Thermally expanded graphite from graphite nitrate cointercalated with ethyl formate and acetic acid: morphology and physicochemical properties

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Abstract. Triple graphite nitrate cointercalation compound with ethyl formate and acetic acid was synthesized and used as a source of the thermally expanded graphite. The effect of the drying regime of the cointercalation compound on its surface morphology as well as ability to the thermal expansion was investigated. Complex studies of the microstructure, morphology, and quality of the obtained thermally expanded graphite by XRD, TEM, and Raman spectroscopy showed that as compared to the initial graphite TEG is less ordered, has a multilayer and insufficiently ordered structure without visible surface defects.

1. Introduction
Thermally expanded graphite (TEG) has an exceptional combination of interesting properties and represents a promising basis for the development of multifunctional materials. Its high porosity, low bulk density and well-developed specific surface determine the excellent sorption properties of TEG [1]. Thermally expanded graphite can be used as a sorbent for various oils and oil products [2–4], organic compounds and heavy metals [5], dressings (especially when healing burn wounds) [6], a catalyst carrier [7, 8]. TEG foil prepared by compression and rolling of expanded graphite is an effective material for the manufacture of heat-resistant gaskets, seals and packing [9–12]. Liquid phase exfoliation of TEG is a promising simple, low-cost method for the preparation of graphene as well as few-layer graphenes [13–17]. This expands the scope of TEG applications and stimulates the development of new composite materials based on it [1, 9, 10].

Acceptor graphite intercalation compounds (GICs) possess ability to volume multiple increasing during heat treatment to produce thermally expanded graphite, thus they are widely used for TEG obtaining on a laboratory and industrial scale [1, 13, 14, 18, 19]. The most known methods for GICs synthesis are liquid phase chemical treatment of graphite by acid solution in the presence of an
oxidizing agent and electrochemical treatment of natural graphite [1]. The latter requires high energy costs and is economically less profitable. Since the properties of the initial GICs determine the structure and properties of TEG based on them [18, 20–22] it is possible to obtain TEGs with desired physicochemical and structural properties by varying the method of chemical treatment of graphite as well as the nature and amount of intercalants [1, 13, 18–25]. Recently the influence of stage number and expansion temperature of the GIC on macro- and microstructure of expanded graphite has been investigated [26]. It was shown that crystallite size is reduced both with decreasing stage number of initial graphite bisulfate and with increasing expansion temperature. Introduction of additional intercalants into the GIC structure leads to changes in their reactivity and often improves their ability to thermal expansion [7, 27]. In the preparation of acceptor-type of graphite intercalation compounds, nitric acid acts as an oxidizing agent and an intercalant at the same time [28]. Therefore, no additional reagents are required to obtain graphite nitrate, and it is a promising precursor for the production of thermally expanded graphite. Moreover, new thermally stable graphite intercalation compounds were obtained via additional intercalation of a series of organic compounds into graphite nitrate [7, 23, 29]. Stabilization of graphite nitrate during its cointercalation with organic compounds is due to their protonation on account of nitric acid contained in the interlayer space. Stability index of cointercalated graphite nitrates was shown to correlate linearly with the calculated proton affinity of the organic cointercalants [27]. Additional stabilization comes from formation of a continuous two-dimensional net of hydrogen bonds among the solvation ligands. Binary graphite nitrate cointercalation compounds have shown to demonstrate high thermal expansion coefficients [7, 27], thus they are promising precursors for TEG production. From this point of view additional information is needed about macro- and microstructure of TEG produced from graphite nitrate cointercalation compounds.

This paper presents the results of complex investigations of structural features of thermally expanded graphite based on graphite nitrate, cointercalated with ethyl formate and acetic acid. Thermal stability as well as effect of the drying mode of graphite nitrate cointercalation compounds (GNCCs) and the ratio of cointercalants in their composition on the thermal expansion process are considered.

