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## Features of Chemical Reactions in the Absence of Solvents under Microwave Action

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### Abstract

Features of a number of chemical reactions in the absence of solvents under microwave action were investigated. The features of microwave heating of phthalic anhydride and glycine before and after melting were studied. It was shown that the microwave synthesis of glycine phthalimide occurs efficiently and with the high yield in the reaction mixture heated above the melting point of phthalic anhydride. Decomposition of intercalation compounds of chlorine trifluoride and intercalation compounds with acetone, acetonitrile, benzene and carbon tetrachloride implanted into the interlayer space of dicarbon polyfluoride was investigated. It was shown that the decomposition of intercalation compounds under microwave heating resulting in the formation of nanostructured graphite occurs at lower temperature values than those involved in conventional convection heating. It was concluded on the basis of experimental results that the absorption of microwave energy is connected with the dielectric properties of the substances intercalated into the interlayer space of dicarbon polyfluoride matrix. Experiments were carried out with Explorer-48 set-up with the microwave unit Discover S-class (CEM Corporation, the USA) operating at the frequency of 2450 MHz under the conditions of controlled power of microwave action within the range 0–300 W.

**Key words:** microwave chemistry, microwave heating, intercalation compounds, dicarbon polyfluoride, solvent-free reactions

### INTRODUCTION

At the present time, a great deal of studies in the field of microwave chemistry is performed in the area of organic chemistry [1–3]. In recent years the direction of synthetic organic chemistry is extensively growing, where the reaction are initiated by microwave radiation. Of particular interest are the reactions those occur without a solvent (so-called solvent-free reactions) [4, 5]. The probability of the fact that a reaction between solid reactants to occur is small, but under the conditions of the microwave synthesis an efficient interaction could be provided by appearing the melt phase of one or more reactants.

The feature of intercalation compounds based on dicarbon polyfluoride consists in the presence of rigid layers of a solid matrix; those impose restrictions on the spatial area of the reactions within the interlayer space of the

matrix. As a result, under thermal or chemical action with respect to corresponding metal compounds intercalated into layered matrices, there could be created the conditions for the formation of fine and anisotropic metal particles or such particles of metal compounds, *i. e.* a layered intercalate could act as a two-dimensional nanoreactor. On the other hand, the thermal decomposition of graphite intercalation compounds with various fluorinated intercalates results in the formation of nanostructured graphite (expanded graphite). The parameters of the functional nanocomposite materials are determined to a considerable extent by the intensity of thermal effects, so the efficient heating with the use of microwave radiation enriches this line of research.

Within the last few years, a systematic research work in performed concerning the obtaining of expanded graphite and graphene layers from graphite intercalation compounds and

oxygraphite using microwave activation for the exfoliation of carbon materials [6–10]. However, in the case of using graphite or oxygraphite matrices one could achieved relatively low expansion level values for the carbon materials (lower than 150 times) and a relatively thick graphene layer stacks (more than 40 nm). In this regard, studying the decomposition of intercalated dicarbon polyfluoride compounds in order to obtain novel expanded graphite and graphene species represents a research field of interest and practical importance.

## EXPERIMENTAL

The experimental studies were carried out using an Explorer-48 unit with a Discover S-class microwave module, operating at a frequency of 2.45 GHz. The power of microwave energy in the resonator cavity was adjusted within the range of 0–300 W with a 1 W increment. The unit under use provides a continuous time recording of the surface temperature of a sample, excess pressure within a microwave vial, the dynamics of changing the microwave power with achieving and maintaining the temperature set points, as well as video registration of reaction mixture behaviour under microwave exposure. A schematic diagram of registering the pressure and temperature values in the course of microwave heating the materials under investigation is demonstrated in Fig. 1.

