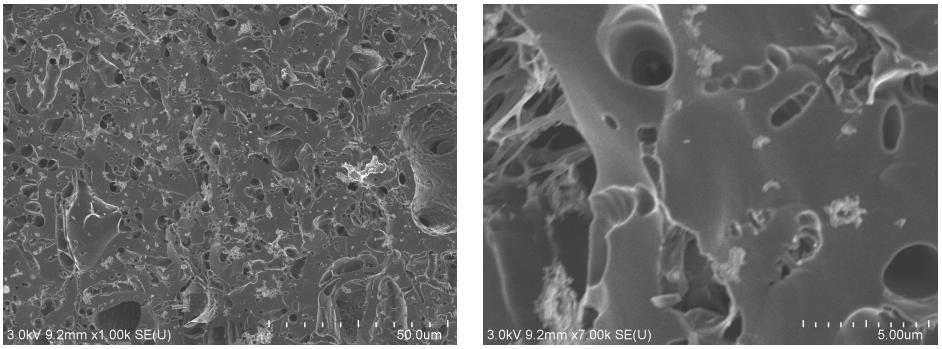

Fig. 1. SEM images of the porous carbon sample.

the dose. Even more, in some cases the increasing irradiation dose causes LII growth followed by LII decrease. Such nonmonotonic behaviour of LII is observed in polymers containing carbon microparticles [10] and in porous surface layers of carbon [11]. For carbon suspensions in transparent polymers, the physical mechanism of the observed growth-and-decay evolution of LII includes pyrolytic transformation of polymer around the laser-heated microparticles, whereas the similar behaviour of LII in porous carbon surface layers is a consequence of transformation of structure of the irradiated layer due to the carbon vaporization, pore expansion, etc.

In the present work, we investigate the evolution of LII of high-porosity carbon samples made of bio-materials (nutshells) by pyrolysis. Complicated structure of such carbon materials is naturally inherited from the morphological properties of the raw material, hence such porous carbon is a promising candidate for various applications. For such porous materials, it is expected that the properties of LII will depend on the structure of the surface layer and on the content of moisture or other substances absorbed in the pores.

2. Methods

Porous carbon samples for measurements of LII were made of walnut shells by heat treatment under the conditions of limited access for air in the electric resistance furnace. The shells were broken into pieces from 0.5 to 1 cm in size and put into the hot furnace in a ceramic crucible covered with a metallic plate. The furnace temperature was set 700°C. Time of heat treatment was set from 0.25 to 1.5 hours. After the heat treatment, the samples were stored in a closed box at room temperature and humidity of approximately 50%. Within several minutes before measurements of LII, the sample was get out of the storage box and broken in two pieces, and the fresh cleavage was irradiated with the laser beam.

SEM images of the sample surface are given in Fig. 1. As is seen from the figure, surface layers of the samples contain a lot of cavities and inhomogeneities of different sizes. For the experiments performed in this paper, an important parameter is the length of temperature diffusion calculated for a time interval of the order of the surface temperature relaxation time. For carbon samples, the mentioned relaxation time can be estimated as several dozens of nanoseconds; hence the temperature diffusion length can be of the order of a micrometer. As is seen from Fig. 1, the irradiated surface contains traces of cavities and other surface inhomogeneities with the sizes comparable with the length of temperature diffusion; hence such surfaces are expected to demonstrate theoretically-predicted peculiarities in LII.

LII was excited by radiation of a Q-switched YAG:Nd^{3+} laser (wavelength 1064 nm, pulse length $\tau \approx 20$ ns, pulse-repetition frequency f from 0.1 to 1 Hz, incident power density I from 10 to 21 MW/cm^2). The pulsed signal of LII was detected by a photomultiplier tube through a single grating monochromator within the spectral interval (600±10) nm. For each laser shot, the PMT pulsed signal was processed with an integrating circuit and digitized with a 10-bit ADC. Hereinafter we denote this time-integrated intensity of LII as I_{LII}. In the experiments, for every laser shot, the laser pulse energy was monitored with a phototube. Every sequence of measurements included 160 laser shots and was performed with a fresh cleavage of the sample. Measurements were conducted at room temperature $T_0 \approx 300$ K and relative air humidity of approximately 50%.

3. Results and Discussion

Under irradiation by a sequence of laser pulses, evolution of the intensity of LII of carbon surfaces is presented in Fig. 2, where the time-integrated intensity of LII is plotted against the number of the laser pulse in the sequence. As is seen from Fig. 2, depending on the laser power density, we can consider two or three stages of evolution of LII with the increase of the laser irradiation dose. The first stage is a relatively quick increase of LII at $N \leq 10$. At this stage, LII increases by more than an order of magnitude during the first 4 to 5 laser shots at the laser power density of 21 MW/cm^2, and approximately 10 shots at 10 MW/cm^2. Such a significant increase of LII can be explained with the use of the following considerations.

