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Polymeric-nanohetermorphous structure of noncrystalline carbon

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The concept of polymeric nanoheteromorphous structure PNS (structural variations at the nanometric level) of noncrystalline substance divides the materials into vitreous and ultradispersible not vitreous substance. In the case of individual chemical substance (element, chemical compound) a special case of the PNS concept is applied. It is important The representation of individual noncrystalline substance (NS) as copolymer nanofragments (dispersed to a greater or lesser extent) is important. They do not exhibit translation symmetry (long-range order), and are characterized by short-range and intermediate order of a given polymorphic modification (PM). The polymorphoid copolymerisation is a necessary and sufficient condition of formation of the noncrystalline state. The noncrystalline carbon can be regarded as dispersed polymorphoids of various carbon forms, characterized by sp^3-hybridization of a chemical bond (diamond bonds), sp^2-hybridization (graphite bonds), sp-hybridization (carbine structure). The noncrystalline carbon (n-C), as well as others non-crystalline materials, differ in the concentration of polymorphoids, determining the structure and properties of a noncrystalline carbon.

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1. Introduction. The formation of the noncrystalline state. Terminology and classification

The main rule of the physico-chemical analysis is the Kournakov - Tananaev rule [1,2]: the properties of the substances are functions of their most fundamental physical and chemical characteristics , i.e. chemical composition, structure, dispersiveness. This is in our opinion the key to the correct solution of the problem of formation and structure of a noncrystalline substance, and also for the general classification of the solid state.

On the basis of the analysis of various noncrystalline substances in the frame of the Kournakov - Tananaev rule, we developed the concept of nanoheteromorphous structures of a noncrystalline substance. This concept originates in the ideas of the years 80 – 90th of the past century [3-11].

The noncrystalline state will be discussed, by avoiding the application of the term "amorphous" because this is, after our opinion, an ambigous term. As it was shown in Minaev's monography [8], some researchers (see references to p. 23 [8]) a vitreous state is a special case of amorphous state, while other researchers affirm that they are identical. There are scientists that consider these states to be completely different.

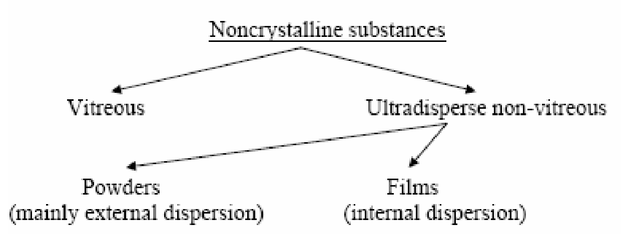
It is interesting, that these points of view are admitted in the works published by one and the same author (see p. 25 in [12]).

After our opinion the non-crystalline solids can be divided, in non-crystalline vitreous, and in non-crystalline small-grained powders. Films of not vitreous substances prepared by sputtering, vapour deposition, drying of gels, etc. form a third class.

According to Kournakov-Tananaev rule [1,2], a key feature of the not vitreous forms of existence of a non-crystalline substance is its high degree of dispersion. The ultradispersed substances or ultradispersed media are macroscopic assemblies of microscopic particles, with size in the range 1-10 nanometers, which are characterized by a high surface/volume ratio, breaking of many chemical bonds and different hybridizations, as well as the increase of sharing of the surface energy [13; 8, p.32].

If for micro (nano) powder dispersion the presence of large quantity of micro (nano) particles is characteristic, for non-crystalline but not vitreous films the continuity of the substance does exist, in spite of the penetration in the bulk mass of large amount of micro (nano) channels, micro (nano) pores and cavities that create the so-called «internal dispersion » [8, p.32]. It exists a large internal surface of the film continuum with an open structure. Feltz [12, p.238] observed that in deposited films of Ge and Si analogs of carbon there were evidenced by small-angle electron scattering voids of size from 0.07 up to 2 nm. As a result, the density of the non-crystalline substances is considerably below the crystal density. For example, for films of silicon and germanium the decrease of density is of 3-15 % [14]. When the extent of copolymerization of structural fragments is smaller, then much greater is the number of the broken bonds. This is characteristic to Si and Ge as opposite to the true glasses. So, in non-crystalline silicon the concentration of not paired spins localized on dangling bonds is 7.5×10^{18} - 2×10^{20} cm^{-3} [15, p.12], i.e. for ~ 10^3 atoms of silicon it exists one dangling bond [12, p.243]. The density of spins of amorphous carbon is 3×10^{19} » [16, 17, p.235], while in vitreous SiO_2 even for strong quenching of a melt from 2000 K the concentration of spins reaches only 10^{13}-10^{14} g^{-1} [17,18]. As a result it is possible to conclude, that « internal dispersion » in noncrystalline C and Si considerably exceeds that in vitreous (glassy) substances.

ThusOne may conclude that the non-crystalline substances can be divided into two basic classes: vitreous and non vitreous ultradispersed substances [8-10], and further in two subclasses: powder and film substances:



Therefore, we have avoided the term "amorphous". Of course, not for the above reasons, the leading journal in the area of disordered materials was named « Journal of Non-Crystalline Solids »

Furthermore, in this paper instead of the term "amorphous carbon" (a-C), we shall use the term «non-crystalline carbon » (n-C).

2. Models and concepts related to the structure of non-crystalline substance

In the first stages of research (in the years ‘60 of the 20-th century) the structure of "amorphous carbon" was considered, as consisting from « diamond-like and graphite-like » areas of short-range order [19, 20, 12]. For the description of the structure it was used the crystallite model. The model was proposed in 1921 by Lebedev [21] and found an experimental confirmation by the work of Randell [22].

For diamond-and graphite-like areas are characteristic sp^3- and sp^2-hybridizations of the chemical bonds, respectively. The presence of sp^3-and sp^2-chemical bonds is demonstrated in many works, in particular [23-26]. In the work of Comelli, etc. (1988) [27], based on EXAFS-investigations (Extended X-ray Absorbtion Fine Structure), it was shown, that in the evaporated samples of non-crystalline carbon there should be two coordinate configurations of carbon atoms, i.e. structural blocks with sp-hybridization of chemical bonds.

