THE ROLE OF AIR IN LASER-INDUCED THERMAL EMISSION OF SURFACE LAYERS OF POROUS CARBON MATERIALS

The influence of the surrounding air on the amplitude and shape of thermal radiation pulses (at a wavelength of 430 nm) during the heating of the surface layer of a porous carbon material (to temperatures of the order of 2000–3000 K) by the radiation of a Q-switched neodymium laser is studied. When the pressure of the surrounding air is reduced to forevacuum conditions, the experiments showed a one-and-a-half-fold increase in the amplitude of pulsed signals of thermal radiation and an increase in the decay time of the glow by about a third. Numerical calculations of the dynamics of the temperature field in the surface layer of the material during the irradiation by nanosecond laser pulses are carried out. An improved model is used in the calculations, which accounts for (i) the porosity of the material and (ii) the temperature dependence of the coefficients of thermal conductivity and the heat capacities of carbon and air. To calculate the thermal conductivity of the porous material, a model of a cubic array of intersecting square rods is used. The satisfactory consistency of calculation results with experimental data is obtained. The above-mentioned improvements of the calculation model made it possible to reconcile the estimates of the thermal characteristics of surface layers of carbon, obtained from the emission decay data, with the reference data published in the literature.

Keywords: laser-induced thermal emission, porous carbon, air.

1. Introduction

Laser-induced thermal emission (LITE) is observed, when the surface layers of light-absorbing materials are heated by pulsed or modulated laser radiation [1–9]. If the material has a sufficiently large absorption coefficient at the wavelength of laser radiation, when irradiated with nanosecond laser pulses, surface temperatures of the order of several thousand degrees can be easily reached, which makes it possible to observe thermal radiation in the visible range using highly sensitive and fast photodetectors. This work will consider just this high-temperature LITE.

A characteristic feature of LITE is a wide spectrum and the strongly nonlinear dependence on the intensity of laser excitation [10, 11]. In some cases, when recording LITE at a fixed wavelength (through a monochromator), the dependence of the thermal emission intensity on the intensity of pulsed laser excitation can be approximated by a power function with the index of the order of 10. In addition, it is worth noting that the characteristics of LITE may depend
on external factors (atmospheric pressure, temperature, humidity) [12], on the surface roughness [13–15], and also on the previous history of the laser irradiation of samples [16,17].

LITE was observed on various carbon materials [10–17], as well as on some semiconductors (Si, Ge, GaSb, InSb) [18,19].

Usually, to describe the laser excitation of the thermal radiation of a surface layer, the classical equations of thermal conductivity are used, together with Bouger’s law for laser radiation, which makes it possible to calculate the kinetics of the temperature field in the surface layer of the irradiated material [15,17]. Optical signals of LITE are calculated using Planck’s formula for blackbody thermal radiation. In some cases, processes of melting of the irradiated material are taken into account [19].

Obviously, LITE carries information about the laser-induced processes in the surface layer, as well as about the optical and thermal characteristics of the material. Important information about the process of laser heating of the surface layers of light-absorbing materials is provided by studies of the kinetics of LITE. As a rule, laser pulses of the order of \(10^{-8}\) s are used to produce LITE. With such excitation, in many cases LITE represents pulses with the duration of the order of the duration of the laser pulse.

As is shown in [17], in some cases, a “slow” component is observed at the trailing edge of the LITE pulse, with the decay time several times longer than the duration of the laser pulse. The analysis [17] showed that the duration of the “slow” decay component is determined by the ratio between some optical and thermophysical characteristics of the irradiated material.

According to the results of the study of LITE decay kinetics, unexpectedly low estimates of the thermal conductivity of surface layers of some carbon materials were obtained in [15,17] – of the order of 0.04–0.06 W m\(^{-1}\) K\(^{-1}\). Such low values of the coefficients of thermal conductivity of carbon materials require additional justification. In the course of works [15,17], in this work, the in-depth analysis of the processes of formation of LITE signals is carried out with regard for the porosity of the carbon material and the temperature dependence of its thermal characteristics, which provides the additional confirmation of the conclusions made in [15,17]. In addition, this paper analyzes the effect of air on the kinetics of thermal radiation during the pulsed laser heating of the surfaces of carbon materials. In particular, the calculations involve the presence of air both above the surface of the irradiated sample and inside the pores. It should be noted that the first report on the experimental evidence of the effect of air on the intensity of LITE of surface layers of carbon materials was given in work [12], but the kinetics of the emission was not investigated.

