Nitration and oxidation of graphite by mechanochemical treatment

V Chaika, V Savin, L Savina and I Zherebtsov
Laboratory of Physical Materials Science IRC, Immanuel Kant Baltic Federal University, 14A Nevskogo Street, 236016 Kaliningrad Russian Federation
E-mail: v_chayka8@rambler.ru

Abstract. When combining special mechanochemical processing of graphite in high-speed and planetary ball mills and heat treatment, it was revealed that condensed graphene oxide is formed, and a nitrogen-containing carbon phase is synthesized. Melamine was used as the material for introducing nitrogen into the system; during the heat treatment it releases ammonia. Besides, it improves the process of compaction of graphite powders into workpieces in the production of refractive X-ray optics. The mechanochemical synthesis of graphite with melamine (not more than 1 wt.%) and two-stage annealing at 360 and 450 °C leads to the formation of some forms of they lead to the formation of graphene oxide and a nitrogen-containing carbon phase. X-ray studies revealed the appearance of peaks that can be attributed to peaks of graphene oxide and carbon nitride. The formed condensed carbon compounds with nitrogen and oxygen are characterized by natural aging.

1. Introduction
One of the known nitrogen-containing carbon materials is graphite carbon nitride (g-C₃N₄) [1]. The increased scientific interest to this compound is due to its promising semiconducting, catalytic and sorption properties attractive for practical use. Graphene oxide (GO) and a family of metal nitride nanostructures may be obtained from the g-C₃N₄. While its hardness and compressibility is a lower than those of diamond-like compounds, its stability under natural conditions is the highest in comparison with the other allotropic forms of nitrogenized condensed carbon compounds [1].

Methods for preparation of the g-C₃N₄ are based on different options of chemical, thermal and hydrothermal treatments at high pressure and high temperature [2,3], vapor deposition, and their various combinations [4].

The methods used to produce GO and graphene-like substances include: (a) chemical reduction using various reagents (e.g., hydrazine) [5]; (b) thermal reduction performed in vacuum or in various gaseous media (e.g., argon, hydrogen, hydrogen/argon mixtures) [6]; (c) electrochemical reduction [7]; and (d) combination of various methods such as chemical reduction and thermal annealing (TA) or thermal reduction and hydrogenation [6]. There are some similarities in the methods used for obtaining the g-C₃N₄ and GO. Particularly, material processing in disintegrators, including ball millings, commonly employed for synthesizing the g-C₃N₄ and GO, especially at the preparatory stages. In recent decades, mechanochemical treatment of powder materials in ball mills and the so-called mechanochemical synthesis (MCS) have shown advantageous results in developing new compound.
Considering the aforementioned, the present paper considers and discusses results of experimental investigations on nitration and oxidation of graphite from a powdered mixture of MPG-7 graphite and melamine by combing the MCS and TA. Melamine is a component that improves the technological process of compaction of graphite powder materials into blanks during the production of refractive X-ray optics [8].

2. Methods and materials
A graphite powder with a fraction of \( \leq 20 \mu m \) was used at initial stage of the MCS processing. The powder of specified dispersion was obtained by grinding a lumpy MPG-7 powder (Graphite Service, Chelyabinsk, Russia) with a size of 1-5 mm in a PM-100 planetary mill (Retch Technology, Hamburg, Germany) for 1 h under fixed conditions [9]. Next, up to 1 wt.% of RN-M40 melamine powder (Roshal Group, Roshal, Russia) was added to the obtained material.

The MCS procedure was carried out for 1 h in various ball mills with different types of headsets: 1) in the PM-100 mill – in a steel glass with steel balls and in an agate glass with agate balls at 300 rpm; 2) in an Emax high-speed ball mill (Retch Technology) – with steel cups and balls with the processing mode of 1500 conventional units. The treatment was carried out in residual air atmosphere. The ratio of the mass of balls to the mass of loading was 9:1. After the MCS procedure, a two-stage annealing of the obtained powder was performed at: \(+360^\circ C\) for 1 h, and at \(+450^\circ C\) for 1 h.