The network model of the “amorphous carbon”, consisting of graphite-like fragments embedded into a matrix of both twofold and fourfold coordinated atoms (sp- and sp^3-hybridizations) has been suggested in the work of Wang, etc. in 1993 [28]. This model has been developed also in the papers [29, 30].

In these papers we explain the structure of noncrystalline carbon in the frame of the concept of polymeric-nanoheteromorphous structure of a non-crystalline substance and its special case: the polymeric-polymorphoid structure of non-crystalline chemical substance (CS). CS is a chemical element or chemical compound.

We refer in the case of the non-crystalline carbon, silicon and germanium [29-34] to the class of “spatially-structured non-crystalline polymers”[35]. (As an exception we used in [35] instead of the word "non-crystalline" the word "amorphous").

From the very beginning of the development of the concept of polymeric-polymorphoid structure of non-crystalline substance (at the end of ’90) there were included both vitreous, and not vitreous (ultradispersed) noncrystalline substances, in particular, C, Si, Ge, $A^{II}B^{VI}$, $A^{III}B^{V}$, etc. [4-8]. The previous name was «neocrystallite». Basically it was a polymorphic-crystallite model of non-crystalline substance, in which crystallites were understood as elementary cells of a crystal lattice (or their fragments) of various crystal polymorphic modifications (PM) [8, p. 49; 9]. However, our understanding of a crystallite contradicted the standard classical definition, which has been given by Poraj-Koshits "…"crystallite “ is extremely small crystal consisting of very small number of elementary cells “ [36], "…" “crystallite” means presence of even restricted long-range order … “ [37]. Thus, our "crystallites" are actually different because there are atomic configurations considerably smaller, than the “extremely small crystals “.

Here the following question arises: what is an extremely small crystal? In our point of view, this is a crystal consisting of two elementary cells of a crystal lattice (ECCL), that makes still possible the "translation symmetry" inherent to crystals. This small crystal has a minimum long-range order: one ECCL can be translated (transferred and combined) in another ECCL. To remove the observed contradiction between our definition and the classical one of a crystallite we have introduced the new concept of “polymorphic-crystalloid” [10, 11, 38, 39], and consequently the “polymeric-polymorphoid structure of the noncrystalline substance » [40, 41]. The term "crystallite" has been replaced by the term "crystalloid", and then – “polymorphoid”. Finally, the definition has been generated: ***the polymorphoid (crystalloid) is a fragment of crystalline structure consisting of a group of atoms, connected among themselves by rules of the stereometry, peculiar to one polymorphic modification of substance and not possessing translation symmetry (long-range order)*** [10, 11, 40, 41.] The polymorphoid itself is the carrier of the medium (intermediate) - range order (MRO, IRO) and is stereometrically defined by a combination of various types of short-range order (SRO) within the limits of polymorphoid, characterized by the parameters of SRO and specific dihedral angles [11]. The long-range order (LRO) in the polymorphoid is absent.

The problem of polymeric-polymorphoid structures of glass and glass forming liquids has been carefully investigated. The new paradigm of the structure of the glass is evidenced, and this allowed to solve the paradox on the “appearance of properties and structures of crystal polymorphic modifications in a glass, which does not contain crystals“ [10,11,42-44].

The main rules of the concept, related to vitreous substances, are valid also for non-vitreous non-crystalline substances. An exception to these rules is related to the glass transition process and to the definition of glass transition temperature, T_g.

We formulate further the basic ideas of the concept of polymeric-polymorphoid structure of non-crystalline ICS state [4,8-11, 38-44]:

- The individual chemical substance in a non-crystalline state represents one-dimensional, two-dimensional, three-dimensional [35]) structures or a mixed copolymer structure made of fragments of various crystalline polymorphic modifications (polymorphoids), not possessing a translation symmetry (long-range order) and characterized by strictly fixed intermediate-range order and short-range orders peculiar to one from two (or more) polymorphic modifications; in noncrystalline CS structure always are present not less than two intermediate-range orders pertinent to the various crystal PM;
- A mutual transformation of polymorphoids of various PM and change of their concentration ratio in noncrystalline CS under the influence of external effects and time is the fundamental reason of structural change and properties of non-crystalline substance within the limits of area of the concentration ratios, which does not result in crystallization of one of PM; outside this area the substance crystallizes in a polymorphic modification, which is stable under given conditions:

$$(T, P, Ph, E, H\ldots, t)$$

$$A_{\text{к}} + B_l + C_m + \ldots + Z_x \Leftrightarrow A_p + B_q + C_r + \ldots Z_y \quad \text{(I)},$$

where A, B, C … Z are polymorphoids of various PM whose concentration k, 1, m … p, q, r … x, changes as a function of processing conditions (temperature T, pressure P, irradiation, electric field E, magnetic field H, etc.), and also as a function of the time of staying in the given conditions) from 0 up to 100 %;

- The polymeric-polymorphoid model of the structure of the non-crystalline substance represents, as well as Zachariasen model (1932) [45], a network model, in which, unlike Zachariasen network combined randomly located polyhedrons as carriers of short-range order, copolymerized polymorphoids, that carry the intermediate (medium)-range order of various crystalline polymorphic modifications.

The last thesis bring together our model and the crystallite models of Frankenheim [46], Lebedev [21] and Goodman [47]. After our ideas in the noncrystalline substance exists aggregated (copolymerized) clusters, and not crystallites - the smallest carriers of long-range order. These are polymorphoids i.e. carriers of intermediate-range orders of various crystalline PM.

Thus, the concept of polymeric-polymorphoid structure of the non-crystalline substance includes all aspects offered by the previous concepts, and supplements them with new peculiarities, allowing to explain all the features of the formation of non-crystalline substances, their structures and relaxation processes [44].