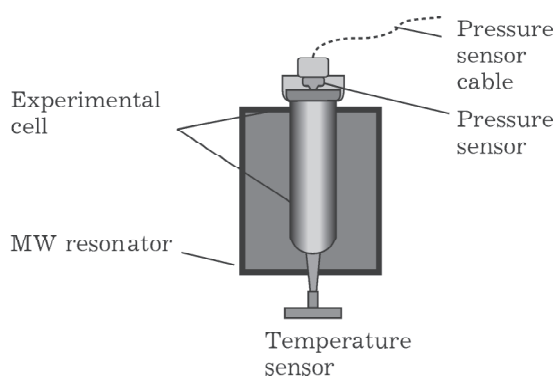
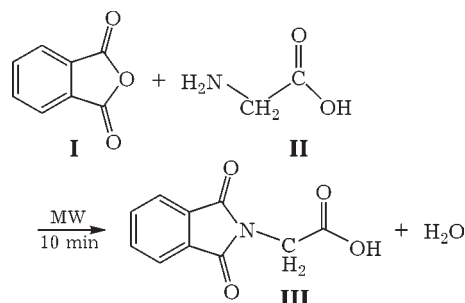


Fig. 1. Schematic diagram measuring the sample temperature and pressure in the course of microwave heating in the Explorer-48 unit.



Scheme 1.

### Studying the reaction between phthalic anhydride and glycine

In order to investigate the possibility of the reaction of glycine phthalimide formation to occur without using a solvent, we studied the interaction of phthalic anhydride **I** (m. p. 131 °C) and glycine **II** (m. p. 240 °C) under the action of microwave activation (Scheme 1).

Primarily, we investigated the dynamics of heating the phthalic anhydride **I** within the microwave reactor via the registration of the rate of changing the temperature depending on the power of microwave radiation (Fig. 2). For the glycine, we obtained similar temperature rise dependences, but at higher temperature values (210–240 °C). It was found that melting the reactants results in the fact that temperature rise rate demonstrates a 30–40-fold increase, which could be caused by an increased mobility of molecular dipoles. It should be noted that the temperature values registered by an external sensor is 25–30 °C lower than the melting point for the reagents under investigation. This discrepancy could be caused by a scheme under use for measuring the temperature by an external sensor located at the bottom of the microwave resonator cavity to measure the temperature of the vial bottom (see Fig. 1). However, appearing the melt zone is observed in the upper part of the sample, further the melt zone moves downwards. In the case when the level of microwave power amounting to 100 W, reaching the melting temperature of phthalic anhydride was unsuccessful during 20 min of microwave heating because of a low efficiency of absorbing the microwave radiation by the solid.

Under the microwave heating of phthalic anhydride there is partial sublimation and the

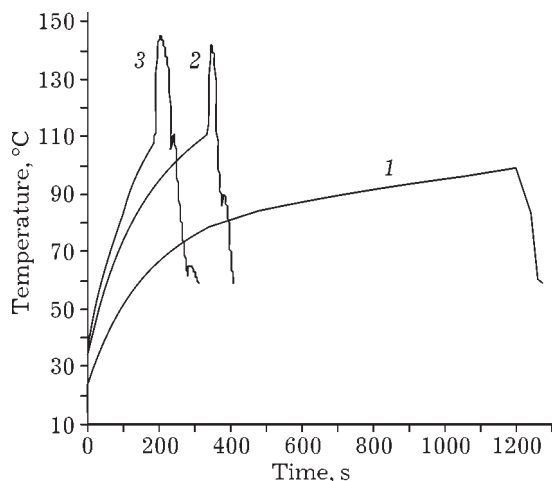


Fig. 2. Dynamics of heating phthalic anhydride at different levels of microwave power, W: 100 (1), 150 (2), 200 (3).

