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SCIENTIFIC PAPER

677.4+544.032.65:677.017.3

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.

Carbon fibrous materials of different shapes (fabric, cloth, felt) are interesting because of numerous good properties: they are thermally and chemically stable, they can have high electrical conductivity, and are easily cut and shaped. That is why they have found wide application as thermal insulators, heating elements, substrates in C/C composites etc. The largest application – in personal protection, environmental protection, medicine – involves activated carbon materials which are obtained by controlled oxidation in the process of manufacturing. These materials are characterized by a large specific surface greater than 1500 m^2/g. They are mostly microporous, with pores < 2 nm, and mesoporous, with pores from 2 to 50 nm, which is a pore distribution convenient for adsorption processes [1].

The area of laser application is very diverse: they are used in different kinds of measurements, the transmission of information, computer engineering, electronics, microelectronics and optoelectronics, detection and automation, defects detection, processing of materials, drilling, soldering, welding, in the aerospace and automobile industry, in military purposes and space exploration [2–7]. Laser–material interaction has been singled out as a special area of study.

It is characteristic for carbon materials that they withstand high temperatures. However, because of the extremely short duration of the laser pulse, it is interesting to see how the material will behave. It is assumed that some reactions take place by a different mechanism than with classical temperature increase. 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 (photolytical 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 CO_2 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 microgeometric 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.

*Paper presented at the "Peti seminar mladih istraživača" (5^{th} Seminar of Young Researchers), Belgrade, December 25–26, 2006.

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Paper received: December 25, 2007.
Paper accepted: Januar 31, 2007.

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 dTex;
- linear mass density of the yarn: 330/60 dTex;
- weaving: flat double;
- interweaving: flat right–right;
- surface mass: 380 – 390 g/m^2;
- material thickness: 1.3 mm.

Felt characteristics:

- fiber type: staple cellulose fiber;
- linear mass density of the fiber: 3 – 4 dTex;
- weaving: needling;
- surface mass: around 500 g/m^2;
- 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 $ZnCl_2$ and NH_4Cl, while the felt was placed only in NH_4Cl 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, λ = 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.

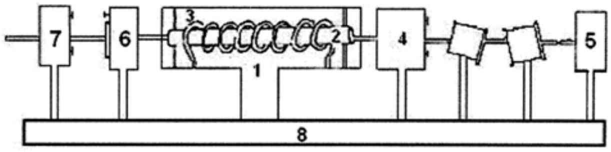

Figure 1. Schematic representation of the "Apollo" ruby laser, model 22
Slika 1. Shematski prikaz rubinskog lasera "Apollo", model 22

The laser energy was measured with a digital energy analyzer (ACM 101) with a calorimetric probe, model L 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 flash lamp.

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.

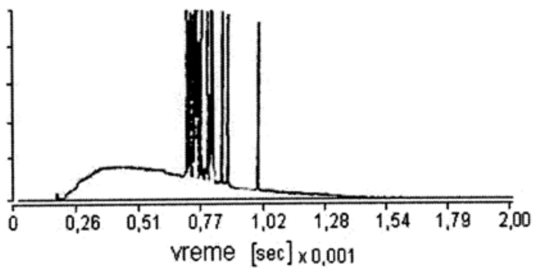

Figure 2. Cumulative diagram of a lamp and laser in a free–generation regime for a lamp voltage of 4.1 kV
Slika 2. Zbirni dijagram lampe i lasera u režimu slobodnog generisanja za napon lampe od 4,1 kV

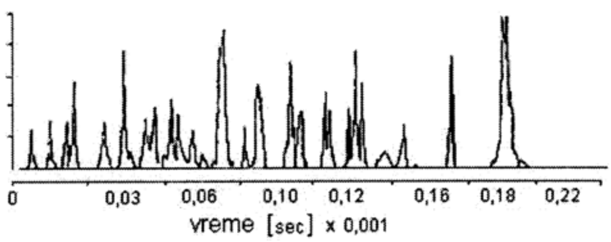

Figure 3. Laser pulse structure in a free–generation regime with prominent spikes
Slika 3. Struktura laserskog impulsa u režimu slobodne generacije sa izraženim spajkovima

