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The Formation of Quasiperiodic Microstructures on the Surface of a Coal Sample under the Action of Laser Radiation

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Abstract

Original structural changes of the surface of a coal sample under the action of pulsed mode laser radiation were studied. It was found that original quasiperiodic columnar structures were formed on the sample surface as a result of the laser action of 10^4 s duration with the frequency of 6 Hz and the single pulse energy density of 1.95 J/cm^2. The diameter of single fragments reached 100 μm with the distance between them attaining 50 μm. On the top of the fragments, there were spherical shapes composed of silicon compounds with a size reaching 10 μm. A scheme of the formation of columnar structure was proposed.

Keywords: coal, surface morphology, pyrolysis, microstructure, laser, catalysis

INTRODUCTION

Natural coal represents a complex multicomponent system consisting of carbon frame and inorganic inclusions, which can be neutral or provide a catalytic impact on the pyrolysis and burning of coal [1–3]. So it is important to define the role of inorganic compounds in the process of coal pyrolysis under laser radiation.

In our previous works, we carried out spectral-kinetic studies of the characteristics of brown coal when exposed to the pulses of neodymium laser in free-running mode (λ = 1064 nm, τ = 120 μs) [4, 5]. Three stages of ignition of highly dispersed coal powders were established with characteristic thresholds related to the initialization of chemical reactions as a result of high-power laser pulses. At the first stage, coal particle heating and the ignition of micro-protrusions took place. The duration of this stage does not exceed the duration of the laser pulse. At the second stage, the evolvement and the ignition of volatile substances take place. The duration of burning of the volatiles equals ~10 ms. At the third stage, the ignition of the coal residues free from volatiles occurs. The duration of the solid residue combustion reaches 150 ms.

The formation of periodic surface structures was previously observed upon the action of laser radiation on ceramics, polymers, and semiconductors [6–14]. Periodic surface structures formed by the action of laser radiation can impart unusual physical or physicochemical properties to the material. For example, surface structuring is used to increase the biocompatibility of implants with living tissues [15], to increase the absorptance of materials [16, 17]. However, despite a significant number of works, most of them are aimed at studying the interaction of laser radiation with metals and semiconductors. There are few studies on the interaction of laser radiation with carbon materials.

In general, the mechanism of the action of laser radiation on a complex multicomponent system consisting of a carbon frame and inorganic inclusions remains uncertain. In this work we have studied the mechanism of the action of laser radiation on a sample of high-ash B grade coal, prepared in the form of a dense tablet. For the first time, the formation of original quasiperiodic columnar structures on the sample surface was detected.

EXPERIMENTAL

Materials and methods

Brown coal of the Tisul deposit (Kuzbass coal basin, Russian Federation) was used in this work. The results of the proximate and ultimate analysis of an analytical coal sample are the following: moisture content W^a = 11.1 %, ash content A^d = 9.5 %, volatile matter V^{daf} = 51.4 %, carbon content C^{daf} = 61.4 %, hydrogen content H^{daf} = 5 %.

The elemental composition of coal ash was measured by the method of atomic emission spectroscopy with inductively coupled plasma (ICP-AES) using an iCAP 6500 Duo L instrument (Thermo Scientific, USA). The data obtained are provided below in Table 1.

In the processes of pyrolysis and combustion of fossil coals, the content of the oxides of catalytic elements plays a critical role [18]; MgO and CaO show the catalytic activity, while Al_2O_3 and SiO_2 do not exhibit it (see Table 1).

Samples were prepared by initial crushing in a jaw crusher, followed by grinding in a ball mill Pulverisette 6 (Fritsch, Germany). After grinding, coal particles were sifted through a sieve with a mesh size of 63 μm and then pressed in a special press mold to obtain experimental coal samples in the form of tablets with a diameter of 4.2 mm, a thickness of 4.7 mm and the mass of 65 mg.

As a source of laser radiation, we used YAG:Nd^{3+}-laser (SOLAR Laser Systems LQ929, Minsk), working in the free-running mode at the wavelength λ = 1064 nm. The energy of the laser radiation was determined using pyroelectric laser energy sensor PE50BF-C (Ophir® Photonics, Israel). The diameter of the laser beam was equal to 4.2 mm, matching the diameter of samples. The instability of the laser pulse energy did not exceed 2 %. The following parameters of the laser radiation were used: pulse duration, 120 μs; the frequency of pulses, 6 Hz; single pulse energy density, 1.95 J/cm^2.