3. Crystalline polymorphic modifications of carbon

Crystal carbon can exist in several polymorphic modifications: diamond, lonsdalite [48], a phase, characterized by face centered lattice [49], graphite (hexagonal, rhombohedral [50], or cubic [51]), spherical variety of fullerenes (C_{60}, C_{70}, C_{72}, C_{78}, C_{82}) [52,53], various forms of nanoparticles (with the size from tens up to hundreds nanometers): nanotubes, "bulbs", "necklaces", spirals, "tripods", fullerene-nanotubules, etc. [53-54], carbine [55-57], existing in the form of cumulene $(=C=C=C=C=)_n$ and polyene $(-C{\equiv}C-C{\equiv}C-)_n$ chains.

For a large variety of diamonds the sp^3-hybridization of carbon atoms is characteristic, for a large variety of graphite and fullerenes, the sp^2 is characteristic while for carbines a sp-hybridization is characteristic.

4. A structure of noncrystalline carbon from the point of view of the concept: polymeric- polymorphoid structure of a non-crystalline substance

In the opinion of Kasatotchkin – (one of the discoverers of the carbine (1960) [58], in “amorphous carbon all three types of hybrid atoms with three types of bonds (diamond, graphite and carbine) are combined. The number of combinations of hybrid atoms in various relationships is very great” [59]. This point of view is in agreement with the concept of polymeric-polymorphoid structure of the non-crystalline substance though some clarification must be done. “The combination of atoms” occurs due to copolymerisation of polymorphoids of various PM (diamond, graphite, carbine). The number of combinations of polymorphoids "is very large”: the structure of the non-crystalline substance, the concentration ratio of polymorphoids of various PM quasi-continuously varies depending on the change of external conditions (temperature, pressure, irradiation, etc.). The non-crystalline substance (including the vitreous substance) is characterized under given conditions by a fixed combination of polymorphoids of various PM, being one from a quasi-continuous multitude of combinations of polymorphoids of the polymorphic modifications sharing the formation of the non-crystalline substances [41].

The specific combination, in particular the specific concentration ratio of polymorphoids (CRP) of various PM defines all the properties of a non-crystalline substance. The quasi-continuum of combinations of CRP resulting in the change of external conditions, defines a quasi-continuum of values of the properties of a given non-crystalline substance.

The presence of sp^3-, sp^2 and sp-hybridizations in non-crystalline carbon is fixed by a detailed diffraction analysis of noncrystalline carbon samples (n-C), based on the data on neutron scattering, EXAFS, electron diffraction, Raman scattering (RS), NMR, molecular-dynamic modeling [28,60-66].

So, in the paper [28] it is shown, that the structure factor S (Q) and the pair correlation function g(r), calculated by tight-binding molecular-dynamics simulations, are in very good accordance with the results of neutron scattering by a sample of sputtered n-C with the density 2.20 gcm^{-3}. The investigated structure represents clusters of graphite-like layers of a size of around 10 Å × 10 Å, containing mainly six-member rings and some quantity of five- and seven-members rings. The graphite-like fragments are embedded in a matrix of both twofold and fourfold coordinated atoms. The majority of twofold and fourfold coordinated atoms serves as bridges that connect the graphite-like clusters.

Other two samples with increased density were studied: 2.44 and 2.69 g/cm^3 (Table 1 [28]).

Table 1. The ratios of various coordinated atoms of amorphous carbon, obtained by the method of tight-binding molecular-dynamics simulations [28].

Density (g/cm^3)	Twofold coordinated atoms (sp-hybridization), %	Threefold coordinated atoms (sp^2- hybridization), %	Fourfold coordinated atoms (sp^3- hybridization), %	Average coordination number, n_c
2.20	12.0	80.6	7.4	2.96
2.44	5.8	80.0	14.2	3.08
2.69	6.5	71.0	22.5	3.16

As apparently from the Table 1, the density of the non-crystalline substance is determined by the relative concentration of the atoms interconnected as a consequence of various hybridizations of electronic shells, i.e. the atoms entering in polymorphoids of various PM [41]. According to the concept of polymeric-polymorphoid structure all other properties of the material are controlled by the ratio of the concentrations of various PM fragments, without long-range order.

In our opinion, the pioneering work [28] contains some inaccuracy in the interpretation of non-crystalline carbon structure. The table 1 given by authors, shows, that hardly it is possible to consider as a matrix the total 19.4 (12.0+7.4) … 29.0 (6.5+22.5) % twofold and fourfold coordinated atoms in relation to 71.0 … 80.6 % of clusters of graphite-like layers, which are interconnected by bridges from these atoms. From the position of the polymeric-polymorphoid concept the structure of non-crystalline substance consisyts of structural fragments (polymorphoids) of all polymorphic modifications participating to the formation of the material, each of which being characterized by its own intermediate order.

The presence in the graphite-like layers of n-C pentagonal rings [28] speaks in favour of the formation of the disordered network and, therefore, fullerene polymorphoids can occur. We hope the future researches, will show to whom polymorphic modification of carbon belongs the case of seven-fold rings of atoms mentioned in [28].

In the papers by Popov and al. [62-66] the level of structural modification of non-crystalline substances are investigated and, in particular, is investigated by electron diffraction the films of the non-crystalline carbon obtained by ion-plasma sputtering of a graphite target at various temperatures. The analysis of the radial distribution of atoms in non-crystalline carbon achieved by the authors, based on the algorithm of Bellman-Zade [67], allowed to estimate for the first time the percentage ratio of quantities of atoms with sp-, sp^2-, sp^3-hybridization of chemical bonds in carbon films (Table 2).

Table 2. Contents of sp^n-components in the films of non-crystalline carbon obtained by ionic - plasma sputtering of a graphite target [62].

