SOME ASPECTS OF FORMING OF MECHANICAL CHARACTERISTICS OF CARBON MATERIALS BASED ON EXFOLIATED GRAPHITE

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Abstract

Structural and phase transformations in precursors of the exfoliated graphite (EG) and an effect of various conditions of heating, extension and chemical modification on structure and physical properties of EG-based carbon materials were studied. Some aspects of the forming of the strength characteristics of low-density materials from EG at the principle stages of their preparation are considered. The preliminary results of obtaining of aggregate models of EG-carbon and EG-carbon-carbon fibre are considered.

1. Introduction

Among the dispersed forms of carbon a special place is occupied by exfoliated graphite. EG is derived as a result of structural transformations of graphite intercalation compounds or their hydrolyzed forms in conditions of fast heating. In particular, in the conditions of heating of residual compounds of graphite bisulfate ($C_{24}^{+}HSO_4^{-}\cdot 2.5H_2SO_4$) up to temperatures 800-1100°C the powder with a specific surface area 50-100 m^2/g can be prepared. The ability of EG to be moulded in a continuous material without binder allows one to use it as a basis for a wide row of carbon materials: electrotechnical, antifriction, constructional, thickeners, fillers of polymers and rubbers [1, 2]. The consumer properties of composite materials (CM) based on EG, including physical and mechanical characteristics, are determined by peculiarities of its crystalline and phase structure, as well as by the strength of bonds between the EG particles, originated during the forming of the material [3, 4]. To adjust a structural state of the surface and the volume of EG particles within certain limits is possible by changing conditions of oxidizing and thermal processing of natural graphite. The chemical modification of the surface of EG particles, in particular thermotreatment with organic compounds, allows to strengthen their interparticle interaction, and the quasi-continuous distributed carbon structure in a graphite matrix changes qualitatively the natural and mechanical characteristics of CM. A considerable increase of the strength characteristics of CM is reached by an introduction of a high-modulus component - carbon fibre into the EG-carbon system.

2. Crystalline structure

The source materials - highly oriented pyrolytic graphite of the mark UT and natural graphite of the mark GAC-2 from Zavalyev's deposit — had the perfect crystalline structure close to a structure of monocrystalline graphite. It allows generalize the results of experiments conducted with each of these materials. The intercalation by a sulfuric acid was conducted by the technique [8] in stoichiometric conditions of oxidation. Crystals of graphite bisulfate were washed by distilled water up to pH 6-7 of flushing waters, and treated in high temperature under atmospheric pressure and final temperatures of heating up to 100, 250, 400, and 1000°C. The endurance at the final temperature lasted till the cessation of the loss of the sample weight. Thus, different states of samples were achieved, which were determined in [9] as residual compounds of graphite bisulfate. The process of intercalation of samples of graphite and various states of residual compounds were controlled with a X-ray diffractometer with CoK_α radiation (λ = 0.17902 nm). Electronic-microscopic analysis was carried out on a device Tesla BS-540 with maximum accelerating power of 120 kV and resolution 0.7 nm. Thinning of samples was conducted by the technique [10]. The mode of matching with a quasimonocrystal source allowed to exclude structural features disconnected with processes of introduction and deintercalation from consideration [7].

Similar to [5, 7], the key feature of the X-ray pattern of residual compounds of graphite bisulfate in the basic state (that is after its heat treatment at 100°C) is a significant broadening of graphite diffraction reflections (002) and the presence of additional peaks. After processing the samples at temperatures up to 400°C the intensity of additional diffraction of reflections is redistributed. The width of the line (002) of graphite matrices decreases too. Such change of diffractogram character testifies on restructuring of residual compounds, which, apparently, ends at 1000°C. On the electron diffraction pattern from a plot of a source sample (Fig. 1, *a*) non-periodically located reflexes, not belonging to a graphite matrix, are visible. The analysis of the dark field images, according to [14], testifies that the structure contains thin flap-type selections of phases, distinct from the matrices, which however have a certain crystal structural conformity with it. With allowance for structural state of the initial sample it is possible to characterize the detected derivations as areas, into a certain degree enriched by the intercalant or its residues. Areas of structural discontinuities (the light fields) have an extended and bent form, both with alternation of dark and light bars and without it. It can be stipulated by the fact that the structure of the indicated areas is similar, but differs by a degree of ordering, including a completely disordered state. The structural discontinuities in the form of flap-type selections, apparently, are the reason of elastic curving of a chip, to which testify the rows of brightly expressed reflexes along certain directions curving of a chip, to which testify the rows of brightly expressed reflexes along certain directions on the picture of microdiffraction (Fig. 1, *a*). Besides distinctly expressed structurally ordered phase derivations of two kinds, residues of intercalant are statistically rare. In areas with obvious texture of a matrix the selections of structural discontinuities of the round form with brightly expressed primary orientation are fixed.

The analysis of the change of a diffractogram, and also the pictures of microdiffraction and appropriate dark and light field of the images of samples after processing at 250 and 400°C (Fig. 1, *d-i*) and during heating at 400°C (*in situ*) [15] detected the following regularities in the change of a structure of residual compounds. The heat treatment of samples at 250°C results in such structural transformations as stratification, which deal mainly with most disordered areas of structural discontinuities, and apparently causes, the transformation in areas with a more ordered structure. Alongside with the deintercalation the probability of derivation of phases of intercalant grows too. The heating up to 400°C results in the dynamic development of processes of structural and phase transformations. Obviously, all areas of structural discontinuities detected in a source sample undergo changes too. The phases of the intercalant residues are formed. These samples are characterised by the greatest diversity both in amount of phases of the intercalant residues and in an amount of areas of structural discontinuities.

The increase of the heating temperature up to 1000°C causes deep structural transformations both of disordered phase derivations and phases of the intercalant residues. It is reflected first of all in the change of a diffractogram. The additional reflections in a small angular area disappear, half-line width of a graphite matrix decreases. However heating and endurance of samples even at 1000°C do not result in full deintercalation.

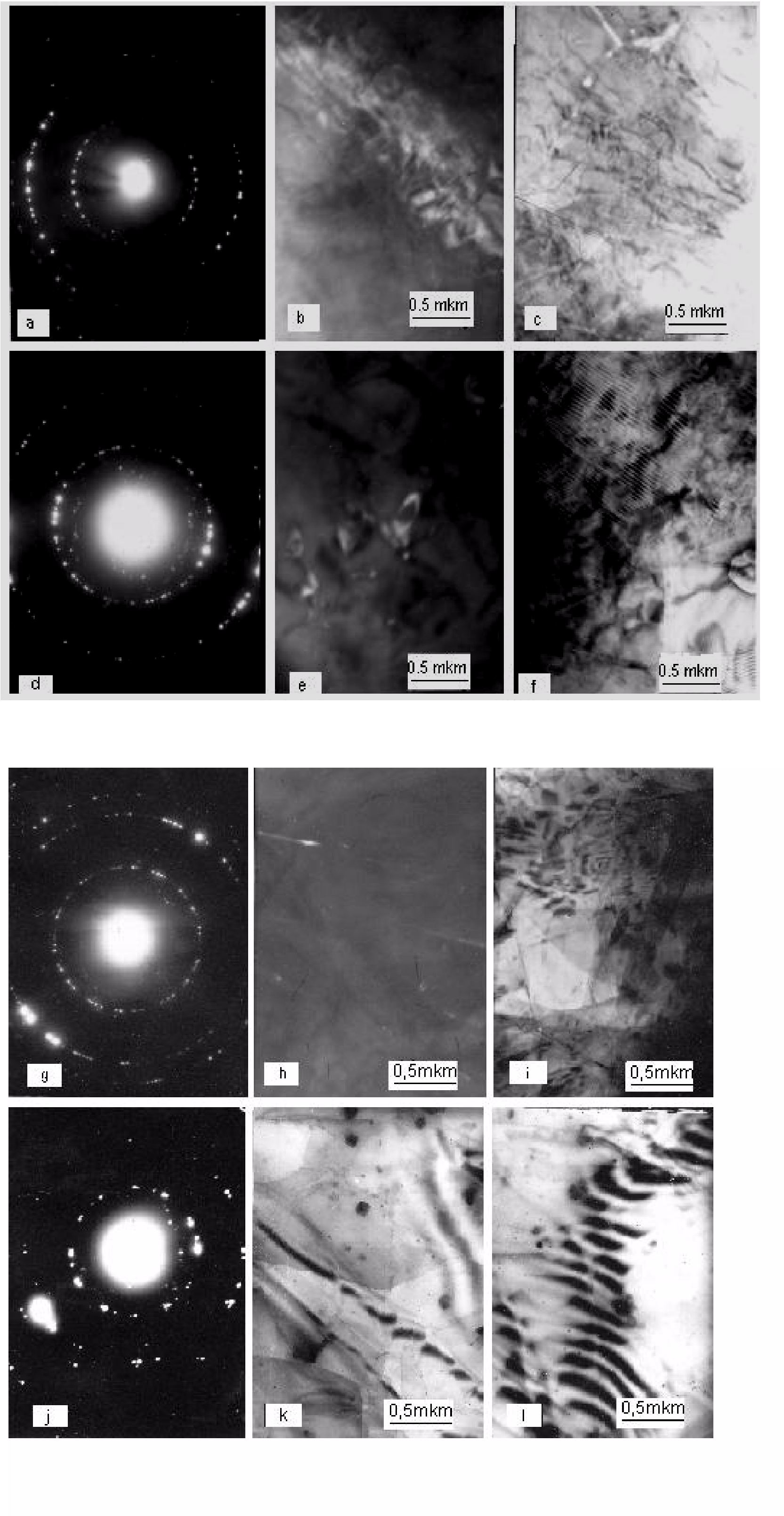


Fig. 1. Electron diffraction patterns and appropriated dark and light fields of the images of specimens of residual compounds of graphite bisulfate, heating under 100 (*a*, *b*, *c*), 250 (*d*, *e*, *f*), 400 (*g*, *h*, *i*), and 1000°C (*j*, *k*, *l*).