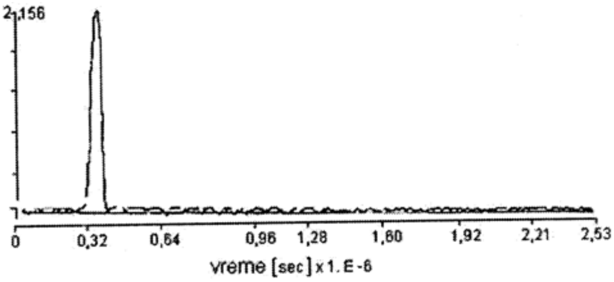

Figure 4. Laser pulse in a Q–switch regime for 4.3 kV voltage
Slika 4. Laserski impuls u režimu Q prekidanja pri naponu od 4,3 kV

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 TEM_{00} mode, which can be seen from the round shape.

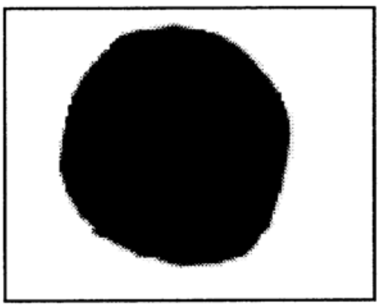

Figure 5. Area of the output laser beam
Slika 5. Površina izlaznog laserskog snopa

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:

Table 1. The conditions of ruby laser interaction with different types of carbon textile material
Tabela 1. Uslovi interakcije rubinskog lasera sa različitim tipovima ugljeničnog tekstilnog materijala

Material	Energy [J]	Energy density [J/cm^2]
1CF	1,7	24,0
2CF	1,7	0,54
1HTF	1,7	24,0
2HTF	1,7	0,54
1CC	0,1	0,08
2CC	1	0,32
3CC	1,6	8,14

$$d_{002} = \frac{c}{2} = \frac{n\lambda}{2\sin\Theta} \qquad (1)$$

where:
n – is the diffraction order; diffraction profile (002) corresponds to the first order of diffraction, $n=1$;
λ – the wavelength of CuKα1 radiation, λ=0.154 nm;
Θ – 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:

$$L\ (\text{nm}) = \frac{K\lambda}{B\cos\Theta} \qquad (2)$$

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 l–2aser 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 2. The conditions of ruby laser interaction with carbonized and heat–treated felt
Tabela 2. Uslovi interakcije rubinskog lasera sa karbonizovanim i termički tretiranim filcom

Material	Energy [J]	Energy density [J/cm^2]	Comment
1CF	1,7	24,0	Damaged
2CF	1,7	0,54	Damaged
1HTF	1,7	24,0	Damaged
2HTF	1,7	0,54	Not damaged

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, Φ, 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

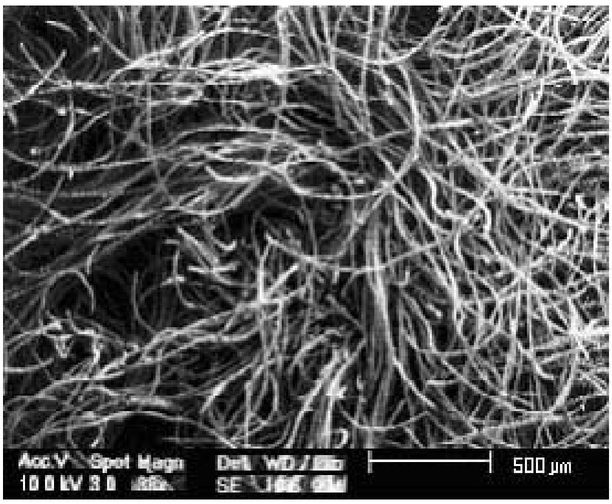

Figure 6. Microphotograph of the specimen 1CF after interaction with a ruby laser (Φ = 24.0 J/cm^2)
Slika 6. Mikrofotografija uzorka 1CF nakon interakcije sa rubinskim laserom (Φ = 24,0 J/cm^2)