2. Methods

In this work, the experiments used a Q-switched YAG:Nd\(^{3+}\) laser (wavelength 1064 nm) with the pulse duration of \(\tau = 20\) ns in the single-pulse mode with the power density of about 15 MW cm\(^{-2}\). A bell-shaped distribution of the laser radiation power density across the beam was achieved by installing a diaphragm inside the laser cavity. LITE was recorded by a Hamamatsu Photonics H1949-51 photomultiplier through a SS-4 glass filter. The signals of the photomultiplier were recorded by a digital oscilloscope with the bandwidth of 250 MHz.

Measurements were carried out using samples of pharmaceutical activated carbon in the form of tablets. An electron microscopic image of the sample surface is given in [17]. The porosity of the material \(\xi \approx 74\%\) was estimated by measuring the weight and dimensions of the samples. Measurements were made at room temperature. Before the measurements, to remove moisture, the samples were previously kept for 15 min at a temperature of \(\approx 150\) °C. A new sample was used for each series of laser pulses. For measurements, the samples were installed in a 4 × 4 × 3 cm chamber connected to a forevacuum pump, which provided a pressure of \(\approx 0.1\) mm Hg.

The following parabolic one-dimensional heat conduction equation was used for computer modeling:

\[
\frac{\partial}{\partial z} \kappa \frac{\partial T}{\partial z} + S = C \frac{\partial}{\partial t} T, \tag{1}
\]

with the heat source function

\[
S = \alpha F, \tag{2}
\]

where the laser radiation power density \(F\) varies according to the expression

\[
F = F_0 \exp \left( -\alpha z - \left( \frac{1}{\tau} \right)^2 \frac{1}{4 \ln 2} \right). \tag{3}
\]
Here, $\kappa$ is the thermal conductivity, $C$ is the specific heat capacity in J m$^{-3}$ K$^{-1}$, $\alpha$ is the absorption coefficient at the laser wavelength, and $z$ is the coordinate along the laser beam.

Thermal radiation signals were calculated using Planck’s formula for blackbody radiation.

Following the approach proposed in [17], the emission decay curves were approximated by the following function with two exponentials:

$$I(t) = A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right)$$

within the interval of about 500 ns after the laser pulse.

### 3. Results and Discussion

First, consider the following results of computer modeling, which indicate the sensitivity of LITE to small variations of the parameters of the irradiated material. For a hypothetical homogeneous material with $C = 1.18 \times 10^6$ J m$^{-3}$ K$^{-1}$, $\kappa = 0.095$ W m$^{-1}$ K$^{-1}$, and $\alpha = 2.6 \times 10^6$ m$^{-1}$, the value of the maximum surface temperature $T_{\text{max}}$ and the corresponding LITE intensity $I_{\text{max}}$ were calculated for variations of parameters $C \pm \delta C$, $\kappa \pm \delta \kappa$, and $\alpha \pm \delta \alpha$. The results are shown in Table 1, where $T_{\text{max}} = 2500$ K.

As can be seen from Table 1, variations of parameters $C$ and $\alpha$ significantly affect the intensity of thermal emission. This fact gives us reason to assume that LITE of porous materials can be sensitive to the presence of a filler in the pores.

Consider the results of measurements of LITE pulse signals under the conditions of atmospheric air and forevacuum. Figure 1 illustrates the behavior of the emission decay time $\tau_2$ (according to expression (4)) for several samples at the normal atmospheric pressure with an increase in the number of laser pulses in the sequence. As can be seen from Fig. 1, $\tau_2$ changes significantly with the increasing dose of laser irradiation. The reasons for the observed changes are not known for sure. It can be assumed that the mentioned changes can be caused by carbon graphitization processes in the surface layer when heated by the laser radiation, similarly to [20]. With accounting for the results shown in Fig. 1, the further measurements in this work were carried out at $N > 10$.

The experiments also showed that pumping out the air leads to noticeable changes of the intensity $I_{\text{max}}$ and of the shape of LITE pulses. In particular, as a result of pumping out to the forevacuum, the value of $I_{\text{max}}$ increases by 1.5 times, and $\tau_2$ increases by approximately 30–35% compared to the measurements at the atmospheric pressure.