As a result of transformations of areas of structural discontinuities at least two phases of the remainders of intercalant of different dispersity are formed. A higher dispersed phase having an obviously expressed texture of a matrix, can be determined as COS from the obtained sets of d/n. The areas with the ordered distribution of the remainders of intercalant are also served.

Thus, the residual compounds of graphite bisulfate (a precursor of exfoliated graphite) at all stages of heat treatment, including high-temperature fast heating with the purpose of obtaining EG, represent structurally a heterogeneous system. It includes chips of graphite, areas of structural discontinuities stipulated by the distribution of the remainders of intercalant with a various degree of ordering, and also at least two phases of the remainders of intercalant of various dispersity. The temperature of processing determines the qualitative structure and quantitative ratio of phase derivations.

3. Structural transition

The structural transformations in samples of residual compounds of graphite bisulfate (GBRC) under volumetric compression were studied by methods of measurement of electroresistance and thermo-emf within the temperature range from 200 to 1200°C according to technique described in [11]. Two variants of structural transitions were considered: "free" extension (the sample was placed on a substrate) and extension to a limited volume (the sample was placed in the form limiting changes of its volume). Overpressure of argon in the high-temperature camera was created by thermocompression [12]. Conductivity and thermo-emf were measured by a four-probe method [13].

The preliminary measurements of temperature of structural transition of GBRC under atmospheric pressure conducted by differential thermal analysis, in accordance with [2], have shown that the temperature range is from 180 to 200°C. The area of maximum rate of weight loss (according to the data of the thermogravimetric analysis) is 200-250°C. The temperature dependencies of electroconductivity (σ) and thermo-emf (S) while "free" expansion were studied under the pressure of 5, 10, and 20 MPa.

While heating the σ value increases to a certain temperature, then it becomes by leaps several tens times less and after that decreases linearly with a constant temperature coefficient (Fig. 2). The thermo-emf decreases from 30-50 to 15-20 μV/K under heating, then it rapidly reduces to the values close to zero or negative ones. The temperatures of the leap of electroconductivity and thermo-emf, that is the temperatures of structural transition, registered when $\sigma(T^{\sigma}_{tr.})$ and $S(T^{S}_{tr.})$ are changed, differ significantly (Fig. 3). The results of their measurement under various pressures are shown in Table 1. Thus, the increasing pressure causes an offset of temperature of structural transition to the area of higher values and the extension of its temperature range (ΔT^{σ}, ΔT^{S}). The dependencies $\sigma(T)$ and $S(T)$ have anomalies at the temperature of about 200°C, that corresponds to the beginning of intensive weight loss of GBRC under normal pressure.

Table 1. Effect of pressure on the temperature of structural transition of residual compounds of graphite bisulfate.

Pressure, MPa	$T^{\sigma}_{tr.}$,°C	$\Delta T^{\sigma}_{tr.}$,°C	$T^{s}_{tr.}$,°C	$\Delta T^{s}_{tr.}$,°C
5	290	65	500	65
10	330	100	555	100
20	345	110	575	110

Note: ΔT - temperature range of structural transition

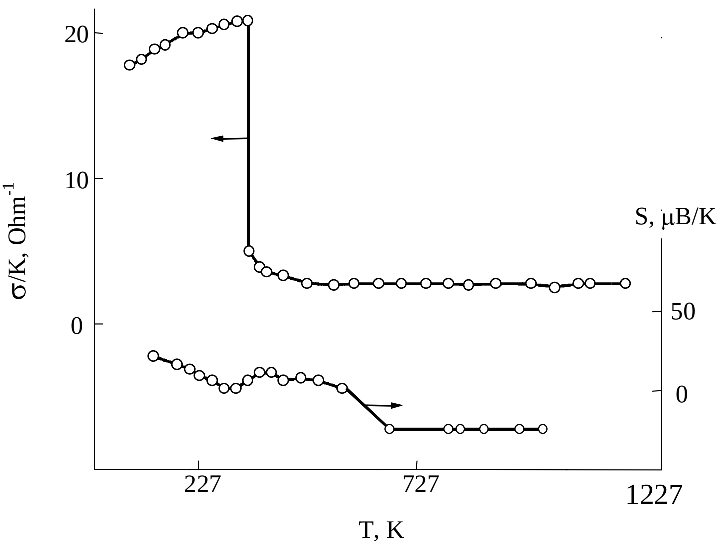


Fig. 2. Temperature dependencies of electroconductivity (σ) and thermo-emf (S) of residual compounds of graphite bisulfate while "free" expansion under pressure of 10 MPa.

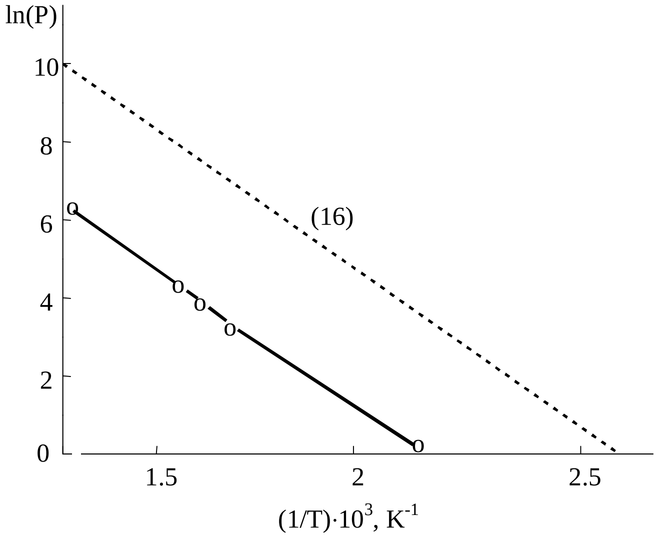


Fig. 3. Dependence of the temperature of the structural transition of residual compounds of graphite bisulfate registered while the leap of electroconductivity under pressure.

The dependence of structural transition temperature on pressure (Fig. 3) registered while conductivity leap has linear character in accord with [16]. The ΔH value, defined according to an inclination of straight line, is 70±2 kJ/mol that almost coincides with ΔH value of graphite-bromine intercalation compound.

In this case the affinity of the ΔH values may testify that the activation process energy of the thermal expansion is determined by properties of a graphite matrix instead of individual intercalant characteristics.

The structural transition of GBRC while expansion in a limited volume was studied under the pressure of 10 MPa. The monotonous change of σ(T) and S(T) is observed when temperature increasing up to 1200°C (Fig. 4). Electroconductivity increases at the temperatures up to 700°C and then slightly decreases within the whole temperature range. When cooling the σ(T) dependence is similar in general to the dependence under heating, however the electroconductivity has smaller values and the inflection point corresponds to 900°C.

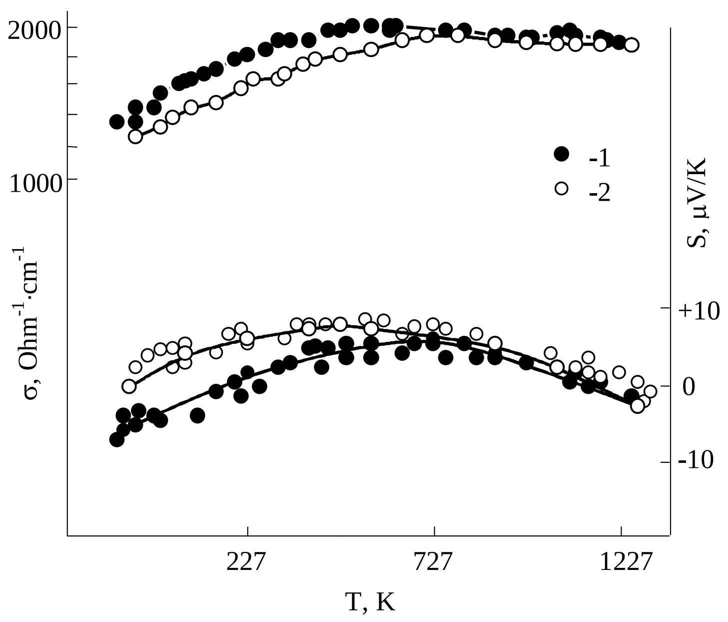


Fig. 4. Temperature dependencies of electroconductivity (σ) and thermo-emf (S) of graphite bisulfate residual compounds while expansion in limited volume under pressure of 10 MPa: *1* - heating; *2* - cooling.

Thus, the leap of electronic properties, which accompanies the structural transition of graphite bisulfate residual compounds under heating, is stipulated by the change of specimen geometry. When the sizes of specimen are fixed by extension to a limited volume the properties are monotonously changed. The hysteresis of temperature dependencies σ(T) and S(T), obviously, testifies to the quasi-continuous "phase" transformations of microareas of the heterogeneous system (residual compounds of graphite bisulfate) almost in the whole studied range of temperatures. The decrease of conductivity and thermo-emf transition to the area of positive values testify that such transformations (intercalant loss, formation of new phases etc.) result in a decrease of total concentration of current charges and a growth of relative concentration of positive charges.

4. Exfoliated graphite moulding

The pressing is the main method of materials moulding from EG. The method of direct pressing (one and double-side) in a mould or rolling of the EG powder is most widespread. The characteristics of EG powder as a moulding material significantly differ from that of powders of other materials. Its particles have a complex structure, advanced surface area, specific “worm-shaped” form, high volatility and propensity to self-compacting.

The pressing of graphite without using a binder is accompanied by formation of bonds of two types: Van-der-Vaals bonds - between graphite planes, and chemical bonds - between active sites, which are available on graphite planes and on the sides of crystallites [18]. The process of EG pressing without using a binder is stipulated by the availability of thermal destruction products of graphite intercalation compounds (GIC) on the surface of EG particles [17]. These products play a plasticizer role, providing sliding of EG layers and its joining during pressing. At the same time the concentration of paramagnetic centres in a briquette is reduced approximately by five orders while EG moulding [18]. It is explained by the fact that a lot of carbon radicals with free bond are formed as a result of thermal splitting of graphite intercalation compounds, which recombine and, apparently, influence the strength of the final product while moulding.