Temperature of substrate, °C	sp^3, %	sp^2, %	sp^1, %
100	65	10	25
150	50	25	25
250	45	50	5
500	5	90	5

The films of noncrystalline carbon obtained in these and other series of experiments [66], differed as a function of the concentration ratio of atoms with various hybridization of a chemical bond. The films differ drastically in their properties. Thus, the width of the optical gap differs by two orders of magnitude (from 0.02 eV for graphite-like films with essential content of sp^2-bonds up to 1.85 eV for films with predominance of diamond-like configuration: sp^3-bonds), and for dark electroconductivity more than by 10 orders (from 7 up to 20×10^{-10} ohm^{-1}.cm^{-1}) [66,63].

It is known, that the diamond (characterized by sp^3-hybridization), is stable at high pressure, and under normal conditions is metastable though can exist indefinitely (Fig. 1 [68]). By heating it turns into graphite. The transition temperature is 600-700 °C for crystals with the size from 0.6 up to 1 mm, and is 450-500 °C for synthetic micropowders. For diamond nanoparticles, it is supposed, this temperature will be even less. The nanoparticles of carbon are supported on a substrate in the experiment of Popov and co-authors, as described in [62-66]. With increasing temperature of the substrate the formed quantity of nanoparticles with sp^3-hybridization (diamond) decreases and the concentration of particles with sp^2-hybridization increases. This is in good agreement with the data reported in [68] on the temperature instability of the diamond crystal. On the contrary, with the decrease of the temperature the number of nanoparticles with sp^3-hybridization increases. It is possible to predict, that at the substrate temperature of < 100 °C, the concentration of sp^3-fragments will be more than 65 %, i.e. the stability of sp^3-nanoparticles will increase with the decrease of the temperature.

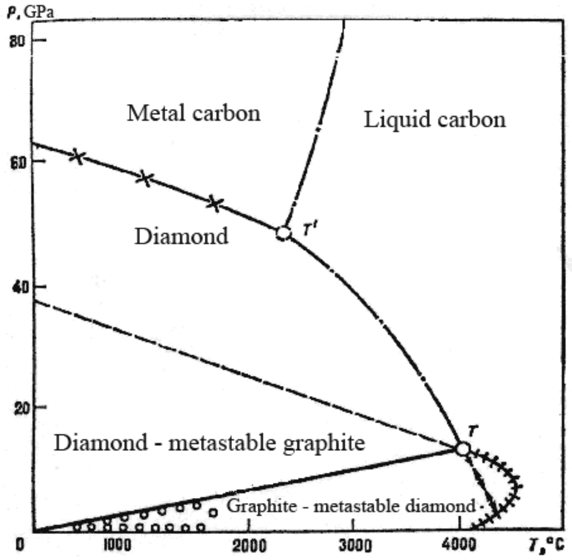


Fig. 1. p-T phase diagram of carbon [68].

——— *curve of graphite-diamond equilibrium;*

┼┼┼┼┼┼┼┼ *curve of graphite melting;*

- - - - - - - - *boundary line of existence of metastable graphite in the field of existence of diamond;*

→←→← *boundary line of existence of metastable diamond in the field of existence of graphite;*

—×— *prospective boundary line diamond - metal carbon (solid phases);*

—·——·— *curve of diamond and metal carbon melting (boundary line of existence of these phases);*

T - triple point: graphite – diamond – liquid carbon;

T ′ - prospective triple point: liquid carbon – diamond – metal carbon;

o o o o o area of crystallization of diamond in metastable conditions.

At the moment of sputtering of a graphite target the formed nanoparticles consist, apparently, of separate atoms of carbon and fragments of graphite, i.e. interconnected six-member rings, separated rings and their fragments. In plasma and on a substrate or near to the substrate, directly before deposition, the products of sputtering of a target turn into particles, characterized by various sp^n-hybridization (n = 1-3). The lower is the temperature, the more graphite-like sp^2-fragments (or separated carbon atoms) turn into fragments with sp^3-hybridization. This means that in the conditions of low temperatures, standard atmosphere pressure and deep dispersion of carbon, the diamond-like nanoparticles are more stable than the graphite-like nanoparticles. As a result on a nanolevel the process of polymorphoids transformation “graphite → diamond” runs. Here we face with the phenomenon of inversion of crystal polymorphic modifications stability (more precisely, stability of polymorphoids), with effect on the occurrence of the enantiotropic polymorphic transformation in the substance characterized routinely in conditions of standard atmosphere pressure by the monotropic polymorphic transformation, in this case, “diamond → graphite”.

Deep dispersion of carbon is a primary factor, i.e. the main reason of the formation of diamond from the atomic carbon or from its graphite-like nanoparticles at low temperatures and standard atmosphere pressure.

The enantiotropy of carbon in conditions of standard atmosphere pressure is actually fixed and in work [68], where on the p-T phase diagram (Fig. 1) in the region of metastability of diamond, the area is fixed at normal and some increased pressure and the temperature goes approximately up to 1500 °C when occurs the “crystallization of diamond in metastable conditions”.

The situation close to that described above, was observed, too, in selenium [69,41] an element characterized usually by a monotropic polymorphic transformation [70]. In [41] on the basis of data from [69] regarding the increase of heat capacity of vitreous selenium in the region of T_g during the increase of its retention interval under T_g after the annealing of the melt, the conclusion was drawn on the increase in polymorphoids concentration of low-temperature PM on the account of the concentration of high-temperature PM.

Thus, both carbon and selenium, are usually monotropic at standard atmosphere pressure. For special conditions the enantiotropy appears. For carbon such special condition is, in particular, deep dispersion of substance during the formation of a non-crystalline state, and for selenium it is the finding of the substance in a vitreous state.

The results, obtained in the paper by Popov et al. [62-66] confirm our concept: structure and properties of a non-crystalline substance, in particular, n-C, are determined by the concentration ratio of polymorphoids of various PM, depending of the source state, conditions of reception, final equilibrium conditions and life time of the substance in the given conditions. The concentration ratio of polymophoids (CRP) of various PM is the major internal parameter of the non-equilibrium thermodynamic system that describes the substance in the non-crystalline state.

