

## Methods of Physicochemical Analysis and Multifractal Parametrization in the Process of Diamond Nanostructured Composites Formation at High Pressures and Temperatures

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### Abstract

To study non-equilibrium processes for the synthesis of materials and coatings at the macro, meso, micro and nanostructured levels, it is advisable to supplement the basic principles of physicochemical analysis: continuity – considering the energy dissipation during the formation of structures and phases; conformity – fractal representations of geometric images; compatibility – studying possible ways of the system evolution. The transition from metastable to non-equilibrium processes in the physicochemical analysis of the state diagrams and the corresponding complex topological and fractal models allows determining the possibility and probability of phase transitions and transformations of the structures, as well as the mechanisms of their realization.

Based on the provisions of the physicochemical analysis of the carbon phase diagram, the thermodynamic conditions for the diamond formation are considered as well as the possibility and probability of different mechanisms for the synthesis of diamond nanostructured materials in non-equilibrium conditions. Depending on the state of the particle surface, it is shown that the synthesis of nanostructured polycrystals from nanoscale diamond powders can occur either by a diffusion mechanism or by a method more similar to the catalytic one using a combination of crystallite and polycrystal growth mechanisms due to the reorganization of graphite microgroupings into a diamond structure.

It is assumed that nanoscale diamond particles have catalytic properties and can act as activators of the graphite phase transformation into diamond at high pressures and temperatures. The process parameters of obtaining diamond polycrystalline materials from detonation nanodispersed diamond powders after chemical cleaning and nanoscale diamond powders with non-diamond forms of carbon on the surface are determined.

### Keywords

Nanoscale diamond particles; physicochemical analysis; multifractal parametrization; carbon state diagram; high pressures and temperatures.

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A distinctive feature of synthetic diamond and diamond-like materials is their high hardness and the ability to produce sharp edges of blade and self-sharpening abrasive tools, which allows ensuring high reliability, durability and long service life of diamond tools [1, 2].

The basis for obtaining diamond nanostructured materials are irreversible phase transformations of carbon and other materials at high pressures and temperatures [1, 2]. For controlled crystallization from melts, it is important to analyze phase state diagrams,

according to which it is possible to choose process parameters, first of all, pressure, temperature, and their changes over time [3, 4].

### The physicochemical analysis of non-equilibrium systems

**Basic principles.** To investigate the structure and phase, to determine their number is performed with the physicochemical analysis of diagrams, i.e. geometric images of relationships: composition – system property

[3]. The basis of the analysis is the principles of continuity and conformity [4] formulated by N.S. Kurnakov, as well as the principle of compatibility proposed by Ya.G. Goroshchenko [5]. Due to the non-equilibrium high-speed processes of synthesis and application of materials at the macro, meso-, micro- and nanostructured levels, their state diagrams are metastable [6]. The analysis is complicated by the fact that the processes take place in short periods of time in limited volumes at high pressure and temperature gradients in the presence of active impurities playing the role of catalysts [7]. As a result, it is difficult to determine the position of points and lines describing phase transitions, and their number which increases with the formation of intermediate phases or transitional structures [3]. In this regard, it is necessary to supplement the basic principles of the analysis of physicochemical diagrams to study non-equilibrium formation processes of the material structures and phases at various levels [1].

**The principle of continuity.** With a continuous change of parameters expressing the state of the system, the properties of its individual phases change continuously. The properties of the system as a whole also change continuously, provided that new phases do not arise and old ones do not disappear [4]. The principle of continuity affects the formation and disintegration of the phases in the physicochemical system, described by the Gibbs equation [8]:

$$F = K + P - C,$$

where  $F$  is the number of homogeneous phases, by which we mean masses differing in composition and thermodynamic properties;  $K$  is the number of components sufficient to determine the composition of any phase;  $P$  is the number of variable fields imposed (pressure, temperature, gravitational, electric, magnetic);  $C$  is degrees of freedom, i.e. the number of parameters that can be arbitrarily changed without changing the number of the system phases [3].

**The principle of conformity.** Each composition of the phases that are equilibrium in the system corresponds to a specific geometric pattern on the diagram. The physicochemical diagram is a closed complex of points, lines, surfaces, where the concept "system" corresponds to the complex in the diagram, and its various elements are in one-to-one correspondence [4].