The scheme of experimental installations is shown in Fig. 1.

The energy of the laser radiation is regulated by neutral light filters, then the laser beam passes the deflecting mirror and lenses and focuses on the sample. Part of the energy of the laser radiation is directed by the beam-splitting plate to the pyroelectric laser energy sensor (PLES) for monitoring the energy of laser pulses.

To carry out an experiment, the sample was placed into the experimental chamber. Then the chamber was sealed, and the chamber was pumped out to residual air pressure of 1 Pa with the help of the pumping system consisting of the shut-off valve, vacuum gauge, and vacuum pump. The inert gas was admitted into the experimental chamber using the inlet system consisting of the shut-off valve, gas pressure regulator, and a gas cylinder. High-purity argon (argon content 99.993 %) was used as the inert gas. After argon admission, the argon pressure in the experimental chamber was equal to $8 \cdot 10^4$ Pa.

The duration of the experiments was 10^4 s. During this time, the sample was subjected to $6 \cdot 10^4$ pulses.

The study of the surface morphology of samples before and after laser treatment was conducted with the help of the scanning electron microscope JSM-6390 LA (JEOL, Japan) with an embedded energy dispersive X-ray analyzer JED 2300 (JEOL, Japan, energy resolution 133 eV).

The surface micrographs were obtained in the mode of registration of back scattered electrons and characteristic X-ray radiation.

The calculation of the contents of each element on the sample surface was conducted from the obtained X-ray spectra (EDX) using the Analysis Station software, version 3.62.07 of JEOL Engineering using the standardless ZAF method.

TABLE 1

Elemental composition of coal ash

Oxide	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O	CaO	TiO_2	Fe_2O_3
Content, mass %	0.3	3.5	18.3	26.7	0.1	14.2	0.6	23.1	0.9	12.3

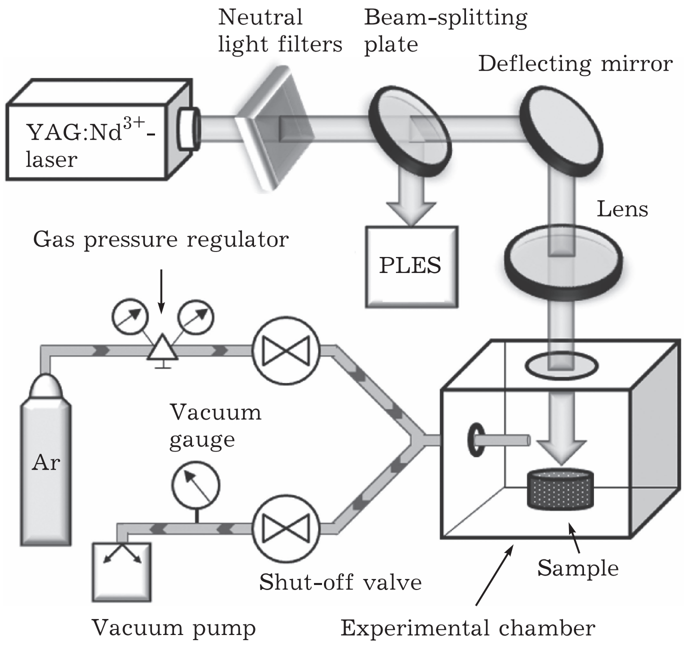

Fig. 1. Functional scheme of the experimental installation.

RESULTS AND DISCUSSION

Figures 2 and 3 show the micrographs of the sample surface before laser irradiation conducted in the mode of registration of back scattered electrons and characteristic X-ray radiation.

Figure 4 shows the micrograph of the sample surface after laser treatment for 10^4 s with the frequency of 6 Hz and single pulse energy density of 1.95 J/cm^2.

The analysis of the micrographs shows that original quasiperiodic columnar structures are formed on the sample surface on the surface of the sample after laser irradiation (see Fig. 2 and 4). The diameter of single fragments reaches 100 μm with the distance between them attaining 50 μm. On top of the fragments, there are oxide compounds of spherical shapes with a size reaching 10 μm.

Figure 5 demonstrates a micrograph of the sample surface after laser treatment for 10^4 s with the pulse frequency 6 Hz, and a single pulse energy density of 1.95 J/cm^2 obtained in the mode of characteristic X-ray radiation.