2. Experimental

At the first stage graphite nitrate cointercalation compounds (GNCCs) were prepared as a starting material for the thermally expanded graphite production. GNCCs were synthesized in a thermostatic reactor at 20 °C. Nitric acid with a density of 1.502 g cm⁻³ (98%) was added to the sample of natural flake graphite GT-1 (Zavalie Graphite Works, Kirovograd region, Ukraine). The mixture was stirred for 10 minutes. Then we added cointercalant(s) and the system was stirred again for 10 minutes. Triple graphite nitrate cointercalation compound (GNCC) was obtained by sequentially adding of organic cointercalants in a ratio of 1 : 1 by volume to the reaction mixture. Organic cointercalants (ethyl formate, acetic acid) were purchased from Merck-Schuchardt and used as received. The consumptions of nitric acid and the cointercalants were 0.6 and 6 cm³ per 1 g of graphite, respectively. Resulted GNCCs were separated by filtration and dried at 20 °C, 40 °C and 105 °C until the sample mass became constant.

Thermally expanded graphite was obtained from graphite nitrate and GNCCs by the thermal shock mode of heating. A stainless cuvette of 150 cm² was placed into a muffle furnace preheated up to 900 °C. About 0.2 g of the graphite nitrate or GNCCs was inserted into the heated cuvette and has been kept in the furnace for 120 s. Then the cuvette with expanded graphite was removed from the furnace, the contents were gently transferred to a graduated cylinder and obtained graphite foam volume was measured. The thermal expansion coefficients (₉) of the graphite nitrate and its GNCCs were determined from the equation:

\[
K_v = \frac{V}{m},
\]

where \(K_v\) – the thermal expansion coefficient, cm³ g⁻¹;
\(V\) – the graphite foam volume, cm³;
3. Results and discussion

3.1 Obtaining and investigation of thermally expanded graphite properties

The synthesis of graphite nitrate cointercalated with ethyl formate and acetic acid was carried out in the following way: at the first stage natural flake graphite was treated with nitric acid (ρ = 1.502 g cm⁻³). Cointercalants (ethyl formate and acetic acid) were sequentially added to the as-prepared graphite nitrate. Resulted GNCC samples were dried at 20 °C, 40 °C and 105 °C until the sample mass became constant. Studies of the surface morphology and elemental analysis of graphite nitrate cointercalated with ethyl formate and acetic acid were carried out by scanning electron microscopy method (SEM). The obtained SEM images of the GNCC are presented in figure 1. All samples have a layered structure. Spontaneous bloating of particles has been observed for GNCC dried at different temperatures (figure 1). Consequently, such compounds can be promising for further production of carbon nanoparticles.

To study the thermal expansion ability of the obtained GNCCs investigated samples were undergoing thermal shock at 900 °C. Graphite cointercalation compounds have a unique ability to expand – increase in volume tens or hundreds of times with rapid heating to high temperature [30, 31]. The formation of gas bubbles precedes the removal of volatile substances from the internal volume of intercalated graphite particles. The increase in gas pressure in GNCCs with increasing temperature leads to deformation of graphite layers during thermal shock and the formation of cracks in flakes (wedge-shaped defects).
In addition, in the process of thermal expansion crystallites are split along the c axis, as well as an increase of the specific surface area of the samples is observed. The large specific surface of the TEG causes its high sorption properties.

The surface morphology of the particles obtained as a result of heat treatment of the investigated GNCCs was studied by SEM. Typical SEM micrographs of thermally expanded graphite obtained from GNCC are shown in figure 2. The width of visible pores in the particles varies from 0.5 to 50 μm.