The selected annealing conditions correspond to the decomposition temperature of melamine [10]. At the first annealing stage, the melamine decomposes with release of ammonia (NH\(_3\)), and melem is formed as a result of the following reaction: \( C_3H_6N_6 \rightarrow NH_3 + C_6H_6N_{10}\). At the second annealing stage, melon \([C_6N_7(NH)(NH)]_n\) polymerization occurs with the release of ammonia (NH\(_3\)) [10]. After this two-stage annealing, the powder material was again subjected to the MCS for 1 h in the same headsets.

A DRON-3M X-ray diffractometer (Burevestnik, Yekaterinburg, Russia) with Cu-K\(\alpha\)-radiation was used for analysis of the materials obtained.

3. Results and discussion
The X-ray diffraction studies show (figure 1) that, the diffraction peaks of graphite weakening and broadening and their center of gravity are shifted towards smaller diffraction angles in comparison with the initial graphite materials for all the three powder samples. This is usual for the MCS processing of the powder due to its grinding, formation and accumulation of various defects, material doping by atoms of the residual atmosphere, and decomposition products of melamine.

![Figure 1. Diffractograms of the powder samples obtained through MCS processing in the Emax (steel set) and PM-100 (steel and agate headsets) ball mills.](image-url)
The maximum attenuation of the intensity of the diffraction peaks is observed for the sample processed in the Emax mill. This result is consistent with its technological characteristics: more high-energy processing, complex interaction of the glass, grinding bodies and powder, accompanied by abrasive and impact effects on the material being processed. When the materials were processed in the PM-100 mill, the abrasive effects prevails [11].

The MCS-processed powder was compacted using a PP 25 manual hydraulic pellet press (Retch Technology) in a cylindrical mold with a diameter of 15 mm and a force of 872 MPa. The obtained samples in the form of tablets poorly kept their shape and showed a tendency to stratification during aging.

The X-ray studies were performed on the flat surface of the compacted powder samples (tablets) with residual mechanical strength. The obtained results demonstrate (figure 2) that, in addition to the main peaks corresponding to graphite, the diffraction patterns of the sample contain a diffusion halo, which is an X-ray scattering characteristic for a substance in an amorphous or glassy state. A diffuse halo with a center of gravity of $2\theta = (12.5 \pm 0.1)^\circ$ (angular degrees) is clearly detected. Slightly diffused diffraction peaks (not related to graphite) are present at $2\theta = (43.5 \pm 0.1)^\circ$, $(79.0 \pm 0.2)^\circ$ and $(83.5 \pm 0.2)^\circ$ (Table 1).

Figure 2. X-ray diffractograms of the samples compacted from the powder processed by the MCS in the Emax (steel set) and PM-100 (steel and agate headset) mills.

In [12], the GO obtained by the Hummers method was subjected to heat treatment. The oxygen content and structural phase changes were analyzed and according to their results, upon the graphite – to GO transition, the graphite peaks (002) at $2\theta = 26.5^\circ$ (Cu-K$_\alpha$-radiation) and (101) at $2\theta = 44.8^\circ$ disappear, and the peak related to the GO (001) becomes apparent at $2\theta = 9.8^\circ$. Due to the introduction of the oxygen atoms into the interlayer space, the hexagonal graphite structure swells in the [001] direction (along the “c” axis). As a consequence, the interplanar distance increases from 0.336 nm for graphite to 0.867 nm for GO. The article [13] presents the results of X-ray diffraction studies on GO obtained by the Hummers method, and the peaks at $2\theta = 10.813^\circ$ and $42.427^\circ$ (Cu-K$_\alpha$-radiation) corresponding to the interplanar spacing of 0.8176 and 0.2129 nm, respectively, were observed.

