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The spectral characteristics of the glow of the flame of coal particles at various stages of ignition during and after exposure to laser impulses

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The results of measurements of the spectral-kinetic characteristics of the glow of the flame of eight brands of stone coals of the Kuznetsk coal basin (Russia) among metamorphism and anthracite are presented during and after exposure to the impulses of the neodymium laser (1064 nm, 120 μs). At the first stage, at the values of the critical density of the laser energy of $H_{\text{cr}}^{(1)}$, the reactive-active micro-extracts on the surface of coal particles are ignited. It was shown that at the second stage, when the critical energy density $H_{\text{cr}}^{(2)}$ is reached, during the radiation impulse, the surface of the coal particles and a flame of 3–4 mm with a height of 3–4 mm occurs. The shape of the flame glow spectra is associated with the contribution of several components: burning carbon particles, excited molecules H_2O^*, H_2^* and CO^*. It is most likely that this stage is associated with thermochemical reactions in the aliphatic part of the coal macromolecule. In the third stage, with an increase in the density of laser energy to the $H_{\text{cr}}^{(3)}$ flame, the height of the flame reaches 3–4 cm. At distances of more than 4 mm from the surface in the spectra of the glow, one component is observed in the time interval of more than 1 ms, the spectrum of which is described by the formula of the bar. It is assumed that the processes in coal particles occurring in the third stage are associated with the ignition of the aromatic part of the coal macromolecules.

Keywords:

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Introduction

It is necessary to study the processes of initiation of thermochemical phenomena in fossil coals in order to expand the understanding of the initiation mechanisms of combustion of solid fuels. This knowledge is needed to develop new ignition and combustion-enhancing technologies for coal combustion and to address the issue of reducing harmful emissions that pollute the environment. It is convenient to use laser pulses [1–4] in the study of coal ignition mechanisms. In this case, the ignition source is remote from the object, which enables both visual observation of the ignition of coal samples and quantitative measurement of the spectral intensity of flame glow in real time using electron-optical methods [1–4] and time-resolved optical spectrometry [5–7].

A number of models of laser ignition of coals have been considered in literature. In the simplest version proposed in [8], the surface of a coal particle is heated to the temperature of thermal decomposition under the influence of initiating laser pulses. The result is the release of volatile substances. Mixing with the oxidizer, they absorb a part of laser radiation, which leads to heating of the gas phase and development of a chemical reaction in it. In this case, the ignition of coal particles can be carried out by two mechanisms: (1) the gas phase is ignited first (homogeneous mechanism); (2) the solid surface of coal particles is ignited first, and then the gas phase is ignited.

In our works [9,10], we have studied the spectral characteristics of ignition of particles of Kuznetsk basin coals during a laser pulse ($\lambda = 1064$ nm, $\tau_i = 120\,\mu$s). Different surface ignition thresholds at which qualitatively different glow spectra are observed have been identified. The first stage is characterized by glow detection threshold H_{cr}^1. A flame of ~ 1 mm can be observed above the particle surface. The glow spectra are non-thermal in nature and are related to the glow of CO (CO_2^*) flame and excited molecules H_2O^* and H_2^*. We attribute this process to the ignition of reactive micro-growths on the surface of carbon particles, as suggested in [11]. As energy density H increases, thermal glow can be observed at a certain stage, i.e., the whole surface of the particle is heated. When H increases further to $H_{\text{cr}}^{(2)}$, radically different glow spectra of a complex character are obtained. CO_2^*, H_2^*, H_2O^*, and burning carbon particles [9,10] contribute to the glow. In our recent work [12], we measured the glow spectra of flames at different distances from the sample during and after exposure to a laser pulse at energy densities $H_{\text{cr}}^{(2)}$ and $H_{\text{cr}}^{(3)}$. Coal particles ($d \leq 63\,\mu$m) of grades DG, G, Zh, and K were used. The stage with characteristic threshold $H_{\text{cr}}^{(2)}$ is usually characterized as the volatile yield and ignition stage [8]. We attribute the third stage with the characteristic