deposition of the compound occurring on the top of the reaction tube. For the equimolar mixture of the reagents the active absorption of microwave energy also begins with appearing the molten phthalic anhydride. However, up to the temperature value equal to 160 °C, there is no formation of glycine phthalimide **III** observed to occur, which is consistent with the

results from [11]. It should be noted that the authors of the mentioned paper argue that the synthesis of glycine phthalimide is possible with use of high-boiling solvents. We have found that the interaction between starting reagents results in the formation of the glycine phthalimide with a high yield, although the reaction requires for a higher melt temperature (200–240 °C). The best result was obtained when the reaction was carried out via two stages. At the first stage, a mixture of solid reactants was heated for 5 min at 130 °C and 200 W microwave power at medium rate of stirring. The reaction mixture was heated for further 5 min at 240 °C at the same level of microwave power and the melt stirring mode. As a result, we obtained the target product **III** with a 90 % yield.

#### Microwave heating of dicarbon polyfluoride intercalation compounds

Under microwave heating the dicarbon polyfluoride intercalation compounds we registered temperature, excess pressure in the vial filled with the substance and the dynamics of chang-

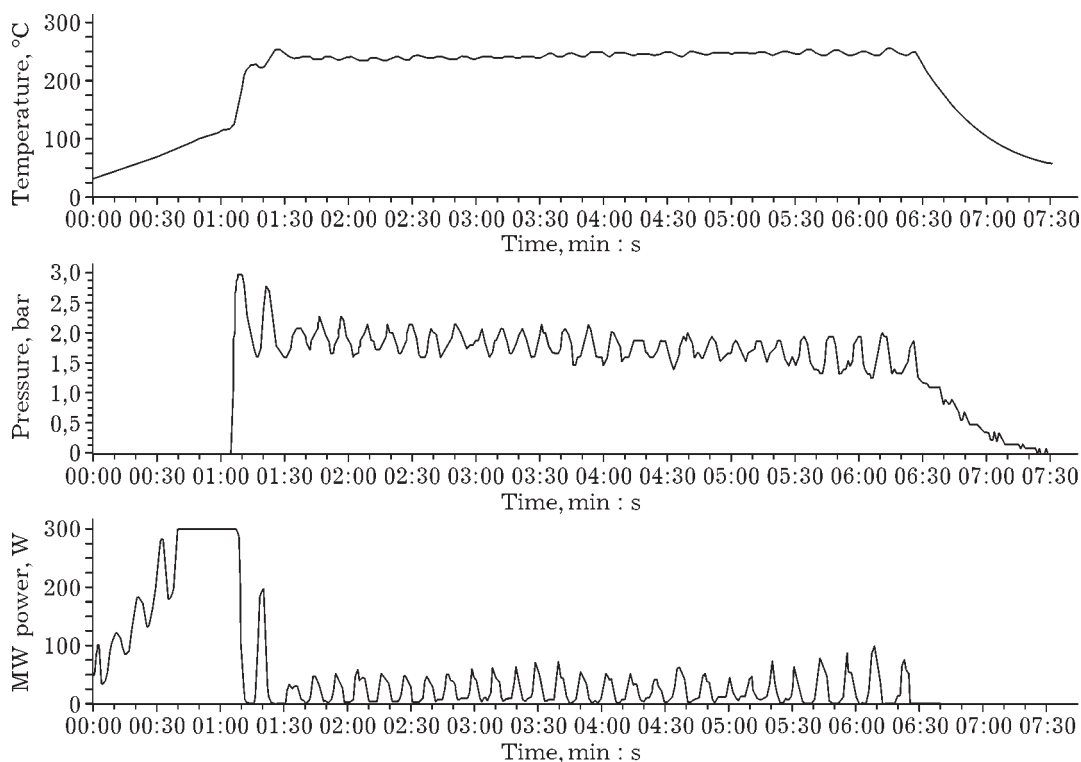


Fig. 3. Dynamics of changing the temperature, pressure, and microwave power in the course of heating the dicarbon polyfluoride intercalation compound with acetonitrile.