The exfoliated graphite moulding has several stages, and morphology and presence of defects of EG particles structure render essential influence on the kinetics of pressing process, i.e. they change dependence of pressed material density (ρ) on pressure P [20]. It is possible to obtain materials with density from 0.1 to 2.2 g/cm^3 by a method of direct pressing.

Other perspective method is the thermal pressing of exfoliated graphite in the closed gas-permeable mould [21]. In this case at first graphite intercalation compounds should be obtained by any known method, then it should be placed in the closed gas-permeable mould and heated up. While heating the GIC powder swells out and renders pressure on the EG powder formed. As the walls of the mould limit the expansion of EG it is packed. The processes of the expansion and packing occur practically simultaneously. By this method it is possible to obtain highly porous graphite materials with apparent density from 0.05 to 0.40 g/cm^3. In order to obtain material with density of more than 0.2 g/cm^3, it is necessary to pack primarily the GIC powder in a mould. The achievement of density of more than 0.4 g/cm^3 is impeded by necessity to apply heat and corrosion resistant moulds and by tendency of swelled graphite to penetrate through the gas went holes.

Pressings of specimens by a method of unilateral moulding with record of the pressing diagram as well as their compression test were conducted on 2167-P50 test unit [22]. To exclude influence of the dynamic factor on process of structural formation, pressing was executed with continuous loading and off-loading and at low speed (10 mm/min). According to the EG pressing diagrams (Fig. 5) the process has complex character; at the same time the elastic after-effect in a material after removal of pressure (curve 2) plays a significant role in creation of a pressed material structure. The dependence of pressed material density on pressure while pressing (curve 1) considerably differs from similar dependence obtained after removal of load and ejecting of compact according to the results of measurement of final density (curve 4). It is explained by elastic dimensional change of pressed materials after removal of pressure. The elastic after-effect is a result of elastic deformation of the mould and clearing of elastic forces in a powder. The crystallographic factor of an anisotropy of particles influences significantly the elastic extension [18]. During EG pressing the stresses in the mould and punches are rather small therefore their elastic deformation may be neglected. At the same the density of pressed materials approaches (Fig. 5, curve 1) to X-ray density of graphite equal to 2.26 g/cm^3 while pressing of high density materials from exfoliated graphite [23]. Apparently, in this case the forces of elastic interaction between graphite planes influence considerably the elastic after-effect. The products of thermal destruction of graphite bisulfate located on planes of EG particles, which play a role of a binder in the process of pressing, become a peculiar damper between layers of graphite. As a result of all this the density of the material is changed by 20-30 % after removal of pressing pressure.

The coefficient of anisotropy K_a of pressed exfoliated graphite was determined as the ratio of intensity of X-ray reflections from the (002) plane measured in parallel and perpendicularly to the direction of application of pressing pressure. The character of change of a given factor depending on pressed material density (Fig. 6) corresponds to the character $\rho = f(P)$ shown on Fig. 5. The pressing process has three stages: I - packing and partial destruction of particles (up to the density of 0.5 g/cm^3); II - mutual moving, splitting, destruction of particles and their fragments (up to the density of 1.3 g/cm^3); III - plastic deformation of fragments of particles in the whole volume [18, 20, 24].

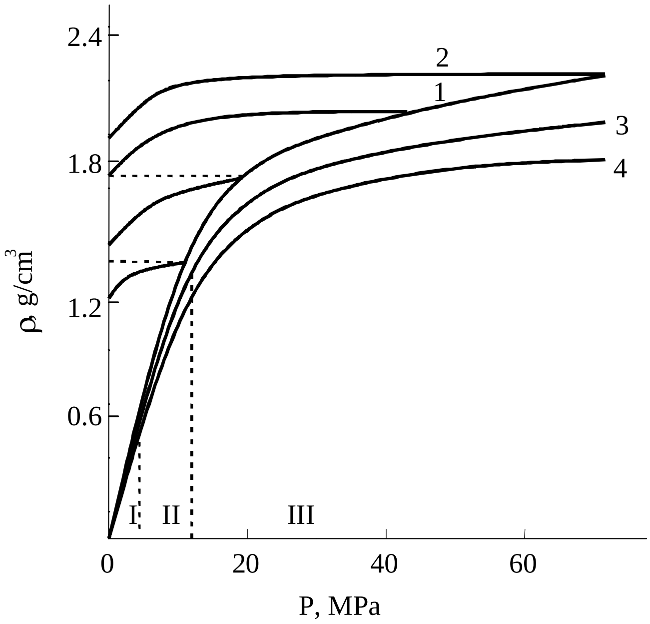


Fig. 5. Dependence of apparent density of pressed exfoliated graphite on pressing pressure while pressing (*1*), unloading (*2*), after removal of pressure (*3*) and after specimen pressing off (*4*).

At the stage I, described by linear change of density depending on pressure of pressing, Ka increases that is apparently connected with deformation of contact surfaces of EG particles and partial orientation of their basic planes perpendicularly to axes of pressing. At the stage II the dependency ρ=f(P) has curvilinear character, and coefficient of anisotropy practically is not changed. It can be explained by crushing and mutual moving of already oriented particles. As a result of such process the increase of anisotropy is stopped, the porosity is decreased and the boundaries of contacts of initial particles are blurred. At the end of this stage the structure of a surface layer acquires homogeneous small fragment character, and the visible boundaries between particles disappear.

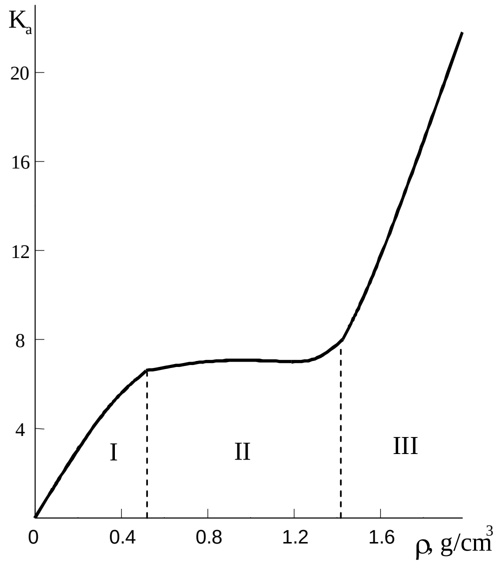


Fig. 6. Change of coefficient of anisotropy depending on apparent density of the pressed material.

The intensive increase of the coefficient of anisotropy at the stage III (Fig. 6) is stipulated by formation of a laminated structure with primary orientation of graphite planes perpendicularly to the direction of effect of the external load. At this stage the reconstruction of macrolayers of materials, their linking and mutual penetration take place that may cause formation of similar to lens microdelamination owing to elastic after-effect after removal of pressure.

5. Mechanical characteristics

According to the sections 3-4 the exfoliated graphite is a complex heterogeneous system, structural state of which is determined by conditions of EG synthesis and defines physical and mechanical properties of obtained materials. Some aspects of the formation of strength characteristics of low-density materials from EG are presented below at main stages of their production: preliminary stage, stage of intercalation and heat treatment and stage of moulding.

The specimens 20 mm in height and diameter made of EG obtained from natural graphite of Zavalyev's deposit (Ukraine) were used for the researches. A powder of natural graphite of GAK-2 mark was processed by the concentrated sulfuric acid in the presence of an oxidizer - ammonium peroxosulfate. After washing and drying the obtained product – compound of intercalant graphite – was subjected to heat treatment at various temperatures, therefore the exfoliated graphite with various bulk densities was obtained. The specimens were produced by the method of unilateral moulding of EG powder in a cylindrical mould as well as by the method of thermochemical pressing of GIC powder in the closed cylindrical gas-permeable steel mould at the temperature of 500°C.

The compression tests - both by method of continuous deformation of a specimen and method of repeated deformation after unload with further increase of load – were conducted until full destruction (for materials with high density) or achievement of 20 % deformation of a specimen. The speed of deformation was 2 mm/min. The loading was executed along the direction of applied pressure while specimens moulding. The value of compression stress at 10% deformation (σ_{10}) was used to compare the characteristics of resistance to compression.

5.1. Influence of granulometric composition. Granulometric composition of the natural flake graphite and the graphite intercalation compounds obtained under standard conditions of compound oxidation are shown in Table 2.

Table 2. Granulometric composition and fraction parameters of natural graphite of GAK-2 mark and GIC powder obtained on its basis.*

Fraction, μm	Mass content, %		Bulk density, g/dm^3			Loss of GIC weight while heat treatment, %
	GAK-2	GIC	GAK-2	GIC	EG	
<100	27	9	446	189	22.5	15
100-200	57	51	469	214	7.0	20
>200	16	40	530	193	4.0	26
Total	100	100	476	200	6.0	22

*- $m_{ox.}/m_{gr.} = 0.7$; the concentration of H_2SO_4 is 93%; the temperature of heat treatment is 800°C.

More than half of particles have dimensions lying within the limits of 100-200 microns. Intercalation results in growth of average dimensions of particles. Bulk density of graphite decreases more than twice. A further heat treatment of each separate GIC fraction has shown that the bulk density of obtained EG decreases when dimensions of particles increase. Larger particles have bigger loss of weight that is higher intercalant content. The intercalation of separate fractions of initial graphite particles in identical conditions and their consequent heat treatment have shown, according to [25], the similar tendency of increase of intercalant content and decrease of bulk density when particles dimensions increase (Table 3). The strength of the pressed EG specimens, obtained from different fractions, also increases when particles dimensions of initial graphite increase in the studied area.

