Structure Modification of Surface of Fine-Grained Graphite and Glassy Carbon under High Power Action by Hydrogen Plasma[1]

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Abstract – The studies of exposing of targets by hot-electron plasma exhaust from the multi-mirror trap GOL-3 are carried out. In experiment conditions the energy density affected the target placed in facility chamber can be varied within 1–30 MJ/m^2 per shot.

In the paper the results of Raman and SEM studies of surface modification of carbon materials with different ordering range of *sp*2 fraction (fine-grained graphite and glassy carbon) exposed by hot hydrogen plasma with energy density up to 8 MJ/m^2 are presented. It is shown that on the depth up to ~80 nm due to this exposing there are obtained two effects – micro structural destruction of the surface and extension of crystallite size of *sp*2 phase, i.e., ordering of nanostructure.

1. Introduction

Carbon based engineering materials are used for different areas of science and technology, in particularly for plasma dumping. High power density loads engage to pick out well-ordered graphite composites possessed by high heat conductivity (CFCs and other). However, they characteristics must be stable under long action by stream of high-energy particles. Such studies with different carbon materials are carried out for a long time (see, e.g., [1–10]). According to referenced data, a nanostructural modification of the materials under high-power action is observed. At the same time, this process can lead to both disordering and extension of crystallite areas. The analysis of the studies shows that surface amorphization is observed due to different defects accumulation at relatively low heat input – under ~0.1 MJ/m^2. In a case of higher heat input the ordering of crystallite structure takes place, one possible mechanism of them is thermal graphitization [11, 12].

In the experiments on plasma confinement in powerful plasma machines the loads on various dumps of fast particles reaches up to several MJ/m^2 and will be up to 30 MJ/m^2 in ITER at various disruptions. These energies must lead to sufficient modification of targets surfaces.

The studies of plasma confinement in multi-mirror trap GOL-3 placed in the Budker Institute of Nuclear Physics [13] and its heating by powerful relativistic electron beam (energy 0.8 MeV, energy content up 200 kJ, duration 8 μs [14]) are carried out. Due to collective interaction, the REB transmits effectively the energy to the plasma electrons and ions (see [15, 16]). Plasma temperature after heating stage reaches ~2 keV. In the exit of the plasma machine the stream of hot plasma and passed electron beam is dumped by collector, placed in splay magnetic field. Common energy density is ~2 MJ/m^2 corresponds to ELMs type I in ITER.

In that conditions the different carbon materials, fine grained graphite MPG-6 and glassy carbon SU-2000, were exposed. Choice of the materials was caused by they find a wide technological application on the one hand, and have different crystalline structure on the other hand. Structure of glassy carbon is amorphous and MPG-6 can be characterized as nanostructured polycrystal.

2. Experiment

For studying the carbon specimens were made in the form of plates of typical size ~20 mm and thickness 2–3 mm. The layout of experiment is shown in Fig. 1.

Relativistic electron beam and hot plasma are dumped by graphite collector in the exit of facility, placed in splay magnetic field. Because of design of magnetic expander the exhaust stream came on target varies within 1–30 MJ/m^2 by placing it on different distances from exit mirror. In the experiments, they were placed in magnetic field 0.28 T.

Specific energy distribution of electron stream measured in similar regimes of facility operation and magnetic field value is shown in Fig. 2 [17].

Spectra shape is determined by features of beam-plasma interaction. Passing through plasma column the relativistic electron beam loses about 40% energy.

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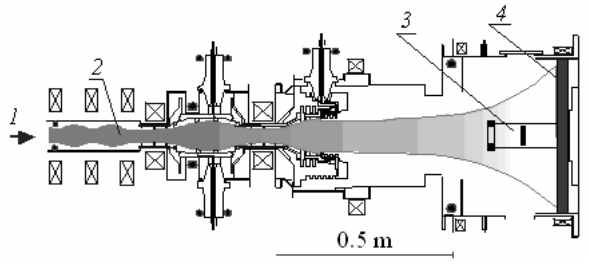


Fig. 1. Layout of experiments on carbon targets exposing by hot-plasma stream on GOL-3 facility: *1* – exhaust of plasma; *2* – end of multi-mirror trap; *3* – target; *4* – plasma dump