According to our results (figure 1 and table 1), the X-ray diffraction peaks of the graphite are shifted towards smaller angles, which is typical for the MCS. And the peaks, presumably corresponding to the GO, are shifted toward larger angles $2\theta= 12.5^\circ$ and $43.4^\circ$ with interplanar
distances of 0.706 and 0.208 nm. Two other peaks at $2\theta = 79^\circ$ and $83.5^\circ$ can also be attributed to the GO structure, since they have a similar appearance (blur). Smaller values of experimental interplanar distances can be explained not only by the imperfect form of the crystal structure due to numerous defects formed during the MCS, but also by the reduced (compared to the other synthesis methods) oxygen content interacting with graphite. The amount of oxygen entering the material is limited by its content in the residual atmosphere of the sealed glass. The MCS process is accompanied by the consumption of oxygen for the formation of volatile, stable oxides of CO$_2$ and CO, which reduces the number of oxygen atoms entering into the synthesis of GO.

The authors of [14] investigated the synthesis and bulk structures of carbon nitrides with different degrees of condensation using thermoanalytical methods. They also note the difference in results when processing in open and closed containers. During the polymerization of melamine in a nitrogen atmosphere at 350 °C, in closed containers, a diffraction peak in the region of $13^\circ$ appears on diffractograms (Cu-K$_\alpha$-radiation). This peak is assigned by the authors to tri-s-triazine blocks (C$_6$N$_7$). Melon chains are built from these blocks, and a variety of compounds with different structures of carbon nitride may be produced from them.

### Table 1. Parameters of the X-ray diffractograms of the samples compacted from MCS powder processed in the Emax (steel set) and PM-100 (steel and agate headset).

| hkl   | PM-100 steel headset | PM-100 agate headset | E$_{\text{max}}$ |
|-------|----------------------|----------------------|-----------------|
|       | $<x>$, degree | H, count | FWHM, degree | d, Å | $<x>$, degree | H, count | FWHM, degree | d, Å | $<x>$, degree | H, count | FWHM, degree | d, Å |
| 001*  | 12.52 | 210 | 3.4 | 7.062 | 12.53 | 172 | 3.37 | 7.056 | 12.47 | 153 | 3.45 | 7.089 |
| 002   | 26.34 | 6457 | 0.68 | 3.379 | 26.33 | 6585 | 0.58 | 3.381 | 26.31 | 3181 | 0.71 | 3.383 |
| 100   | 42.48 | 32 | 0.49 | 2.125 | 42.56 | 63 | 0.89 | 2.122 | 42.4 | 31 | 0.37 | 2.129 |
| 100*  | 43.33 | 47 | 1.71 | 2.086 | 43.7 | 68 | 1.3 | 2.069 | 43.21 | 55 | 1.77 | 2.091 |
| 101   | 44.79 | 57 | 2.39 | 2.021 | 44.81 | 70 | 2.44 | 2.020 | 44.54 | 57 | 2.27 | 2.032 |
| 004   | 54.25 | 298 | 1.15 | 1.689 | 54.29 | 300 | 0.93 | 1.688 | 54.23 | 147 | 1.16 | 1.689 |
| 110   | 77.55 | 48 | 0.85 | 1.229 | 77.47 | 77 | 0.81 | 1.231 | 77.47 | 29 | 0.43 | 1.231 |
| 79.1  | 10 | 1.29 | 1.209 | 78.68 | 24 | 1.03 | 1.215 | 79.24 | 35 | 1.61 | 1.227 |
| 83.43 | 26 | 2.7 | 1.157 | 83.45 | 33 | 2.41 | 1.157 | 83.44 | 20 | 3.03 | 1.157 |
| 006   | 86.47 | 31 | 1.96 | 1.124 | 86.51 | 30 | 2.18 | 1.124 | 86.28 | 17 | 2.6 | 1.126 |

Note: hkl with an asterisk (*) refers to GO.

Given that the synthesized MCS powders and compacts based on them are in a state of “undersaturation” (“underdevelopment”) with the oxygen, then in a state of natural aging in air, these processes can continue in the direction of enrichment of the material with the oxygen. In this work, a repeated study of this material was carried out after being kept in vivo within two months. The MCS powders were re-compacted in a cylindrical mold with a diameter of 10 mm and a force of 624.6 MPa.

