

Surface microstructure of thermoexfoliated graphite

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The surface microstructure of thermoexfoliated graphite (TEG) particles produced by thermoexfoliating graphite intercalation compounds with different intercalants of acceptor type at different temperatures has been investigated using optical microscopy and X-ray analysis. The surface microstructure has been found to depend essentially on the substance used as intercalant, the temperature of thermoexfoliation as well as particle sizes of initial graphite used for intercalation and thermoexfoliation. By varying intercalants and temperatures applied for thermoexfoliation, it is possible to obtain microstructures with the desired values of such parameters as grain sizes, uniformity and dispersity of grain structure on the developed surface of TEG.

Методами оптической микроскопии и рентгеновского анализа исследована микроструктура поверхности частиц терморасширенного графита (ТРГ), полученного при разных температурах терморасширения интеркалированных соединений графита с разными интеркалянтами акцепторного типа. Показано, что упомянутая микроструктура существенно зависит от природы вещества-интеркалянта, температуры терморасширения и размеров частиц исходного графита. Варьированием типа интеркалянта и температуры терморасширения можно обеспечить необходимые значения параметров микроструктуры, таких, как размеры зерен, однородность и дисперсность зернистой структуры развитой поверхности ТРГ.

It is known that fast heating (thermal shock) of the graphite intercalation compounds (GICs) results in formation of a new modification of graphite materials, so-called thermoexfoliated graphite (TEG). The unique thermal and plastic properties of TEG provide possibilities of its application in many branches of industry, e.g., chemical, nuclear, and heat power, and others. Moreover, the thermoexfoliated graphite is a material of good prospects for preparation of modified graphite, i.e., the graphite with modifier particles distributed on its surface. Various inorganic substances such as metals, metal oxides, salts, as well as organic substances can be used as modifiers. Distribution of the modifier particles on graphite surface depends essentially on the surface microstructure. That is why the necessity of investigation of TEG particles surface microstructure in depending on ob-

taining conditions is defined by problems of graphite modification. In [1, 2], the TEG particle surface morphology has been studied as depending on structure of initial graphite and intercalant type. Substantial distinctions in the morphology of TEG particles obtained using acceptor and donor GICs were revealed by authors in [2]. In this work, results of optical microscopic investigations in surface microstructure of thermoexfoliated graphite particles produced by thermoexfoliation of GICs with different acceptor intercalants and at different temperatures.

The initial graphite used for preparation of intercalation graphite compounds was natural graphite of different fractions, from 160 to 400 μm . Intercalation of SbCl_5 and ICl was carried out to stages 2 and 3 by single-zone method [3] at 493 K and 313 K, respec-

tively. Graphite bisulfate $C_{24}HSO_4 \cdot 2H_2SO_4$ was prepared using the persulfate and dichromate techniques [4]. The stage of the produced GIC samples as well as phase composition of thermoexfoliated graphites was determined using a DRON-3M X-ray diffractometer in Co radiation. Thermoexfoliation of the intercalated graphite samples was performed in a laboratory furnace, temperature stability was ± 10 K. In order to produce thermoexfoliated graphite, small portions of GIC powder were quickly poured into quartz cup preliminary heated to the temperature of thermal shock.

Investigations of graphite surface microstructure were performed using a Micmed-1 optical microscope. Microscopic studies of graphite particles were carried out at magnification $\times 225$, the surface fine structure was studied using objectives that allowed $\times 900$ and $\times 2250$ magnification to be obtained in oil immersion.

In initial state, the GAK brand graphite is a silver-colored powder consisting of regularly shaped flat particles (Fig. 1a). Graphite platelets contain a number of planes shifted horizontally with respect to one another and as a result, the platelets have a staircase appearance. The particle thickness is about 30 to 40 μm , the step height being 3 to 5 μm . The large horizontal planes of graphite are broken into grains of regular geometry about 100 μm in size which, in turn, consist of small (10 to 30 μm) blocks. The block surfaces are smooth in some areas or covered with flakes about 5–6 μm in other ones.