The stated facts and conclusions are in accordance with the data of Raman-spectroscopy, reported in the papers [60,61].

Regarding the availability of diamond and graphite polymorphoids in noncrystalline carbon it is possible to draw a conclusion on their presence, by comparing the Raman-spectra of these forms. In Fig. 2 [60, 61] are presented the spectra of crystalline diamond (a), graphite

(b) and microcrystalline graphite (c), with the main |Raman lines.

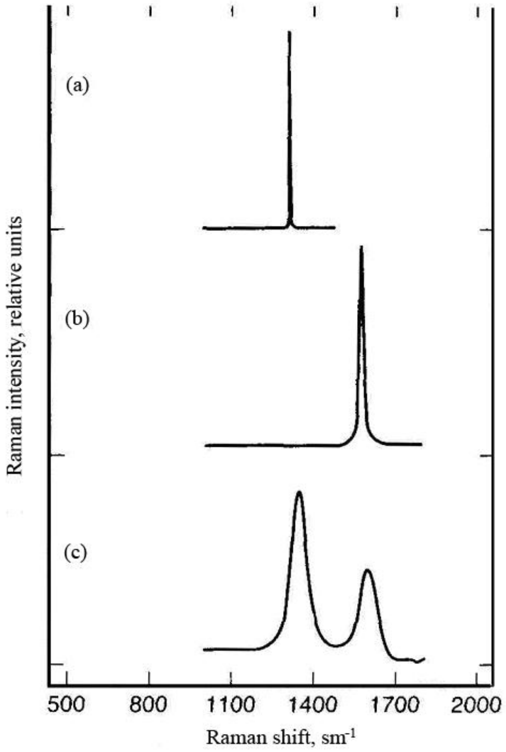


Fig. 2. Raman spectra of diamond (a), graphite (b) and microcrystalline graphite (c) [60,61].

For Raman-spectrum of diamond the narrow line of 1332 cm^{-1}, and for graphite - a narrow line of a longitudinal oscillatory mode of 1581 sm^{-1} (among Raman active oscillatory modes of graphite the authors of [60, 61] mark also the modes of 42 and 2710 cm^{-1}) are characteristic. The microcrystalline graphite shows the widened D-band of 1355 cm^{-1} (band of diamond - Diamond) and the widened G-band of 1580 cm^{-1} (band of graphite - Graphite). The broadening of the bands is explained by the authors by a deviation from highly-ordered structures of diamond and graphite. On Fig. 3 (a, b) are given Raman-spectra of polycrystalline and highly-oriented pyrolytic graphite, respectively. Fig. 4 (a, b) shows the non-crystalline kinds of carbon – glass-like carbon (a) and the mineral "coal" (b). As regarding non-crystalline samples it is spoken, that they have "some characteristic features of graphite". Obviously, the authors take into account the lines of 1591 cm^{-1} (Fig. 4a) and 1584 cm^{-1} (Fig. 4b), close to the oscillatory mode of graphite of 1581 cm^{-1} . From the point of view of the concept of polymeric-polymorphoid structures of the non-crystalline substance in Fig. 2-4 we also have "some characteristic features" of diamond: a line at 1355 cm^{-1} (Fig. 2c), a line at 1357 cm^{-1} (Fig. 3a), a line at 1343 cm^{-1} (Fig. 4a) and a line at 1360 cm^{-1} (Fig. 4b). All listed lines are close to the narrow line of diamond situated at 1332 cm^{-1}. The authors of the papers [60, 61] point out that the discussed Raman-spectra "can be used for getting the information on the degree of disorder and on the nature of local chemical bonds", but do not develop further this idea.

In the following we discuss the data of the Raman-spectra from the point of view of the concept of nanoheteromorphous structure of the non-crystalline material [41,71,44].

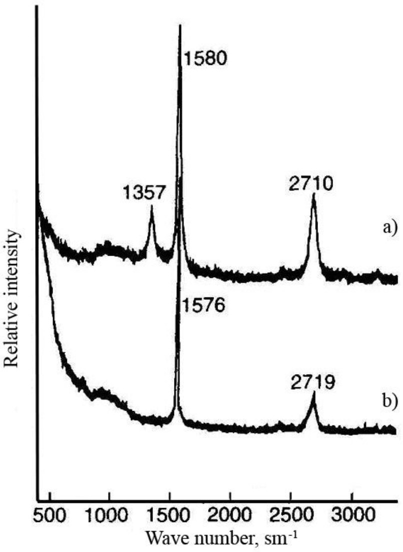


Fig. 3. Raman spectra of polycrystalline (a) and high-oriented pyrolytic graphite (b) [60,61].

In the Raman-spectrum of highly-oriented graphite (Fig. 2b) there is lacking the band that characterizes the diamond (1332 cm^{-1}). Only undistinguished display of fluctuations in the spectral area of 1330-1360 cm^{-1}, characteristic for diamond-like base units is observed in highly-oriented pyrolytic graphite (Fig. 3b) A poly-crystalline graphite shows significant intensity of a band at 1357 cm^{-1} (Fig. 3a). And, finally, in microcrystalline graphite (Fig. 2c) high intensity of the 1355 cm^{-1} line that characterizes a polymorphic modification of diamond, comparable with the intensity of a line is observed at 1343 cm^{-1} in non-crystalline vitreous carbon (Fig. 4a).

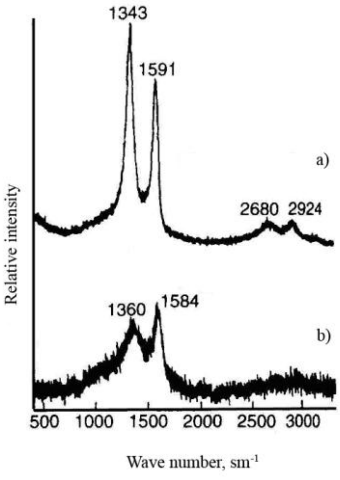


Fig. 4. Raman spectra of noncrystalline carbon: vitreous carbon (a) and black coal (b) [60,61].