According to the principle of conformity: the components  $K$  in the physicochemical system are the points of the diagram that form the graph nodes or the polyhedron vertex  $B$  for the complex; the variables imposed on the field system  $P$  are surfaces or faces  $G$  of the complexes. The lines connecting the vertices  $B$

or intersecting the faces  $G$ , formed by the appearance of new and disappearing of the old phases  $F$  during decomposition, should be marked by the edges  $P$  of the formed graph or polyhedron.

Instead of the correspondences  $K \rightarrow B$  and  $P \rightarrow G$ , we can consider  $K \rightarrow G$  and  $P \rightarrow B$  due to the fact that the formed graph edges  $P$  can be obtained by connecting the vertices  $B$  and intersecting the faces  $G$  [9].

**The principle of compatibility.** Any set of components, regardless of their number and physicochemical properties, can constitute a system. A diagram of any system contains all the elements of the private subsystems of which it is composed. In a common system, the elements of private subsystems are combined with geometric images that arise as a process mapping, with the participation of all components of the common system [5]. The conclusion follows from the principle: the system cannot be divided into pure components that do not contain impurities of other components, since substances exist naturally in a mixture representing a multi-component system [4, 5].

The emerging geometric image can be considered as a multidimensional graph (polyhedron), the projection of which on the plane is the polygon representing a closed graph. If a graph consisting of connected pieces, the total number of which is  $C_v$ , is embedded in a plane, then it breaks it up into a certain number of faces  $G$  [9]:

$$G = C_v - B + P + 1.$$

Then for a connected graph on the sphere ( $C_v = 1$ ), the Euler formula is valid:

$$B + G - P = 2 = C_v + 1 = X$$

The ratio holds for any convex polyhedron. The number  $X$  is the Euler characteristic which shows how many dents ending in holes a polyhedron has. The number of holes is determined by the ratio  $d_0 = 1 - X / 2$  [3, 9].

**Thermodynamics of non-equilibrium processes in a dissipative system.** The Gibbs equation is intended for the analysis of a closed, equilibrium physicochemical system [8]. It is also applicable to an open system, when external flows of energy and substances are dissipated by dissipative structures [6]. The dissipation function  $\psi$  at the absolute temperature  $T$  and the entropy production  $\sigma$  [10]:

$$\psi = T\sigma = Td\varepsilon / d\tau,$$

due to the second law of thermodynamics increase ( $\psi \geq 0$ ,  $\sigma \geq 0$ ) with time  $\tau$ .

In closed conditions, in the process of evolution with  $d\varepsilon \geq 0$ , the system moves to equilibrium, in which  $\varepsilon = \max$ ,  $d\varepsilon = 0$ . The entropy production does not increase  $d\sigma \leq 0$ . In the open system, the condition of evolution is preserved  $d\sigma^* \leq 0$ , and the equilibrium condition implies  $\sigma = \min$ ,  $d\sigma = 0$ . For the time derivative:

$$d\sigma/d\tau \leq 0.$$

According to the fundamental Prigogine – Glensdorf theorem [10], in time evolution  $\tau$  to a stationary state, arbitrary systems with immutable boundary conditions fulfill:  $d\sigma \leq 0$  – the evolution condition;  $d\sigma = 0$  – the stationary condition;  $\delta\sigma \geq 0$  – the stability condition.

As a result, the Gibbs equation with constraints on the entropy production, according to the Prigogine-Glensdorf theorem, allows us to consider open non-equilibrium systems [6, 10].

Since between the system of arbitrary, unlimited composition, described by the Gibbs equation:  $K + P - F - C = 0$ , and the state diagram, i.e. the geometric image of a system of any dimension, described by the Euler formula:  $B + G - P - X = 0$ , there is a unique correspondence. The degrees of freedom of the system should be considered as the Euler characteristics of the polyhedron:

$$X = C = C_v + 1 = 2 - 2d_0.$$

The number of connected pieces of the graph  $C_v$  and the number of holes  $d_0$  of the geometric image make it possible to distinguish groups of interdependent parameters in the system [6]. According to the Gibbs equation, the degrees of freedom  $C$  in the system allow controlling the forming phases  $F$  in the processes of synthesis and application of materials with an unchanged number of components  $K$  of the used substances and flows of input energy  $P$  [1, 6].