Table 3. Dependence of loss of GIC weight, EG bulk density and strength of specimens on initial graphite dispersity.*

Initial graphite fraction, mkm	Loss of weight of GIC, %	EG bulk density, g/dm^3	Specimen density, g/cm^3	σ_{10}, MPa
> 100	13	26	0.6	1.1
100-200	19	6.5	0.6	1.35
>200	28	3	0.6	1.55

∗ $m_{ox.}/m_{gr.}$=0.7; concentration of H_2SO_4 is 93.64%; $T_{h.tr.}$=800°C

5.2. Influence of acid concentration and heat treatment. Fig. 7 shows the results of researches of dependencies of EG bulk density on conditions of chemical and consequent thermal treatment of initial graphite. When one of process parameters (amount of an oxidizer or concentration of sulfuric acid under intercalation, temperature of heat treatment) was changed, other parameters remained constant and corresponded to standard conditions determined in [26]. As Fig. 7 shows, EG bulk density is monotonously reduced when the amount of oxidizer or concentration of acid or temperature of GIC treatment are increased. The value of EG bulk density is the most sensitive to concentration of sulfuric acid: decrease of concentration by 10% results in 10-times increase of bulk density. The increase of the amount of an oxidizer in the process of intercalation or temperature of heat treatment in the studied interval results in almost identical decrease of bulk density. More intensively the bulk density is changed when the amount of an oxidizer increase to approximately 0.7 kg of an oxidizer per 1 kg of graphite. The further increasing of the ratio $m_{ox.}/m_{gr.}$ changes insignificantly the value of bulk density. In Tables 4, 5 the results of compression tests of specimens made of EG, obtained with different concentration of sulfuric acid (Table 4) and temperatures of heat treatment (Table 5) are shown. When the concentration of sulfuric acid increases the strength of specimens monotonously increases. In the dependence of strength on heat treatment temperature the maximum is observed at the temperature of about 600°C. It would be expected that EG specimens that have equal density obtained of EG powder with equal bulk density should have identical strength.

Table 4. Dependence of compression stress of specimens (σ_{10}) on concentration of sulfuric acid ($m_{ox.}/m_{gr.}$=0.7; T_{htr}=1000°C).∗

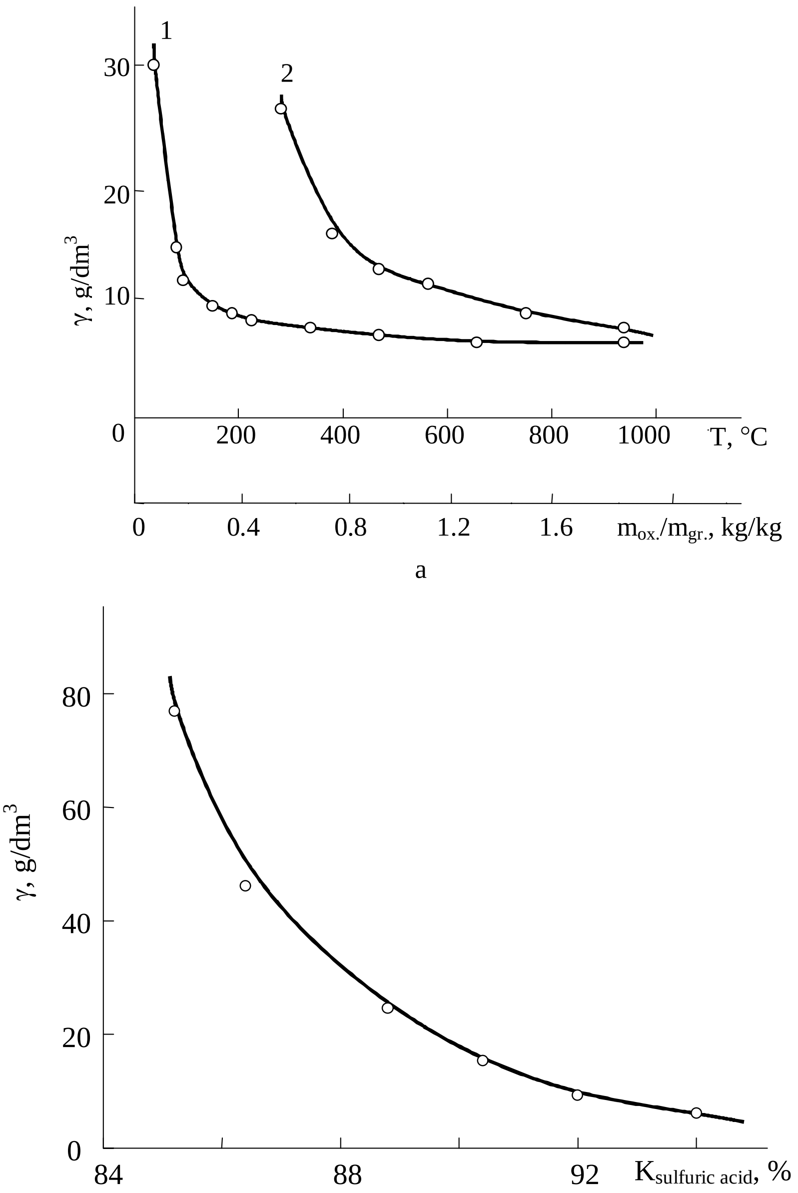
Concentration of H_2SO_4, %	85.3	86.4	88.7	93.64
σ_{10}, MPa	1.15	1.7	2.1	2.9

∗Specimens density – 1.0g/cm^3

Table 5. Dependence of compression stress of specimens (σ_{10}) on temperature of GIC heat treatment ($m_{ox.}/m_{gr.}$= 0.7; concentration of H_2SO_4 is 93%)∗.

$T_{htr.}$,°C	300	400	600	800	1000
σ_{10}, MPa	1.8	2.76	3.14	3.04	2.9

∗ Specimens density – 1.0 g/cm^3



a

b

Fig. 7. Dependencies of EG bulk density on: (*a*) *1* – oxidizer/graphite ratio (concentration H_2SO_4 is 93%, $T_{h,tr}$=850°C); *2* – temperature of heat treatment of GIC (concentration H_2SO_4 is 93%, $m_{ox.}/m_{gr.}$=0.7); (*b*) H_2SO_4 concentration ($m_{ox.}/m_{gr.}$=0.7, $T_{h,tr}$=1000°C).

However, the analysis of results of strength tests has shown (Table 6) that as well as in case of different bulk density at various temperatures (Table 5) there is a certain maximum of strength of specimens made of EG, which was obtained at 600°C.

Table 6. Dependence of compression stress of specimens (σ_{10}) on heat treatment temperature while identical EG bulk density (Y=11 g/dm^3; specimens density 1.0 g/cm^3).

T,°C	400	600	800
σ_{10}, МПа	2.80	3.15	2.85

*($m_{ox.}/m_{gr.}$= 0.7; concentration of H_2SO_4 is 93%).

Such effect, obviously, is stipulated by features of thermal decomposition of compounds of graphite intercalated with sulfuric acid. The temperature dependence of rate of GIC-H_2SO_4 weight loss has two maximums: first at the temperature of about 250°C and second - in the range from 600 to 850°C [27]. Therefore on a surface of EG particles obtained at 400°C there is a considerable amount of products of graphite bisulfate decomposition (sulfate sulfur and sulfur chemically bound with carbon of graphite) [28]. At temperatures of about 800°C and higher the amount of residual compounds of sulfur decreases considerably (second peak of thermogravimetric curve, [27]), that, apparently, worsens the pressing ability of EG and, accordingly, decreases the strength of specimens. Furthermore, EG obtained at 600°C is characterised by high degree of discontinuity of particles structure [20] which requires more significant costs of energy for its modification while deformation. Therefore specimens of low density (up to 1.3 g/cm^3) made of EG obtained at 600°C, have higher resistance to deformation [29].

Fig. 8 shows general dependencies of compression strength on bulk density of EG, obtained under various conditions of intercalation and heat treatment. For the analysis the following specimens made of exfoliated graphite were used: specimens obtained under standard intercalation conditions of oxidation and at variable temperatures of heat treatment; under condition of variable sulfuric acid concentration and constant content of an oxidizer and at constant temperature; obtained under standard intercalation conditions at step rise of heat treatment temperature from 200 to 600°C with interval of 30 minutes after each 100°C as well as specimens obtained by crushing particles of EG, produced under standard conditions, in distilled water. As Fig. 8 demonstrates, the most significant decrease of specimens strength is observed when the bulk density increases at the account of decrease of temperature of GIC heat treatment (curve 1) and decrease of concentration of sulfuric acid in the process of graphite intercalation (curve 2). Despite of considerable increase of EG bulk density (5-8 times) at the account of gradual GIC heating, obtained under standard conditions of intercalation (curve 3), or at the account of liquid-phase crushing of EG (curve 4), significant decrease of compression strength is not observed. Therefore, the strength of pressed exfoliated graphite depends not only on the degree of structure loosening (value of a specific surface area or bulk density value) but also on a physical and chemical state of the surface of EG particles that is determined as by properties of initial graphite so by conditions of chemical and consequent thermal treatments of graphite.

5.3. Influence of graphite over oxidation on the mechanical characteristics. The graphite intercalation with sulfuric acid in the presence of strong oxidizers ($KMnO_4$, $K_2Cr_2O_7$, $(NH_4)_2S_2O_8$, SO_3 etc.) is rather complex process, which determines to the large extend properties of obtained materials. The authors of works [30, 31] have shown that the GIC phase composition depends on oxidising mixture redox-potential, which in its turn depends on concentration of a sulfuric acid and amount of an oxidizer in mixture. Authors affirm that the bulk density of obtained EG is the function of GIC phase composition and practically does not depend on the nature of an oxidizer. The authors of work [32] assert that while chemical oxidation of graphite in the presence of strong oxidizers GIC intercalated layer composition includes peroxodisulfuric HS_2O_8-anions.

The similar GIC hydrolytic deintercalation may cause formation of surface layer of graphite oxide in amount up to 6-10 wt. % [33] and increase the strength of final materials.