One can see in Fig. 5 that sphere-like formations are fused oxide compounds of silicon and iron. The spherical form indicates that the compounds of silicon and iron are heated up to the

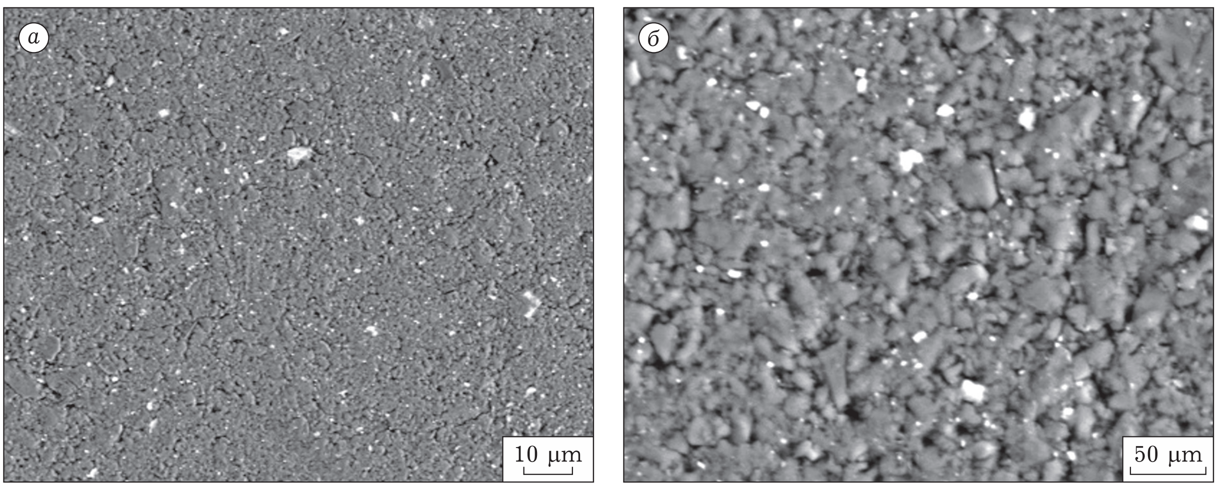

Fig. 2. Micrographs of the sample surface before laser treament at different magnifications.

melting point during the laser treatment. According to [19], the melting point of SiO_2 equals 1995 K, and that of Fe_2O_3 is 1838 K. Thus one can conclude that during the laser treatment the temperature of the sample surface can exceed 2000 K.

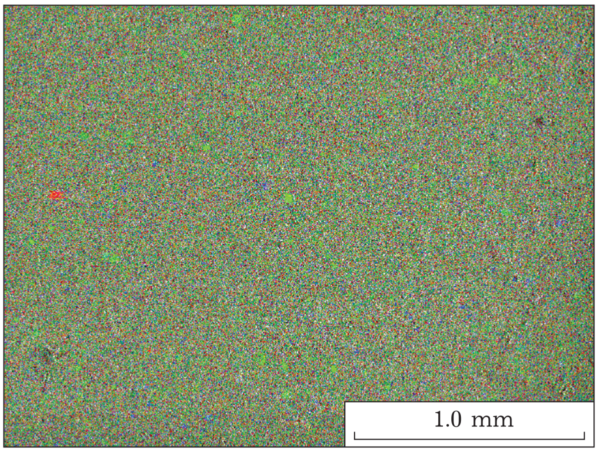

Fig. 3. Micrograph of the sample surface before laser treatment obtained in the mode of characteristic X-ray radiation. Blue – Fe, red – Ca, green – Si.

Table 2 shows the chemical composition of the surface giving the relative content of elements before and after laser treatment for 10^4 s with the frequency of pulses 6 Hz, and a single-pulse energy density of 1.95 J/cm^2.

It can be seen from Table 2 that pyrolysis and thermal decomposition of the coal organic mass occur as a result of the laser irradiation, leading to a significant decrease of carbon concentration on the surface and an increase of the surface concentration of inorganic components of the mineral part of coal.