![Figure 1. SEM images of graphite nitrate cointercalated with ethyl formate and acetic acid dried at 20 °C (a, b), 40 °C (c, d) and 105 °C (e, f).](image1)

![Figure 2. SEM images of thermally expanded graphite obtained from graphite nitrate cointercalated with ethyl formate and acetic acid – dried at 20 °C.](image2)

Obtained GNCC demonstrates good thermal expansion ability. Thermal expansion coefficient obtained for considered GNCC sample along with corresponding values for graphite nitrate as well as binary GNCCs on the base of ethyl formate and acetic acid are listed in table 1. In all studied cases, the use of cointercalant(s) leads to an increase in the $K_T$ value in comparison with corresponding value for the graphite nitrate. The values of the expansion coefficient of the triple compound D exceed the $K_T$ values for the corresponding binary compounds B and C. This fact indirectly indicates an increase in the intercalants molar content in the obtained triple graphite nitrate cointercalation compound D.
Table 1. The thermal expansion coefficients of the graphite nitrate and its cointercalation compounds.

| GNCCs       | Cointercalant(s)                                | $K_v$, cm$^3$·g$^{-1}$ |
|-------------|-------------------------------------------------|------------------------|
|             |                                                 | 20 °C  | 40 °C  | 105 °C |
| A           | HNO$_3$                                         | 249    | 230    | 11     |
| B           | HNO$_3$ / ethyl formate                          | 318    | 290    | 55     |
| C           | HNO$_3$ / acetic acid                            | 354    | 310    | 72     |
| D           | HNO$_3$ / ethyl formate / acetic acid            | 378    | 321    | 97     |

Reflexes, which are typical for the graphite phase, are observed on the X-ray diffraction pattern of thermally expanded graphite obtained from compound D – dried at 20 °C (figure 3). The absence of uncharacteristic reflexes for crystalline graphite on TEG XRD patterns was established by the XRD method, residual intercalation compounds were also not detected – there are no reflexes typical for the initial GNCC (figure 3a). Broadening, splitting and shift of the reflexes towards larger angles on the X-ray diffraction pattern occurs upon GNCC thermal expansion. TEG is less ordered than initial graphite (figure 3a).

Figure 3. XRD patterns of initial graphite (a - 1), compound D – dried at 20 °C (a - 2) and thermally expanded graphite obtained from compound D – dried at 20° (b).

The microstructure and morphology (figure 4) of initial graphite and thermally expanded graphite obtained from compound D – dried at 20 °C, were investigated by transmission electron microscopy (TEM). The experimental interplanar spacing ($d$) determined by equation (2) were compared with available data [32] for selected area electron diffraction patterns interpretation. The spots on the graphite and TEG selected area electron diffraction pattern (figure 4) are blurred and represent a full bright circle. The intensities of inner hexagon ($I_1$) and outer hexagon ($I_2$) spots are matching. There are a lot of reflexes on the circles which indicate the presence of a multilayered and insufficiently ordered structure without visible surface defects of the samples.
Figure 4. Bright field TEM images and electron diffraction patterns of the a) initial graphite and b) thermally expanded graphite obtained from compound D – dried at 20 °C.

The (100) and (110) crystallographic planes are defining planes for hexagonal lattice systems. Results listed in table 2 show that there is no complete correspondence between the experimentally obtained and the literature data due to the different nature of the compared graphites. Comparative analysis of the TEG and initial graphite interplanar spacing shows that thermal expansion leads to interplanar spacing decrease for the (100) plane.

Table 2. The initial graphite and TEG interplanar spacing determined by the selected area electron diffraction pattern analysis.

| Sample                                           | d (hkl), Å |
|--------------------------------------------------|------------|
|                                                  | 100        | 110        | 105        |
| Data from [32]                                   | 2.134      | 1.232      | 1.133      |
| Initial graphite GT-1                           | 2.118      | 1.181      | 1.133      |
| TEG obtained from compound D – dried at 20 °C    | 2.103      | 1.181      | 1.133      |

The quality of thermally expanded graphite obtained from compound D – dried at 20 °C, was also estimated by Raman spectroscopy, since each compound has its own unique vibrational spectrum. Allotropes of carbon have their characteristic peaks [33] (G-peak at ~1580 cm⁻¹, 2D-peak at ~2700 cm⁻¹, and D-peak at ~1350 cm⁻¹). D-peak is responsible for the structural perfection of samples and the intensity ratio of $I_D/I_G$ indicates the level of defects. D-peak appearance can be attributed to edge effects and it not lead to the appearance of defects on the sample surface.