In this work the influence of concentration of an oxidizer in the system "graphite - $(NH_4)_2S_2O_8$ - H_2SO_4" and sulfuric acid concentration on the strength of pressed EG (with conditions being equal) was studied. For tensile tests the specimens like strips of variable cross-section 100 mm in length, minimum width of 5 mm and thickness of 0.3 mm were used. Specimens were moulded by a method of unilateral pressing of EG powder obtained at the temperature of 800°C. The density of specimens was 0.9 g/sm^3. For compression tests specimens of 20 mm diameter and height were produced by a method of thermochemical moulding at the temperature of 500°C in the closed gas-permeable mould; density of specimens was 0.07 g/sm^3. Fig. 9 shows dependency of EG bulk density and specimens tensile strength on amount of an oxidizer per unit of graphite mass with constant content of sulfuric acid in reactionary mixture.

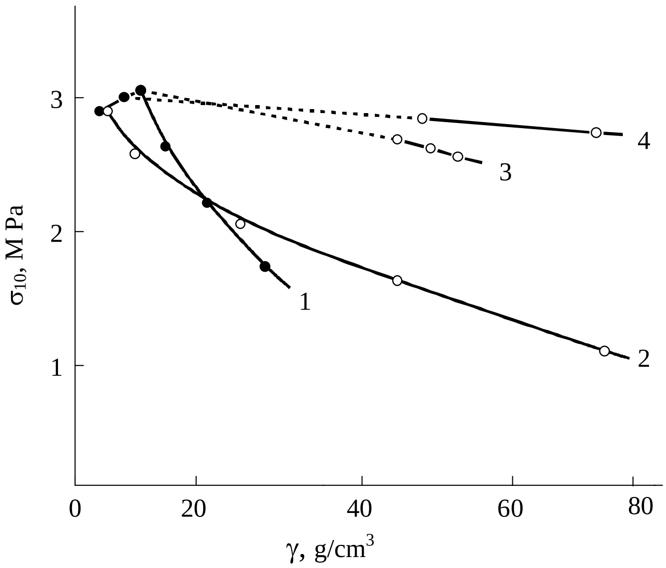


Fig. 8. Dependence of compression strength (σ_{10}) of specimens on change of EG bulk density (Y) while:
1 - change of temperature of GIC treatment (concentration of H_2SO_4 is 93%, m_{ox}./m_{gr}.=0.7); *2* - change of concentration of a sulfuric acid under intercalation ($m_{ox.}$/$m_{gr.}$=0.7; HTT=1000°C); *3* - step GIC heating from 200 to 600°C ($m_{ox.}$/m_{gr}=0.7; concentration of H_2SO_4 is 93%); *4* - liquid-phase crushing of EG particles ($m_{ox.}$/m_{gr}.=0.7; concentration of H_2SO_4 is 93%, HTT=800°C). The density of the specimens is ρ=1g/cm^3.

The sharp decrease of bulk density, when the amount of an oxidizer increases, is accompanied by considerable increase of tensile strength, which is obviously caused by increase of EG specific surface area, and accordingly by increase of amount of active sites of its surface. In the section of bulk density stabilisation the further strength growth is apparently caused by increase of amount of free radicals of EG surface owing to introduction of peroxodisulfuric acid anions in graphite and its further decomposition [33]. The further increase of oxidizer amount results in a sharp strength decrease owing to as GIC particles sticking together in drying process so EG particles in process of heat treatment. In this case active sites recombine that results in EG compactibility deterioration and, accordingly, in material strength decreasing. The similar picture is observed for dependencies of thermochemical moulded GIC compression strength on amount of oxidizer in reactionary mixture (Figs. 10, 11).

The graphite crystals swell much more in the intercalation process than while intercalation under stoichiometric conditions. This process is accompanied by significant decrease of bulk density of dried GIC (Fig. 10). The swelling of graphite crystals is apparently caused by not only interlayer intercalant introduction, but also by intensive extraction of oxygen between carbon layers owing to partial decomposition of introduced HS_2O_8-peroxosulfate ions. When graphite-acid mass ratio is equal to 2 (Fig. 10, curve 1) and at certain amount of an oxidizer the GIC bulk density begins to increase owing to the particles sticking together in drying process. The particles sticking together is apparently caused by formation under these conditions of considerable amount of graphite oxide on the surface of particles in GIC hydrolysis process [33]. The character of change of compression strength of specimens (Fig. 11) and the reasons of this change are similar to ones described above for tensile strength. In this case with greater amount of sulfuric acid in reaction mixture the specimens strength becomes slightly higher (Fig. 11, curve 2) than the similar one with smaller amount of acid (Fig. 11, curve 1).

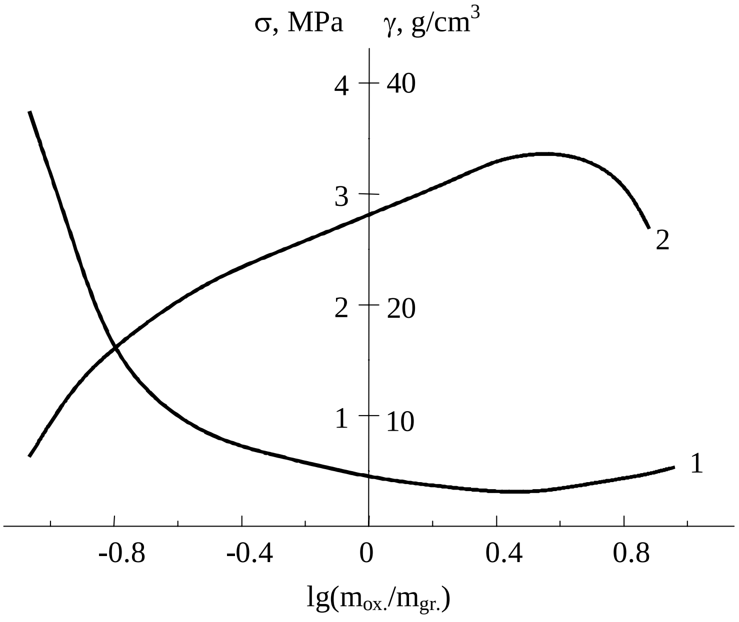


Fig. 9. Dependency of EG bulk density (Y) (*1*) and specimens tensile strength (σ_t) (*2*) on oxidizer-graphite mass ratio ($\rho_{sp.}$=0.9 g/cm^3, $m_{ac.}/m_{gr}$=2).

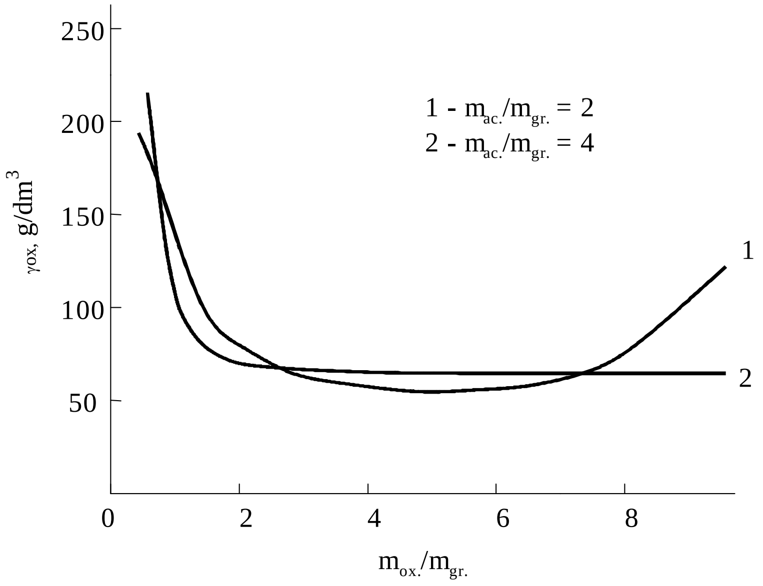


Fig. 10. Dependency of GIC bulk density on the oxidizer-graphite mass ratio.

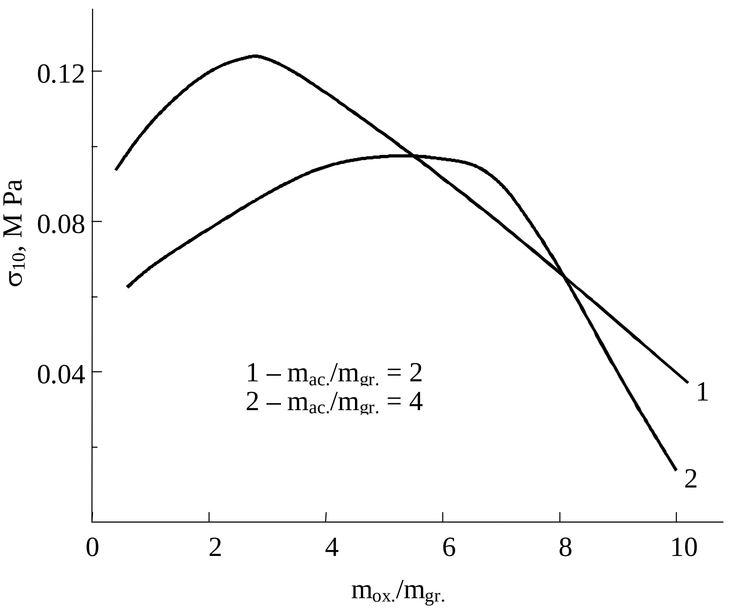


Fig. 11. Dependency of specimens compression strength (σ_{10}) on the oxidizer-graphite mass ratio.

5.4. Influence of material density. The experimental researches have shown that a loading mode (continuous or repeatedly-static with increasing load) does not influence on value of stress while given deformation. Fig. 12 shows the data of strength of single-axis compression of specimens with different density made of EG powders obtained at various temperatures of the GIC heat treatment. As it is shown, the results of tests are well approximated by piece-wise linear dependence, which has some characteristic section. Temperature of the GIC heat treatment changes the compression resistance of specimens. The analysis of the deformation diagrams has allowed to determine the reasons of this change (Fig. 13). So, when specimens have low density, irrespective of the EG powders obtaining temperature, the diagram of specimens deformation is similar to the deformation diagram of cellular polymeric materials with a small initial linear section stipulated by packing of weak structure elements, section of elastic deformation of "frame work" of structure and section of plastic deformation (Fig. 13, *a*).

