INTERACTION OF RUBY LASER WITH CARBON FIBROUS MATERIALS*

Carbon fibrous materials are interesting because of their good properties and numerous possible applications. The characteristics of these materials can be programmed by careful selection of the modification process parameters. The laser technique can be successfully employed for these purposes. The high temperatures arising in the material during a short laser pulse can cause a number of changes in the material. Carbon fibrous materials with different textile shapes, during different stages of processing, were exposed to laser radiation. A ruby laser (λ = 694.3 nm) was used to modify the material. The structural changes were examined by scanning electron microscopy and X-ray diffraction. It was established that the radiation of this laser induces structural changes leading to a better arrangement of the turbostratic carbon fiber structure.

One of the first investigations was the application of lasers in coal pyrolysis [8]. The laser technique can be used to study the kinetics of processes, e.g. the oxidation of graphite [9], to obtain carbon material in the interaction of laser radiation with poly(vinyl chloride) (PVC) [10], as well as to obtain graphitic carbon from the liquid phase (photolithical graphitization) [11]. The pulse laser ablation of graphite in vacuum leads to the condensation of carbon atoms, ions and clusters, and their precipitation on the surface of the substrate. The films obtained are extremely smooth, of the nanometer order, and are referred to as amorphous carbon, a-C [12]. By exposing polycrystalline graphite to the continuous radiation of a CO₂ laser, and to quick cooling in liquid nitrogen, a diamond structure is formed at atmospheric pressure [13]. The laser technique can also be applied in the pyrolysis of cellulose [14].

Recent studies in the USA have been oriented towards the application of lasers in the expanding area of nanomaterials, more precisely, the synthesis of carbon nanotubes by laser assisted chemical vapor deposition (LCVD) [15]. An interesting area of study is also the heat conduction in porous carbon materials subjected to the action of laser radiation. It has been established that the porosity, pore size and their microporous distribution have a great impact on the heat response of the material. It is also possible to mathematically calculate these influences using different models [16].

The aim of this paper was to analyze the effect of laser radiation on carbon fibrous materials. The high temperatures arising during the short period of laser pulse action can cause numerous changes in the material. Carbon fibrous materials with different textile shapes, during different stages of processing, were exposed to laser radiation. A ruby laser was used to modify the material. The morphological, structural, destructive and non-destructive changes were examined.

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EXPERIMENTAL

The carbon textile material used here was manufactured using a facility for textile materials of viscose origin. The main parts of this facility are: an impregnation device, a heat treatment furnace and a material flow system. Viscose cloth and felt were used to manufacture the carbon textile material.

Cloth characteristics:
- fiber type: rayon fiber;
- linear mass density of the fiber: 5.5 d/10x;
- linear mass density of the yarn: 330/100 d/10x;
- weaving: flat double;
- interweaving: flat-right-right;
- surface mass: 380 – 390 g/m²;
- material thickness: 1.3 mm.

Felt characteristics:
- fiber type: staple cellulose fiber;
- linear mass density of the fiber: 3 – 4 d/10x;
- weaving: needling;
- surface mass: around 500 g/m²;
- material thickness: 3.2 mm.

The process of manufacturing the carbon textile material included pretreatment, carbonization and heat treatment. Carbonization and heat treatment are processes of thermal processing the material up to 1000 and 2800 °C, respectively, in inert atmosphere.

In the process of pretreatment the cloth was placed in a 5–8% aqueous solution of ZnCl₂ and NH₄Cl, while the felt was placed only in NH₄Cl solution.

Thermal processing included carbonization, in the interval from 900 to 1000 °C, or heat treatment up to 2000 – 2200 °C. These operations were conducted in inert nitrogen atmosphere. The samples were manufactured in a semi-industrial furnace.

A ruby laser, λ₀ = 694.3 nm, was used to modify the material.

The experiments were conducted using an "Apollo" ruby laser, model 22, the schematic representation of which is given in Figure 1 [17].

This laser is characterized by a high level of coherency (time and space) and a high degree of plane polarization. It can operate in the free-generation as well as in the Q-switch regime.

Apart from the optical, optoelectronic and mechanical components of the laser, there is a control system, power supply and cooling system. The main parts of the laser system are designated in Figure 1. The laser head (1), contains a ruby rod (2) and a flashing lamp (3). A Pockels cell (4), aperture (6) and resonant mirrors (5 and 7) are included in the other optical elements. The laser elements are placed on a specially prepared optical bench (8) made of reinforced and heat-treated aluminum.