#### ***The fractal dimension of the dissipative system.***

Due to the sensitive dependence on the initial conditions, it is rational to present the state of the physicochemical system as an attractor. The sensitive dependence on the initial conditions requires the dimension of the attractor, satisfying the inequality  $C > 2$  [11].

The three-dimensional flow in the phase space should provide  $C < 3$ , since the volumes in the phase space decrease with time in the case of a dissipative system (possessing an attractor). Therefore, the volume of the attractor must be zero, which in the three-dimensional phase space leads to the inequality  $C < 3$  [1, 11].

An attractor that can represent a chaotic mode (and thus have the sensitive dependence on the initial conditions) must be such that the inequality  $2 < C < 3$  is fulfilled. Attractors that satisfy this inequality have a non-integer fractal dimension [11, 12]. A dissipative dynamical system can become chaotic if the dimension of the phase space is greater than two. Such chaos (with a small number of degrees of freedom) is due to the sensitive dependence on the initial conditions of trajectories on the strange attractor. In order to avoid the unpredictability of the behavior of deterministic flows of energy and substances during their dissipation, the system needs to provide less than three degrees of freedom.

The emergence of new and the disappearance of old phases and structures under the condition of intermittent, abrupt state changes raise the question of the structural and phase stability of the physico-chemical system. This requires studying the state of the dissipative system in the vicinity of remarkable points of diagrams and especially singular points in which the composition is preserved with changing external conditions.

***The study of singular elements of the topological model.*** The singular points in the diagram show the formation of new, undissociated, chemical compounds – daltonides. In contrast, partially dissociated compounds, bertholides, form maxima and minima on the lines, but do not form singular points on the diagram [3].

According to *the principle of conformity*, a certain geometrical image must correspond to each phase in the diagram, and in accordance with *the principle of continuity*, this image must be continuous. However, when an undissociated compound is formed, not one but two curves correspond to the liquid phase, the singular intersection point of which shows the composition of the formed chemical compound.

To eliminate this contradiction N.S. Kurnakov and S.F. Pearl proposed to consider these two lines as two branches of the same curve which intersects itself. The intersection is a double nodal point, in the neighborhood of which the stability of the emerging states of the system should be considered [4].

It should be noted that a loop added at the singular point is not purely hypothetical. The formation of the loop, according to *the principle of compatibility*, shows the formation of a new undissociated chemical compound from the compound dissociated in the solution – the transformation of bertholides into daltonides, with the formation of a singular point at which the number of degrees of freedom  $C$  of the system does not change [6].

The development of the principles of the physicochemical analysis based on the thermodynamics of non-equilibrium systems allows analyzing transients and structures, describing the degrees of freedom  $C$  of the system with non-integral values and forming phases – with fractal and multiplicative parameters  $F$ .

### Fractal parameterization of cluster structures

**Fractal parameterization and percolation of media.** The synthesis of nanostructured materials, the modification of surface layers by energy flows, the deposition of films and coatings are accompanied by the formation of layered structures. The transition zones are formed between the layers, the dimensions of which affect the material properties [6].

The study of interfacial surfaces, the determination of the optimal modes of formation of structures and the boundaries of the layers allows to control the quality of the product [1]. The boundaries of the layers can be considered by analogy with the deviations and irregularities of the profile of a rough surface ( $Ra - Rz$ ) [13].

When studying the geometric deviations of the layers boundaries due to a combination of different scale levels of deviations, it is advisable to use fractal representations [1, 12]. The fractal structures of materials and surfaces are very diverse [12]. The most frequently used constructions of inhomogeneous surfaces are based on models of regular fractals – the Koch curve and the Minkowski fractal [14]. Fractals are used to generate objects of a quasi-periodic nature. Their use allows modeling processes that are irregular in nature [12]. The theory of fractals reflects the specific structure of clusters and is promising for describing the properties of inhomogeneous materials [15]. It is similar to the percolation theory for describing the behavior of systems near topological phase transitions, which, by their physical nature, can be very diverse.