TABLE 1

Decomposition temperature of intercalation compounds under investigation observed in the case of microwave and conventional (convective) heating, °C

Samples	Microwave heating	Convection heating
$C_2F \cdot ClF_3$	270–280	590–600
$C_2F \cdot C_6H_6$	180–190	275–285
$C_2F \cdot CCl_4$	190–200	405–415
$C_2F \cdot CH_3COCH_3$	95–105	175–185
$C_2F \cdot CH_3CN$	115–125	190–200

ing the microwave power. Figure 3 demonstrates a typical form of ejecting the experimental results obtained by means of microwave heating the samples of dicarbon polyfluoride intercalation compounds with various organic intercalates embedded in the interlayer space.

It should be noted that primarily we investigated the microwave heating of dicarbon polyfluoride intercalation compounds with chlorine trifluoride ( $C_2F \cdot xClF_3$ ). When the microwave power within the resonator was equal to 300 W, the duration of heating the intercalated compound obtained from graphite with particle size of 6–7  $\mu m$  up to its decomposition temperature (Table 1) exceeded 40 min. No decomposition was registered for the chlorine trifluoride intercalation compounds obtained from graphite with a particle size amounting to about 630  $\mu m$  at this value microwave power action (300 W).

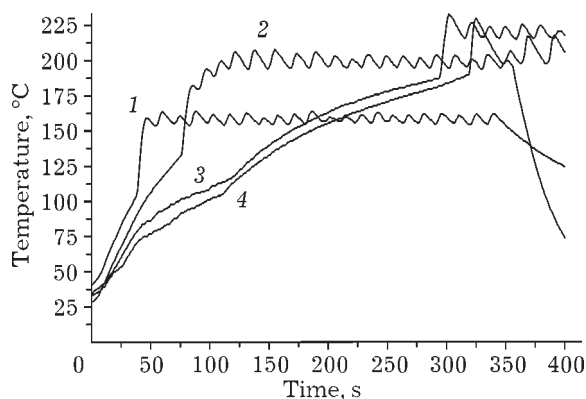


Fig. 4. Outside temperature of the ampoule with the substance depending on time in the course of microwave heating the dicarbon polyfluoride intercalation compounds with organic substances: 1 – acetone, 2 – acetonitrile, 3 – carbon tetrachloride, 4 – benzene.

In the case of dicarbon polyfluoride intercalation compounds with organic substances, there are two processes with different time behaviour observed under microwave heating. In the case of dicarbon polyfluoride intercalation compounds with benzene and carbon tetrachloride, the temperature rise for initial samples in the course of microwave heating is characterized by a low rate, and the decomposition of these compounds to form carbon nanostructure occurs at higher temperature values (Fig. 4). On the contrary, the dicarbon polyfluoride intercalation compounds with acetone and acetonitrile under microwave heating are characterized by a rapid rising the substance temperature in the vial, which is accompanied by the formation of nanostructured carbon. In the course of the formation of nanostructured carbon (expanded graphite) there is an abrupt increase in the rate of temperature rise observed, as well as the formation of volatile and gaseous products in significant amounts due to evolving both intercalation compounds and the products of their interaction with the material of the fluorocarbon matrix from the interlayer space of the matrix. The prolonged heating of the resulting carbon material is characterized by significant oscillations in the microwave power, temperature and pressure in the vial (see Figs. 3, 4), which is not typical for microwave heating of homogeneous systems.

Information concerning the decomposition temperature values for intercalated compounds under investigation with the formation of nanostructured carbon under convective and microwave heating is presented in Table 1.

#### *Obtaining the nanostructured carbon under microwave heating the dicarbon polyfluoride intercalation compounds*

As noted above, in the course of microwave heating the dicarbon polyfluoride intercalation compounds there is extended (nanostructured) carbon observed to be formed. Upon the decomposition of dicarbon polyfluoride intercalated compounds the material volume exhibits an almost 2500-fold increase, whereby the resulting carbon material has a very low bulk density (0.4–1.0 g/L) and high specific surface value (>300  $m^2/g$ ).