As is shown in [15, 17], the LITE decay curves of various carbon materials contain slow components with the decay time $\tau_2$ of the order of $10^{-7}$ s. This fact makes it possible to estimate the thermal conductivity of surface layers, and the estimates are close to the typical values of the thermal conductivity of gases. Taking this into account, we will analyze the possible role of air that fills the pores and surrounds the sample.

For the thermal conductivity $\kappa$ of a porous carbon material with a filler (air), we use the model of a cubic array of intersecting square rods [21, 22]

$$\kappa_p = \left[\kappa_c + \frac{2\beta(1 + \beta)\kappa_\alpha\kappa_c}{\kappa_\alpha + \beta\kappa_c} + \beta^2\kappa_\alpha\right](1 + \beta)^{-2}, \quad (5)$$

where $\kappa_\alpha$, $\kappa_c$ are thermal conductivities of air and carbon, respectively; $\beta$ is the parameter that depends on the porosity of the material and is determined from
the equation
\[ \xi = 1 - \frac{1 + 3\beta}{(1 + \beta)^3}. \]

For \( \xi = 0.74 \), we get \( \beta = 2 \).

For the specific heat \( C \) and the absorption coefficient \( \alpha \) of the porous material, we use the expressions
\[ C = \xi C_a + (1 - \xi) C_c, \text{ and } \]
\[ \alpha = (1 - \xi) \alpha_c, \]
where \( C_a, C_c \) are the specific heats of air and carbon, respectively, \( \alpha_c = 10^7 \text{ m}^{-1} \) — carbon absorption coefficient. We neglect the absorption of laser radiation in air.

For calculations, the reference data on thermal conductivity and specific heat of air and carbon were represented by analytic expressions in the form of polynomials \( \sum_{i=0}^{5} a_i T^i \). The approximation parameters are shown in Table 2, and the corresponding temperature dependences are shown in Fig. 2.

In the absence of reference data for \( \kappa_a \) in the temperature range of \( >2000 \text{ K} \), an extrapolation was carried out. Regarding the approximation of \( C_a \), data on the temperature dependence of the air density from work [23] were additionally used.

As for the carbon material from which the porous samples are made, its thermal characteristics remain unknown. It can be assumed that, as a result of heating during the irradiation with a sequence of laser pulses, the graphitization of the material occurs in the surface layer, similarly to [20]. Then, to estimate the thermal conductivity \( \kappa_c \), we can use the averaged recommended data from [27] for graphite. Despite the significant scatter of experimental data in [27], it is noted that, at temperatures above room temperature, the thermal conductivity of graphite changes proportionally to \( T^{-1} \). Accordingly, in this paper, the temperature dependence of \( \kappa_c \) is represented by the expression
\[ \kappa_c = \kappa_0 T_0 / T, \] (6)

where \( \kappa_0 \) is the thermal conductivity of carbon at room temperature \( T_0 \). In further calculations, \( \kappa_0 \) is used as a fitting parameter to achieve the consistency of the calculation results with the measurement ones.

The analytic expressions that correspond to the temperature dependences of the thermal characteristics of air and carbon shown in Fig. 2 were used to calculate the shape of LITE signals using Eqs. (1)–(3). In the calculations, the power density of laser radiation \( F_0 \) was adjusted so that the maximum value of the surface temperature \( T_{\text{max}} \) was \( 2500 \text{ K} \), which roughly corresponds to the experimental conditions. The value of the parameter \( \kappa_0 = 4 \text{ W m}^{-1} \text{ K}^{-1} \) was selected based on the best coincidence of the duration \( \tau_2 \) of the slow component of LITE decay with the measurement results. It should be noted that the value \( \kappa_0 = 4 \text{ W m}^{-1} \text{ K}^{-1} \) approximately...
The results of calculations are shown in Fig. 3. Curve 1 in Fig. 3 corresponds to the absence of air both above the surface of the sample and inside the pores. For comparison, Fig. 3 (curve 2) shows the results of calculations for a hypothetical porous medium with a temperature-independent thermal conductivity 0.86 W m$^{-1}$K$^{-1}$ and specific heat $4.53 \times 10^6$ J m$^{-3}$K$^{-1}$, which correspond to the values of $\kappa_c$ and $C_c$ at a temperature of 1400 K (average between 300 K and 2500 K). As can be seen from the figure, the consideration of the temperature dependences of $\kappa_c$ and $C_c$ in the calculations leads to a noticeable lengthening of the emission oscillogram (curve 1 in Fig. 3) compared to the case (curve 2 in Fig. 3), when the material parameters ($\kappa_c$ and $C_c$) do not depend on temperature.