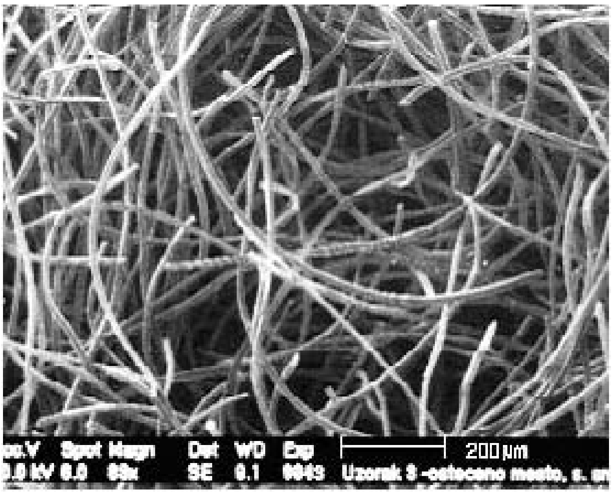

Figure 7. Microphotograph of the specimen 2CF after interaction with a ruby laser (Φ = 0.54 J/cm^2)
Slika 7. Mikrofotografija uzorka 2CF nakon interakcije sa rubinskim laserom (Φ = 0,54 J/cm^2)

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 Φ = 0.54 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 Φ = 24.0 J/cm^2 this is not the ca-

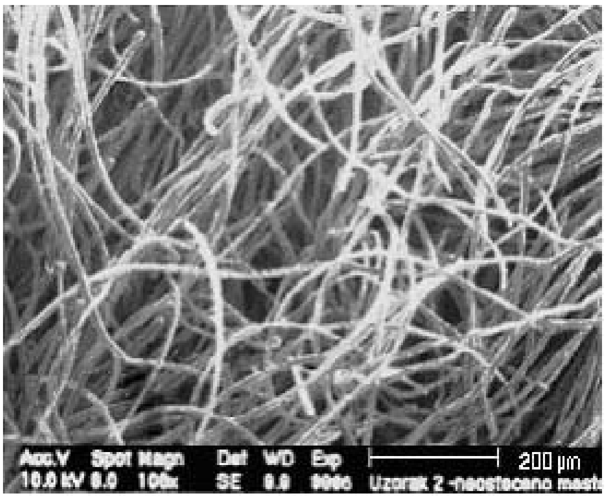

Figure 8. Microphotograph of the specimen 1HTF after interaction with a ruby laser (Φ = 24.0 J/cm^2)
Slika 8. Mikrofotografija uzorka 1HTF nakon interakcije sa rubinskim laserom (Φ = 24,0 J/cm^2)

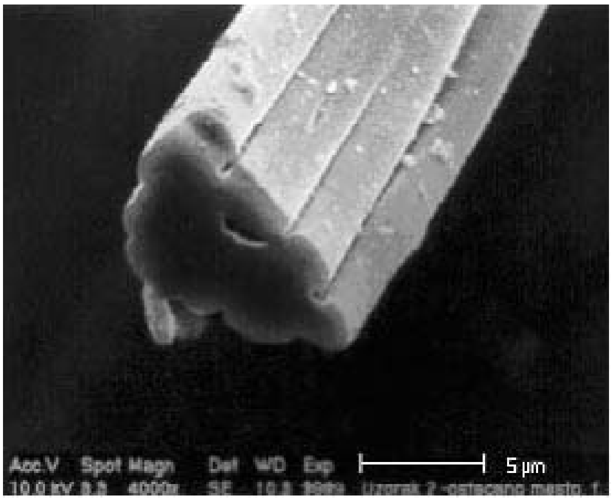

Figure 9. Microphotograph of the fiber of 1HTF cut by a ruby laser focused beam
Slika 9. Mikrofotografija vlakna 1HTF presečenog fokusiranim snopom rubinskog lasera

Table 3. The results of X-ray diffraction analysis of carbonized cloth before and after modification by a ruby laser
Tabela 3. Rezultati rendgensko-difrakcione analize karbonizovane pletenine pre i posle modifikacije rubinskim laserom

Specimen and energy density [J/cm^2]	2Θ [^{o}]	d_{002} [nm]	L_c [nm]	L_c/d_{002}	L_a [nm]
CC	24,53	0,363	0,840	2,3	3,389
1CC, Φ = 0,08	24,82	0,358	1,039	2,9	3,955
2CC, Φ = 0,32	24,43	0,364	1,083	3,0	4,435
3CC, Φ = 8,14	25,57	0,348	1,149	3,3	4,003

se (Fig. 8), –2and the fiber cut is smooth and flat, as if melted (Fig. 9).