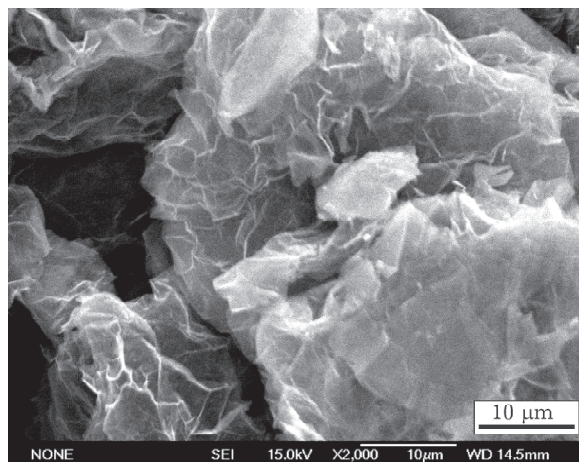


Fig. 5. Morphology of the nanostructured carbon material obtained under microwave heating the dicarbon polyfluoride intercalated compound with acetone.

In appearance, the resulting expanded graphite (EG) represents a lint-like material composed of helical fibres from 2–3 to 10–12 mm long. The length of carbon fibres depends on the particle size of the graphite used for the synthesis of the starting carbon compound intercalated with chlorine trifluoride (in the first case the size of graphite particles is equal to 6–7  $\mu\text{m}$ , in the second case the size is about 630  $\mu\text{m}$ ). The thickness of fibres obtained in the course of the decomposition ranges from 0.1 to 1.0 mm.

Depending on the source of the initial intercalant, the expanded graphite contains more than 90 mass % of carbon, 3–6.5 mass % of fluorine, and about 2 mass % of chlorine [12]. This fluorine and chlorine atoms those are strongly (chemically) bonded with carbon atoms thus they could not be completely removed even in the course of the calcination of expanded graphite up to 300  $^{\circ}\text{C}$  in an atmosphere of hydrogen. A typical morphology of the carbon material obtained from the intercalated compound with acetone was determined by means of a JEOL-JSM6700F scanning electron microscope (Fig. 5).

## RESULTS AND DISCUSSION

The ability of a substance to absorb the microwave energy is connected either with the existence of electronic or ionic conduction currents therein, or with biasing currents caused

by the polarizability of the substance in the field of electromagnetic wave [13]. In the absence of conduction currents, the energy input from the alternating electromagnetic field to the substances under investigation could be connected with the ability of polarizing the substances, whereas the greatest contribution to the substance polarizability is made by electric dipole moments of the constituent molecular components. When alternating electric field is applied across a substance, the electric dipoles (polar molecules or other separate atomic groups) following the oscillating field change their spatial orientation. In order to absorb the energy of electromagnetic wave in the substance *via* its interaction with the dipole moments of atomic groups composing the molecule, it is necessary that the bond between the dipole with surrounding atoms in the material provided a certain freedom of the dipole movement. In case when the dipole is rigidly bound with the matrix of the substance and the amplitude of its movements in the field of the wave is low, no significant absorption of electromagnetic energy via this mechanism should occur.

It is just the dipole hindrance of phthalic anhydride and glycine molecules in the solid state that causes a low rate of heating the substances under microwave action. The loss tangent values ( $\text{tn } \delta$ ) those characterize the ability of a substance to convert the microwave energy into heat do not exceed 0.001 for these compounds, which just determines the low heating rate. Upon reaching the melting temperature, a considerable increase in dipole mobility occurs, which results in a rapid rise in the temperature of the substances under investigation. However, to measure the values of  $\text{tn } \delta$  under melting these compounds was not yet possible.