Table 1. Results of technical analysis of analytical coal samples

№	Coal grade	Technical analysis, %			C, %
		W^a	A^d	V^{daf}	
1	Grade D, „Kamyshansky“	7.6	6.2	44.5	74.4
coal mine 2	Grade DG, „ V.D. Yalewski“	5.7	4.7	42.6	74.3
mine 3	Grade G, „Kirov“	1.2	3.3	40.4	81.3
mine 4	Grade Zh, „Tikhov“	0.8	7.8	33.3	80.2
mine 5	Grade K, „Koksovy site“	0.6	4.9	21.3	87.7
LLC 6	Grade OS, „Tomusinsky“	0.1	6.7	19.8	84.8
coal mine 7	Grade SS, „Bachatsky“	1.3	4.7	19.0	83.8
coal mine 8	Grade T, AO „Kuznetsinveststroy“	0.5	6.2	14.4	89.7
9 coal mine	Grade A, „Bungursky“	0.4	3.6	7.7	89.6

Note. W^a — analytical moisture, A^d — ash content, V^{daf} — volatile matter yield.

$H_{cr}^{(3)}$ threshold to the ignition of a non-volatile residue of coal macromolecules.

In the present work, the range of coal samples used (including those studied earlier) was expanded to nine grades, which represent more fully the metamorphism series. Flame spectra at energy densities $H_{cr}^{(2)}$ and $H_{cr}^{(3)}$ were measured and analyzed.

Samples and experimental procedures

Coals of the Kuznetsk coal basin (Russia) of different stages of metamorphism were studied: long-flame (D), long-flame gas (DG), gas (G), greasy (Zh), coke (K), lean caking (OS), low caking (SS), lean (T), and anthracite (A).

The coals were ground using an AGO-2 ball mill and sieved using a vibrating sieve with mesh size $d = 63\,\mu$m. Thus, the coal samples were fractions with a broad size distribution with $d \leq 63\,\mu$m. The results of technical analysis of coals and carbon content in the organic mass are given in Table 1. Samples with bulk density $\rho = 0.5\,$g/cm^3 and a mass of 20 mg were placed in a copper capsule with a diameter of 5 mm and a depth of about 2 mm and examined.

The diagram of the experimental setup and the technique of measuring flame spectra were discussed in detail in [6].

The samples were ignited using a pulsed neodymium laser operating in the free generation mode ($\lambda = 1064\,$nm, $\tau_i = 120\,\mu$m). The section of flame glow located at the required height from the optical axis was projected onto a spatiotemporal slit $0.1 \times 0.2\,$mm in size using a lens. The image of the glowing slit was projected to the input of the polychromator using a lens and converted to a spectrum in the range 350–750 nm. The spectrum strip was transferred to the photocathode of a linear sweep photo-chronograph, which produced a time sweep of the spectrum. The light matrix on the output screen of the photo-chronograph was read by a CCD matrix and transferred to a computer for further processing. The vertical columns of the matrix can be used to plot the glow spectrum at the required moment of time, while the horizontal rows produced the dependence of glow intensity on time at a given wavelength. Correction of the glow spectra to the spectral sensitivity of the measuring path was performed using a TRSh-2800-3000 reference incandescent lamp [13]. The spectral resolution was 10 nm, and the temporal resolution was determined by the applied sweep of the photo-chronograph. In the present work, the temporal resolution at the applied sweep was $2\,\mu$s, which is much longer than the laser pulse duration.

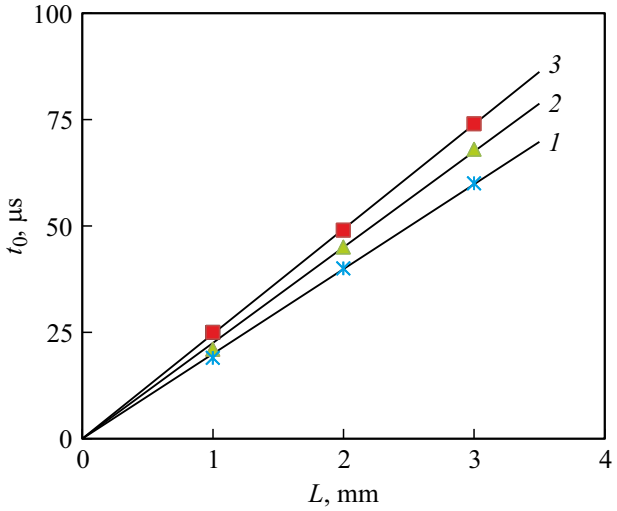

Figure 1. Dependences of flame occurrence times on the distance to the surface of coal samples exposed to energy density $H_{cr}^{(2)}$. *1* — Grade A, *2* — grade SS, and *3* — grade D.