Graphite of 400 μm fraction intercalated with $SbCl_5$ is a dark gray powder with metallic glance. The size of the particles located parallel to graphite layers remains essentially unchanged in the intercalated powder. The platelet thickness increases. The grains forming graphite planes are reduced in size down to 50 μm , and the blocks that the grains consist of are reduced down to 15 μm . The reduction of block sizes is caused by formation of cracks and fractures as well as by turning of some graphite planes at an angle in relation to the horizontal plane. The flakes remain but in rare places on the graphite surface. The particle edges in the places where they are formed by protruding planes contain visible precipitations of intercalant at the borders of grains and blocks. Graphite of 400 μm fraction intercalated with ICl is a powder with

the same metallic glance as the initial graphite. Particle sizes of intercalated graphite are not increased in comparison with the initial graphite. The particle thickness increases but not so much as in graphite intercalated with $SbCl_5$. The borders of grains and blocks are rectilinear and retain regular geometric form. Grain sizes are about 25 to 100 μm , block sizes are about 10 μm . There are intercalant precipitations at the edges of particles, grains and on the surface of graphite planes. On the surface of 400 μm fraction graphite intercalated with H_2SO_4 (1b), there are no flakes similar to those on the surface of initial graphite. The grains into which graphite planes are broken are large and their sizes are not changed considerably as compared to the initial graphite. There are areas on the surface with twins, cracks, traces of microexplosions and regions where deeper planes are as if elevated above the top plane level. The lines of fracture diverge from explosion centres and from elevated planes in straight parallel lines.

Thus, under intercalation, the initial graphite particles are thickened without their sizes being changed along the a plane. Essential are the differences between surface structure of the particles of graphite intercalated with different intercalants. For instance, the graphite surface structure does not change considerably due to intercalation with iodine chloride. Grain sizes are not changed significantly in comparison with graphite intercalated with stibium chloride, with its grains somewhat reduced in size. As for graphite intercalated with sulphuric acid, the average grain size remains the same but surface structure is significantly "worse": graphite particles are covered with microcracks, traces of microexplosions, deeper planes coming out on the surface, etc.

The intercalant removal from graphite matrix is accompanied by arising of strong mechanical stresses. As a result, the particle planes are transformed into large voluminous layered structures branching in different directions. Particle sizes of thermoexfoliated graphite and their dependence on intercalant type, particle sizes of the initial graphite, and thermoexfoliation temperatures are presented in Table.

It is seen from the Table that the thermoexfoliated graphite particle sizes depend essentially on all the parameters mentioned above. For example, at the temperature as low as 473 K, the particles of GIC with

sulphuric acid become 20 to 30 times thicker than those of initial graphite, while the particle thickness of GIC with stibium chloride and iodine chloride does not enlarge so much. However, when the thermoexfoliation temperature elevated up to 1173 K, the maximal enlargement of particle thickness is observed for 400 μm fraction of graphite intercalated with stibium chloride. It is 140 times larger than the thickness of initial graphite particle. In graphite of the same fraction intercalated with sulfuric acid by dichromate method, the particles become 100 times thicker; in GIC prepared by persulfate method, they enlarge by 75 times and intercalation with iodine chloride results in a 65-fold enlargement of the particle thickness.