The specific feature of heating the dicarbon polyfluoride intercalation compounds consists in the transparency of proper fluorographite matrix for passing microwave radiation therethrough. This fact is indicated also by data on low heating rate in the case of the intercalated compounds of benzene and carbon tetrachloride incorporated in the interlayer space of the matrix, even at the maximum power of the microwave radiation amounting to 300 W. The loss tangent values for the dicarbon polyfluoride intercalation compounds with chlorine

trifluoride, benzene, and carbon tetrachloride are equal to 0.002–0.003, which determines a low rate of microwave heating. Both benzene and carbon tetrachloride exhibit a zero dipole moment, so the process of microwave heating and decomposition of these compounds with the formation of nanostructured carbon occurs with a considerably lower rate and at higher temperature values. The fact that the mentioned heating non-polar substances are heated under these conditions could be connected with the process of a dipole polarization of the molecules in a strong microwave field.

The efficient heating of the dicarbon polyfluoride intercalation compounds occurs due to the absorption of microwave energy by an intercalated (*i. e.* embedded in the fluorographite matrix) compound that exhibits a dipole mobility. The bulk, but not only the surface-controlled (as it is in the case with a conventional external supply of heat energy) nature of heating the samples under irradiation is an important feature of the microwave field. Given that the container wherein the sample is placed, is made of glass, *i. e.*, the material that exhibits almost no absorption of the microwave radiation, in the course of the experiments on heating in the field of microwave energy there can be achieved a rapid temperature rise uniform-

ly throughout all the volume of the material contained in the ampoule.

The molecule of chlorine trifluoride has a slightly distorted T-shaped structure. The dipole moment of the chlorine trifluoride molecule, is almost insignificantly less than the dipole moment of water (0.554 and 1.86, respectively) [14], but, in our opinion, it is sufficient to provide a high absorption level for microwave energy in the substance. Consequently, the low rate of temperature increase in this substance under microwave heating could be caused either by the formation of chlorine trifluoride dimeric molecules with a zero dipole moment within the interior interlayer space, or by chemical bonding between chlorine trifluoride with the fluorocarbon material of the matrix, which bonding reduces to a considerable extent the dipole mobility of the chlorine trifluoride intercalated into the interlayer space.

Unlike the intercalation compounds with chlorine trifluoride, the intercalated compounds with acetone or acetonitrile are characterized by a high dipole moment (2.84 and 3.44 D for acetone and acetonitrile, respectively) [15]. The loss tangent values for these compounds are significantly higher to be equal to 0.044 and 0.063, respectively. The process of the decomposition of these compounds to form a carbon nano-

