



Changes of the structure of fullerite and graphite during their mechanical activation



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ABSTRACT

The results of the comparative study of deformation-induced structural changes in fullerite $C_{60/70}$ and graphite during their mechanical activation (MA) have been presented in the paper. It was shown that intensive deformation resulted in the destruction of the crystalline structure of fullerite $C_{60/70}$, with the formation of a fullerite-like phase at the initial stage and an amorphous graphite-like phase at long periods of MA, with time values determined by the energy density of the process. It was stated that the process of the destruction of fullerite crystalline structure was accompanied by deformation-induced destruction of fullerene molecules. It was also found that during MA the crystalline structure of graphite C_g had essentially lower deformation stability than the crystalline structure of fullerite $C_{60/70}$.

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1. Introduction

Since the end of the 20th century, when fullerenes were discovered, they have attracted close attention of researchers. They are regarded as future-oriented materials to be used as photodetectors and optoelectronic devices, films, superconductor materials, dyes for copiers, as data storage medium with super high storage density, as additives for rocket propellants and lubricants, hydrogen-storage materials, etc. [1–3]. Fullerenes are also considered to be promising materials in biology and medicine as anticancer and antiviral agents.

Prior to using fullerenes in modern nanotechnologies, it is essential that they should be converted into a nanostructured form. A widely used method of particle size reduction is mechanical activation (MA) in activator mills. It is however necessary to take account of the possible structural changes in fullerenes in process of their MA.

The data presented in literature on the sequence of the structural changes in fullerenes during their high-energy milling and on their deformation stability, are controversial [4–9]. Depending on MA conditions, namely, energy density of a mill used and mechanochemical treatment medium (air, vacuum, inert medium),

metastable crystalline/amorphous carbon structures can be formed – from amorphous-like fullerite C_{60} to graphite-like or diamond-like carbon. In Ref. [8] it was shown that depending on the energy density applied and the following annealing, the temperature evolution of amorphous fullerenes formed during MA can result in either structural reordering with the formation of a fullerite crystalline phase or the formation of a diamond-like amorphous phase ($>600^\circ\text{C}$).

Since MA changes the sorption properties of fullerenes, it is possible to obtain fullerene-containing compounds of different chemical compositions. Thus, MA of fullerenes in hydrogen medium is used to produce fullerene hydrates $C_{60}H_n$ [7]; in oxidizing medium MA is applied to produce the mixtures of polyoxide fullerenes of different compositions - $C_{60}O_n$ [10,11], etc. Also, MA is now widely used to obtain more complex modified fullerene structures with targeted chemical properties [12–15].

The initial samples were monofullerite C_{60} [5–7] and a more available mixture $C_{60/70}$ [4,5,16], which was not subjected to the preliminary separation into fractions in a liquid chromatograph. Fullerite $C_{60/70}$ prepared by crystallization from toluene solution, represents molecular complexes $C_{60}-C_{70}-C_6H_5CH_3$ (crystalline solvates), with the molecules of fullerenes and the solvent held together by weak Van der Waals forces. It is known that toluene can be removed by durable annealing in conditions of dynamic vacuum ($\sim 200^\circ\text{C}$) and/or by sublimation of the sample [17]. However, no

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research data is available in literature on the behavior of toluene in molecular complexes C_{60} – C_{70} – $C_6H_5CH_3$ after MA.

The research results on nanosized carbon obtained in process of MA of graphite and carbon nanotubes are presented in papers [18–22] and [23–25], respectively. In Ref. [7] it was suggested that nanostructured carbon was prepared using fullerite as a precursor as a less stable carbon phase than graphite. At the same time, no comparative studies of the deformation behavior of fullerite and graphite have been performed in uniform experimental conditions. The only exclusion is paper [26] devoted to the preparation of compounds Fe–fullerite and Fe–graphite, where it was demonstrated that graphite underwent amorphization after as little as 2 h of MA, while fullerite preserved fairly high crystallinity. However, no detailed analysis of the structural changes in fullerite and graphite was given in the paper.

In this paper we present the results of the comparative study of deformation-induced changes in fullerite $C_{60/70}$ and graphite C_g during their MA in uniform experimental conditions.

2. Experiment details

Fullerite and graphite were taken as samples. Fullerite was obtained by electric-arc evaporation of graphite rods, followed by fullerene extraction with boiling toluene from fullerene-containing soot, in a Soxhlet apparatus. Fullerite was then crystallized from the solution using a rotation evaporator. The initial graphite was in the form of shavings obtained by mechanical crushing of graphite rods OSCh 7-2. The composition of the initial mixture $C_{60/70}$, according to HPLC and TGA, was as follows: 82.18% C_{60} ; 14.08% C_{70} ; 2.81% $C_{60}O$, $C_{60}O_2$ and $C_{70}O$; 0.93% C_{76} , C_{78} , C_{82} , C_{84} %; 1.1% of residual toluene.

For comparison, both fullerite and graphite samples were simultaneously processed in two drums in a planetary ball mill AGO-2 (cured stainless steel as balling drum material, \varnothing 8 mm balls from ball-bearing steel). MA was performed in a preliminary vacuumed mill ($P = 10^{-3}$ MPa) at energy densities $J_{m1} = 2.2$ and $J_{m2} = 4.3$ wt/g in inert medium $P_{Ar} = 0.1$ MPa for time intervals from 15 min to 28 h. After MA process was finished, the milling drums were held unopened for 24 h at room temperature, and then some quantity of the powder was selected for analysis. Holding at room temperature was conditioned by high reactivity of the powders and the possibility of their inflammation in the presence of ambient oxygen.