The authors of [20, 21] noted that the mineral mass of coal can affect the reactivity of the coal organic mass. It was shown in [22–24] that additives of alkaline and alkaline earth metals have a catalytic effect on the process of coal pyrolysis. Among alkaline earth metals, the compounds of calcium [3–5] exhibit the highest catalytic activity, while the compounds of magnesium and barium are less active [4, 25]. Demineralization of coal leads to a reduction of the reactivity of the coal organic mass [26, 27].

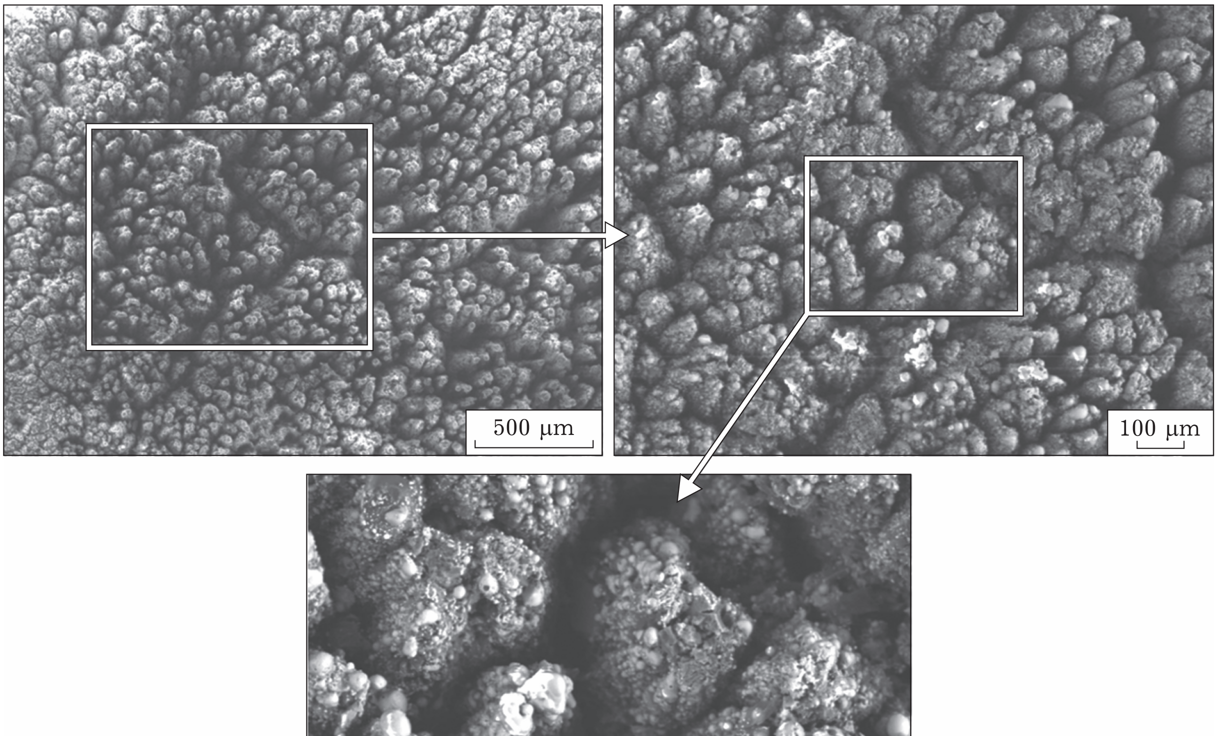

Fig. 4. Micrograph of the sample surface after laser treatment.

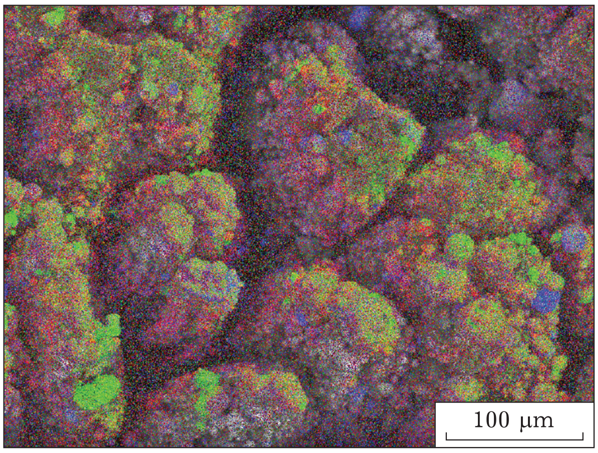

Fig. 5. Micrograph of the sample surface after laser treatment, in the mode of characteristic X-ray radiation. Blue – Fe, red – Ca, green – Si.