The expected result, which has practical significance, was obtained: the pressed samples retain their shape well, do not stratify, and have sufficient mechanical strength for research. Figure 3 presents the diffraction patterns of such tablets.

All previously detected peaks significantly reduce their intensity and broadening. The peak of an amorphous halo at $2\theta = 12.5^\text{th}$ shifted towards smaller angles by an amount beyond the experimental error ($2\theta = 11.5 \pm 0.1^\circ$). The obtained results are in good agreement with the assumption that the process of saturation of the MCS powder with the oxygen and the physical-chemical processes of interaction of graphite with elements present in the bulk of the powder material or coming there from the atmosphere continue during aging under natural conditions. As a result, on the diffractograms of tablets from such MCS powders at small angles, four distinct diffraction peaks appear at angles of $2\theta =$...
6.6°, 7.1°, 8.2°, and 17.8° (figure 4). Moreover, if the first three peaks in the three samples are slightly shifted, then the latter has a constant location and intensity (Table 2).

Figure 3. X-ray diffractograms of the samples compacted from the powder processed by the MCS in the Emax (steel set) mill after being kept for 60 days.

Figure 4. Fragment of X-ray diffractograms of tablets from the MCS powder after being kept for 60 days.
Table 2. Results of calculations of diffractograms of the samples obtained by compaction of MCS powder, which was kept under natural conditions for 60 days.

| hkl | PM-100 steel headset | PM-100 agate headset | E<sub>max</sub> |
|-----|----------------------|----------------------|--------------|
|     | <x>, H, FWHM, degree | <x>, H, FWHM, degree | <x>, H, FWHM, degree |
|     | d, Å                  | d, Å                  | d, Å         |
| 6.64| 19 0.54 13.296 6.62 17 0.43 13.336 6.41 17 0.19 13.774 |
| 7.17| 13 0.4 12.314 7.18 23 0.12 12.297 6.97 14 0.62 12.667 |
| 8.2 | 43 0.64 10.769 8.19 41 0.88 10.783 8.16 42 0.59 10.822 |
| 11.53| 31 2.6 7.666 11.64 36 2.8 7.593 11.17 13 5.19 7.912 |
| 16.61| 28 2.56 5.331 16.44 24 2.49 5.386 |
| 17.8 | 522 0.28 4.977 17.8 569 0.27 4.977 17.8 514 0.28 4.977 |
| 002 | 26.15 1866 0.73 3.404 26.23 1833 0.54 3.394 26.14 861 0.68 3.405 |

The appearance of similar peaks at low angles is noted by the authors of [15] when studying the melamine polycondensation in a nitric medium at high pressure and temperature. The analysis of the chemical composition of the material obtained showed that graphite forms C<sub>3</sub>N<sub>4</sub>. However, the rhombic cell modeled by the authors for the structure obtained was not confirmed and requires further refinement and development.

4. Conclusion

A method of mechanochemical treatment of graphite in ball planetary and high-speed mills of MPG-7 graphite powder with additions of melamine powder in an amount of up to 1 wt.% in combination with heat treatment (annealing) and aging (under natural conditions) was proposed for providing synthesis of the condensed matter state by combining carbon with nitrogen and carbon with oxygen.

The effect of the following MCS technological parameters of the process was shown: ball mill type (PM-100 and Emax; headset (steel, agate); processing modes (load, energy, time, process sequence).

It was confirmed that, according to the proposed modes, during the MCS, the synthesis of condensed carbon compounds with nitrogen and carbon with oxygen proceeds in a new crystalline and/or amorphous-crystalline state.

For the formation of condensed carbon compounds with nitrogen and oxygen that are formed during the mechanochemical synthesis, the phenomenon of aging under natural conditions was found to be inherent.

The aging processes are associated with physicochemical regularities (absorption, diffusion, catalytic chemical reactions of atoms and molecules of absorbed elements with graphite and derivatives formed during its mechanochemical processing) occurring in the activated powder material upon contact with the atmosphere.

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