Usually, a percolation model is considered for a lattice system in which nodes or bonds are selected with probability  $x$  [16]. With a small  $x$ , the selected sites are mostly isolated, but with an increase in their concentration, clusters appear, i.e. groups of bound particles. With further growth of  $x$ , the aggregation takes on an avalanche-like character and happens simultaneously: particle – particle, particle – cluster, cluster – cluster.

The most important characteristic of the percolation system is the percolation threshold  $x_c$ , when the quantity turns into quality while passing through it. In the system of selected nodes, the

connectivity caused by the appearance of a percolation hypercluster extending across the entire system becomes global [15, 16]. The topological phase transition which has occurred means that the formed structure begins to play the role of the formed independent phase.

Multiscale aggregation implies that the different hierarchical levels of the process are interrelated. Therefore, a characteristic spatial scale is introduced in the system using the correlation radius  $r$  during aggregation. In turn, the density of the fractal cluster  $\rho$  changes according to the power law [14, 15]:

$$\rho(r) = \rho_0 (r/r_0)^{D-d},$$

where  $\rho_0$  is the density of the cluster particle material;  $r_0$  is the average particle radius;  $D$  is the fractal dimension;  $d$  is the Euclidean dimension of space.

The critical indicators of the percolation theory allow to determine the fractal dimension of percolation clusters:  $D(2) = 1.90$  for two-dimensional space and  $D(3) = 2.54$  for three-dimensional space [15].

**The transformation of fractal structures on interfaces.** The analysis of fractal dimensions when changing the basis and increasing the complexity of its meander (Table 1) allowed to form the basic principles of the transformation of fractal structures, their percolation and degeneration during the formation of the interfaces, structures and layers of the product [1].

The increase in the number of elements of the base is easier than increasing the complexity of the meander. With 6 or 10-element meanders having a 3 or 4-element base, the process develops according to the pre-simulation scenario. With 8 or 14 meanders having a 3 or 4-element base, the fractal approaches degeneration.


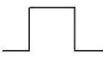


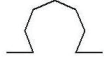




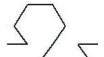

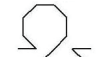

From the structural and energy standpoint, the following sequence of stages in the development of the interfaces of the phases, structures, and layers seems to be appropriate: the growth of structures; increasing the number of elements of the fractal base; the complication of fractal meanders; percolation of layers on the interface; fractal degeneration.

As the fractal structures grow, due to the appearance of defects when the growth mechanism fails, the number of base elements increases. The accumulation of defects leads to a change in the transformation mechanism of the interfaces by the complication of fractal meanders. When the reserves of complication are exhausted, the surfaces are transformed according to a percolation scenario, accompanied by the formation of phases, the growth of structures and the interpenetration of layers.



Table 1

The analysis of fractal dimensions

Meander number, $n$		1	2	3	4	5	6
Fractal fragments	(3 + $n$ )-elements: 3-element base						
	(4 + 2 $n$ )-elements: 4-element base						
							
Dimensions	$D_3^n = \frac{\lg(3+n)}{\lg 3}$	1.262	1.465	1.631	1.772	1.893	2.000
	$D_4^n = \frac{\lg(4+2n)}{\lg 4}$	1.293 (1.404)*	1.500	1.661	1.793	1.904	2.000
Dimension change	$\Delta^n = D_4^n - D_3^n$	0.031 (0.142)*	0.035	0.030	0.021	0.011	0.000
	$\Delta_3 = D_3^n - D_3^{n-1}$	—	0.203	0.166	0.141	0.121	0.107
	$\Delta_4 = D_4^n - D_4^{n-1}$	— (0.111)*	0.207 (0.096)*	0.161	0.132	0.111	0.096

\* Possible existence of transitional structures.

This transformation leads to the degeneration of fractals, the formation of new structures and phases. The change of transformation mechanisms of the interfaces in the material occurs due to the complication of fractals, through their percolation to degeneration, due to multi-scale aggregation and is accompanied by the growth of fractals, an increase in the number of base elements and the possible complication of fractal meanders [1].