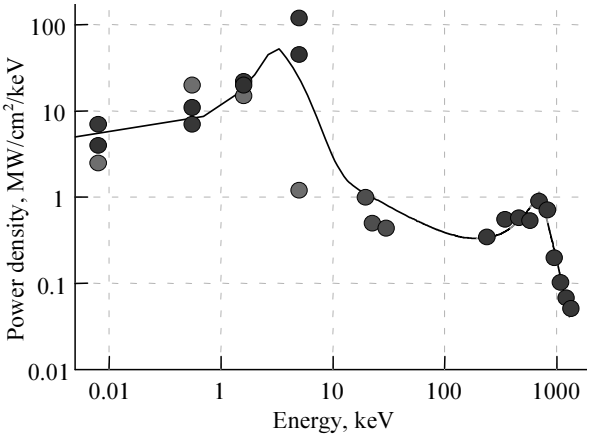


Fig. 2. Energy distribution of power density of irradiating electron stream

The last is transmitted, mainly, to epithermal electrons. About 3% of beam energy (~5 kJ) remains in plasma, heating it up to temperature of 2 keV at density ~10^{21} m^{-3}. Hot plasma gradually flows out through the ends of multi-mirror trap during ~1 ms.

The total energy density reached the target was measured by heat radiation obtaining from its surface and by bolometer. The methodic is described in detail in [18]. Following an experiment the energy density was 2.1 MJ/m^2 per shot.

Energy release distribution versus carbon target depth is shown in Fig. 3, *a*.

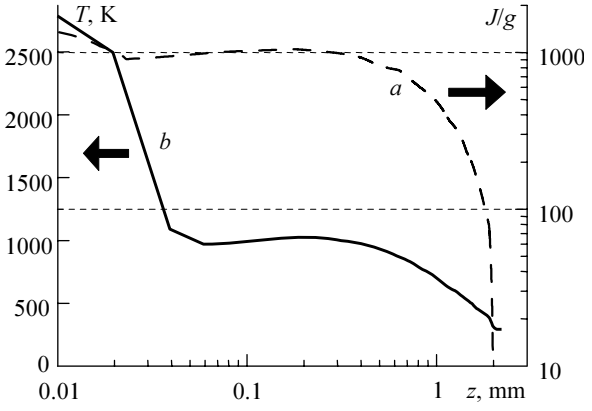


Fig. 3. Energy release (dashed) and temperature (solid) distribution versus carbon target depth just after REB ending. Distributions are calculated by EMSH [21] and DISWALL [20] codes using Fig. 2 dependence

One can see, that high-energy electrons (0.1–1 MeV) with ranges ~1 mm heat bulk of target up to ~1000 K. Superficial layer on the depth of ~20 μm (see Fig. 3, *b*) overheats by energy release from epithermal electrons and hot plasma ions. The value of volumetric energy release in this area reaches 50 kJ/g, that sufficient greater than enthalpy of phase change of microstructural graphite destruction (~10 kJ/g, [19]). However simulation of heat transport by DISWALL code [20], show that maximal temperature does not exceed 3000 K that is below sublimation temperature (4100 K).

3. Results

For obtaining of nanostructure modification the Raman spectroscopy was used. The method based on measuring of profiles of *G*- and *D*-vibration graphite modes before and after exposing. Changes of they intensities and widths by Tuinstra–Koening correlation [22, 23] give the opportunity to estimate crystallite size of sp^2 phase (L_a):

$$C(\lambda)/L_a(\text{Å}) = I_D/I_G,$$

where: $\lambda = 514.5$ nm is the wavelength of excited light, $C(\lambda) \approx 44$Å. The method gives averaged L_a size on the carbon layer depth of 50–100 nm depending on material.

Before exposing graphite specimens MPG-6 were burnished for micro structural modification obtaining (see SEM photo in Fig. 5, *a*). Its initial Raman spectrum is shown in Fig. 4 (top curve). One can see sharp *G*- (1623 cm^{-1}) and *D*-peaks (1360 cm^{-1}) are present.