![Figure 1. Schematic representation of the "Apollo" ruby laser, model 22](image)

Slika 1. Schematski prikaz rubinskega lasersa "Apollo", model 22

The laser energy was measured with a digital energy analyzer (ACM 101) with a calorimetric probe, model 1 AL-25.

The analysis of the results is complex because the processes in question are of very short duration. Special electronics were used to determine the shape and length of the pulse, and the corresponding diagrams are given on Figures 2–4.

Figure 2 shows a laser and lamp pulse, i.e. only the peak of the emitted lamp signal. Laser radiation emission starts when the threshold voltage of 3.9 kV is brought to the flashlamp.

The diagram of the laser pulse in a free-generation regime is given in Figure 3 [17]. The pulse length is 250 to 350 µs. The pulse has a classic shape and is made of a large number of relaxation oscillations ("spikes"). The figure shows a signal with only 512 points out of the 2048 recorded. It can be deduced from the diagram that the spike length is about 5 µs.

![Figure 2. Cumulative diagram of a lamp and laser in a free-generation regime for a lamp voltage of 4.1 kV](image)

Slika 2. Zbirni dijagram lampje in lasersa v režimu slobodnega generiranja za napon lampje od 4,1 kV

![Figure 3. Laser pulse structure in a free-generation regime with prominent spikes](image)

Slika 3. Struktura laserskega impulsa v režimu slobodne generacije sa izraženimi spajkoma
Figure 4. Laser pulse in a Q-switch regime for 4.3 kV voltage

Slika 4. Laserski impuls u režimu Q prekidanja pri naponu od 4.3 kV

Measurements of the laser pulse characteristics using an EG & SGD 040 radiometric system show the real shape of the laser signal (Figure 4).

The laser was used in the Q-switch regime and the pulse length was 30 ns. Focused and unfocused beams were used, as well as different positions of the specimens regarding the focus of the lens. The focus length of the lens was 100 mm. The specimens were under a right angle to the laser beam. The unfocused beam is presented by the area in Figure 5, so its size was of the same order as the specimen. The laser operated in the TEM₀₀ mode, which can be seen from the round shape.

Figure 5. Area of the output laser beam

Slika 5. Površina izlaznog laserskog snopa

The specimens were subjected to a ruby laser, operating in a monopulsed regime. The experimental conditions are given in Table 1. CF denotes carbonized felt, HTF heat-treated felt, while CC is carbonized cloth.

Scanning electron microscopy, SEM and X-ray diffraction analysis were used to analyze the morphological, structural, and also destructive and non-destructive changes.

A Philips XL-30 DX4i scanning electron microscope was used. The electronic optics were integrated with the outer system and automated by a basic program. The interface with expanded logic is given in MS Windows.

The structural characteristics — interlayer distance \(d_{002} (c/2)\), crystalline height \(L_c\) and width \(L_a\) — were determined by X-ray diffraction analysis using a D 500 Siemens device with CuKα1 radiation. The interlayer distance was assessed from the angle position of diffraction profile (002) using Bragg's law:

\[
d_{002} = \frac{c}{2} = \frac{n\lambda}{2 \sin \theta}
\]

(1)

where:

- \(n\) — is the diffraction order; diffraction profile (002) corresponds to the first order of diffraction, \(n = 1\);
- \(\lambda\) — the wavelength of CuKα1 radiation, \(\lambda = 0.154 \text{ nm}\);
- \(\theta\) — the diffraction angle.

The size of the crystallite along the c-axis, called the crystallite height \(L_c\), and along the a-axis, the crystallite width \(L_a\), were determined from the half-width of the diffraction profile using Scherrer's equation:

\[
L (\text{nm}) = \frac{K\lambda}{B \cos \theta}
\]

(2)

where:

- \(L = L_c\) or \(L_a\), is the size of the crystallite, height and width [nm];
- \(B\) — the peak half-width in radians;
- \(K\) — the shape factor. For \(L_c\) this factor is 0.89, and for \(L_a\) it is 1.84.

**RESULTS AND DISCUSSION**

Numerous processes occur in a material subjected to laser radiation — heating, surface oxidation, fiber damage, structural changes — which affect the material properties. For a process to take place, the laser radiation has to exceed a certain threshold which depends on the material and laser characteristics.