#### The multifractal analysis of material structures.

The formed principles of fractal structures transformation on the interfaces of the phases, structures and layers allow to analyze the processes of synthesis of nanostructured materials, to determine the formation mechanisms and quantitative characteristics of nanostructures.

The analysis of the structures of synthesized materials was carried out using the method developed at the Baikov Institute of Metallurgy and Materials Science, RAS. The developed computer program MFRDrom allows processing images up to 2000–2000 pixels in the range of the control parameter  $q \in [-200; +200]$  [17, 18]. The program processes images from a scanning electron microscope and provides information for particular parameters of multi-fractal spectra based on the results of statistical

processing of correct spectra with an arbitrary sample of image processing scales. The information analysis was carried out according to the following multi-fractal parameters [17]:

$\Delta_q = D_1 - D_q$  is the degree of ordering and symmetry breaking for the overall structure configuration as a whole. An increase (in absolute value) in  $\Delta_q$  shows that a greater number of periodic components occur in the structure, while the system is pumped with information (negentropy) and the degree of symmetry breaking increases in it;

$f_q$  is a measure of the structural homogeneity, an indicator of the distribution of the structural unit elements in the Euclidean space encompassing the structure. The larger  $f_q$ , the more uniform the structure is for the canonical versions of the spectra, and vice versa, for the pseudospectra;

$D_0, D_1, D_2, D_q$  and  $D_{-q}$  are the elements of the spectrum of Renyi dimensions which characterize the distribution of the measure in the studied space regions;

$D_0$  is the Hausdorff-Besikovich dimension (in the study of the multi-fractal properties of regular fractal structures, the fractal dimension appears as  $D_0$ );

$D_1$  is the informational dimension;

$D_2$  is the correlation dimension.

Strictly speaking, the term “dimension” is applicable only to  $D_0$ , since the value  $q = 0$  removes the differences between the measures of different cells, and we are dealing with the configuration of the carrier “in its pure form”. The values of the remaining “dimensions”  $D_q$  are determined both by the configuration of the carrier and its measure. In other words, they are also called generalized Renyi entropies [17, 18]. The Renyi entropy spectra  $D_q$  at large positive  $q$  reach saturation. The characteristics of  $D_q$  carry some quantitative information about the thermodynamic conditions of the structure formation under study. It can be said that large values of  $D_q$  (for  $q \gg 1$ ) correspond to large values of entropy [17, 18].

To ensure the performance of materials during operation, the ability of their structures to adapt to external loading is of great importance. The adaptation refers to the ability of the material structure to transform without any irreversible damage (destruction).

The transition from the reversible material damage to the irreversible one is a non-equilibrium phase transition. Understanding the mechanism of this transition provides important information about the critical state of the material, within which the structure is able to adapt to changing external conditions without losing its integrity.

**The adaptation of material structures to external loads.** The conditions for reaching the boundary state of inorganic fractal media were considered in [19] and it was found that the relationship between the fractal dimension  $D_f$  and the Poisson ratio  $\nu$  for flat fractal media is determined by the relation

$$D_f = 1 + \nu.$$

If we take into account that the adaptation of the material structure to an external effect is related to the symmetry violation, which is realized under different deformation mechanisms (re-crystallization, quasi-elastic, elastic-plastic, plastic and percolation), then this ratio has the following form for multi-fractal structures:

$$D_q^C = 1 + \nu_{\text{eff}}^*,$$

where  $\nu_{\text{eff}}^*$  is the critical effective Poisson's ratio controlling the transition from one adaptation mechanism to another;  $D_q^C$  is the threshold value of  $D_q$  corresponding to the loss of stability of the

structure adaptation to external effects during the implementation of this deformation mechanism.

Therefore, when changing the deformation mechanism that controls the structure adaptation to an external effect when the maximum degree of symmetry is reached, the critical value of the degree of order  $|\Delta_q^C|$  is determined by the achievement of the critical value of the effective Poisson ratio  $\nu_{\text{eff}}^*$ . The self-similar transition from one controlling mechanism of the structure deformation to another is determined by the principle of cumulative feedback, according to which the final value  $(\Delta_q^C)_{i+1}$  for the previous adaptation mechanism is the initial one for the subsequent one.

