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STRUCTURAL CHANGES IN INDUSTRIAL GLASSY CARBON AS A FUNCTION OF HEAT TREATMENT TEMPERATURE ACCORDING TO RAMAN SPECTROSCOPY AND X-RAY DIFFRACTION DATA

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Changes in the structure of glassy carbon as a function of heat treatment temperature is investigated by Raman spectroscopy and X-ray diffraction measurements. It is shown that the glassy carbon samples studied can be described as poorly ordered turbostratic nanographite. An increase in temperature leads to some ordering with preservation of the general structural motif. Based on spectroscopic evidence, graphene sheet curvature in the high-temperature glassy carbon samples is suggested.

Keywords: Glassy carbon, nanographite, Raman spectroscopy, X-ray diffraction.

1. Introduction

Glassy carbon (GC)[1] is an sp^2 carbon material (CM) produced by the pyrolysis of suitable thermoreactive organic polymers. Due to GC’s unique physicochemical properties, such as isotropy, chemical inertness, high mechanical strength, low density, impermeability to gases and liquids, extreme resistance to chemical attack, electrical conductivity, heat conduction, biocompatibility [1,2], this material is widely used in modern high-technologies. GC, produced by the carbonization of oxygen-containing polymers, belongs to the so-called “non-graphitizable” CM which do not transform to graphite even at temperatures of up to 3000 ^{o} [2,4]. Several models were proposed for GC structure based on X-ray and neutron diffraction data as well as those of Raman spectroscopy, SEM, TEM and AFM [4-8], and on model calculations [9,10], however, its atomic-scale structure is not fully elucidated.

Our aim was to follow structural changes in the samples of a typical non-graphitized CM, fabricated at the pilot factory of the State Research Institute of Graphite (NIIGrafit, Moscow) by carbonization of phenol-formaldehyde resin SFG-3038, and heat-treated in a step-wise manner under an inert atmosphere in the interval from 1020 to 2700 °C (the samples are marked as GC1020 etc). To characterize the samples, elemental analysis, Raman spectroscopy and X-ray diffraction (XRD) data were used. The latter measurements were non-destructive and were carried out sequentially, without preliminary sample preparation.

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[1] “Glassy carbon” is a trademark commonly used instead of IUPAC recommended [1] term “glass-like carbon”.

2. Experimental

Raman spectra were obtained using a laser Raman spectrometer LabRAM (Jobin Yvon). The spectra were excited by a 632.8 nm line of a He-Ne laser, laser power not exceeding 1 mW. The spectra registered from different spots of the sample shears appeared identical, thus pointing to the sample homogeneity. X-ray diffraction patterns were measured in the Bragg-Brentano $\theta/2\theta$ geometry using a DRON-3 automated diffractometer (CuKα radiation, scanning step 0.02°). The curve-fitting analysis of the Raman band contours and diffraction patterns was carried out using a standard Origin 7.5 program with appropriate Lorentzian, Gaussian or Voight functions.

3. Results and Discussion

Raman spectra of GC from various origins have been published and interpreted in many papers, starting from the classical work of Koenig (see, e.g. [11-20]). First-order Raman spectra of GC differ from those of graphite in the widths of the D and G lines and in their intensity ratio, $I_D/I_G > 1$, the latter is also typical for other nano-sized disordered sp^2 CM [14-16,20], as well as in the presence of the line in the region of $\sim$1100 cm^{-1}. The region 1000–3200 cm^{-1} of the Raman spectra obtained for the samples studied is presented in Fig. 1 and characterized in Table 1. The overall spectral pattern agrees well with the literature data; in all spectra, the ratio $I_D/I_G > 1$. However, in the Raman spectrum of GC1020, the G and D lines are broadened compared to the spectrum of a typical GC [20]. The second-order Raman spectrum of this sample exhibits very broad and weak bands, typical for all strongly disordered sp^2 carbons [13,20]. All this is not surprising, because it is well-known [2,3,13] that at the initial stage of the resin pyrolisis (up to $\sim$1400 °C), primary carbonization and polymerization of the organic substance takes place with the formation of randomly oriented graphene layers, however, containing an appreciable fraction of heteroatoms. Indeed, according to our elemental analysis data, the sample GC1020 contains only 75% of carbon. Thus, the sample marked GC1020 is in essence not a real glassy carbon. Heat-treatment of GC samples up to 1450 ° increases the carbon content to 98% and in the GC1650 sample it reaches the value of 99.5 %. The Raman spectra exhibit noticeable changes (Fig. 1,3,4, Table 1). The D and 2D lines shift slightly and gradually narrow. The G line becomes more and more asymmetric, and in the spectra of GC2100 and higher, a weak line at 1620 cm^{-1} (D$'$) becomes clearly visible, which points to a turbostratic structure, i.e., to the absence of strict periodicity along the **c** axis [19,20]. The latter conclusion is also confirmed by a gradual formation in the second-order spectrum of an intense symmetric line at 2650 cm^{-1}, corresponding to an overtone 2D. Thus, it is evident from the Raman spectra that an increase in the annealing temperature leads to partial ordering of the condensed aromatic clusters in the **ab** plane (two-dimensional “quasi-crystallization”) [19].