Raman spectroscopic studies were carried out for triple compound D – dried at 20 °C, and TEG prepared from it (figure 5).

Figure 5. The Raman spectra of 1) graphite nitrate sequentially cointercalated with ethyl formate and acetic acid – dried at 20 °C, 2) thermally expanded graphite.

Structural reorganization of the triple compound D after its thermal expansion was clearly demonstrated by the change in the shape and position of the G-peak and 2D-peak as well as the
appearance of the $D$-peak ($\sim$1342 cm$^{-1}$). Graphite nitrate cointercalation compound has an asymmetric 2D-peak at $\sim$2700 cm$^{-1}$ after GNCC thermal expansion the 2D-peak position shifts to lower wave number ($\sim$2668 cm$^{-1}$). $G$-peak position also shifts from $\sim$1594 cm$^{-1}$ to $\sim$1573 cm$^{-1}$. The ratio of $I_D/I_G$ for TEG was 0.04. This value indicates that obtained TEG is almost free of defects and has good structural perfection. The results of Raman spectroscopy agree well with the XRD and TEM data. The obtained data also confirm that in the process of thermal expansion crystallites are split along the $c$ axis.

3.2. The effect of the cointercalants ratio in the GNCC composition on the value of the thermal expansion coefficient

The effect of the organic cointercalants ratio in the composition of graphite nitrate cointercalated with ethyl formate and acetic acid on the thermal expansion coefficient was studied. For this, the volume ratio of ethyl formate and acetic acid was varied in the process of graphite nitrate intercalation. Samples were dried at a temperature of 40 °C. The value of thermal expansion coefficients for graphite nitrate cointercalation compounds with different ratio of organic cointercalants are presented in the Table 3. It was found that the $K_V$ value for graphite nitrate cointercalated with ethyl formate and acetic acid, does not depend on the initial ratio of organic cointercalants taken for synthesis, and average out 321 cm$^3$·g$^{-1}$.

Ability to thermal expansion of studied GNCCs samples was found to enhance when they were stored in ambient conditions for 24 days. Observed increase of the value, when averaged, was 27 units (for compound D samples dried at 20 °C, 40 °C, and 105 °C, $K_V$ values were 405, 348 and 124 cm$^3$·g$^{-1}$ correspondingly). The achieved values of the thermal expansion coefficient for these samples did not change after storage time extension up to 100 days.

**Table 3.** Thermal expansion coefficients of graphite nitrates cointercalated with ethyl formate and acetic acid, with different ratio of organic cointercalants.

| Ethyl formate | Acetic acid | $K_V^1$, cm$^3$·g$^{-1}$ | $K_V^2$, cm$^3$·g$^{-1}$ | $\Delta$ |
|--------------|------------|--------------------------|--------------------------|-------|
| $V_1$, cm$^{-1}$ | $n$ | $V_2$, cm$^{-1}$ | $n$ | | |
| 2.0 | 0.12 | 10.0 | 0.88 | 318 | 345 | 27 |
| 4.0 | 0.26 | 8.0 | 0.74 | 322 | 348 | 26 |
| 6.0 | 0.41 | 6.0 | 0.59 | 337 | 360 | 23 |
| 7.1 | 0.51 | 4.9 | 0.49 | 311 | 337 | 26 |
| 8.0 | 0.59 | 4.0 | 0.41 | 315 | 345 | 30 |
| 10.0 | 0.78 | 2.0 | 0.22 | 325 | 355 | 30 |

Notes:
1. $K_V^1$ – thermal expansion coefficient after 1 day of GNCCs synthesis
2. $K_V^2$ – thermal expansion coefficient after 24 days of GNCCs synthesis
3. $\Delta = K_V^1 - K_V^2$
4. $n$ – mole fraction of the cointercalant
5. $V$ – volume of cointercalant