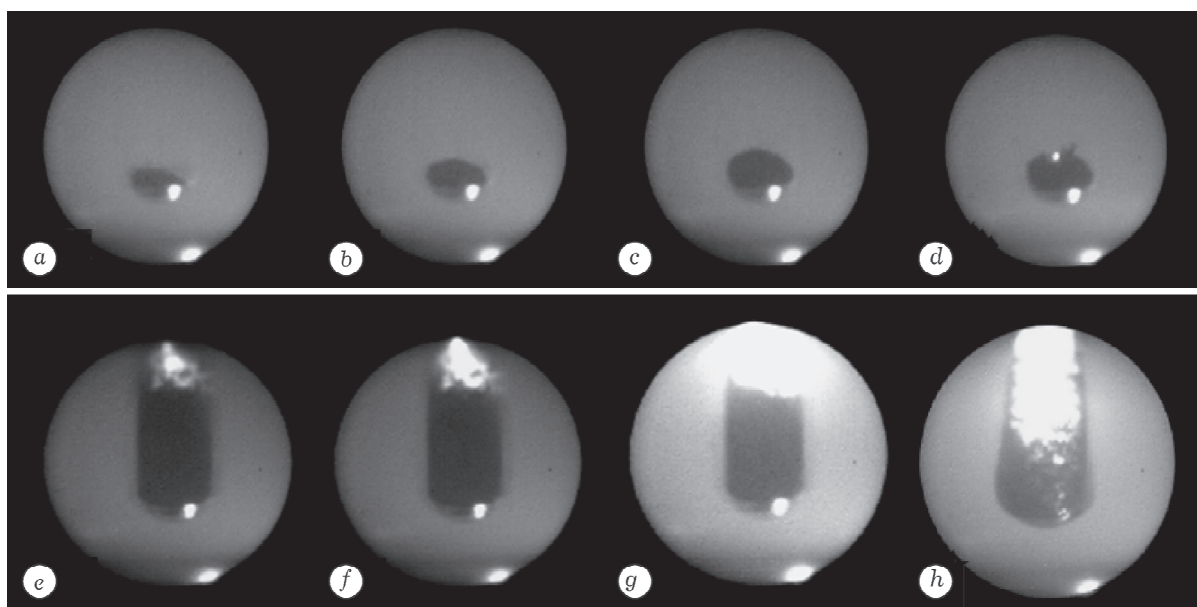


Fig. 6. Photographic pictures of changing the volume of dicarbon polyfluoride intercalation compound with benzene under microwave heating (*a-d*) and those of the formation of a corona discharge on the surface of the expanded graphite obtained (*e-h*). The increment of the pictures, s: 60 (*a-d*), 0.25 (*d-h*).

structure occurs rapidly and at relatively low temperature values inherent in the outer layers of the fluorocarbon matrix (see Fig. 4).

Upon reaching a certain temperature in the course of microwave heating the sample of an intercalated compound in the experimental cell, a considerable amount of volatile and gaseous products is formed due to their evolving from the interlayer space of the matrix wherein they are generated both by the intercalate, and by the products of its interaction with the fluorocarbon material of the matrix. The course of this process can be illustrated by the dynamics of changing the pressure under microwave heating the dicarbon polyfluoride intercalation compound with acetonitrile (see Fig. 3). One could see that the moment of abrupt increasing the pressure corresponds to jumping the temperature rise to a set point, which ends by decreasing the power input into to the resonator to almost zero value.

Further maintaining the preset temperature value is provided by a periodic supplying to the relatively short-time pulses of microwave radiation into the resonator cavity. Such a behaviour of the temperature and pressure values, in our opinion, could be caused by the formation of high-split graphite in the course of the degradation of the intercalation compounds under study at a certain temperature. In this case such an abrupt increase in the temperature occurs due to the fact that high split graphite which absorbs microwave energy with a high efficiency forms in the product obtained in the course of the microwave treatment. The loss tangent value for high-split graphite  $\tan \delta = 1.21$ , which is significantly higher as to compare with that inherent in the intercalated dicarbon polyfluoride compounds with polar substances (acetone and acetonitrile).

As mentioned above, prolonged heating the carbon material obtained is characterized by significant oscillations in the microwave power, temperature and pressure in the vial. These features could be connected with the formation of a high-frequency corona discharge on the surface of the resulting carbon material, which was detected in the course of video recording the process of forming the expanded graphite resulting from microwave action. At the initial stage, there is a partial decomposi-

tion of dicarbon polyfluoride intercalation compounds observed to occur with a slight increase in the volume of the initial sample (Fig. 6, *a-d*). For the intercalation compounds with acetone and acetonitrile the duration time of preliminary stage ranges within 30–40 s, whereas for the compounds with benzene and carbon tetrachloride this value is equal to 5 min. Then there is an abrupt (for 1 s or less) increase in the volume of the carbon stuff, whose surface is just a place for the corona discharge to appear (see Fig. 6, *e-h*).

The surface layers of nanostructured carbon exhibit a minimum density and minimum distortion level of the carbon fibres formed, whereon by a high-frequency corona discharge is formed. The structure of carbon fibres is presented in Fig. 7.