From the above results it is possible to draw the conclusion, that with the increase of the degree of the failure of the crystalline structure (due to the modification of the crystallization conditions), if the amount of graphite increases and the area characterized by continuous ordered structure decreases, in graphite develops polymorphoids, and, at certain concentration, the graphite crystals transforms into non-crystalline carbon.

The process of failure of the crystalline structure of a given polymorphic modification under external factors is a process of formation in the material of structural fragments (polymorphoids) of other polymorphic modifications, accompanied by the appearance of various structural defects. These defects are formed due to stereometrical hindrance that impedes on the correct formation of the chemical bonds in the lattice. This conclusion based on the analysis of the experimental facts, is in agreement with one of the main points of view of the polymeric-polymorphoid concept applied to the structure of the non-crystalline solids, generalized in the formula (I), given in section " 2 ". In Minaev's papers of the beginning of 90th years [7; 8, p. 47] it is shown, that an important consequence is: “In the presence of only one polymorphic modification we are dealing with ideal monocrystalline substance. The very small quantities of others PMs allow to get only monocrystals in which it is possible to control defects and dislocations, by moving the relative PM concentrations by external factors (T, P, Illum., E, H …). The increase in concentration of others PMs yields a polycrystalline substance. The coexistence of comparable quantities of PM result in the formation of non-crystalline substances (e.g. a-Si, a-C, a-As, a-$A^{III}B^{V}$, glassy materials).

In the papers [7, 8] there were not presented the experimental proofs of the given conclusion. In fact the conclusion is the forecast concerning the formation of non-crystalline, and crystalline state. After more than one and a half decade it is possible to confirm, *exempli gratia*, (Fig. 2,3,4,5 [60,61]), that the forecasting is largely confirmed for the case of carbon.

In our opinion, the density defect is strongly related to the structural problem discussed above. The defect density represents the change of density of a real crystal compared to the roentgenographic ideal value [72]. The author considers as the probable reason of occurrence of defect of density the formation of different polymorphic modification with the structure slightly differing from the matrix structure, which is “ distributed in a crystal in the form of more or less stretched areas and does not form a self-contained phase”. The phenomenon is rather close to that of the “real monocrystal containing microquantities of others PM” [7,8], discussed above.

Furthermore, the author of the paper [72] considers two possible limiting cases. In the first one there are not formed regions (areas) of the new PM independent phase. The system is homogenous. Examples are germanium, the compounds of type $A^{III}B^{V}$ (with the exception of BN). In the second case, under usual conditions coexists the cubic and and hexagonal phase with prevalence of the more table cubic phase. An example is the compound silver iodide.

Other aspect of the problem is the following: the character of the change of Raman-spectra modification and, in particular, the ratio of the intensities I_D/I_G D-and G-bands (bands of diamond and graphite) proves that it is possible to enhance the dispersion of the monolithic crystalline structure, e.g. by mechanical crushing.

It seems that the ratio of the intensities I_D/I_G D-and G-bands defines the concentration ratio of different hybridizations of the chemical bonds.

In the Fig. 5 [60,61] is shown the dependence of the ratio of I_D/I_G D-and G-bands of Raman-spectrum on the size of the graphite nanocrystal, L_a. The size lays within the limits of 3 - 300 nanometers, as determined from X-ray scattering. The dependence [60,61] is linear when L_a and I_D/I_G are represented in double logarithmic scales. When the degree of dispersion increases the ratio I_D/I_G grows from ~0.02 up to ~1.0. The linear relation demonstrates the increase of the amount of diamond polymorphoids when dispersion of the material increases, i.e. actually fixes the process of dispersion transformation graphite in the non-crystalline substance, consisting of polymorphoids of both carbon PM.

The transformation of graphite polymorphoids in diamond polymorphoids during crushing is confirmed also by electro-physical data. In the paper [73] the increase of the band-gap width of graphite from zero up to 0.65 eV is produced during the transformation from bulk crystal to clusters of size around 15 Å. It is known, that the band-gap width of diamond is 5.6 eV [74, volume 5, p. 303].

Thus, the analogy with the behaviour of the ratio of Raman – spectrum bands I_D/I_G is good for the cases: a) diminishing of the particle size during the dispersion of graphite (300 → 3 nanometers) and b) diminishing of the crystallite size during transformation from monolithic highly-oriented pyrolytic graphite (Fig. 3b) to poly-crystalline graphite (Fig. 3a) and further to micro-crystalline graphite, Fig. 2b, (original: " intramonolithic dispersion"). In both cases the intensity ratio I_D/I_G increases, so the concentration ratio of diamond and graphite polymorphoids increases.

In essence, various ways of decrease of the sizes of crystallites in material leads to the increase of concentration of new polymorphic modifications. The decrease of the size of the crystallites, and of the long-range order (down to the size of two shortest translations in a crystalline lattice) lead to the formation of the non-crystalline substance built from various polymorphoid modifications.

What is the reason of the occurrence of structural fragments of new crystallographic modification during the decrease of the crystallite size? One of the reasons can be the following:

It is known, that the force caused by the surface tension, tends to reduce a free surface of a body up to the least possible limits for a constant volume [74, V. 4, p. 101]. This causes a certain excessive pressure within the substance.

This pressure is, apparently, larger, when the dispersion is larger. Therefore, is related more to the ratio surface/volume, and less to the size of crystallites.