3.3. Thermal stability of graphite nitrate cointercalation compounds

Thermal stability of graphite nitrate cointercalation compounds (Table 4) was evaluated by the ratio of the thermal expansion coefficients of products dried at 105 °C and 20 °C:

$$K_\nu = \frac{K_V^{105}}{K_V^{20}},$$

(3)
where $K^{105}_V$ и $K^{20}_V$ – thermal expansion coefficients of GNCCs obtained using the same intercalant(s) and dried at 105 ºC and 20 ºC correspondingly; $K_{st}$ – thermal stability coefficient.

The thermal expansion coefficient is mainly determined by the moles number of gaseous products formed from intercalated particles. Gaseous products in the initial stages of heating do not have time to leave the volume of the solid due to the high heating rates, and almost all moles are involved in the deformation recorded in the macro-index – the thermal expansion coefficient.

The $K_{st}$ is an assessment of thermal stability, since the comparison is made for products dried at different temperatures. Drying of the obtained GNCCs at 105 ºC leads not only to the removal of weakly bound surface particles, but also to a larger (in the case of low stability of the obtained GNCC) or less (in the case of high stability of the obtained GNCC) part of the intercalated particles. The heat treatment temperature of 105 ºC was selected on the basis of data indicating complete decomposition of graphite nitrate at 110 ºC for an hour.

There is a significant difference in the $K^{105}_V$ and $K^{20}_V$ values for graphite nitrate and its GNCCs, (table 4) due to the significant decomposition of obtained GNCCs during heat treatment at 105 ºC. There is a much smaller number of intercalated particles in the volume of this sample in comparison with GNCC dried at 20 ºC, – a small moles number of gas are formed inside the graphite matrix during thermal shock, i.e. its volume is less. It has been established that the intercalation of the third cointercalant into the graphite matrix leads to an increase in the thermal stability of the resulting GNCC – the triple compound D has a higher $K_{st}$ value in comparison with the graphite nitrate and compounds B and C (table 4).

**Table 4.** Coefficients of thermal expansion and thermal stability of the graphite nitrate and its cointercalation compounds.

| GNCCs | Cointercalant(s) | $K_V$ cm$^3$·g$^{-1}$ | $T_{drying}$, ºC | $K_{st}$ |
|-------|------------------|----------------------|-----------------|---------|
| A     | HNO$_3$          | 287                  | 20              | 0.04    |
| B     | HNO$_3$ / ethyl formate | 318              | 55              | 0.17    |
| C     | HNO$_3$ / acetic acid | 354              | 72              | 0.20    |
| D     | HNO$_3$ / ethyl formate / acetic acid | 378              | 97              | 0.26    |

4. Conclusion

Thus, the effect of the drying regime of graphite nitrate cointercalated with ethyl formate and acetic acid on its surface morphology as well as ability to the thermal expansion was studied. An increase in the drying temperature of the samples leads to a decrease in the thermal expansion coefficient. It was shown that the initial ratio of organic compounds in the process of triple GNCCs obtaining does not effect on the value of the thermal expansion coefficient, and the storage of such cointercalates in air at room temperature for 24 days leads to an approximately 10% increase in their thermal expansion ability. The value of the thermal expansion coefficients does not change after storage time extension up to 100 days.

It was found that the sequential treatment of graphite nitrate with two cointercalants leads to an excess of the thermal expansion coefficient of triple CCNG compared to the $K_V$ values for the corresponding binary cointercalates, and the intercalation of the third cointercalant into the graphite matrix leads to an increase in the thermal stability of the obtained CCNG.

Systematic studies of the microstructure, morphology, and quality of the obtained thermally expanded graphite by XRD, TEM, and Raman spectroscopy showed that compared to the initial graphite TEG is less ordered, has a multilayer and insufficiently ordered structure without visible surface defects.
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