Features of Raman spectra of mechanically activated graphite

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Abstract. The prolonged mechanoactivation treatment (MAT) of graphite and carbon materials causes nonequilibrium processes, accompanied by stepwise changes in the characteristics of the structure of the material and its phase constituents. Using the techniques of electron microscopic analysis and Raman spectroscopy, the research task was to study the effect of short-term high-energy MAT on the possibility and regularity (sequence) of the transformation of chemical bonds between carbon atoms in the produced micro- and nanopowder materials. To compare the rate of change, graphite MPG-7 was processed for no more than an hour at 1000 and 1500 rpm. The changes were evaluated not only by the shift of the Raman spectrum lines, but also by the structural ordering of the substance and the degree of disorder, by the degree of amorphization. Similar nonlinear parameter changes for the two processing modes are detected. It is shown that treatment with less energy for an hour leads to a greater accumulation of energy in the material, which is reflected in the internal pressure corresponding to the difference Raman spectrum lines (S1-D1).

1. Introduction

At present, the number of works in the field of nanotechnology and nanocarbon materials is continuously increasing. Wide varieties of processes used: heat treatment, intercalation, chemical oxidation, irradiation, laser ablation, etc. [1, 2]. Increasingly popular is the mechanoactivation treatment (MAT) of carbon materials.

When MAT graphite and carbon materials in the reactor system, non-equilibrium processes occur, usually accompanied by stepwise (jumplike) changes in the characteristics (near and long-range order parameters) of the material structure and its phase components [3]. Most of the studies were carried out for MAT samples after a long hours of treatment for 1, 3, 5, 10, 25, 50, 75 hours. Therefore, one of the goals of this study was to analyze the processes in a short-term treatment of less than an hour in a high-energy ball system at the E_max plant.

To ensure increased sensitivity and reliability of the analysis of structural changes in carbon materials, Raman spectroscopy methods are often used. In literary data, the overwhelming majority of Raman studies of graphite pertain to annealing, pressure treatment, laser treatment, and there are practically no data from Raman studies on the effect of MAT on structural changes in graphite [4, 5, 6].

Processing in small time intervals in high-energy MAT systems leads not only to crushing of graphite, its stratification, grinding of crystallites, but also often to higher-energy step transitions (jumps) of chemical processes (chemical reactions), including subsequent spontaneous transition to lower-energy metastable stable states.
Taking into account the foregoing, using the techniques of electron microscopic analysis and Raman spectroscopy, the research task was to study the effect of short-term high-energy MAT on the possibility and regularity (sequence) of the transformation of chemical bonds between carbon atoms in the micro-and nanopowder materials formed.

2. Materials and Methods

The material for MAT was graphite MPG-7. The treatment was carried out in a high-energy ball mill E\textsubscript{max} at a mass ratio of balls to a loading weight of 4.5: 1. Continuous processing time is 10, 30, 50 and 60 minutes at 1000 rpm and 20, 40, 60 minutes at 1500 rpm in the residual air atmosphere.

Electron microscope studies were carried out on a JEOL scanning electron microscope to refine the chemical composition, particle size and shape. Characteristics of the scanning electron microscope JEOL: resolution 0.8 nm (15 kV), 1.2 nm (1 kV), 3.0 nm (15 kV, 5 nA, working section 10 mm); accelerating voltage 10 V - 30 kV; cathode - Schottky; beam current - 1 pA - 200 nA; range of magnifications from x25 to x1000000.

Raman spectra were obtained on a LabRAM HR Evolution Raman spectrometer using a wavelength of 633 nm. The laser power is about 10 milliwatts, the grating is 600 divisions per millimeter, the accumulation of 10 seconds 3 times.

3. Results

According to electron microscopic studies, the initial graphite has a layered structure with a visible layer thickness of \( \approx 5 \, \mu m \). The content of impurities according to the certificate does not exceed 0.05% by weight.

After MAO, crushed graphite has particles that can be conditionally divided into three morphological groups. The smallest particles are usually equiaxed, and their number increases with increasing processing time. The second group is "scales". Their size in one direction, perpendicular to the layers, is much smaller than the other two dimensions. With increasing processing time, their thickness becomes smaller, the scales are shortened 3-5 times and, in practice, disappear. The third group includes large particles of \( \approx 60-80 \, \mu m \) fragmentation form. Their dimensions are reduced to 20-50 microns, the shape becomes more rounded, but then the size is somewhat increased, and the number of such particles is reduced. Moreover, it should be noted that the rounded shape appears not so much due to the rolling or shaping of the previously fragmented shape, but due to the adherence of thin short flakes (Fig. 1). For particles after treatment at 1500 rpm, the presence of loose flakes is more typical, the sizes of which are reduced.

![SEM image of the particles after 60 minutes MAO 1000 (a) and 1500 (b) rpm](image-url)
Figure 2 shows a fragment of the spectrogram of the initial graphite. The spectrum features are mainly determined by the level of clustering (condensation) of carbon atoms, the degree of ordering of atoms in sp2-hybridization, the disruption of C-C bonds, the fraction of the phase with sp3-hybridization of carbon [7].