As the thermal shock temperature is elevated to 1573 K, the particle thickness still increases but only slightly and attains 3.5 mm in GIC with ICl, that is approximately 90 times larger than the particle thickness in initial graphite; particle sizes in GIC with H_2SO_4 prepared by both methods are 4.8 mm and 4.5 mm, respectively, which exceeds approximately 110–120 times the size of initial graphite particle. Particle size in GIC with SbCl_5 practically does not change or even becomes a little smaller; this may be due to particles scorching at this temperature. Depending on particle sizes of initial graphite, the particle thickness in thermoexfoliated graphite has been found to be smaller for smaller initial particles (in practice, the thickness of particles in all graphite fractions is considered to be the same). For example, the maximal thickness of thermoexfoliated particle in GIC with SbCl_5 prepared at 1573 K is 5.5 mm for fraction 400 μm and 1.1 mm for fraction 160 μm which indicates 35-fold enlargement of initial particle, i.e. for fraction 400 μm

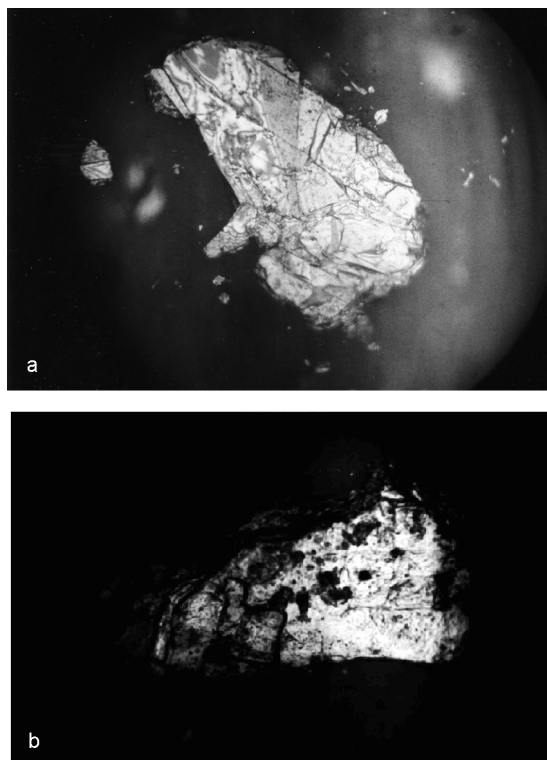


Fig. 1. Particle surface structure: a) initial graphite; b) GIC with H_2SO_4 ; optical microscopy, $\times 225$.

the graphite particle thickness becomes 4–5 times larger than that for fraction 160 μm .

In the course of thermoexfoliation, the granular structure of graphite changes due to size reduction of grains. As the investigations in surface topology of thermoexfoliated graphite have shown, the graphite granular structure depends on the thermoexfoliation temperature and the intercalant type.

Particle surface topology was investigated for graphite of fraction 400 μm intercalated with stibium chloride, iodine chloride and sulphuric acid, and thermoexfoli-

Table. Average size of TEG particles l (mm)

T, K	Intercalant						
	SbCl_5				ICl	H_2SO_4 (d)	H_2SO_4 (p)
	2 stage, 400 μm	3 stage, 400 μm	2 stage, 315 μm	2 stage, 160 μm			
473	0.35				0.5	1.5	0.7
573			0.4	0.3			2.0
773		0.6	0.7	0.4	0.8	2.0	
1073		2.2		0.5	2.0		2.4
1173	5.5	4.0	4	0.8	2.6	4.2	3.0
1573	5.0	4.5	3	1.1	3.5	4.8	4.5

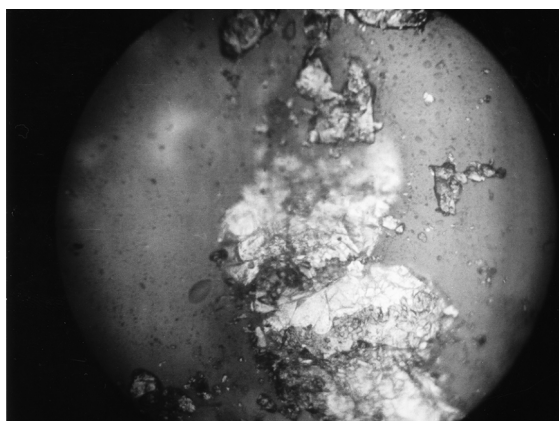


Fig. 2. Particle surface structure of TEG obtained from GIC with H_2SO_4 at 473 K; optical microscopy, $\times 225$.

ated at the temperatures 473 K, 773 K, 1173 K, and 1573 K.