The sample surface was placed perpendicular to the laser beam and parallel to the optical axis of the measuring path. The sample could move vertically so that the spatiotemporal slit highlighted different sections of the flame.

Experimental findings

Spectral-kinetic characteristics of coal flame glow during and after exposure to a laser pulse were measured at energy

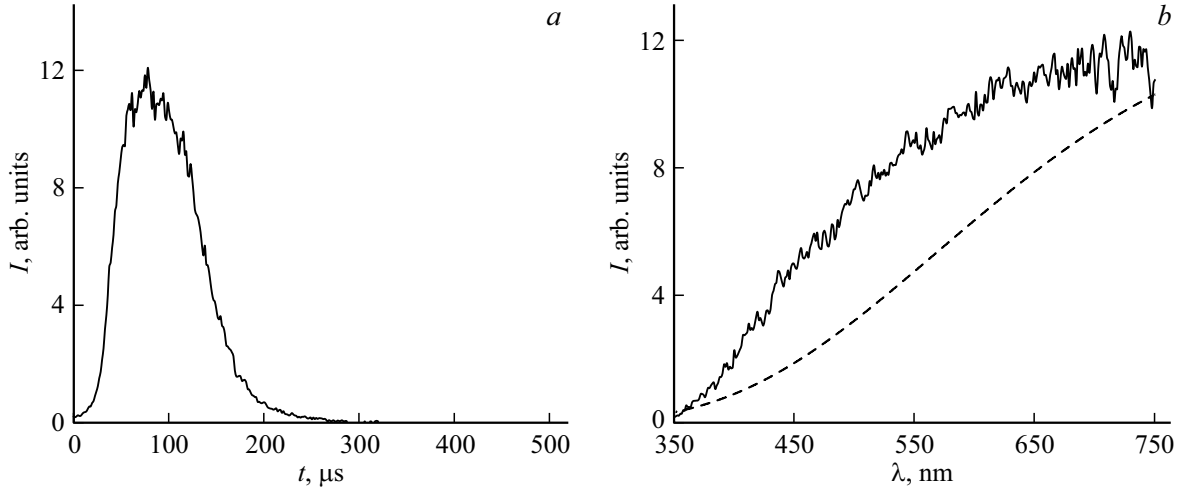

Figure 2. Time dependence of flame glow intensity (a) of grade OS coal particles and glow spectrum (b) at a distance of 1 mm from the sample surface and a time of 100 μs when exposed to energy density $H_{cr}^{(2)}$.

Table 2. Thresholds $H_{cr}^{(2)}$ and $H_{cr}^{(3)}$ for long-flame (D), long-flame gas (DG), gas (G), greasy (Zh), coking (K), lean caking (OS), low caking (SS), lean (T), and anthracite (A) coal grades

№	Coal grade	$H_{cr}^{(2)}$, J/cm^2	$H_{cr}^{(3)}$, J/cm^2
1	D	2.4 ± 0.1	3.1 ± 0.3
2	DG	1.6 ± 0.3	2.4 ± 0.4
3	G	1.8 ± 0.2	3.3 ± 0.2
4	Zh	1.1 ± 0.1	5.5 ± 1.0
5	K	0.9 ± 0.1	6.2 ± 0.4
6	OS	1.1 ± 0.1	7.5 ± 0.8
7	SS	1.0 ± 0.1	7.9 ± 0.8
8	T	0.9 ± 0.1	8.5 ± 1.1
9	A	1.10 ± 0.05	9.3 ± 1.1

densities corresponding to volatile ignition thresholds $H_{cr}^{(2)}$ and non-volatile residue ignition thresholds $H_{cr}^{(3)}$. The values of $H_{cr}^{(2)}$ and $H_{cr}^{(3)}$ for all coal grades used were measured in [14] and are given in Table 2.