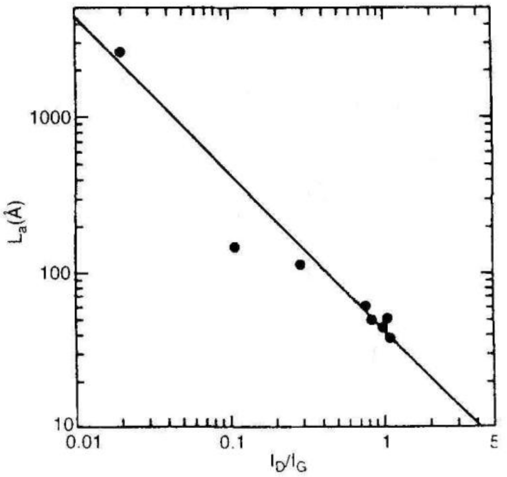


Fig. 5. The relation between the nanopaticle size (L_a, Å) of graphite and the intensitiy ratio of Raman D (diamond) - and G (graphite) bands I_D/I_G (in double logarithmic scales) [60,61].

This finds a good confirmation in the work [75] where it is shown the changes of the lattice constants of the crystals Si, GeO_2, Sn, MgO during dispersion down to the sizes of 100-10 nanometers. In particular, the cubic silver iodide at undergoes a phase change to hexagonal polymorphic modification during the decrease of the size of aerosol particles down to 50 nanometers. Such changes cannot be caused, in opinion of the author, by reasons related to surface because the particle has a surface corresponding to tens and hundreds atomic layers, i.e. full volume of a particle. Therefore the modifications are related not with the surface, but to other factors, for example with the "intrinsic pressure" [76].

As follows from the phase diagram of carbon [68] (Fig. 1), the increase of the pressure at normal temperature translates carbon from the region in which graphite is stable and diamond is metastable, in the region in which diamond is stable, and graphite is metastable. This is the reason of transformation of graphite polymorphoids in diamond polymorphoids.

Apparently, the same reason (increase of intrinsic pressure) causes also the formation of fragments with sp^3-hybridization during sputtering of a graphite target at the low temperatures of the substrate (increase of the dispersiveness !), as described above on the basis of the results of works of Popov et al. [62-66].

On the other hand, the increase of temperature at higher pressure, as shown in the phase diagram (Fig. 1 [68]), reverts carbon from the region of stability of diamond to the region of stability of graphite and consequently, during the increase of the substrate temperature from 100°C up to 500°C (Table 2), the fraction of fragments in a film with sp^3-hybridization of chemical bonds drops from 65 % up to 5 %, and in the same time the fraction of graphite fragments (with sp^2-hybridization) increase from 10% up to 90%.

In this connection it is interesting to remark that up to 90 % fraction of basical units of diamond (sp^3-hybridization) has been fixed in a film of so-called diamond-like carbon, DLC, ("amorphous material without long-range crystallographic order" [77], obtained by the thermoionic vacuum arc (TVA) method. Here the ratio of the sp^3/sp^2-hybridized bonds has been determined according to the x-ray photoelectronic spectroscopy data.

The Raman-spectroscopy has been applied also for the identification of the carbon phases in the deposited film. In Fig. 6 [77] is shown the Raman-spectrum of a film in which two asymmetric bands of diamond (D) and graphite (G) were observed, and, also, the results of the analysis of the spectrum with the application of Gaussian function.

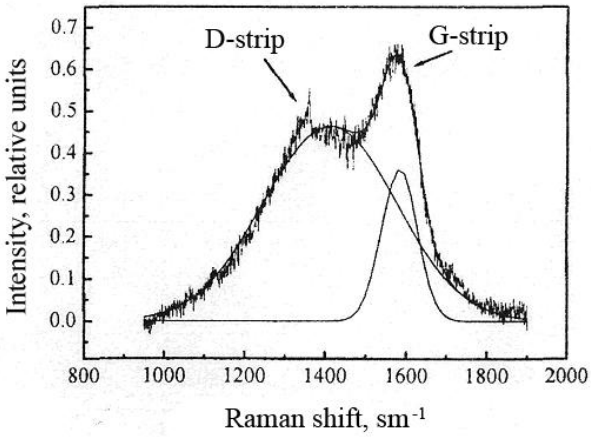


Fig. 6. The Raman spectrum of films of the noncrystalline diamond-like carbon obtained by a thermo-ionic vacuum - arc method. The Gaussian distribution is shown for the D-and G-bands [77].

One can conclude that different methods of preparations of non-crystalline change essentially the concentration ratio of polymorphoids of carbon films (from 90 % sp^2 up to 90 % sp^3).

One more question is important: which is the limit ratio of polymorphoids, in this case, diamond and graphite? It is possible to get more than 90 % of that and other fraction in the noncrystalline film? To have an answer to this question it seems to be necessary, to perform special experiments.

In our point of view the Raman-spectroscopy of crystal carbine films and of the non-crystalline carbon that contains a given fraction of fragments with sp-hybridization of a chemical bond have not been yet carried out. It is possible to predict with confidence, that changing the concentration ratio of polymorphoids of three polymorphic modifications (Tables 1,2) - diamond, graphite and carbine, - will offer the answer in the corresponding Raman-spectra. It is, of course important to determine carefully the change of the ratio of bands intensities ($I_{diamond}/I_{graphite}/I_{carbine}$), responsible for structural fragments with sp^3-, sp^2-and sp-hybridization of the chemical bonds.

Another problem to be solved is: which is the ratio in the non-crystalline carbon of the:

a) *Cumulene* $(=C=C=C=C=)_n$ and *polyene* $(-C\equiv C-C\equiv-)_n$ chains in carbine polymorphoids, characterized by sp-hybridization of bond;

b) Flat fragments, fragments of spheres, cylinders (tubules) and "bulbs", characteristic for various modifications of graphite, fullerene and other nano-particles in which atoms are linked through sp^2-hybridized chemical bonds;

c) Three-dimensional diamond, lonsdalite poly-morphoids and, probably, nanofragments of others PM, characterized by more complex hybridization of chemical bonds, for example, with participation of d-electrons.