Curve 3 in Fig. 3 is obtained at the presence of air both above the surface of the sample and inside the pores, and the thermal characteristics of air depend on the temperature according to Fig. 2. Comparing oscillograms 1 and 3 in Fig. 3, it can be seen that the presence of air significantly affects both the amplitude and the duration of the emission pulse. Thus, curve 1 in Fig. 3 has $I_{\text{max}}$ 2.15 times greater than curve 3. In addition, $\tau_2$ for curves 1 and 3 are 135 and 72 ns, respectively. The mentioned regularities roughly correspond to the results of experiments: due to air removal, $I_{\text{max}}$ increases by 1.5 times, and $\tau_2$ increases from 100 to 134 ns.

Curve 4 in Fig. 3 corresponds to the hypothetical situation, when air is present only above the sample surface and is absent in the pores. Calculations show that the air above the sample surface causes a decrease in $I_{\text{max}}$ by about 1.32 times (compared to curve 1), and the decay time $\tau_2$ for curve 4 is about 132 ns. Thus, the results of the calculations show that the presence of air above the sample surface has little effect on the decay time $\tau_2$. Besides, it can be expected that, for carbon materials with closed pores, pumping out the air over the sample will affect the magnitude of LITE signals.

Under the pulsed laser heating of surface layers of light-absorbing materials, optical LITE signals are formed in the surface layer with a thickness of the order of $\Delta = \alpha^{-1}$. In addition, an important parameter is the distance that the heat flow travels during the time of the order of the laser pulse duration. This value can be approximately estimated as $\delta = \sqrt{\frac{\Delta}{\tau_i}}$. As is shown in [17], the slow decay component of LITE appears in the materials with a low thermal conductivity, when the depth of penetration of the laser radiation into the material $\Delta$ significantly exceeds the distance of heat propagation during the duration of the laser pulse $\delta$. Herewith, the value of $\tau_2$ is determined by the ratio $\Delta/\delta$. In particular, for
values of $\tau_2$ of the order of 140 ns, the value of $\Delta/\delta$ can be of the order of 10 $[17]$. 

Figure 4 shows the results of modeling the behavior of the $\Delta/\delta$ parameter over time during the laser excitation of LITE without air (corresponding to oscillogram 1 in Fig. 3). As is seen from Fig. 4, at room temperature, $\Delta/\delta \approx 2.7$, which is significantly less than the estimates made in $[15,17]$. With increasing time, as a result of the laser heating of the material, the parameter $\Delta/\delta$ increases to 12–13 in the interval $t = 50–200$ ns, where the slow component of LITE is measured. Thus, the approximate estimates in $[15,17]$ agree satisfactorily with the results of simulations in this work.

It should also be noted, as is shown in $[15,17]$, $\tau_2$ can be affected by the shape of the laser pulse and by the roughness of the irradiated surface, which allows reducing the $\Delta/\delta$ estimate. This circumstance gives reason to expect that the thermal conductivity of carbon at room temperature $\kappa_0 = 4$ W m$^{-1}$ K$^{-1}$ used in this paper for the modeling is underestimated, since the roughness of the surface was not taken into account in the calculations.