Under exposure to energy density $H_{cr}^{(2)}$, a flame of 3–4 mm is visually observed above the samples in the metamorphism series. Experimentally measured records at a fixed wavelength showed a lag in the onset of the glow flame that increased with distance from the sample surface to the optical axis. Figure 1 shows the dependences of flame appearance times on the distance to the surface of samples of some coal grades. It is characteristic that the dependences have a linear character and start at the origin of coordinates (within the experimental error). As shown in our previous work [12], the spectral-kinetic characteristics of the flame glow of coal flames of grades DG, G, Zh, and K at distances of 1 and 2 mm from the sample surface are very different, but qualitatively similar for all coal grades.

Figure 2 shows the time dependence of flame glow intensity of OS grade coal particles and the glow spectrum at a distance of 1 mm from the sample surface at a time point of 100 μs. Qualitatively similar dependences were observed in our previous work [12] for DG coal and for all coal grades in the metamorphism series used in the present work.

Figure 3 shows the time dependences of glow intensity of coal particles of all studied grades at a distance of 2 mm from the sample surface under exposure with energy density $H_{cr}^{(2)}$.

Two or three maxima of flame glow intensity were observed in the kinetic dependences (Fig. 3).

The glow spectrum in the first maximum for D grade coal is shown in Fig. 4. Qualitatively similar spectra were observed for all studied coal grades. The glow spectra of all coal grades in the second and third maxima are described by the Planck formula. The color temperatures at the maxima (T_2 and T_3, respectively) determined by optical pyrometry [15] are presented in Table 3.

When coal samples are exposed to energy density H_{cr}^{3}, a flame with a height of ~ 3 cm is visually observed above the surface. The time dependences of flame glow intensity for D coal and the glow spectra at distances of 6 and 8 mm are shown in Figs. 5 and 6, respectively. The glow spectra are described by the Planck formula with color temperature $T = 2000$ K. Qualitatively similar kinetics and glow spectra are observed for the other studied coal grades. Table 4 presents the color temperature values of coal flames determined from the measured spectra by optical pyrometry at a distance of 8 mm from the surface of samples [15].

Discussion

An important conclusion follows from the results presented in Fig. 1: heating to the ignition temperature of the sample surface when exposed to an energy density of $H_{cr}^{(2)}$ begins directly during a laser pulse. This results in the release of a volatile gas phase, which is ignited immediately.

Table 3. Color temperatures in the maxima of glow intensity at time points *2* and 0 *3* (Fig. 3)

	D	DG	G	Zh	K	OS	SS	T	A
T_2, K	2400	2400	2000	2200	2100	1800	2100	1800	2100
T_3, K	1800	1800	1900	2000					

Table 4. Color temperature of coal flames at a distance of 8 mm from the sample surface