X-ray diffraction data are fully consistent with the above Raman spectroscopy data (Fig. 2). The diffraction pattern of GC1020 reveals three very broad peaks at $2\theta = 24.0$, 43.6 and 79.7°, which can be assigned to 002, 100 and 110 indices of the graphite lattice. No general-index lines (e.g., 101) were observed. Furthermore, the 100 and 110 lines were strongly asymmetric due to the Warren effect [21,22]. This indicates that the sample GC1020 can be formally described as a nanostructured turbostratic graphite without register in the orientation of adjacent graphene layers and with a very small size of ordered domains. In contrast to bulk graphite, this sample is not prone to preferred orientation. The sample GC2700 additionally contains an admixture of ordered polycrystalline graphite, which is evidenced by the occurrence of 002 line at 26.47° with FWHM of 0.65° (the area under the peak

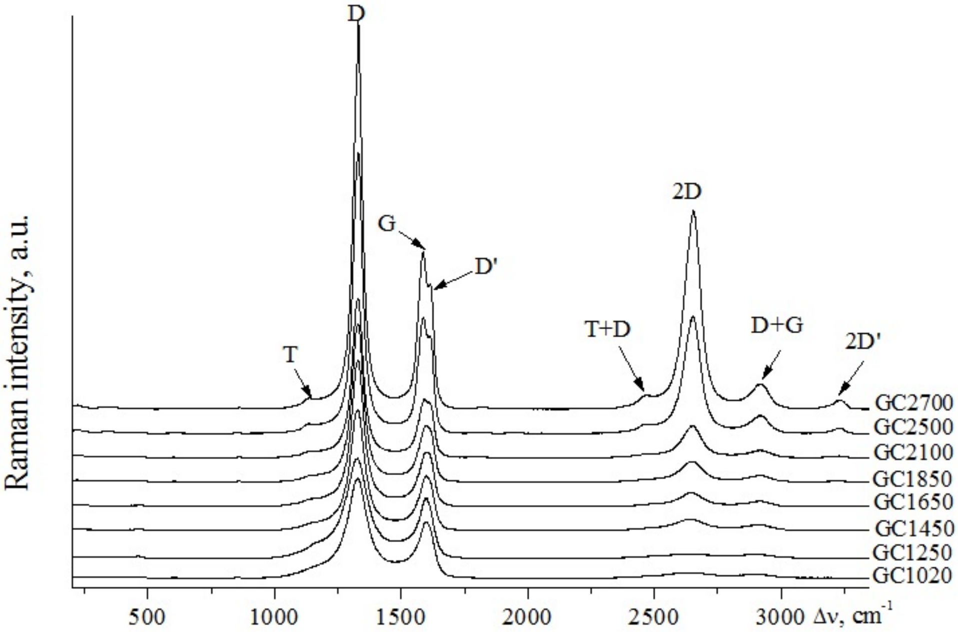

FIG. 1. Raman spectra of the GC samples annealed at different temperatures

TABLE 1. Frequencies ($\Delta\nu$) and half-widths (FWHM) of the D and 2D Raman lines *

Heat treatment temperature ($^\circ$C)	$\Delta\nu$ of the D line (cm^{-1})	D line FWHM (cm^{-1})	$\Delta\nu$ of the 2D line (cm^{-1})	2D line FWHM (cm^{-1})
1020	1324.5	107	2637	233
1250	1326.5	92	2638	213
1450	1326.5	69	2639	148
1650	1328	59	2643	113
1850	1328	53	2645	102
2150	1328	48	2647	88
2450	1329	42	2649	72
2700	1329	40	2650	67

* The values presented are the results of averaging of 5 independed series of experiments.

corresponds to ~15% of that of the glassy carbon component). No graphite admixture was observed by other diffraction measurements using synchrotron radiation (to be published) on similarly prepared samples.

An increase in annealing temperature leads to the emergence of very weak bands in the low-frequency region of the Raman spectra from 200–500 cm^{-1} (Fig. 4). Analogous bands were observed for carbon tubular cones, whiskers, polyhedral crystals and nano-onions [23,24], the authors associate them with graphene sheet curvature. For the latter CM, a high Raman intensity of the 2D overtone was observed, the same is true for GC2500 and 2700 (Fig. 1). By analogy, it can be suggested that these facts speak for applicability to the high-temperature GC samples studied of the structural model proposed by Harris [7], which is based on fullerene-related basic units with a high curvature and on the presence of closed voids.