Calculations of LII signals were based on a model described in [11, 14, 16]. High-porous carbon material was given as a surface layer with a train of three spherical cavities. An illustration of a model of the high-porous material used for calculations is shown in the insert in Fig. 3. LII was excited by a laser pulse (λ_{laser} = 1064 nm, τ_{laser} = 20 ns) with power density of 10 MW/cm^2. LII signal was calculated within spectral interval of $\Delta\lambda$ = 1 nm, LII detection wavelength was λ = 600 nm. Spherical cavity radius was R = 500 nm, the distance between cavities (cavity-to-cavity thickness) was d = 100 nm. As seen from Fig. 3, a decrease of a depth of pore allocation due to laser-induced evaporation of the roof carbon layer over the cavity leads to an increase in LII signal and can be considered as a one of the reasons of an increase in I_{LII} observed in experiments (Fig. 2).

The second stage of evolution of LII under the laser irradiation is a slight decrease of I_{LII} at N from 10 to 30 (see Fig. 2). This stage is best pronounced at the laser power density 18 and 21 MW/cm^2 (Fig. 2-(c), (d)). The observed decrease of LII with the increase of N can be caused by the processes of opening of pores as a consequence of laser-induced vaporization of the surface layer of the sample. When the cavity opens, it transforms into the pit, and the LII signal decreases. Computer simulations show, that laser-induced opening of undersurface pores can lead to the decrease of LII of the pore area in 4-5 orders (depending on the depth of the pit which arises when the pore opens) [16]. The pore-opening mechanism can be a noteworthy competitor for the above-considered mechanism of laser-induced increase of LII due to the vaporization of roofs of the cavities. The fact, that the second stage of evolution of LII is not observed at $I =$ 10 and 14 MW/cm^2 (Fig. 2-(a),(b)) can be a consequence of competition of the above-mentioned mechanisms of LII at different laser intensities.

Another possible mechanism of the LII decrease with the laser irradiation dose is a characteristic feature of LII of rough surfaces. As is known for rough surfaces [11, 14], laser-induced thermal emission from top areas of the surface relief is dominant. Then, the laser

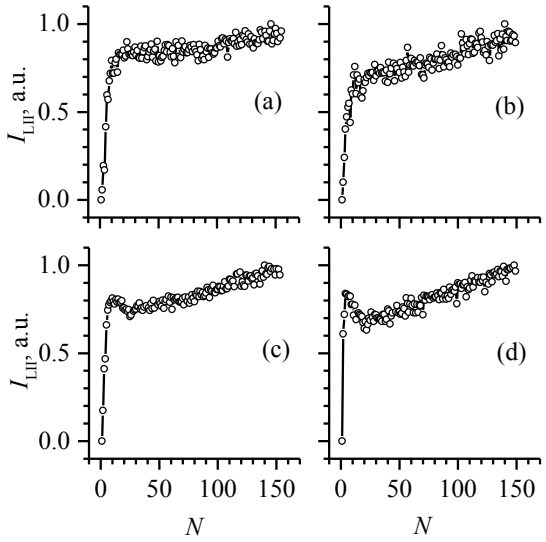

Fig.2. Typical graphs for time-integrated intensity of LII, I_{LII} , as a function of the laser pulse number in the sequence, N, for different laser power densities: $I =$ 10 (a), 14 (b), 18 (c), and 21 MW/cm^2 (d). Laser pulse-repetition frequency $f =$ 1 Hz.

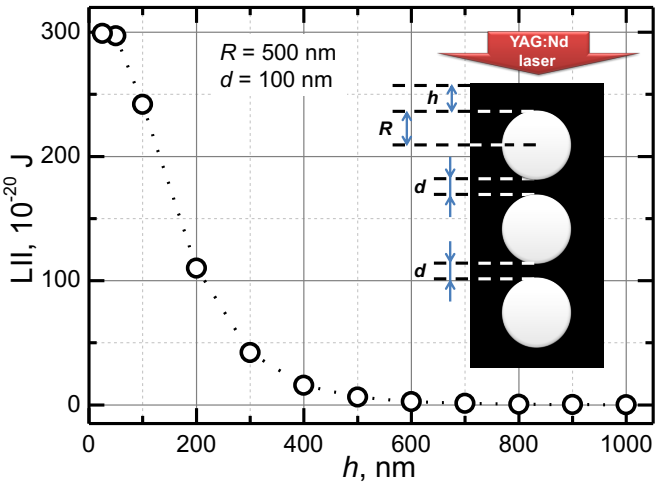

Fig. 3. Dependence of calculated total emitted LII energy (J) over the whole irradiated surface on the height of roof layer over the undersurface cavity (surface-to-cavity thickness) *h* under the action of laser pulses with power density of 10 MW/cm^2.

irradiation causes primary vaporization of these areas, hence with the increase of irradiation dose the roughness height decreases, as well as the LII signal I_{LII} .