	D	DG	G	Zh	K	OS	SS	T	A
T, K	2000	1900	1900	1900	2000	1800	1800	2000	2000

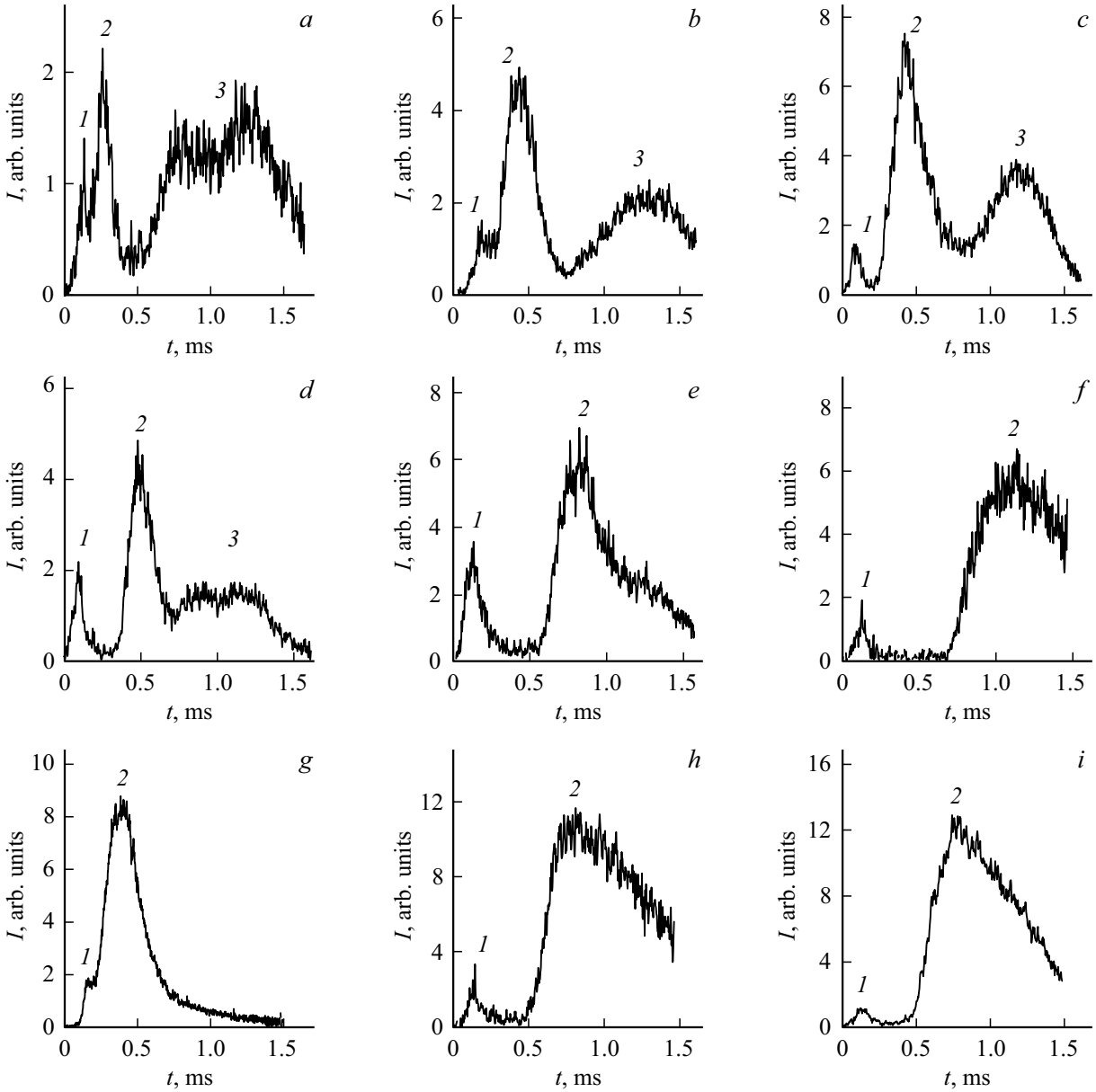

Figure 3. Time dependences of glow intensity of coal particles at a distance of 2 mm from the sample surface when exposed to energy density $H_{cr}^{(2)}$. Coal grades: *a* — D, *b* — DG, *c* — G, *d* — Zh, *e* — K, *f* — OS, *g* — SS, *h* — T, and *i* — A.

According to the slope of the straight line in Fig. 1, the velocity of volatiles escape under exposure to a laser pulse can be determined as $V = 45-50$ m/s.

The first results of the study of the spectral-kinetic characteristics of flames of four coal grades (DG, G, Zh, and K) exposed to energy density $H_{cr}^{(2)}$ are presented and discussed in detail in our work [12]. As was shown in the previous section, the regularities found in [12] under energy densities $H_{cr}^{(2)}$ can be extended to all hard coal and anthracite grades studied in this work. Thus, a brief discussion below is based on [12].

At a distance of 1 mm, SO flame contributions were detected in the composition of the emission spectrum, i.e., when the surface is ignited, carbon monoxide is emitted, ignited in reaction with air oxygen

$$2CO + O_2 \rightarrow 2CO_2^* \qquad (1)$$

and glows in the 350–550 nm spectral range [16,17].

It was also found that the glow of excited molecules H_2O^* and H_2^* in the spectral range 550–750 nm [16,17] can contribute to the spectra. In addition, escaping glowing (or burning) carbon particles with a Planck spectrum [12] contribute to the glow spectra. Consequently, the glow spectrum shown in Fig. 2 is a superposition of the glow spectra presented above. Qualitatively similar spectra were observed for all studied coal grades.

The kinetics of coal flame glow in Fig. 3 has a similar character for all coal grades. The glow in the first maximum is due to the release of volatiles under exposure to a laser pulse. The glow spectrum (Fig. 4) occupies the 550–750 nm spectral range, which implies that it is associated with the glow of excited molecules H_2O^* and H_2^* [16,17]. Further, as a result of development of chemical reactions in coal particles, two or three maxima are observed in the millisecond time interval (Fig. 3), the glow spectra of which are described by the Planck formula with color temperatures presented in Table 3.