Under microwave action on the carbon material previously obtained *via* decomposing the

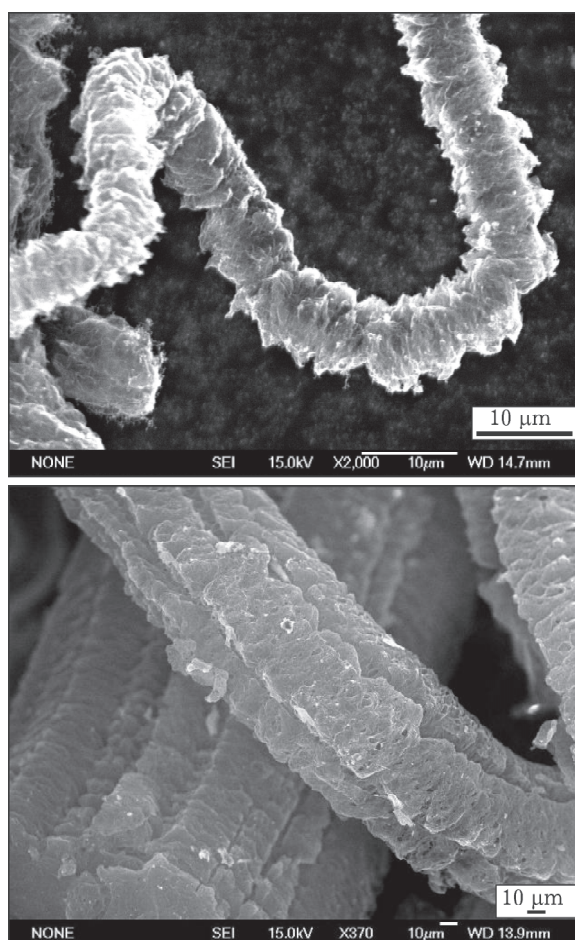


Fig. 7. Electron microscope image of carbon fibres on the surface of a nanostructured carbon material.

dicarbon polyfluoride intercalation compounds and then thoroughly degassed, the formation of the surface discharge is observed at low levels of microwave energy equal to about 20 W. The intensity of the discharge glow increases with the power of the microwave irradiation. The formation of the corona discharge occurs also the graphite particles are treated by microwave radiation. However, the beginning of the glow is observed to occur at high enough levels of microwave power (about 200 W). This phenomenon could be caused by the size of the graphite particles those are substantially larger than that for the carbon material obtained *via* ISFG decomposition (the linear size of the graphite particles reaches 2 mm, the thickness of the flakes amounting to 50  $\mu\text{m}$ ). This indicates that the formation of the discharge on the surface of the material is determined by the geometrical characteristics of the latter.

It was found that in the regions of forming the high-frequency corona discharge there are local zones formed with high temperature gradients high electron density. These data could provide a basis for the development of microwave methods for modifying of different materials.

## CONCLUSION

Microwave heating dynamics was studied for phthalic anhydride and glycine before and after melting the substances under investigation. The synthesis of glycine phthalimide is demonstrated to occur in the melt of phthalic anhydride heated up to 200–240 °C.

We investigated for the first time the features of microwave heating the dicarbon polyfluoride intercalation compounds with chlorine trifluoride and various organic intercalates (acetone, acetonitrile, benzene, and carbon tetrachloride).

The efficiency of microwave heating the dicarbon polyfluoride intercalation compounds was demonstrated to be determined by the dielectric the properties of compounds embedded in the matrix.

It has been established that under microwave heating the dicarbon polyfluoride intercalation compounds the decomposition of the

substance is accompanied by the formation of high split graphite. The process temperature for the formation of high split graphite under microwave radiation is to a considerable extent lower than the temperature values inherent in for the case of traditional convection heating.

It is demonstrated that the microwave action on nanostructured graphite obtained in the course of decomposing the intercalated compounds results in the formation of periodic high-frequency corona electric discharge on the surface of a carbonaceous material.

## Acknowledgement

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