From the resulted data on the structure (concentration ratio of polymorphoids of various PM) and on the properties of the films deposited from the substance dispersed in plasma [62-66], evaporated by thermoionic vacuum-arc method [77], ultradispersed (300 … 3 nanometers) powders obtained by crushing of graphite [60, 61,73], and also the crystal graphite possessing “intra-monolithic dispersion” (Fig. 3 [60, 61]), it is possible to draw the following conclusions:

- during the dispersion of the substance (in particular carbon) by all ways listed above owing to increase of intrinsic pressure in micro(nano)-blocks in monolithic substance and in micro(nano)-particles in milled substance, it is obtained a polymorphic transformation of the polymorphic modification stable under normal conditions (graphite), into the modification stable at higher pressure (diamond) and metastable under normal conditions;
- the changes of the properties of the substance during dispersion occur owing to the change of its structure expressed in the change of the concentration ratio of polymorphoids of various polymorphic modifications in substance.

In the cases of Si, Sn, AgI, GeO_2, MgO [75] similar processes seem to exist.

One can suppose that these conclusions can be propagated for the majority of individual chemical substances.

The formulated conclusions allow to alter a little bit the classical rule of the physical and chemical analysis, the rule of Kournakov-Tananaev [1,2]: the property of the substance is a function of its most fundamental physical and chemical characteristics (chemical composition and structure) is lastly determined by specific polymorphic modifications and dispersiveness of the substance.

5. Certification of the structure of the non-crystalline substance

After our opinion the further development and active application of the concept of polymeric-polymorphoid structure of a noncrystalline substance consists in the large-scale researche on the formation of all the modifications possible for simple and complex substances, i.e. detection and study of all polymorphic modifications, and, also, the definition of external conditions (temperature, pressure, etc.) that limit their existence [78] are necessary. This will create a basis for getting new non-crystalline substances and for a deeper understanding of the already known disordered solids.

The major stage of development of the concept should be the elaboration of specific approaches for a quantitative estimation of the concentration ratio of polymorphoids of various PM in liquid and solid non-crystalline substances [78,79]. The ratio of major polymorphoids is the most important parameter of a nonequilibrium thermodynamic system of non-crystalline substance. This parameter should be used in the designation and standardization of the structure of the non-crystalline substances. The opportunity of application of the certification using polymorphoid concentration as the main controllable parameter, has been discussed in 1993 [38] and thereafter retried in 1996 [11] and 2000 [79]. The first example of such simplified certification (with the density of the substance based on the concentration of various polymorphoids) is that given in Table 1 [28]. The data on CRP of polymorphoids with sp^3-, sp^2-and sp-hybridization of chemical bonds of films of carbon (Table 2 [62]) together with the data got in the study of the properties of these films [62-66] enable us to start j7ust now to certificate some solids on the basis of the parameters such as “width of an optical band gap” and “dark electric conductivity”. The certification of graphite powders can be implemented on the basis of the "CRP-particle size", according to [60,61] (Fig. 5) as it is obvious, that the ratio of the bands of the Raman-spectrum, I_D/I_G, is proportional to CRP of diamond and graphite polymorphoids. Obviously, it is simply to expand these dependences, having other determined properties of noncrystalline substance with a known set of CRP of various PM. More complicated will be the determination of the concentration ratio of polymorphoids in noncrystalline “amorphous diamond”, built, apparently, mainly from diamond polymorphoids with face-centered cubic and hexagonal lattices (in both sp^3-hybridization of chemical bonds), and also from polymorphoids of a crystal modification characterized by cubic volume-centered unit cell [49].

For the estimation of CRP, the comparison of Raman-spectra of the non-crystalline substance with its various crystal PM or of radial distribution function of atomic and electronic density of non-crystalline substance [28,60-66] and crystalline PMs, as well as other methods can be useful. An estimation of CRP will become a powerful tool for the creation and updating of technologies of production of non-crystalline substance with well defined structure and controlled properties necessary for the technologists.

6. Conclusions

In the analysis of the structure and properties of non-crystalline substances is not correct to apply for their characterization the term "amorphous", an ambiguous word used by various researchers.

It is useful more correct to divide the noncrystalline substances into vitreous and nonvitreous (ultradispersible) substances. The last category is subdivided into powders with mainly external dispersiveness and films with high internal dispersiveness (micro-and nanochannels, pores, cavities, torn off chemical bonds).

The analysis of the data on structure of non-crystalline carbon n-C, obtained by electron-, neutron-, X-ray diffraction techniques, EXAFS, NMR, Raman-spectroscopy and molecular-dynamics simulations, implemented on the basis of the concept of polymeric-nanoheteromorphous structures of noncrystalline substance, allows to draw the following conclusion: the noncrystalline carbon is nonvitreous, internally dispersed copolymer of the structural fragments without long-range order (polymorphoids): at least three polymorphic modifications of diamond, graphite, carbine, built from atoms with sp^3-, sp^2-and sp-hybridization of chemical bonds, respectively.

The data of Raman-spectroscopy obtained for samples with a various degree external dispersiveness (powders) and intramonolithic dispersion (characterized by limited extent of long-range order of crystalline regions in a line: high-oriented graphite, poly- and microcrystalline graphite) show an increase in the ratio of intensities of I_D/I_G bands (diamond and graphite) with the development of the dispersion of both kinds, and increase in the concentration ratio of diamond and graphite polymorphoids in the dispersed substance.

The concentration ratio of structural fragments of carbon with various hybridization of the chemical bonds (sp^3-, sp^2-and sp-) in the sputtered films and in dispersed powders changes according to the change of conditions of film preparation, in particular, temperatures of the substrate, and the degree of crushing of graphite samples, resulting in the change of the intrinsic pressure in the particles. The concerned fragments with sp^3-and sp^2-hybridization of the chemical bond agree completely with the p-T phase diagram of carbon.

The concentration ratio of polymorphoids of various polymorphic modifications can and should be used for designing and standardization of the structures.

The main rule of the physical and chemical analysis, the rule Kournakov-Tananaev is pointed out. A new formulation is proposed: the property of substance is a function of its most fundamental physical and chemical characteristics: chemical composition and structure. The structure is determined by specific polymorphic modifications (in the case of individual chemical compound) and on dispersiveness of the substance.

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