It follows that the development of exothermic reactions in coal particles results in the initiation of combustion with complex kinetics in the millisecond time interval, leading to the escape of glowing carbon particles (possibly tar, as was proposed in [18]). It was shown in theoretical studies [19,20] that aliphatic chains have the lowest thermal stability in the macromolecule of coal. Therefore, the observed products are produced upon exposure of coal particles to energy density $H_{cr}^{(2)}$ as a result of partial destruction of the aliphatic part of coal macromolecules. Remarkably, there is no CO flame at a distance of 2 mm from the surface (reaction 1). Consequently, when carbon monoxide escapes from carbon particles, it is ignited near the surface by a heterogeneous mechanism, and there is no CO flame at distance $L \geq 2$ mm.

The flame height increases to 3 cm when the samples are exposed to energy density $H_{cr}^{(3)}$. At distances of 6 and 8 mm (Figs. 5, 6), the glow kinetics is described by a single component with a thermal spectrum at $T = 2000$ K

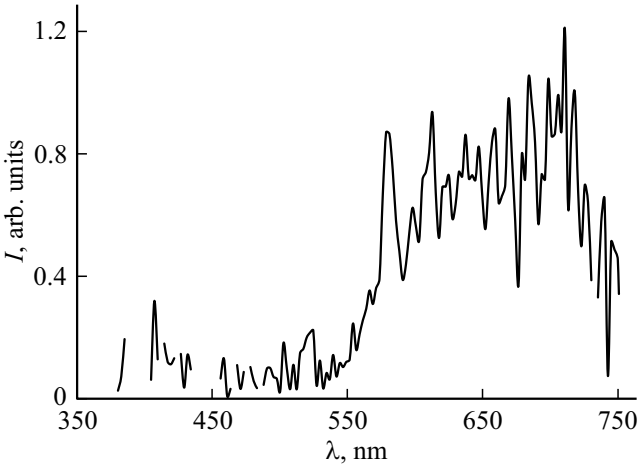

Figure 4. Glow spectrum in the first maximum for coal Grade D (Fig. 3, *a*, peak *1*).

for coal grade D. The measurement of kinetics and glow spectra at a distance of 1 cm from the sample surface for all the studied coal grades showed that all spectra are described by the Planck formula with color temperatures presented in Table 4. This result allows us to conclude that at distances $L > 4$ mm upon exposure to energy density $H_{cr}^{(3)}$, the overwhelming contribution to the glow spectra of coal flames is produced by escaping red-hot and, more probably, burning carbon particles, which are formed by ignition of the aromatic part of coal macromolecules as a result of thermochemical reactions. Perhaps, this process is also accompanied by the release of volatiles that boost carbon particles. However, their glow is either lacking in the 350–750 nm spectral interval or its contribution to the glow spectra is small compared to the Planck glow of carbon particles.

Conclusions

1. When coal particles with size $d \leq 63\,\mu$m in the metamorphism series of coals from grade D to grade A are exposed to energy density $H_{cr}^{(2)}$ during a laser pulse, heating and ignition of the particle surface occurs.

2. As a result of heating, carbon monoxide escapes and ignites by a heterogeneous mechanism near the particle surface at a distance of ~ 1 mm, and excited molecules H_2^* and H_2O^* escape to a distance up to 3–4 mm directly during the laser pulse.

3. As a result of development of chemical reactions in coal particles, burning carbon particles (possibly tar) escape to a height of 3–4 mm within a time interval of ~ 1 ms.

4. The processes described in paragraphs 2 and 3 are most likely related to thermochemical processes in the aliphatic chains of coal macromolecules that contain the observed components.