Graphite with a perfect crystal macrostructure has only one (G) line of the first order at 1582 cm\(^{-1}\). The G-type vibrations of graphite molecules are formed by carbon atoms located in sp2-states and located in the plane of graphite meshes; a similar mode is present in all cases when carbon atoms contain carbon atoms with double bonds, i.e., this mode refers not only to six-membered (aromatic) carbon rings. As noted in the paper [8], in the spectrum of graphite having defects of graphene layers, and also in the case where the size of the crystallites or domains is small, there are additional lines of the first order: in the region of 1355 cm\(^{-1}\) - D1, about 1620 cm\(^{-1}\) - D2, as well as several weaker lines in the region of 1400-1500 cm\(^{-1}\) - D3 and 1100-1200 cm\(^{-1}\) - D4. In Fig. 2, all the lines indicated with some deviations are visible. Since the intensity of the D1 line, the small lines D2 and D3 are practically invisible. On the one hand, the intensity of the D1 line is strictly related to the proportion of six-membered (aromatic) carbon rings. If the aromatic clusters are small, then the position of the maximum shifts to the region of higher frequencies; when the amount of undistorted aromatic rings is reduced, for example, in the transition of nanocrystalline graphite to amorphous carbon, the frequency and intensity of the D1-maximum decreases. The presence in the graphene layers of not only six-membered carbon rings also reduces the amplitude of the D1 peak and increases its width [8]. This can serve as an explanation for the displacement of the position of the D1 line (instead of 1355 cm\(^{-1}\), the line is at 1331 cm\(^{-1}\)). But, on the other hand, as noted by the authors of [9], the 1332 cm\(^{-1}\) line corresponds to the diamondlike structure.

Processing the material for 60 minutes at 1000 rpm leads to structural changes (Fig. 3). The D4 line practically disappears on the spectrogram, but the D3 line (1453.5 cm\(^{-1}\)), although shifting, becomes more clear. Lines D1 practically does not change the intensity, but shifts to the region of large values up to 1339.95, which allows to assert about the decrease in the sizes of aromatic clusters. Line D2 shifts from 1616.26 cm\(^{-1}\) to 1606.03 cm\(^{-1}\). But due to the expansion, peak G absorbs this line. In addition, a burst of 1532.37 cm\(^{-1}\) appears, which, according to the authors [10, 11], corresponds to nanographite, interlayer
defects, disordered sp3 clusters, or disorder in the form of amorphous carbon. It is proposed to denote this line G (k).

In the second-order spectral region for the original graphite, there are higher harmonics of graphite dispersion: 2720 cm\(^{-1}\) - S2 (the most intense line), 3240 cm\(^{-1}\) - S4 (weak but clear maximum), and 2450 cm\(^{-1}\) Raman lines, S1 and 2935 cm\(^{-1}\) - S3. For MAO graphite, after 60 minutes, these lines are strongly shifted towards smaller values: 2691.78; 3232.12; 2447.15 and 2924.5 cm\(^{-1}\), respectively, although the ratio of line intensities is preserved. There is also a small reflex in the region of 2000 cm\(^{-1}\), which corresponds to the onset of the carbon amorphization process [12].

When considering the Raman spectra of graphite MAO with a shorter processing time (Figure 4 a), a nonuniform shift of the lines of both the first and second order is observed (Fig. 5). The greatest displacement is observed after 50 minutes of treatment.
Analysing the features of the change in the Raman spectrum of MAO graphite at 1500 rpm (Fig. 4 b), attention is drawn to the presence of an halo in an amorphous type after 40 minutes of processing both for first-order lines and for second-order lines, and in the region of second-order lines its intensity is greater. After 60 minutes, the halo decays, the spectrum is characterized by an increased noise background and the presence of many small peaks. Thus, the amorphization process started after 40 minutes relaxes after 60 minutes and the structure of the powder particles is ordered.

The difference in the structural ordering of substances can be revealed by using the ratio $R_3$ of the widths of the lines $S_2$ and $G$ [8] (see Table 1).

![Displacement of Raman spectra of MAO graphite](image)

**FIGURE 5.** Displacement of Raman spectra of MAO graphite

| rotation | 1000 rpm | 1500 rpm |
|----------|----------|----------|
| time, min | 10 | 30 | 50 | 60 | 20 | 40 | 60 | note |
| $R_3' = \frac{A_{S2}}{A_G}$ | 2,531 | 1,647 | 1,638 | 3,401 | 1,872 | 3,241 | 5,822 | Structural ordering |
| $R_1 = \frac{I_{S1}}{I_G}$ | 0,254 | 0,615 | 0,6667 | 0,417 | 0,54 | 0,576 | 0,124 | Degree of disorder |
| $S_1-D_1$, cm$^{-1}$ | 1134,09 | 1131,02 | 1132,7 | 1107,2 | 1137,26 | 1120,79 | 1066,46 | Change in internal pressure |

The generally accepted parameter of the degree of disordering of $R_1$ correlates with the parameter $R_3$ of the structural ordering. According to the data in Table 1, up to 50 minutes of treatment, the degree of disorder increases, and after 60 minutes an increase in the order in the powder structure occurs. An
estimate of the change in internal pressure from the difference in line values (S1-D1) also shows a decrease to 60 min processing.

Figure 6 shows the relationship of the degree of disordering of R1 with the change in internal pressure (S1-D1). On the chart, extremums are clearly visible, corresponding to the decay of disorder.

4. Discussion

It is shown that under graphite MAT for an hour, uneven changes occur both in particle morphology and in structural ordering. The level of disorder at MAT 1000 rpm is 50 min higher than at 1500 rpm. The process of amorphization more readily occurs at 1500 rpm, but by 60 minutes, a certain relaxation occurs, leading to an increase in the structural ordering of the particles. This occurs when the degree of disordering of R1 is of the order of 0.6-0.67 and when the internal pressure corresponding to the difference (S1-D1) 1133 cm⁻¹ is reached. Thus, at MAT, the processes of energy accumulation and relaxation alternate much in shorter time intervals than previously thought.

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