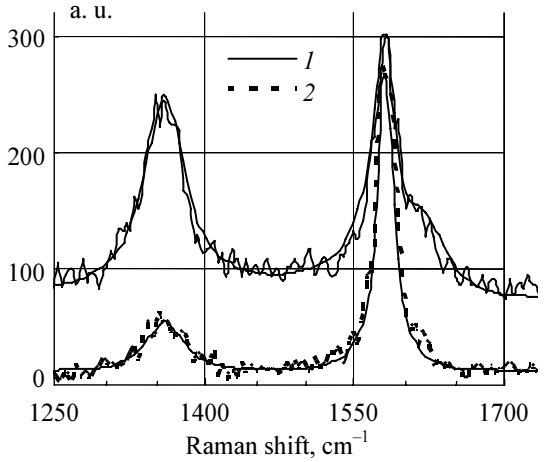
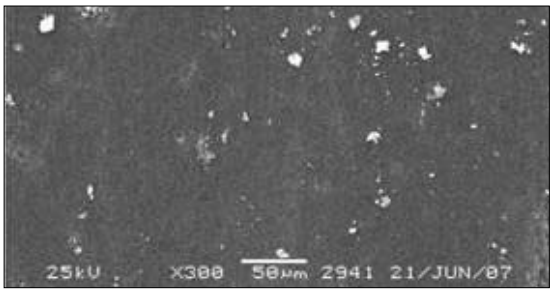


Fig. 4. Fitted Raman dispersion spectra of fine grained graphite MPG-6 before (solid line) and after (dashed) exposing

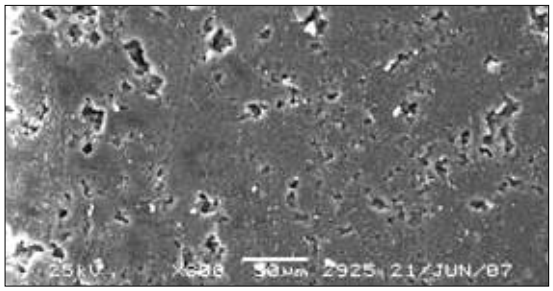
So additional *D′* peak is obtained at 1623 cm^{-1}. Spectrum is fitted by asymmetric Breit–Vigner–Fano profile (*G*) and two Lorenzian profiles (*D*, *D′*) with 28 and 50 cm^{-1} widths correspondingly. The spectrum allows to characterize this material according with [2] as nano-structured graphite. Peaks ratio is $I_D/I_G = 0.81$

that allow to estimate [1] graphite crystallite size of 50 Å.

The specimen was exposed by four repeated plasma impact up to 8 MJ/m^2 total heat load. The exposed surface has defects of erosion of ~10 μm characteristic dimension obtained by SEM (see Fig. 5, *b*).



a



b

Fig. 5. SEM image of fine grained graphite MPG-6 before (*a*) and after (*b*) exposing

It agrees with MPG-6 grains size covering the range of 10–100 μm. This process can be obtained because of grains binding energy some less of microstructural graphite destruction ~10 kJ/g.

In Raman spectrum changes take place after irradiation. Width *G*- and *D*-peak diminished on 5–8 cm^{-1}, asymmetry of *G* peak reduced and peaks ratio decreased up to 0.17 that testifies arising of crystallite size up to 260 Å.

The Raman spectrum of glassy carbon is shown in Fig. 6 (bottom).

In the spectrum *G*- (1594 cm^{-1}) and *D*- (1360 cm^{-1}) peaks with widths of 95 и 90 cm^{-1} correspondingly are seen. As graphite procedure was used for fitting. Obtained spectrum allows us to characterize the studied material according with [22] as carbon with amorphous structure.

For such materials the Tuinstra–Koening correlation stops to hold. And for estimation of graphite (sp^2-phase) ordering sizes the correlation proposed in [22] can be used. The result is about 9.6 Å.

The specimen was exposed by three repeated plasma impact up to 6 MJ/m^2 total heat load. In Fig. 7 the surface SEM photos before (a) and after (b) exposing are shown.

Some scales ~100 nm thick are seen on surface after exposing. They are situated on all specimen surface.