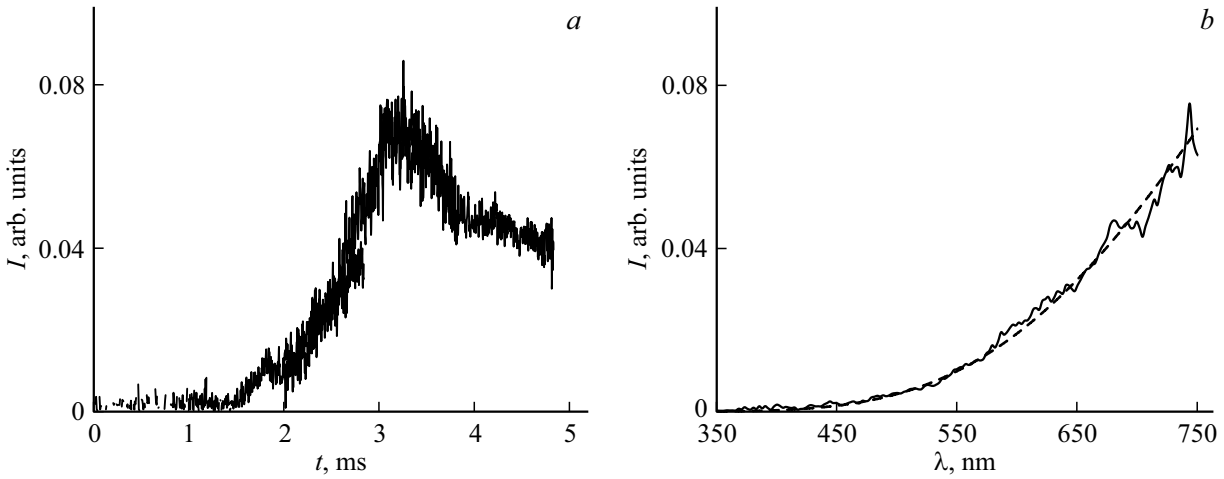

Figure 5. Time dependences of glow intensity (a) of flames for coal grade D and glow spectra (b) at a distance of 6 mm from the sample surface when exposed to energy density $H_{cr}^{(3)}$.

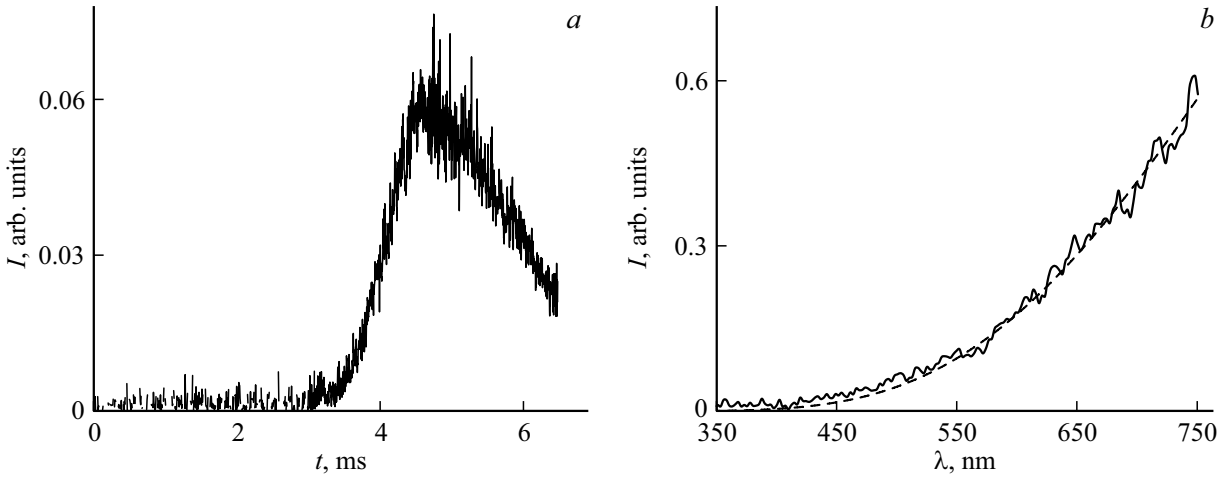

Figure 6. Time dependences of glow intensity (a) of flames for coal grade D and glow spectra (b) at a distance of 8 mm from the sample surface when exposed to energy density $H_{cr}^{(3)}$.

5. Exposure of coal particles to energy density $H_{cr}^{(3)}$ produces flame ~ 3 cm in height. At distances $L > 4$ mm from the surface, a single glow component with its spectrum described by the Planck formula is observed on timescales greater than 1 ms.

6. It is most likely that the processes in coal particles occurring under exposure to energy density $H_{cr}^{(3)}$ are related to thermochemical processes in the aromatic part of coal macromolecules.

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Conflict of interest

The authors declare that they have no conflict of interest.

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