Fig. 2 presents the surface of graphite particle intercalated with H_2SO_4 and exfoliated at 473 K. As it is seen from the Figure, the particle surface is highly inhomogeneous. The large grains of about $40\ \mu\text{m}$ in size are present, but most of the surface has fine-grained structure with grain sizes not exceeding $5\ \mu\text{m}$. The grains are irregular in shape. There are many traces of microexplosions, the areas with smaller grains are as though half-raised above the surface plane. There are separate surface islets coated with a thin film. The surface structure of TEG particles prepared from GIC- SbCl_5 at 473 K shows a similar image. The surface is highly inhomogeneous: the areas with fine-grained structure containing grains of nearly $5\ \mu\text{m}$ are observed along with the areas containing large grains of about $15\ \mu\text{m}$. The block boundaries are rectilinear and the lines of twinning and microcracks are observed in a large number. In GIC with ICl thermoexfoliated at 473 K, grain sizes practically did not change as compared to those in the initial GIC- ICl and are of 25 to $60\ \mu\text{m}$ size. However, individual grains of about $20 \times 10\ \mu\text{m}^2$ (1–2 in sight) cause the plane layering throughout particle height as if by being half-raised above the sample surface. The grain boundaries are rectilinear, grain sizes decrease when passing to the particle edges as compared to those at the particle center. There are precipitations of intercalant at the edges of particles and grains, as well as areas coated with a thin film.

Thus, the thermal shock temperature of 473 K results in considerable inhomogeneity

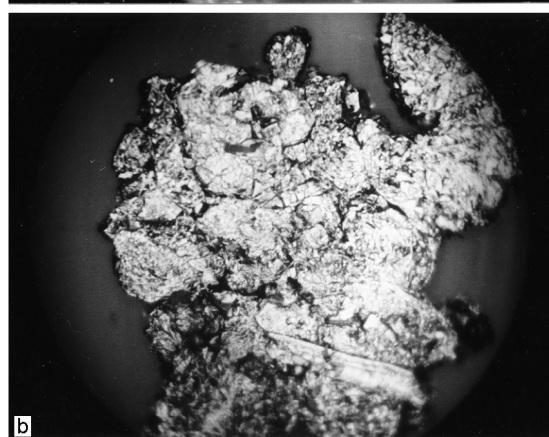
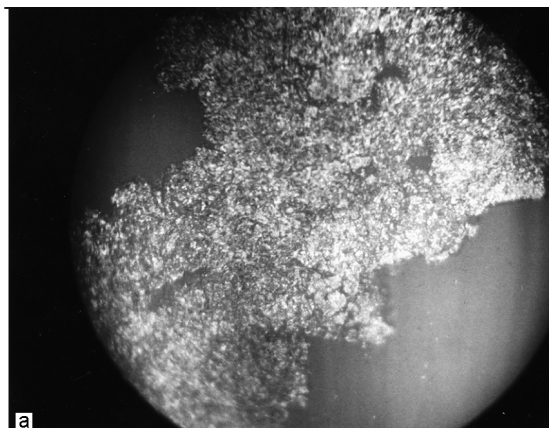


Fig. 3. Particle surface structure of TEG obtained at 1173 K from GICs with SbCl_5 (a); ICl (b); optical microscopy, $\times 225$.

of the surface structure in graphite intercalated with stibium chloride and sulphuric acid. Relatively large grains together with small grain area are present on the particle surface in these GIC, thus differing their surface structure from that found in GIC with ICl thermoexfoliated at the same temperature where the grains practically do not change in size with respect to the initial GIC.