The critical value  $D_q^C$ , when  $|\Delta_q| = |\Delta_q^C|$ , can be used to calculate the  $Z_A$  index, which integrally takes into account the stock of the structure ability to adaptation in order to maintain the sustainable development of the system and its integrity at the macro level.

Since the symmetry breaking due to external influence manifests itself in the form of specific multi-fractal structures, it is obvious that multi-fractal parametrization of material structures, that are subject to different types of effects, is a direct method for determining the adaptive properties of the structure [20].

The concept of fractal symmetry of the material structure and the interpretation of the multi-fractal nucleation as a result of breaking symmetry developed on its basis allows using the information on symmetry breaking to analyze the mechanism of a fractal structure adaptation to an external effect. Taking into consideration this fact, a connection between the critical value of the generalized Rényi dimension  $D_q^*$ , corresponding to the degeneration of the multi-fractal set with maximum symmetry breaking, and the degree of order of the structure  $|\Delta_q|$  for this state is established.

The degeneration of the multi-fractal upon reaching the maximum symmetry breaking is determined by the condition:

$$D_q^* = (1 - |\Delta_q|/2) D_1 = A_m^{\max} D_1,$$

where  $D_1$  is the boundary value  $D_q$  the boundary value corresponding to the multi-fractal nucleation at a given  $\Delta_q$ ,  $A_m^{\max} = 1 - |\Delta_q|/2$  is the maximum value of a measure of the structure ability to adapt  $A_m$ , which is reached at  $D_q^*$ .

The map of the material structure to the external effects in general form is formed from three areas – adaptation, degradation and irreversible damage (destruction). The adaptation area is bounded by a vertical line at  $\Delta_q = 0$ , a horizontal line with  $D_q^* = 2$  and an oblique line  $D_q^C$  characterizing the transition from reversible to irreversible damage.

The boundary separating the adaptation area from the degradation area corresponds to a vertical segment at  $\Delta_q = 0.5$ , which corresponds to the amorphization of the crystal structure in local areas of metals and alloys subjected to deformation [21].

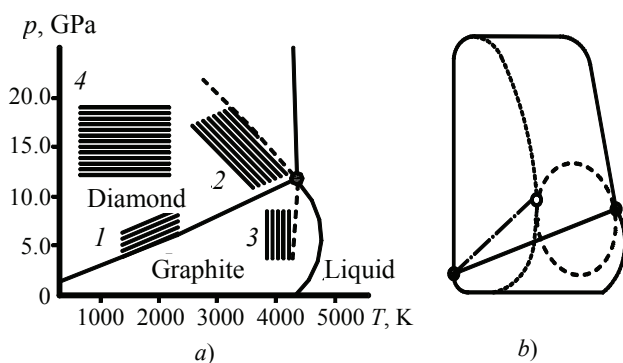
The capacity of the structure ability to adapt  $Z_A$  to an external effect is calculated by the formula:

$$Z_A = D_q^* - D_q^C.$$

The maps of the material structures adaptation to external influences, presented as dependencies of fractal dimensions on the degree of order in the areas of the material adaptation and degradation, make it possible to visually compare structures in a batch of products, as well as compare structures of different parts of the product surface with each other.

### The graphite-diamond state diagram

**The carbon phase state diagram.** According to the thermodynamics of open non-equilibrium systems based on the self-organization principles [1, 6], we consider the synthesis of superhard materials [2, 7] using the example of carbon phase diagrams. These diagrams [1, 7] show the boundaries between graphite, diamond and their liquiduses (Fig. 1). At pressures



**Fig. 1. Carbon state diagram (a) and the topological model corresponding to the system (b):**

- 1 – catalytic synthesis of diamond from graphite;
- 2 – direct transition of graphite to diamond;
- 3 – direct transformation of diamond into graphite;
- 4 – direct conversion of graphite to lonsdaleite

above 60 GPa, there is a section indicating the existence of the metallic carbon-3 phase [2, 7].

The study of Me–C systems at high pressures showed [1, 7] that diamond originates and grows in conditions of supersaturated carbon solution in a metal that is supersaturated with respect to diamond, but is not sufficiently saturated with respect to graphite.