TABLE 2

The content of chemical elements on the surfaces of the sample before and after laser treatment

Element	Before irradiation		After irradiation	
	Mass, %	Error, %	Mass, %	Error, %
C	66.41	0.09	30.78	0.08
O	29.19	0.68	32.78	0.20
Na	0.04	0.20	0.18	0.11
Mg	0.15	0.15	1.03	0.08
Al	0.80	0.14	4.38	0.07
Si	1.12	0.14	6.55	0.07
S	0.44	0.11	0.67	0.05
K	0.03	0.17	0.40	0.08
Ca	1.13	0.20	12.41	0.09
Ti	0.02	0.25	0.38	0.12
Fe	0.68	0.47	10.44	0.21

The formation of columnar structures on the surfaces of the samples at laser irradiation is explained by the presence of mineral inclusions in the coal. During the laser treatment, mineral inclusions that do not exhibit catalytic properties are subjected to thermal impact, and they screen the underlying organic mass of coal from the direct laser effect. The unshielded organic mass of coal, being in contact with catalytically active mineral inclusions, is exposed to the laser impact that causes intensive catalytic pyrolysis. Thus deep voids are formed between the screened columns.

So, we propose for the first time the following scheme of the original columnar structure formation on the coal surface exposed to laser radiation (Fig. 6). For clarity, the oxide inclusions not showing catalytic activity and providing the screening effect are marked on the diagram as Si, and the inclusions having the catalytic activity as Ca.

A similar formation of quasiperiodic surface structures was observed on the surfaces of metals or semiconductors after laser treatment with the intensity close to the threshold of the melting point of the material; under these conditions, a periodic grid-type structure with a period approximately equal to the radiation wavelength is formed [6]. At high temperatures of the laser treatment, material evaporation and ablation can occur. The laser impact with the radiation intensity exceeding the threshold of ablation leads to the formation of quasi-periodic cones on the surface of materials [11, 28]. An analogous effect also was shown in [12] in the ablation of several polymers containing foreign micro-inclusions, leading to the formation of cone structures.

The phenomenon similar to the formation of columnar structures as a result of the combination of catalytic action and the screening effect discovered by us was previously observed in the study of the effect of laser radiation on two other objects. The screening effect was noted when using phase masks in [29], and in [30] the catalytic effect of barium in gasification of graphite was found.

CONCLUSIONS

The original structural changes with the formation of columnar structures on the surface of a coal sample under pyrolysis by pulsed-mode laser radiation are discovered. The laser irradiation of

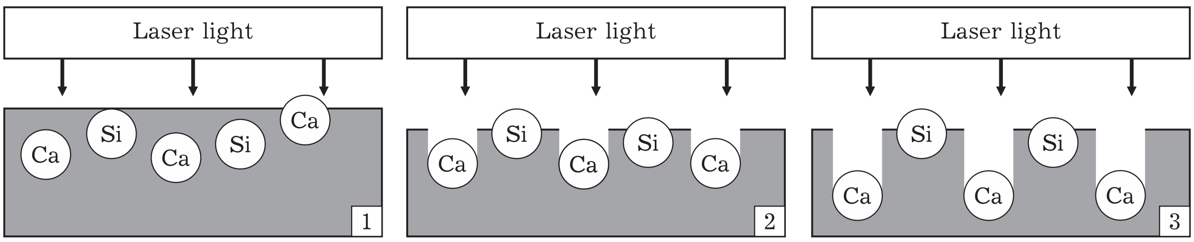

Fig. 6. Scheme of the formation of columnar structure.

10^4 s duration with the frequency of 6 Hz and single pulse energy density of 1.95 J/cm^2 focused on the surface of a coal sample was used.

The diameter of a formed single columnar fragment reaches 100 μm with the distance between them attaining 50 μm. On the top of the fragments, there are spherical shapes composed of melted silicon compounds with a size close to 10 μm.

We propose a scheme of the formation of columnar structure as a result of a combination of the catalytic action of CaO + MgO and the screening effect of SiO_2 in ash composition during the fossil fuel thermal pyrolysis process under pulsed laser irradiation.

The elucidated phenomena must be taken into account in modeling the pyrolysis and the first stages of combustion of different ranks of coal under traditional thermal processes as well.

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