The particle surface of TEG prepared from GIC with SbCl_5 at the thermoexfoliation temperature 773 K retains its inhomogeneity though the maximal grain size decreases to $7\ \mu\text{m}$. Large grains are coated with a thin film. The particle surface is fractured with fractured planes facing different directions. The area of a fractured part located in one plane attains about $30\ \mu\text{m}$. The TEG particle surface of prepared from GIC with ICl at the thermoexfoliation temperature 773 K becomes more fine-grained, but the grains retain their regular geometrical shape; grain sizes vary from $60\ \mu\text{m}$ to $5\ \mu\text{m}$. The number of large

and small grains is approximately the same, the large and small grains being distributed uniformly. The particle surface is flat and mosaic though there are individual elevated areas. Large parts of the surface are coated with a film. The TEG particles prepared from GIC with H_2SO_4 at the thermoexfoliation temperature 773 K have been found to possess fine-grained structure. There are also individual separate islets of 10 to 15 μm coated with film.

When the thermal shock temperature is increased to 1173 K, the particle surface of TEG prepared from GIC with SbCl_5 consists of evenly distributed grains from 7 to 20 μm in size, the number of large grains being much smaller (Fig. 3a). The division into large grains disappears almost completely. The places where deeper planes merge on the particle surface can be distinguished. The particle surface of TEG prepared from GIC with ICl at the thermoexfoliation temperature 1173 K consists also of uniformly distributed large and small grains (Fig. 3b). The difference between these GICs is that the large grains in GIC with ICl comprise about 50 % in the visible part of the surface; the grains retain their rectilinear borders and there are areas on the surface with the preserved thin film. The particle surface of TEG prepared from H_2SO_4 at the thermoexfoliation temperature 1173 K consists of uniformly distributed grains from 8 μm to 2 μm in size, with the larger grains located near the particle center, and the size of smaller grains decreases towards the particle boundaries.

Fig. 4 presents the surface structure of TEG particles obtained at 1573 K from GICs with SbCl_5 (4a), ICl (4b), and H_2SO_4 (4c). As it is seen from the Figures, the particle surface of TEG prepared from GIC with SbCl_5 represents a fine-grained homogeneous structure. The surface is very uneven, the grains are irregular in shape. The grain sizes vary from 3 μm to 1.5 μm . The particle surface of TEG prepared from GIC with ICl is inhomogeneous. There can be found both large grains of about 15 μm and smaller ones with average size of 5 to 6 μm , all grains preserving linear edges and regular geometrical shape. In contrast with particles of TEG prepared from GIC with SbCl_5 , there are regions with preserved film coating on the surface, despite of such a high thermoexfoliation temperature. The particle surface of TEG prepared from H_2SO_4 represents the most homogeneous