When studying the mechanism of diamond formation, it is necessary to consider nucleation. The crystal nucleus has a certain structure, size and surface properties. When it appears, the metastable phase becomes more stable. It has been established [7] that graphite crystallites are sources of diamond crystallization centers and are particles of graphite with a high degree of order. When dissolved by metal, these particles reach a certain size and become centers of diamond crystallization.

The diamond formation at static pressures in a carbon dissolving system is the growth of crystals from a supersaturated carbon solution in the molten metal, while the growth of crystals is due to the diffusion of carbon atoms through the molten metal. The sources of crystallization centers are graphite crystallites [7].





At pressures greater than 12 GPa and temperatures above 4000 K, the direct transformation of graphite of martensitic type into diamond takes place when the graphite lattice is transformed into a diamond one without the presence of a metal, i.e. a carbon solvent. It is natural to assume that at pressures and temperatures lower than those corresponding to the direct transition, in the presence of a carbon solvent, crystals can grow due to the diffusion of its atoms and graphite microgroups through the molten metal.

**The topological model of a non-equilibrium system.** Based on the experiments [2, 7], taking into account the introduction of additional components and the formation of new system bonds with a change in the number of degrees of freedom, its stability and equilibrium, the topology of the carbon state diagram was considered. The model was built according to the phase state diagram based on the analysis of the number of degrees of freedom in the system (Table 2) in metastable states, taking into account the stability of non-equilibrium processes during the system evolution to a stationary state.

The analysis of the bonds formation on a topological model shows that the addition to the singular (dark) point only of a loop covering metastable states (the dashed line) provides the system with three degrees of freedom ( $C=3$ ) and the prospect of transition to a chaotic state without stabilizing non-equilibrium processes. The stabilization in one of the

Table 2

## Formation of bonds in the carbon state diagram

Formation of the system bonds (see Fig. 1b)	Degrees of freedom of the physico-chemical system $B + G - P = C_v + 1 = C$
	$2 + 3 - 3 = 1 + 1 = 2$
	$2 + 5 - 4 = 2 + 1 = 3$
	$3 + 6 - 6 = 2 + 1 = 3$
	$3 + 7 - 8 = 1 + 1 = 2$

points (light) of the limit state (the dash-dotted line) with the introduction of an additional component is also impossible, since  $C=3$ . Therefore, considering the node (the bright point) as the formation of a new chemical compound with the addition of lines separating it from the solution (the dotted line), it is possible to ensure the stability of the system during its evolution to a stationary state ( $C=2$ ).

Thus, the synthesis of diamond goes through direct and catalytic routes or perhaps a combination of them. The synthesis of diamond from graphite, depending on the conditions of diamond crystals formation, can be carried out by various mechanisms:

1) extreme conditions (direct transfer of graphite to diamond without carbon solvents) when the transformation of the graphite lattice into diamond (martensitic type) occurs;

2) the synthesis of single-crystal diamond (low supersaturation) when the crystal growth occurs due to the diffusion of carbon atoms through the molten metal;

3) the synthesis of polycrystalline diamond (high supersaturation) when the growth of crystals is due to the diffusion of microgroups which include graphite and carbon atoms through the molten metal.

**The carbon phase diagram based on the particle size.** The boundary of the diamond and graphite stability area was first defined in [22] and then refined in [2, 7]. For graphite and diamond crystals of small sizes, where the contribution of surface energy to the thermodynamic potential is significant, the conditions of the graphite – diamond phase equilibrium differ from the carbon states predicted by the conventional phase diagram. There are suggestions [23] that, using the nanoparticles, the diamond becomes a thermodynamically stable form of carbon.

The boundary of the diamond stability area should then be described by a certain surface in the space of pressure, temperature, and dimensions ( $r, e$ ) of crystallites [24]. An example is the graphite-diamond phase equilibrium surface constructed with the experimental data in the interval  $T = 0-3000$  K (Fig. 2).