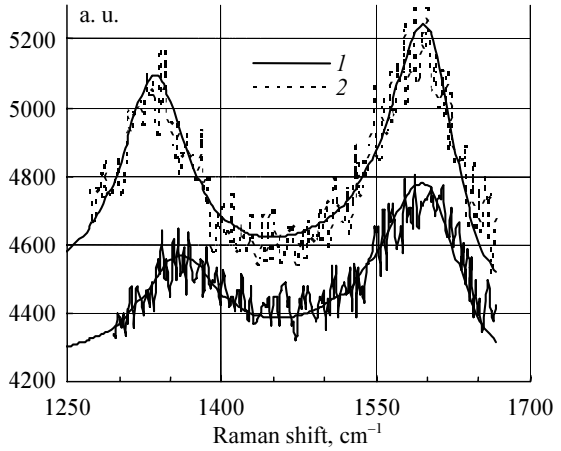
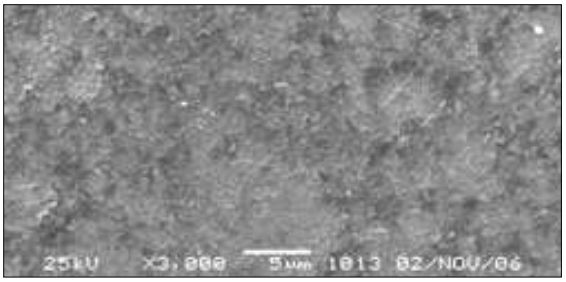
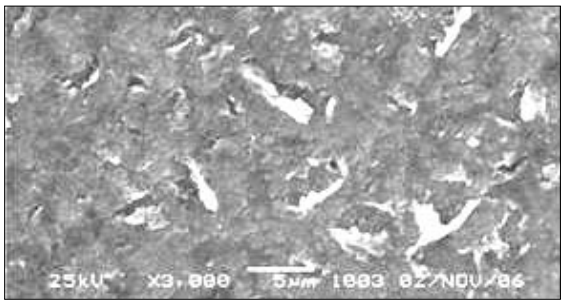


Fig. 6. Fitted Raman dispersion spectra of glassy carbon before (solid line) and after (dashed) exposing



a



b

Fig. 7. SEM image of glassy carbon before (*a*) and after (*b*) exposing

In Raman spectrum of glassy carbon changes are seen after exposing (Fig. 6, top curve). *D* peak shifted to 1335 cm^{-1}, widths both peaks diminished to 80 cm^{-1} and peaks ratio increased to 0.72. That testifies to graphitization of specimen surface and allows estimating sp^2-phase ordering sizes as 11.5 Å.

4. Discussion

In [12] it is shown that carbon materials can be divided into graphitized and un-graphitized by heat treatment at 2000–3000 K. The typical graphitized materials have texture with turbostatic orientation reached over sizeable distances. Under heating, it assists to gradual azimuth rotation of some layers up to matching with neighbors organizing in scope the graphite structure. In the typical un-graphitized materials, the local well-

ordered zones are appreciably less and placed confusedly therefore ordering increase under heat treatment results in small crystallite arising with mutual chaotic ordering.

The obtained results show the change of superficial structure modification of carbon materials under hot-electron plasma exposing of 6–8 MJ/m^2 density load for several milliseconds. In both MPG-6 and glassy carbon specimens the extension of sp^2-phase crystallites size is obtained by Raman spectroscopy. But because of glassy carbon belongs to un-graphitized materials the graphitization value is small sufficiently.

Supposed mechanism responsible to structure ordering can be thermal graphitization. However, in [12] was pointed that this process has a long time. In particular, for enlargement of La up to 100 nm for initially turbostatic orientation one needs a day at 2700 K and some minutes at 3300 K.

In [24] was pointed that at these experimental conditions of graphite exposing from the surface an enough target atoms amount flies down forming dense gas-plasma cloud close to the surface. These atoms deposit partly back on the target after shot ending. Bulk fine-disperse particles of target material get detached as well at the same time. Because of they are situated in dense surface plasma with temperature of a few electron volts these particles can heat up to sublimation temperature. It can lead to significant fast thermal graphitization of grains whereupon they precipitate partly on target substrate. The presence of many flakes on glassy carbon targets can testify this process.

As was mentioned above the calculated surface temperature of targets reaches ~3000 K. But processes superficial structure modification of target can lead simultaneously to reduction of heat transport between grains and increase of surface temperature. That can quicken of graphitization process as well.

5. Conclusion

The studies of behavior of essential structurally-different carbon materials, fine-grained graphite and glassy carbon, under hot-electron plasma exposing were carried out. The total heat load was 6–8 MJ/m^2 at impact time of ~5 μs. The Raman spectra from targets surface shown graphitization process of both substances on the depth at least of ~50 nm. It appears by enlargement of sp^2-phase crystallites size.

The most probable mechanisms of specimens superficial graphitization are thermal treatment and re-precipitation of carbon from dense gas-dust phase being close to the surface and appeared at target destruction by powerful plasma stream.

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