The effect of a laser beam in a given operating regime on the structural changes of carbon textile was analyzed by X–ray diffraction of the carbonized cloth before and after interaction with a ruby laser. The results are given in Table 3.

Two wide peaks around $2\Theta \sim 24^o$ and 44^o were observed and attributed to (002) and (001) reflexions. These peaks as well as values of the interalyer distance d_{002} of around 0.34 to 0.37, indicate a so–called turbostratic structure, which is characteristic for all carbon materials. It has been established that ruby laser radiation affects the arrangement of this structure – crystal growth occurs, in height as well as in width. The crystallite height L_c increased from 0.8 to 1.15 nm, so the number of graphene layers increased from 2 to 3. The crystallite width increased from 3.4 to 4.4.

CONCLUSION

Structural changes arising due to the effect of ruby laser radiation on carbon fibrous materials were examined.

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. Deteremination 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

This research was supported by the Ministry of Science and Environmental Protection, Republic of Serbia, under Contract No. 142016. We would like to thank the Military Technical Institute for help in the experimental work.

ABREVATIONS AND SYMBOLS

CF – carbonized felt
HTF – heat treated felt
CC – carbonized cloth
λ – wavelength
d_{002} – interlayer distance
L_c – crystalline height
L_a – crystalline width
n – diffraction order
Θ – diffraction angle
B – peak half–width in radians
K – shape factor
Φ – energy density of laser radiation

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IZVOD

INTERAKCIJA RUBINSKOG LASERA SA UGLJENIČNIM VLAKNASTIM MATERIJALIMA

(Naučni rad)

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Ugljenični tekstilni materijali interesantni su za proučavanje zbog dobrih osobina i brojnih mogućnosti primene. Svojstva ovih materijala mogu se programirati pažljivim izborom parametara procesa modifikacije. U tu svrhu uspešno može da se koristi i laserska tehnika. Visoke temperature koje nastaju u materijalu za kratko vreme delovanja laserskog impulsa mogu izazvati niz promena u materijalu. Ugljenični vlaknasti materijali u različitim tekstilnim oblicima, u toku različitih stupnjeva procesa, izlagani su dejstvu laserskog zračenja. Korišćeni su karbonizovani filc, termički tretirani filc i karbonizovana pletenina. Za modifikaciju materijala korišćen je rubinski laser (λ=694,3 nm). Laser je radio u režimu Q prekidanja, a dužina impulsa je 30 ns. Korišćen je fokusiran i nefokusiran snop i različiti položaji uzoraka u odnosu na položaj žiže sočiva. Ispitane su strukturne promene korišćenjem skenirajuće elektronske mikroskopije, SEM, i rendgenske difrakcione analize. SEM metodom ispitani su uzorci karbonizovanog i termički tretiranog filca. U slučaju kada se koristio nefokusirani snop, a meta bio termički tretiran filc, nije došlo do vidnih promena na materijalu. U svakom slučaju, kada je gustina energije lasera veća (fokusiran snop) i oštećenje je veće. Oštećenja su uočena kod svih uzoraka pri interakciji sa fokusiranim snopom laserskog zračenja. Iako su u filcu vlakna haotično uređena, vidi se da je oštećenje sa fokusiranim snopom nešto dublje prodrlo u filc u odnosu na dejstvo nefokusiranog snopa. Može se takođe reći da i temperatura termičkog tretiranja materijala ima uticaj na dejstvo interakcije sa laserom, jer filc koji je termički tretiran do 2200 ^{o}C, pri uslovima korišćenim u eksperimentu nije pretrpeo oštećenje u slučaju interakcije sa nefokusiranim snopom. Dejstvo fokusiranog snopa na ovaj uzorak izraženo je znatno manje nego u slučaju karbonizovanog filca, a presečeno vlakno je glatko i ravno, kao da je istopljeno. Rendgenskom difrakcionom analizom utvrđeno je da zračenje rubinskog lasera najviše utiče na mikrokristalnu strukturu ugljeničnog tekstilnog materijala, tj. dovodi u većoj ili manjoj meri do sređivanja turbostratične strukture karbonizovane pletenine – dolazi do rasta kristalita, kako u visini tako i u širini.

Ključne reči: Ugljenični vlaknasti materijal • Rubinski laser • Modifikacija • Oštećenja • Turbostratična struktura •

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