Finally, the third stage of evolution of LII under the laser irradiation is a gradual increase of LII at $N > 30$. For understanding this stage, consider the following simple estimate. As far as the thermodynamic parameters of the samples used in this work are unknown, for estimations we use the values, which are typical for similar porous carbon materials [17–19]:

thermal conductivity 0.055 W/m/K, specific heat 1000 J/kg/K, density 180 kg/m^3. For a time interval of Δt =1 s (which corresponds to the laser pulses repetition rate) we estimate the length of propagation of temperature as $\Delta l \approx \sqrt{\frac{\kappa}{\rho C_p}\Delta t} \approx 0.5$ mm. With keeping in mind this estimate, we can consider laser heating of a sample with the thickness Δl under irradiation by a single laser pulse with the power density of I. The increase of the sample bulk temperature after irradiation by a single laser pulse can be estimated $\Delta T = \frac{I\tau}{\Delta l \rho C_p} \approx 20$ K for $I = 10$ MW/cm^2. The obtained value of ΔT is overestimated because the calculation does not account for heat flux from the sample into the surrounding air and to the sample fixtures. Besides, this estimate does not account for temperature dependence of the parameters involved. Nevertheless, it is plausible to suggest that the sample surface temperature can gradually increase from pulse to pulse by at least several Kelvins, and this circumstance should be taken into account in the interpretation of the experimental data.

In the experiments, the maximal surface temperature (which corresponds to the maximum of LII pulse) can be close to the temperature of vaporization of carbon $T_{\max} \approx 4000$ K. Then, according to the approach shown in [13], we can estimate LII signals for the initial sample temperature T_0 and for $(T_0 + \mathrm{d}T)$ as the blackbody emission corresponding to the surface temperature $T_{\max}$ and $(T_{\max} + \mathrm{d}T)$, respectively. Note should be made that here the same value of $\mathrm{d}T$ is used as the increment of T_0 and as the appropriate increase of $T_{\max}$. For example, suppose $T_{\max} = 3900$ K and $\mathrm{d}T = 10$ K; then the increase of I_{LII} due to the increase $\mathrm{d}T$ can be estimated as $I_{\mathrm{LII}}(3910\,\mathrm{K})/I_{\mathrm{LII}}(3900\,\mathrm{K}) \approx 1.027$. This estimate is made with the use of equations described in [13]. As far as the data presented in Fig. 1 give the increase of LII of the order of 30% per 100 laser shots, we can adjust the value of $\mathrm{d}T$ to be equal to 1 K, and then the calculations give us the increase of LII $I_{\mathrm{LII}}(3901\,\mathrm{K})/I_{\mathrm{LII}}(3900\,\mathrm{K}) \approx 1.0027$. This estimate is in agreement with the observed increase of LII at the third stage of its evolution with the increase of laser irradiation dose (see Fig. 2).

For the additional confirmation of the proposed mechanism of LII increase at the third stage of its evolution with the laser irradiation dose, we measured the $I_{LII}(N)$ curves at different rates of the laser pulse repetition. The results are given in Fig. 4, where the graphs correspond to different values of pulse-repetition frequency at a fixed laser power density $I =$ 18 MW/cm^2. As is seen from the figure, at higher interval between the laser pulses the third stage of evolution of LII with N becomes almost flat. This fact is in agreement with the proposed model, which supposes that the sample surface needs time to cool down at the time interval between the laser shots.

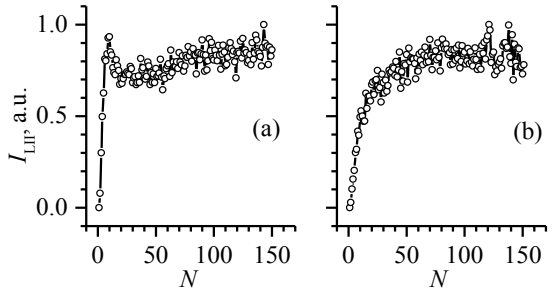

Fig. 4. Time-integrated intensity of LII, I_{LII}, as a function of the laser pulse number in the sequence, N, for pulse-repetition frequency $f = 1$ (a) and 0.1 Hz (b).

4. Conclusion

The experimental results show that porous carbon material demonstrates unexpected behaviour under irradiation by a sequence of laser pulses. To our knowledge, it is the first time we observe the three-stage evolution of LII with the laser irradiation dose. In this paper, plausible explanations are proposed for the observed features of LII. The proposed mechanisms account for separate aspects of interaction of powerful laser radiation with porous media, however, the exact comprehensive model for interaction of porous carbon with pulsed laser radiation is far from being completely developed. The processes resulting in the emission of LII in porous media are complicated and include additional unknown features. For example, the preliminary experiments and computer simulations show that LII of porous carbon can be sensitive to the amount of moisture in the environment where the sample was stored, that makes such materials promising for applications as sensors, and also makes LII promising for monitoring of clogged filtering elements, absorbents, etc.

Acknowledgements

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