The visual-optical experiments have shown [20] that it was stipulated by the above-mentioned description. The axis of a hysteresis loop is placed inside it that testifies to energy dissipation in material due to significant structure reconstruction under deformation. In the density range approximately from 800 to 1300 kg/m^3 the structure of the material has finely grained character, when the EG particles are already destroyed [24]. In the process of repeatedly-static compression of such structure the line of repeated loading begins to acquire positive curvature similar to the shape of the off-loading curve and the hysteresis loop axis begins to exceed its limits (Fig. 13, *b*). This testifies that most part of energy dissipating in the material is used for deformation of structure formed during moulding, and to a less degree is stipulated by the structure reconstruction. Mostly laminated structure with interlayer defects of continuity forms in EG specimens with density of more than 1300 kg/m^3 according to the visual-optical microscopy. While continuous or repeatedly static single-axis compression of such structure the deformation curve has S-shaped form. The hysteresis loop axis while repeatedly-static compression considerably exceeds the limits of a hysteresis loop, and the curve of repeated deformation is similar to the shape of the curve of the initial section (Fig. 13, *c*). Such character of deformation of specimens is apparently stipulated by effect connected with the presence of the lens-visible pores and microseparations in laminated structure. While deformation of these structures, their elastic resistance similar to lens-visible springs and consequent manifestation of elastic loss of stability are realized; in this case the initial section of deformation curve has positive curvature. As a result of collapse of pores and microseparations the section of the consequent increase of stress and compression deformation has linear character before the moment of a plastic deformation inside the material layers. Collapse of microseparations does not provide their disappearance, therefore the initial section of the compression diagram after relief and repeated application of load is non-linear till specimen destruction. The analysis of the deformation diagrams has shown that irrespective of the EG obtaining temperature the inclination corner of hysteresis loop axis differs from the inclination corner of the initial section tangent line α_o, which reflects an initial rigidity of a structure “frame” (Fig. 13). Subsequently the "frame " rigidity can be estimated by tangent of the inclination corner of the hysteresis loop axis tgα, changing character of which reflects ability of a material to cyclic hardening or loss of strength during the process of deformation. It has been determined that during process of repeatedly-static compression the tangent of inclination corner of hysteresis loop axis ambiguously depends on exfoliated graphite obtaining temperature (Fig. 14). So, tgα of hysteresis loop axis of low-density specimens has a downward tendency when deformation increases (line *I*), and its value does not depend on EG obtaining temperature. The material is cyclically losing strength up to density approximately equal to 800 kg/m^3. For the specimens with density of 800-1300 kg/m^3 tgα is changed insignificantly when deformation increases (lines 2-5), and in this case materials are cyclically stable, but they have different rigidity of structure “frame" depending on EG obtaining temperature. While the density of more than 1300 kg/m^3 tgα increases when deformation increases (lines 6-9), in this case materials are cyclically loss strength, and specimens of exfoliated graphite obtained at 600°C have higher ability to cyclic hardening.

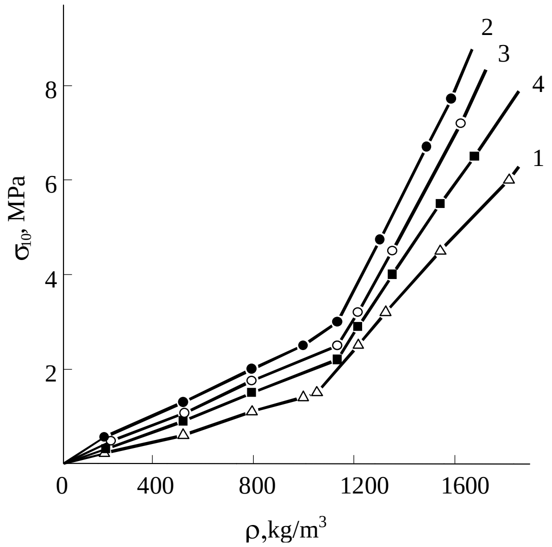
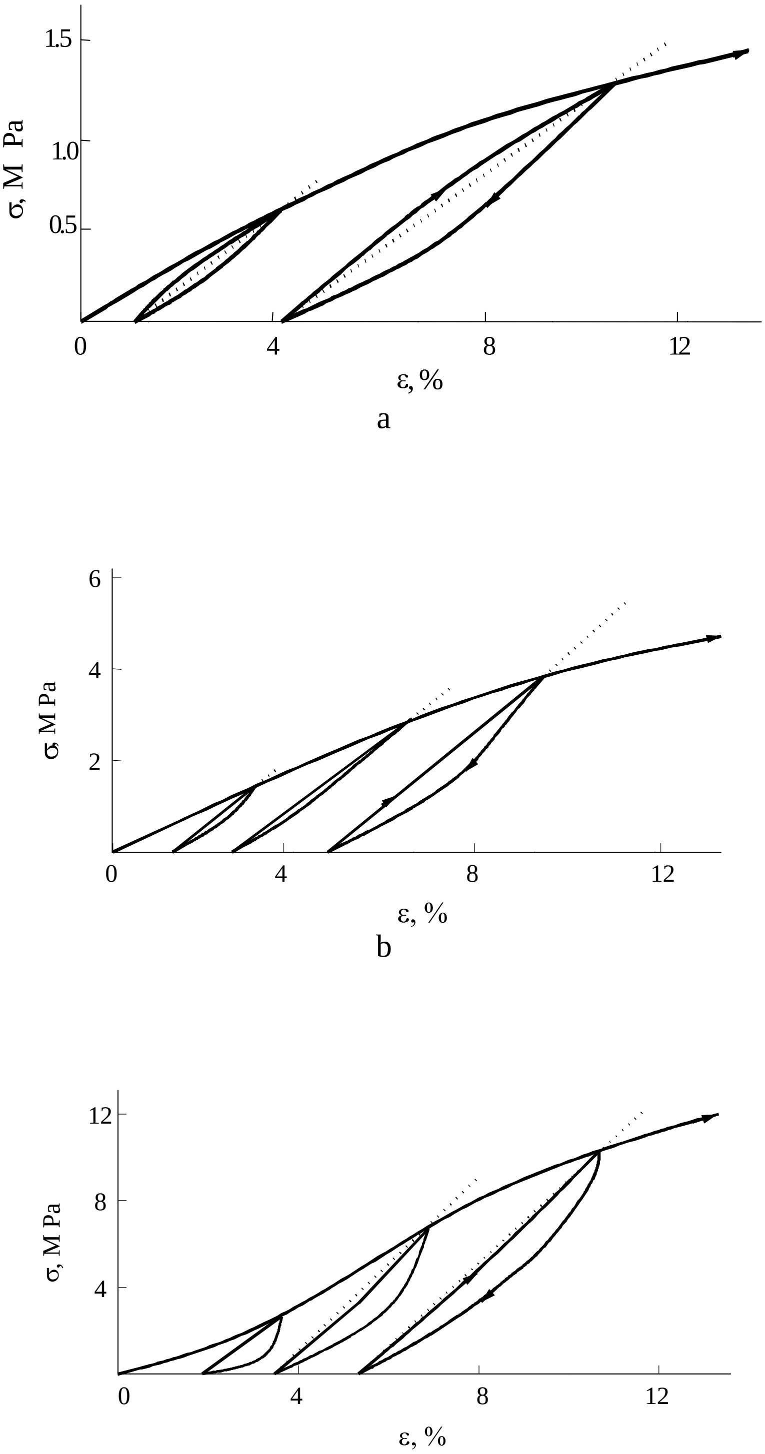


Fig. 12. Dependences of compression strength (σ_{10}) on the bulk density of the EG specimens obtained at treatment temperature: *1* – 400, *2* – 600, *3* – 800, and *4* - 1000°C.



a

b

c

Fig. 13. Diagrams of repeatedly-static single-axis compression deformation of EG specimens with density: *a* – 500; *b* – 1300; and *c* – 1700 kg/m^3.

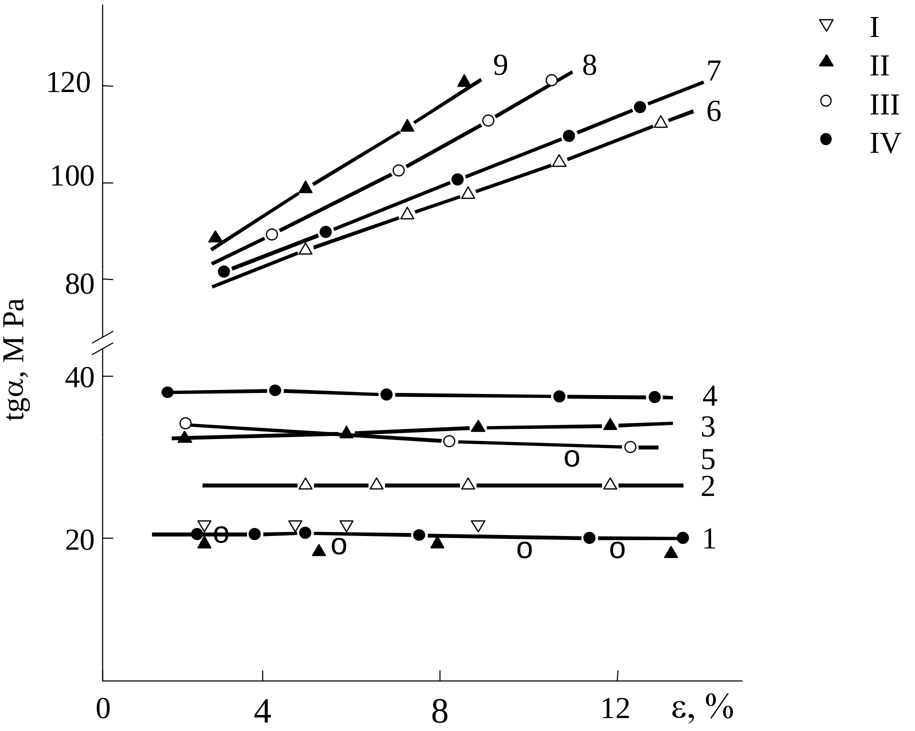


Fig. 14. Dependence of tangent of inclination corner of hysteresis loop axis on general compression deformation of specimens with density of 500 (*1*), 900 (*2-4*), and 1700 kg/m^3 (*5-9*) of EG obtained at the temperatures of 400 (*I*), 600 (*II*), 800 (*III*), and 1000°C (*IV*).