The interaction of a ruby laser with carbon textiles, carbonized and heat-treated felt, causes changes in the material. The experimental conditions

<table>
<thead>
<tr>
<th>Material</th>
<th>Energy [J]</th>
<th>Energy density [J/cm²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1CF</td>
<td>1.7</td>
<td>24.0</td>
</tr>
<tr>
<td>2CF</td>
<td>1.7</td>
<td>0.54</td>
</tr>
<tr>
<td>1HTF</td>
<td>1.7</td>
<td>24.0</td>
</tr>
<tr>
<td>2HTF</td>
<td>1.7</td>
<td>0.54</td>
</tr>
<tr>
<td>1CC</td>
<td>0.1</td>
<td>0.08</td>
</tr>
<tr>
<td>2CC</td>
<td>1</td>
<td>0.32</td>
</tr>
<tr>
<td>3CC</td>
<td>1.6</td>
<td>8.14</td>
</tr>
</tbody>
</table>
Table 2. The conditions of ruby laser interaction with carbonized and heat-treated felt
Tabela 2. Uslovi interakcije rubinskog lasera sa karbonizovanim i termički nitanim filcem

<table>
<thead>
<tr>
<th>Material</th>
<th>Energy [J]</th>
<th>Energy density [J/cm²]</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1CF</td>
<td>1.7</td>
<td>24.0</td>
<td>Damaged</td>
</tr>
<tr>
<td>2CF</td>
<td>1.7</td>
<td>0.54</td>
<td>Damaged</td>
</tr>
<tr>
<td>1HTF</td>
<td>1.7</td>
<td>24.0</td>
<td>Damaged</td>
</tr>
<tr>
<td>2HTF</td>
<td>1.7</td>
<td>0.54</td>
<td>Not damaged</td>
</tr>
</tbody>
</table>

for specimens the surface of which was analyzed by SEM are given in Table 2.

The damage of textile material during interaction with a ruby laser is shown in the microphotographs in Figs. 6 to 9. The laser energy used in the experiment is the same, only the energy density, \( \Phi \), varies depending on whether the target is focused or not.

In case of an unfocused beam, no visible changes occurred when heat-treated felt (HTF) was the target. When the energy density is larger (focused beam), the damage is larger. Damage was observed in all specimens in the case of interaction with a focused laser beam (Figs. 6 and 8). Although the fibers in felt are disordered, it can be seen that the damage caused by a focused beam has penetrated somewhat deeper (Fig. 6) compared to the effect of an unfocused beam (Fig. 7).

It can also be concluded that the temperature of heat treatment has an impact on the effect of laser interaction, because felt heat-treated up to 2200 °C, under the conditions used in the experiment, did not suffer any damage in the case of interaction with an unfocused beam. The effect of a focused beam on this specimen was considerably smaller (Fig. 8) than in the case of carbonized felt (Fig. 6).

Damage also occurs when carbonized and heat-treated felt, are subjected to a ruby laser due to heating and surface oxidation. The energy density threshold which leads to the damage is different. In carbonized felt, an energy density of \( \Phi = 0.54 \text{ J/cm}^2 \) is sufficient for the oxidation to be more intensive and combustion to occur (Fig. 7). In heat-treated felt, this energy density did not cause any visible damage, since the material had already been exposed to high temperatures in the manufacturing process. For an energy density of \( \Phi = 24.0 \text{ J/cm}^2 \) this is not the ca-
These changes depend on the characteristics of the radiation applied, as well as on the properties of the carbon fibrous material. Depending on the experimental conditions, destructive and non-destructive changes can occur. Both kinds of changes are of interest. Determination of the energy density thresholds which lead to changes in the material is very important, because it enables the establishment of the optimal processing parameters (e.g. cutting complicated shapes). Also, it is important for future work to know what kind of changes can be expected from particular combinations of laser radiation and carbon textile material.

It has been established that ruby laser radiation mostly influences the microcrystalline structure of the carbon textile material, i.e. it leads more or less to a better arrangement of the carbonized cloth turbostratic structure.

A mathematical model, which will primarily describe the conductive thermal fields induced in activated carbon textile materials due to the interaction with laser radiation, will be developed.

ACKNOWLEDGEMENTS

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ABBREVIATIONS AND SYMBOLS

CF – carbonized felt
HTF – heat treated felt
CC – carbonized cloth
\( \lambda \) – wavelength
\( d_{02} \) – interlayer distance
\( I_{c} \) – crystallite height
\( I_{a} \) – crystallite width
\( n \) – diffraction order
\( \theta \) – diffraction angle
\( B \) – peak half–width in radians
\( K \) – shape factor
\( \Phi \) – energy density of laser radiation

REFERENCES

IZVOD

INTERAKCIJA RUBINSKOG LASERA SA UGLJENIČNIM VLAKNASTIM MATERIJALIMA

(Naučni rad)

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Key words: Carbon fibrous material • Ruby laser • Modification • Damages • Turbostratic structure •