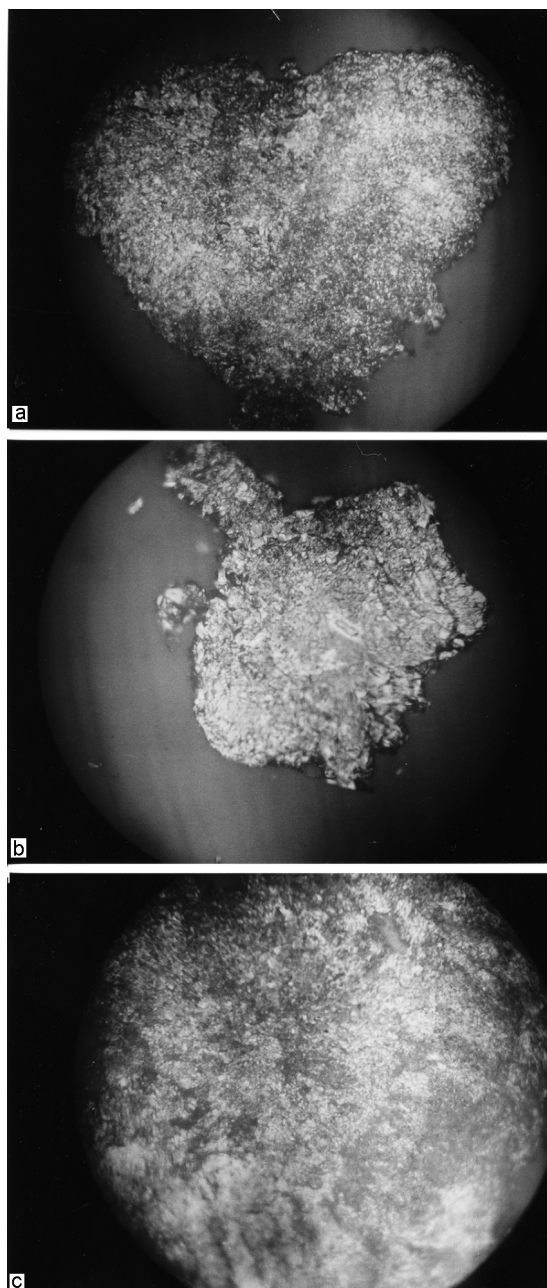


Fig. 4. Particle surface structure of TEG obtained at 1573 K from GICs with SbCl_5 (a); ICl (b); H_2SO_4 (c); optical microscopy, $\times 225$.

fine-grained structure with average grain size of about 1 μm .

Thus, the performed investigations in the dependence of the particle surface structure in GICs prepared by intercalation of different materials and thermoexfoliated at different temperatures have shown that the intercalant nature influences considerably intercalation process. GICs have similar particles structure irrespective of the intercalant nature. However, the thermoex-