Concerning the role played by air in the formation of LITE signals in the surface layers of porous carbon materials, the following fact should be taken into account. As is known, the application of the parabolic equation of heat conduction (1) is based on the assumption that the rate of establishing the local thermodynamic equilibrium $\tau_e$ is significantly shorter than the characteristic times of temperature change in the studied system $\tau_T$. As the calculations show, at the leading edge of the LITE signal (Fig. 3, curve 1), the temperature growth rate reaches about 100 K ns$^{-1}$. As an example, for estimating $\tau_T$, let us take the time during which the emission intensity $I$ increases by 10% near the maximum of the derivative $dI/dt$. From Fig. 3, curve 1, the estimate $\tau_T \approx 0.1$ ns follows. For a lower bound of $\tau_e$ in air, we can use the well-known expression for the average lifetime of gas molecules between collisions $\langle \lambda \rangle = \left(\frac{\sqrt{2\pi d^2 n}}{V} \right)^{-1} \left(\frac{8kT}{\pi m} \right)^{-1/2}$, where $\langle \lambda \rangle$ is the average free path length, $\langle V \rangle$ is the average speed, $d$ is the diameter of a molecule, $n$ is the concentration of molecules, $k$ is the Boltzmann constant, and $m$ is the mass of a molecule. Hence, for a temperature of 300 K, we obtain estimates of $\tau_e \geq 0.16$ ns and $\tau_e \geq 1240$ ns for pressures of 760 and 0.1 mmHg, respectively. For a temperature of 2500 K, the same estimates will be 0.47 and 3580 ns. Thus, during the formation of the leading edge of the LITE pulse, the condition $\tau_e < \tau_T$ can be violated for heat conduction processes in air, which can lead to additional errors in the calculations.

4. Conclusions

Thus, the results of measurements and calculations obtained in this work indicate the following. First, accounting for the temperature dependence of thermal characteristics of the irradiated material makes it possible to satisfactorily describe the shape of LITE signals without the need to involve abnormally low values of the thermal conductivity of carbon. The satisfactory agreement between the results of calculations and the results of measurements is observed at a moderate value of the thermal conductivity of carbon at room temperature $\kappa_0 = 4$ W m$^{-1}$ K$^{-1}$. The difference of $\kappa_0$ from the typical values of the thermal conductivity of carbon materials can be explained by the presence of a large number of defects in the thin surface layer of the material, as well as by the processes of the graphitization of the material during the laser irradiation. Second, the obtained results indicate the important role played by air in the formation of LITE signals in the surface layers of porous carbon materials. The presence of air above the surface and in the pores of the studied porous material has a noticeable effect on the kinetics of LITE. In particular, air significantly shortens the emission decay time and reduces the amplitude of LITE signals. Finally, as the numerical estimates show, in the considered case of LITE, the rate of growth of the surface temperature may exceed the rate of establishment of a local thermodynamic equilibrium in air. Such a situation requires a separate study that goes beyond the scope of this work.

The work was carried out with the support of the Ministry of Education and Science of Ukraine in accordance with Agreement No. BF/30-2021 dated August 4, 2021.


Received 29.04.23

C. E. Zelenskyi, O. S. Kolesnik, V. P. Yashchuk

**РОЛЬ ПОВІТРЯ В ІНДУКОВАНОМУ ЛАЗЕРОМ ТЕПЛОВОМУ ВИРОБЛЮВАННІ ПОВЕРХНЄВИХ ШАРІВ ПОРУВАТИХ ВУГЛЕЦЕВИХ МАТЕРІАЛОВ**

Досліджено вплив оточуючого повітря на амплітуду і форму імпульсів теплового випромінювання (на довжині хвилі 430 нм) при нагріванні поверхневого шару порувацього ву-
глецевого матеріалу (до температур порядку 2000–3000 K) випромінюванням неодимового лазера з модуляцією добротності. Експерименти показали, що при зменшенні тиску оточуючого повітря до умов форвакууму спостерігається півтораразове збільшення амплітуди імпульсних сигналів теплового випромінювання і зростання часу загасання світіння приблизно на третину. Проведено чисельні розрахунки динаміки температурного поля у поверхневому шарі матеріалу при опроміненні наносекундними лазерними імульсами. У розрахунках використано удосконалену модель, яка враховує (i) поруватість матеріалу і (ii) температурні залежності коефіцієнтів теплопровідності та теплоємності вуглецю і повітря. Для розрахунку теплопровідності порува того матеріалу використано модель кубічного масиву квадратних стрижнів, що перетинаються. Отримано задовільну узгодженість результатів розрахунків з результатами експериментів. Вищезазначені удосконалення розрахункової моделі дозволили узгодити оцінки теплових характеристик поверхневих шарів вуглецю, отримані за даними загасання світіння, з довідковими даними, опублікованими у літературі.

**Ключові слова:** індуковане лазером теплове випромінювання, поруваційний вуглець, повітря.