5.5. Influence of moulding method. The comparative X-ray phase analysis of natural graphite and EG specimens obtained by the free expansion and by expansion in limited volume of graphite intercalation compounds has been conducted. The general shape of diffractograms has appeared to be similar. However, noticeable difference was observed in profiles of reflections (002), half-width of which was 18.5, 28.0 and 21.0 minutes accordingly. Physical broadening of X-ray reflection is determined, as it is known, by limits of coherent dispersion areas and value of microstresses, that is characteristic for the structural state of a crystal (degree of disordering). Thus, the indicated values of half-width of reflections (002) testify that the expansion in limited volume results in considerably smaller disordering of EG structure in comparison with a material obtained by free expansion. The single-axis compression tests were conducted. Specimens for mechanical tests have been produced by two methods: unilateral pressing of EG powder in a cylindrical mould and expansion in limited volume of residual compounds of graphite bisulfate (thermochemical moulding). Diameter and height of compression specimens were 20 mm. The tests were conducted using 2167-P50 test unit under condition of repeated-static loading with an increasing load and record of the deformation diagram. The vector of loading was directed in parallel to axis of pressing and deformation speed was 2 mm/min.

The method of repeated-static compression was used to study how the indicated differences in a structural state influence mechanical properties of materials. To exclude the influence of specimens macrostructure features, in particular their anisotropy, specimens had identical low density (~0.1 g/cm^3). Having such density they are practically isotropic. The analysis of dependencies σ_c on ε (Fig. 15) shows that the character of deformation of specimens, obtained by the free expansion of graphite bisulfate residual compounds, has mainly elastic character.

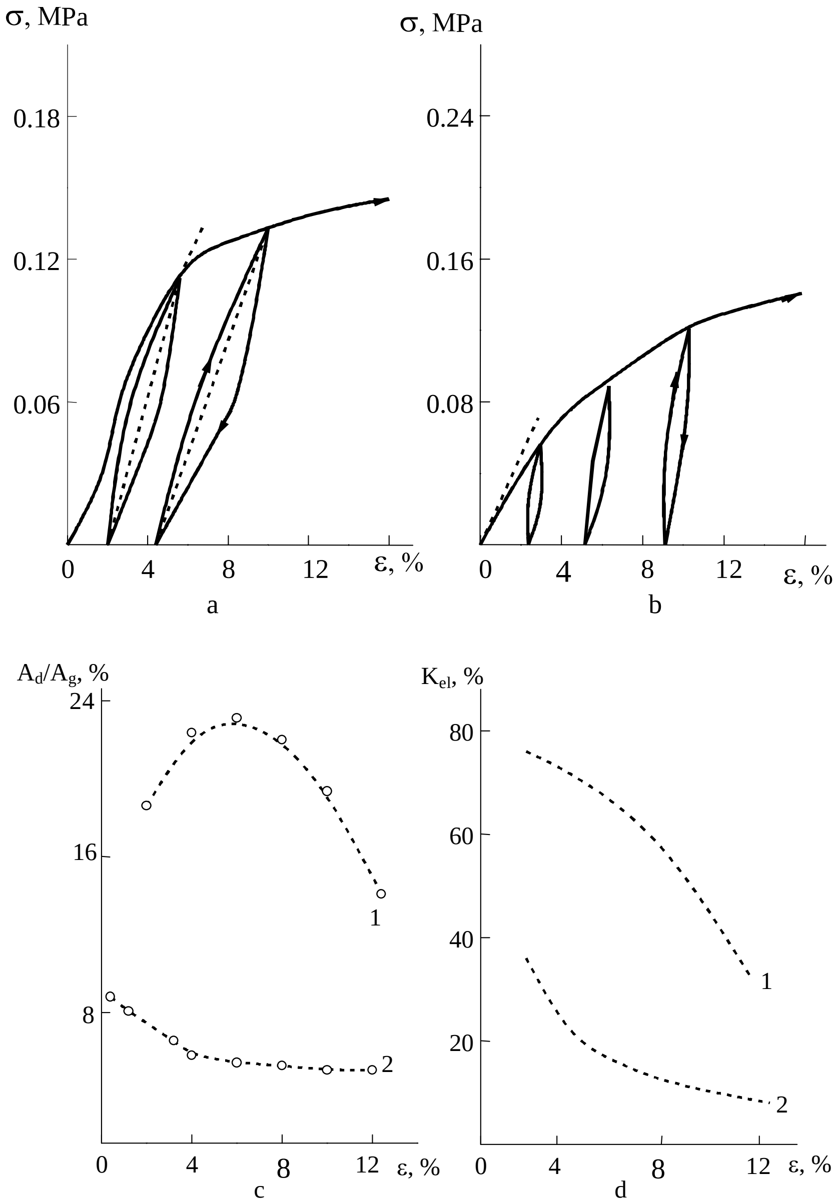


Fig. 15. Dependencies of compression stress (*a*, *b*), dissipated deformation energy share (*c*), and elasticity coefficient (*d*) on compression deformation of specimens obtained by methods of EG unilateral pressing (*a, 1*) and GBRC expansion in limited volume (*b, 2*).

It is explained by the fact that while expansion in free volume the particles acquire properties of elastic elements with high residual stresses owing to high structure disordering caused by deformation and curving of plane carbon layers and creation of specific defects of a graphite crystalline lattice and honeycomb structure [5]. It determines the specificity of deformation process of specimens consisting of such particles (Fig. 15, *a*). At the first stage of compression after deformation of weak elements of "frame" formed owing to elastic after-effect while specimens moulding, the process enters a stage of elastic deformation of "frame". After that, the compression passes to stage of elastic-plastic deformation of the structure elements. The curve of unloading-repeated loading form a wide hysteresis loop, and at the same time dissipated deformation energy A_d (the square of a hysteresis loop) constitute a significant part of general energy A_g., used for deformation of the material (square under the curve of deformation). When deformation increases the share of dissipated energy initially increases (Fig. 15, *c*, curve 1) and the internal stress and defectiveness of structure are increased. When the critical level of internal stresses achieved the elements of the structure stop to act as elastic elements and the processes of local and general destruction of particles begin. As a result the share of dissipated energy considerably decreases, and the deformation acquires mainly plastic character (Fig. 15, *d*, curve I).

While expansion of GBRC in limited volume the process of appearance of residual stresses connected with disordering of the structure, is apparently accompanied by their simultaneous relaxation owing to interaction of particles while stacking in the mould. Due to this the plasticity of the structure elements of the specimens is increased, and the compression diagram is essentially changed (Fig. 15, *b*). The elastic-plastic deformation begins practically at the same time when compression stress begins to increase, the share of dissipated deformation energy is insignificant (Fig. 15, *c*, curve 2) and continuously reduces when deformation increasing. The deformation has mainly plastic character (Fig. 15, *d*, curve 2).

Thus, the difference in a structural state of the graphite particles obtained by the extension of graphite bisulfate residual compounds in free and limited volumes, results in change of character of resistance to compression of materials made of these particles.

6. Effect of chemical modification of EG surface by thermosetting polymers on mechanical characteristics of composite materials

The distribution of a thin layer of a polymeric material on the EG advanced surface and consequent its carbonization in a compact form allows to create a composite material including two mutually penetrating structures of crystalline graphite and amorphous carbon material. Thus, at the account of combination of EG plasticity and amorphous carbon hardness, taking into account their high adhesive interaction, it is possible to regulate mechanical characteristics of such composite material and to create EG-carbon-carbon fibre systems. The average characteristics of the studied specimens are shown in Table 7.

The comparative analysis of the compression diagrams of specimens of “pure" EG and EG-carbon compositions (Figs. 16, 17) have shown that the carbon component of specimens causes considerable change in behaviour character of a material during compression process.

During the process of repeated-static compression of EG specimens the lentil-shaped hysteresis loop of large area is observed that testifies to significant dissipation of deformation energy in the material connected with restructuring during deformation. In this case the share of elastic component of deformation ($K_{el.}$), which can be determined as the ratio of elastic component of deformation after unloading ($\varepsilon_{el.}$) to general deformation achieved on the moment of unloading ($\varepsilon_{g.}$), continuously decreases when deformation increases. While large deformations (more than 10 %) plastic component prevails in deformation process.

Table 7. Initial and final parameters of specimens of EG-carbon and EG-carbon-carbon fibre (CF) compositions.

Composition	Concentration of polymer in initial mixture, wt. %	Initial density of specimens, g/cm^3	Final density of specimens, g/cm^3	Carbon concentration in specimens, %
EG-carbon	30	1.20	1.10	22
EG-carbon	50	1.20	1.07	35
EG-carbon	70	1.20	1.00	47
EG-carbon-CF	30	1.20	1.06	21
EG-carbon-CF	50	1.20	0.97	47
EG-carbon-CF	70	1.20	0.99	61

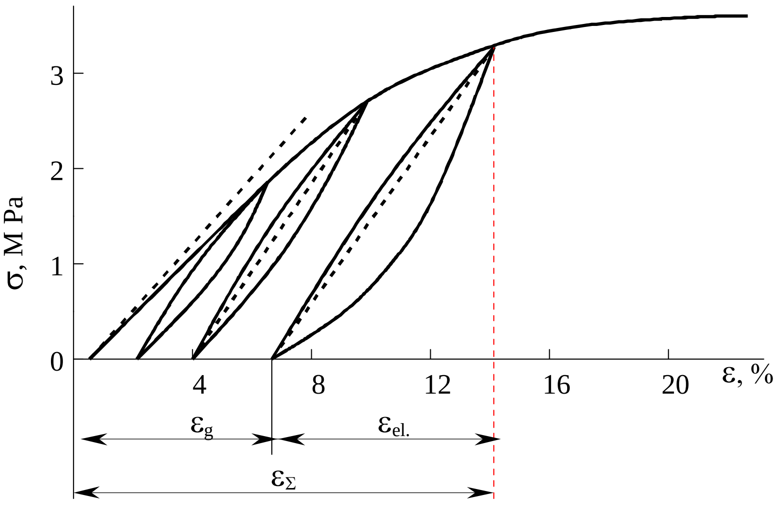


Fig. 16. Repeatedly-static single-axis compression deformation diagrams of EG.