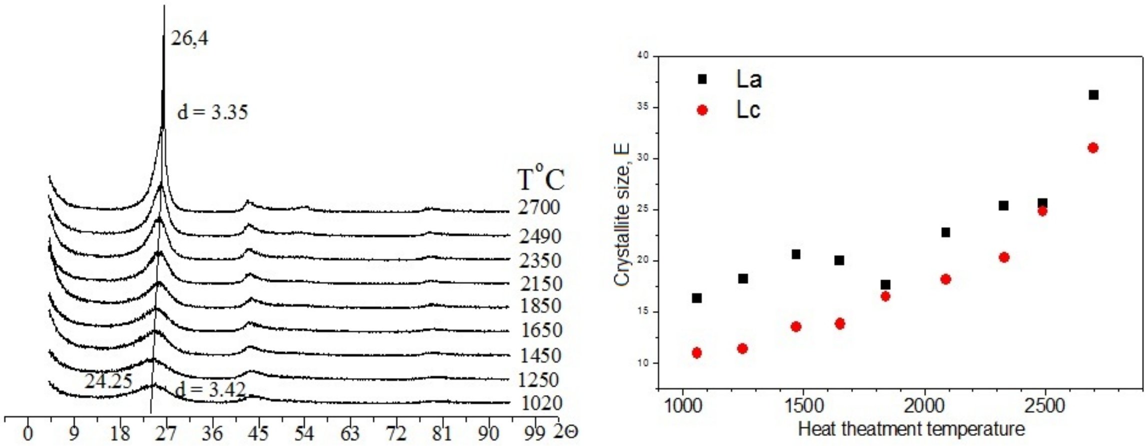

FIG. 2. X-ray diffraction patterns of glassy carbon samples treated at different temperatures (left) and estimates for crystallite sizes L_a and L_c (right)

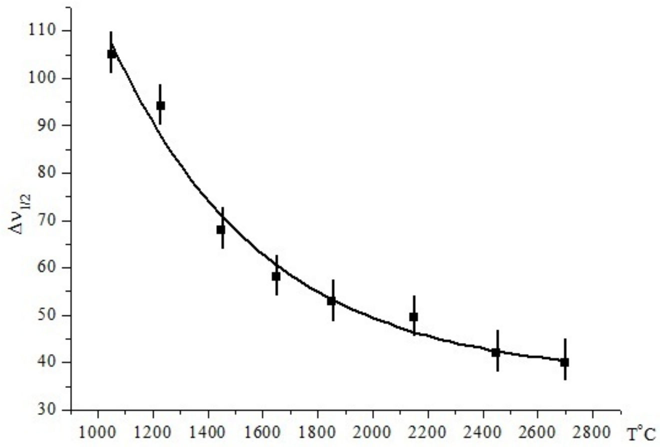

FIG. 3. Dependence of the D line half-width on the heat-treatment temperature

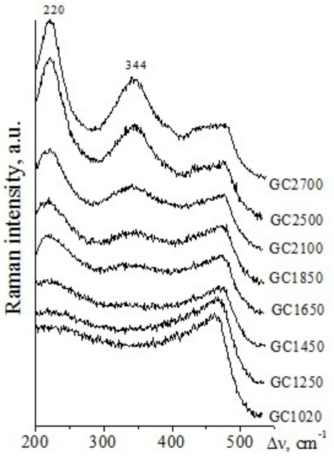

FIG. 4. Low frequency Raman region of the spectra obtained

Diffraction patterns of GC samples also evolve as the temperature increases (Fig. 2). The diffraction lines become narrower, the dominant 002 line slightly shifts to a larger scattering angle (to $2\theta \sim 25.5°$), whereas the 110 line slightly shifts to smaller angles (Table 2).

All these changes clearly indicate that some ordering and an increase in effective crystallite size occurred with preservation of the graphite-like main structural motif.

To estimate dimensional characteristics of GC structural units, the X-ray diffraction data were used (a model approach with use of the Debye formula). The results are presented in Fig. 2, right panel.

Thus, both the X-ray and Raman data show that an increase in the heat-treatment temperature leads to a noticeable ordering of aromatic nanoclasters in directions parallel and normal to the graphene layers. However, the general structural motif, that is, poorly ordered turbostratic graphitic nano-particles is still preserved herewith. Gradual formation of a series of new low-frequency weak features in the Raman spectra suggests carbon layer curving which unfortunately has no distinct manifestation in the diffraction data.

TABLE 2. Changes in the profile parameters of 100 and 002 lines as a function of heat treatment temperature

Heat treatment temperature (°C)	FWHM of 100 line (°)	FWHM of 002 line (°)	Position of 002 line (°)
1020	4.2	7.7	23.97
1250	4.0	6.9	23.91
1450	3.2	5.8	24.58
1650	3.3	5.9	24.67
1850	2.9	5.2	24.92
2100	2.5	4.4	25.17
2450	2.5	3.9	25.21
2500	2.2	3.1	25.53
2700	2.4	2.8	25.34

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