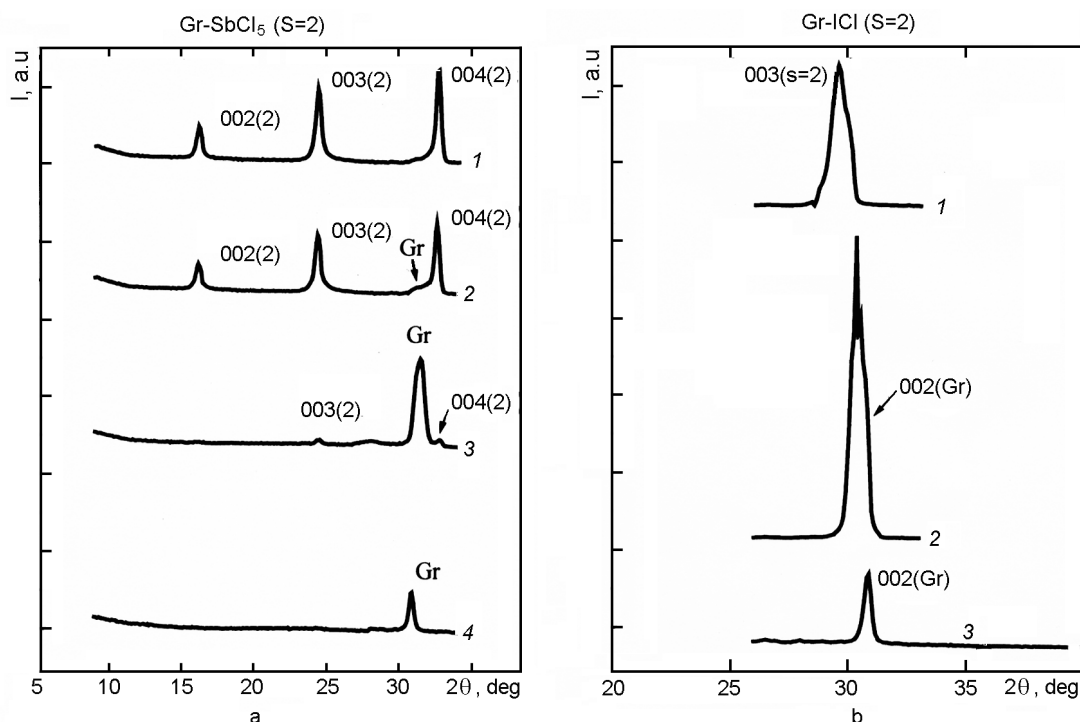


Fig. 5. X-ray diffraction patterns for GIC with: a) SbCl_5 : initial GIC (1) and exfoliated at temperatures (K): 473 (2), 773 (3), 1573 (4) b) ICl : initial GIC (1); exposed at room temperature during 24 hours (2), exfoliated at 1573 K (3).

foliation at minimum temperature (473 K) results in differences of surface structure in particles with various intercalants. For example, at 473 K, the particle surface structure for GIC with stibium chloride and sulphuric acid becomes very inhomogeneous. This is essentially different from what has been observed for GIC with iodine chloride. The thermal shock at this temperature practically does not influence its surface structure and grain sizes are almost the same as in the initial GIC. At the maximum temperature (1573 K) applied for GIC thermoexfoliation in our experiments, the surface of graphite particles in GIC- SbCl_5 and GIC- H_2SO_5 represents a fine-disperse homogeneous structure with grains from 1 to 3 μm in size. At the same time, the particle surface of TEG prepared from GIC with ICl remains slightly inhomogeneous: grain sizes are from 2 to 15 μm , with the grains preserving their rectilinear edges.

The differences in thermoexfoliation process of GICs with different intercalants are confirmed by X-rays analysis. Fig. 5 presents diffraction patterns of initial GICs with SbCl_5 (5a, curve 1) and ICl (5b, curves 1 and 2), and diffraction patterns of TEG obtained from these GICs at different temperatures. As it is seen from curves 1 (Fig.

5), the obtained GICs are monostage compounds for which intensity of lines from intercalant layers exceeds essentially that of lines from graphite layers. The graphite line with intensity comparable to that of the intercalant one is already present in the diffraction curve for a sample of GIC with ICl exposed under room conditions during 24 hours. Consequently, the GIC with ICl is unstable. The intercalant release from this GIC starts at room temperature due to high volatility of ICl . This process has not an "explosive" character and does not result in a change of the particle surface structure. For GIC with SbCl_5 , the low intensity line corresponding to reflections from graphite layers appears only at thermoexfoliation temperature 473 K, that is, the intense intercalant release from the GIC starts at this temperature.

At the thermoexfoliation temperature 773 K, the graphite line intensity for TEG obtained from GIC's with SbCl_5 exceeds substantially the intercalant line intensities. At the thermoexfoliation temperature 1573 K, the diffraction patterns for both TEG samples are identical, that is, the intercalant is absent in both samples. However, the character of intercalant release from the GICs is different. This follows from distinctions in the particle surface

structure of TEG obtained at various temperatures from GICs with different intercalants revealed by optical microscopy.

Thus, investigations of TEG particle surface structure depending on the intercalant nature and thermoexfoliation temperature by means of optical microscopy revealed that variation of intercalants and thermoexfoliation temperatures makes it possible to obtain microstructures with the desired values of such parameters as grain size, uniform-

ity and dispersity of grain structure on the developed TEG surface.

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Мікроструктура поверхні терморозширеного графіту

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Методами оптичної мікроскопії та рентгенівського аналізу досліджено мікроструктуру поверхні частинок терморозширеного графіту, отриманого при різних температурах терморозширення з інтеркальованих сполук графіту з різними інтеркалянтами акцепторного типу. Показано, що згадана мікроструктура істотно залежить від природи речовини-інтеркалянту, температури терморозширення та розмірів часток вихідного графіту. Варіюванням типу інтеркалянту і температури терморозширення можна забезпечити необхідні значення параметрів мікроструктури, таких, як розміри зерен, однорідність і дисперсність зернистої структури розвитої поверхні ТРГ.