The introduction of carbon component within the limits of the studied concentration changes behaviour character of materials while compression (Fig. 17). The diagrams of deformation become similar to the diagrams of plastic materials compression, which has ability of deformation without destruction [29]. Such materials are characterized by the positive curvature of the diagram in the section of elastic-plastic deformation and forestalling stress growth while increase of deformation. As it is shown in Fig. 17, for the studied compositions of the unloading-repeated loading diagram the hysteresis loop also forms. This loop has also lentil-shaped form under condition of small deformations. However, when deformation increases the loop begins to curve and hysteresis loop axis exceeds its limits. This, apparently, testifies to formation of the closed hollow defects of a lens-visible shape in the studied materials while large deformations. During repeated loading such defects are deformed as the lens-visible springs and cause such shape of the hysteresis loop. Under condition of small deformations the stress values in the EG-carbon compositions differ insignificantly from the same values for initial EG specimens. However, while large deformations the compositions EG-carbon have considerably large strength.

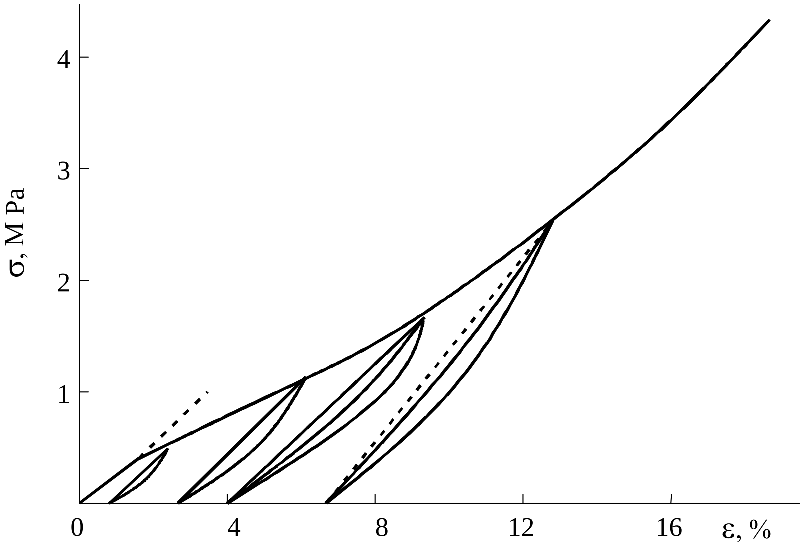


Fig. 17. Diagrams of repeatedly-static single-axis compression deformation of EG-carbon composite materials.

As it is shown in Fig. 18, the change of carbon component concentration within studied limits has little influence on compression resistance, and the studied compositions have approximately equal strength.

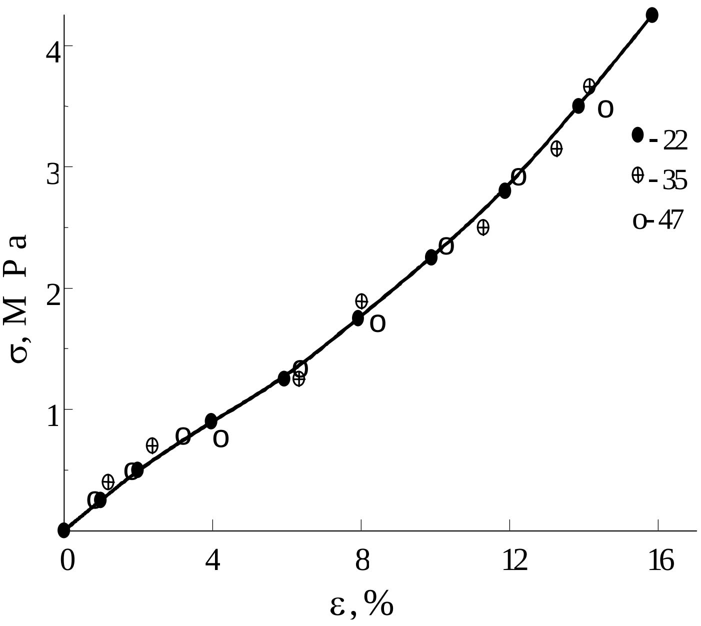


Fig. 18. Compression deformation diagrams of EG-carbon composite materials with carbon concentration 22, 35 and 47 wt. %.

The share of elastic component of deformation for the studied compositions, as well as for "pure" EG, continuously decreases when deformation increases, although while large deformations some stabilisation of elastic properties of materials (Fig. 19, curves 1-3) is observed.

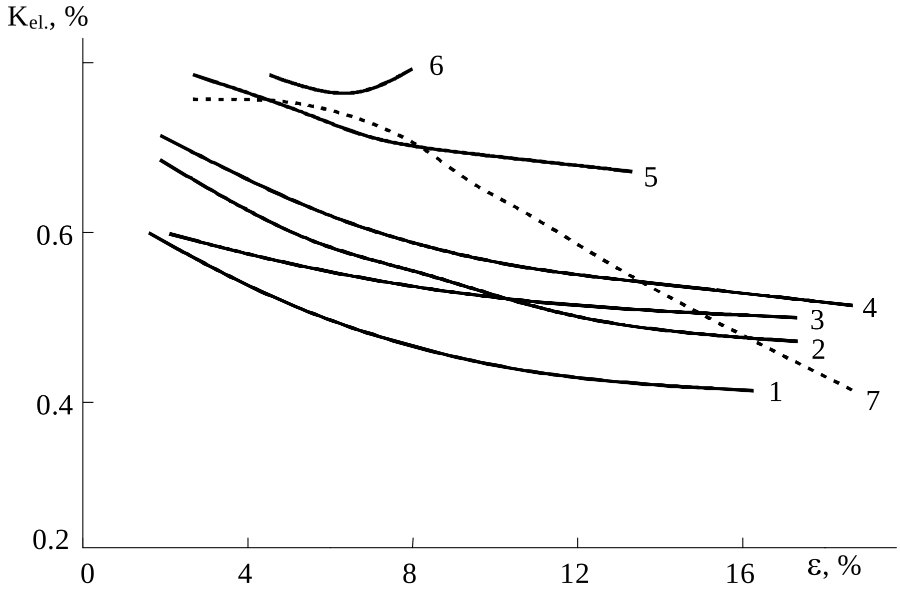


Fig. 19. Dependencies of elastic coefficient on specimens deformation for EG-carbon (*1-3*); EG-carbon-CF (*4-6*); and EG (*7*).

As it is shown in the compression diagram of EG-carbon-carbon fibre compositions, the introduction of small amount of carbon fibre into material influences considerably behaviour character and strength of composition during compression (Fig. 20).

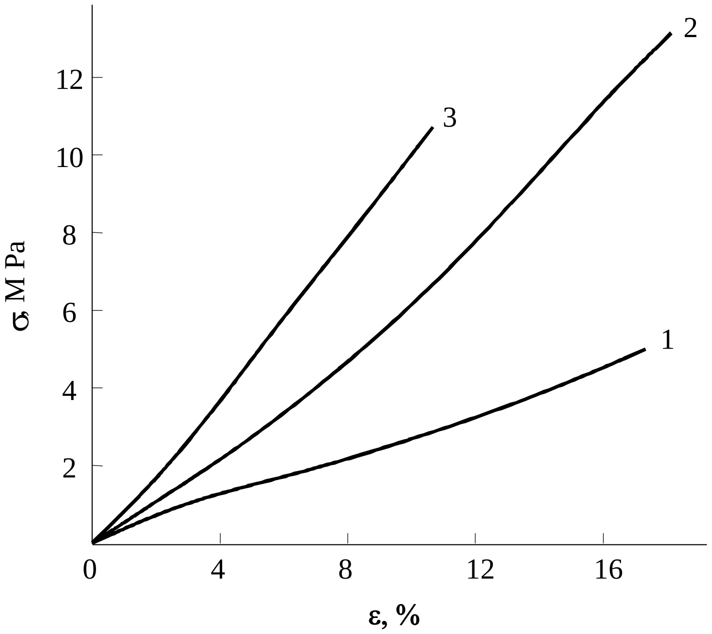


Fig. 20. Compression deformation diagrams of EG-carbon-carbon fiber composite materials with carbon concentration 21 (*1*); 47 (*2*) and 61 wt. % (*3*).

If at small carbon concentration the compression diagrams differ insignificantly from the diagrams for EG-carbon compositions as to the character and stress level, the compression diagrams acquire practically linear character as far as the specimens destruction, and the destruction has a brittle character while increase of the carbon component concentration. The strength of specimens is increased by a factor of 3-5, and the share of elastic component prevails in deformation process (Fig. 19, curves 5,6). An elasticity coefficient $K_{el.}$ increases even before specimen destruction in case of EG-carbon-CF compositions with concentration of carbon of 61 wt. %.

Thus, the introduction of carbon component in EG changes the behaviour character of materials during compression and increases their strength while large deformations. Within the studied interval of carbon concentration (20-45%) it has little influence on compression resistance, therefore specimens have approximately identical strength. The deformation of EG-carbon-carbon fibre composition with large carbon concentration mostly has elastic character. The strength of such compositions exceeds the strength of EG-carbon materials by a factor of 3-5, and the destruction has a brittle character.

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