X-ray diffraction analysis of the samples before and after their MA was performed using diffractometers BRUKER D8 ADVANCE ($CuK\alpha$ radiation) and DRON-4 ($MoK\alpha$ radiation). To determine short-range order in the structure of MA-material from the experimental diffractograms obtained using $MoK\alpha$ radiation, we calculated structural factors (SF), and used a radial-distribution method for this [27,28]. The stability of the molecular state of fullerene was determined using the data obtained from IR-spectroscopy, UV-spectroscopy and qualitative chemical analysis. In the latter case, the samples were dissolved in toluene, and, judging by the color intensity of the solution, the presence or absence of fullerenes was determined. The IR-investigation was performed using an FSM1202 Fourier spectrometer with the resolution of 1 cm^{-1} (14 scans). To take transmittance spectra, fullerite powders were pelletized together with KBr in the ratio of 1:250 mg. Absorption spectrophotometry (UV-spectroscopy, λ 650, fullerene solutions in toluene) was used for the quantitative evaluation of the stability of fullerene molecules after their MA; molar absorption coefficients for the wavelengths 400, 410 and 472.8 nm were calculated in Ref. [29].

Electron-microscopic investigations were performed with the aid of a scanning electron microscope Jeol JSM 6360LA. Raman

spectra (RS) were taken at room temperature with a spectrometer DFS-24. Ar laser LGN-503 with the wavelength $\lambda = 514.5$ nm and laser power $P \sim 30$ – 50 mW was taken as a source of radiation.

3. Results and discussion

3.1. Structural changes in fullerite $C_{60/70}$

The initial particles of fullerite $C_{60/70}$ 200–800 μm in size were flat-shaped (Fig. 1a) and had a developed loose surface (Fig. 1b). Mechanical milling resulted in particle size reduction and morphological changes in the powders. After 1 h milling ($J_m = 2.2$ W/g), we obtained particles of a stone-like shape 200 μm in size (Fig. 1c). Further MA resulted in the decrease of particle sizes down to 2 μm (24 h MA, Fig. 1d).

Fig. 2 demonstrates the diffractograms of $C_{60/70}$ -samples mechanically activated under different milling conditions ($J_{m1} = 4.3$ W/g (a) and $J_{m2} = 2.2$ W/g (b)). We can see that after high-energy deformation processing, the crystalline structure of fullerites underwent some changes. Judging by the spectra, the structural state of the initial $C_{60/70}$ mixture (0 h MA) is characterized by the presence of FCC- C_{60} , HCP- C_{70} and a crystalline solvate C_{60} – C_{70} – $C_6H_5CH_3$, the molecules of fullerenes and the solvent in which are bound by Van der Waals forces. The most intensive lines correspond to FCC- C_{60} (due to its larger fraction in the sample). The spectra taken after mechanical activation were characterized by considerable broadening of diffraction lines and decreased intensity, which evidenced grain-size reduction and accumulation of micro distortions in the crystal under high deformation. For the times of milling 2 and 4–8 h at J_{m1} and J_{m2} , respectively, fullerite reflexes were virtually indistinguishable. Up to the above times, the $C_{60/70}$ mixture preserved its crystalline structure. Further milling resulted in the emergence of amorphous halos in the X-ray diffraction patterns in the area of main fullerite peaks, which shifted towards the main (002) graphite peak after 3.5 and 28 h MA ($\sim 26.5^\circ$). The latter fact indicates the total destruction of the crystalline structure of $C_{60/70}$.

It is known that diffraction pattern with broad diffuse halos can correspond not only to amorphous material, but also to polycrystals with the coherent scattering region sizes < 1 – 3 nm [30]. In this connection, to examine in detail the structural states of mechanically activated fullerites $C_{60/70}$ using X-ray diffraction data, the structural factors of the samples were calculated, and also Raman spectroscopy was applied.

Fig. 3 demonstrates the results of structural factor (SF) calculations for $C_{60/70}$ at different MA times. The SF of the initial material is characterized by three strong peaks: $s_1 = 0.74\text{ \AA}^{-1}$, $s_2 = 1.25\text{ \AA}^{-1}$ and $s_3 = 1.44\text{ \AA}^{-1}$ (Fig. 3 0 h MA), typical of fullerene C_{60} , judging by their positions. The absence of maximums typical of fullerene C_{70} , can be explained by its small quantity in the sample. As a result of ball milling, the peaks s_1 , s_2 and s_3 begin to broaden. After 8 h MA, the peaks s_2 and s_3 coalesce into one broad line with the maximum position $s'_2 = 1.29\text{ \AA}^{-1}$. The appearance of this line implies the amorphization of fullerite during MA, i.e. its crystalline lattice is demolished. Further increase of MA time to 28 h terminated in the total destruction of the structure of molecular crystal. A line $s_1 = 1.75\text{ \AA}^{-1}$ with its position typical of graphite was detected in SF curve of the corresponding sample. Hence, the material obtained represents amorphous carbon with graphite-like short-range order. Besides, a line at 3.09 \AA^{-1} is present in the spectrum of SF calculated for the samples subjected to 8, 16 and 28 h MA. This line is explained by the presence of iron contamination originating from a steel milling container and balls. Chemical analysis also proved the presence of iron in the material.

Thus, it can be stated that the sample, the diffractograms of

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