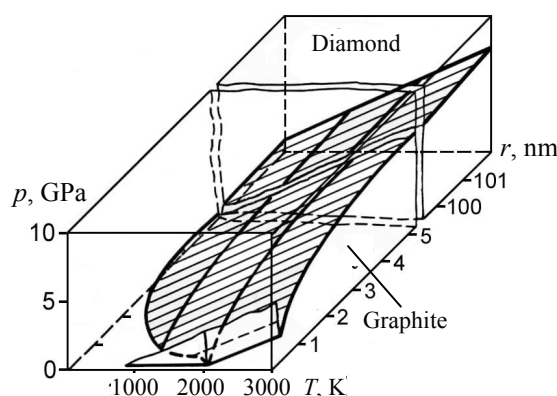


Fig. 2. The carbon phase diagram based on the particle size [24]

When the crystallite size decreases ( $r \leq 10$  nm), the phase equilibrium surface significantly deviates from the plane towards low pressures, and at  $r \approx 1$  nm, the diamond is stable in the absence of external pressure to  $T \leq 2,000$  K. The size range in which one can actually expect the appearance of crystallites with a diamond structure in the absence of pressure is  $r \approx 0.3-1.5$  nm.

One of the ways to transfer graphite to diamond is local heating of crystallites formed on the sample surface. As a result, films with properties close to those of diamond crystals are formed.

For nanodispersed diamond particles of detonation synthesis, the thickness of the surrounding amorphous carbon layer is the order of the interatomic distance [25]. In the case of shock-induced coalescence of detonation nanodiamonds under weak dynamic loading with an amplitude of 10 GPa, nanoclusters with excited crystal lattices interact with each other. As a result, covalent bonds can be formed between the outer atoms of the crystal grains of the contacting particles. Due to the short duration of the pressure pulse, ( $10^{-5}$  s), it can be assumed that the growth of particles occurs mainly under metastable conditions for diamond on the carbon phase diagram (the absence of pressure and elevated residual temperatures).

During the cooling of the sample, two subsystems of particles with average sizes of  $1.5 \cdot 10^{-5}$  and  $1.5 \cdot 10^{-4}$  m are formed. The combination of calculation and experimental data favors the growth model of diamond-like structures under loads that exclude the formation of a liquid phase. This is confirmed by a number of experiments in which the transformation of nanoparticles of graphite, onionic carbon into diamond by heating without external pressure was observed [26]. At relatively low static pressures corresponding to the stability area of graphite, for example, diamond crystals



100–800  $\mu\text{m}$  in size were obtained from a fullerene-containing mixture at  $P = 2$  GPa and  $T > 1300$  K in the presence of carbon metal-solvents [7].

**The synthesis of nanostructured diamond-based materials.** Due to low compaction ability and tendency to collective re-crystallization of nanoscale diamond particles, the search for new technological solutions that would allow obtaining high-density nanostructured material on their basis is necessary. The use of traditional methods of pressing and sintering for the production of nanostructured ceramics based on diamond turned out to be ineffective [27].

Pressings from nanoscale diamond powders have a high initial porosity (up to 60 %), while the content of oxygen-containing impurity groups, gases on the surface of particles can be up to 15–20 %. Therefore, during high-speed sintering under static and dynamic conditions in the pressure range of 2–8 GPa, the sintering mechanisms change drastically compared with the sintering of micron-sized diamond powders [27–29].

The technology of polycrystalline materials from nanoscale diamond powders at high static pressures should be considered.

#### An experimental technique in high static pressure conditions

The thermobaric treatment of nanoscale diamond powder was performed in an “anvil with a well” high-pressure apparatus at pressures of 2.5, 5.0 and 7.7 GPa and temperatures from 1,400 to 2,400  $^{\circ}\text{C}$ . As a pressure transmitting medium, a container of lithographic stone was used, inside of which a tubular graphite heater with

the test material was placed. To estimate the pressure in the synthesis chamber, a calibration method, based on the comparison of the press effort and the pressure of the polymorphic transformation in the reference material, which used Bi and PbSe, was used at room temperature. The temperature control was performed using chromel-alumel and platinum – platinum – rhodium thermocouples.

The nanodiamond powder of detonation synthesis produced by NP CJSC “Sinta” (Minsk, Belarus) with a particle size of 4–10 nm, purified from non-diamond forms of carbon and containing non-combustible impurities in an amount of up to 1 wt. % was used during the experiment.

The cylindrical samples with a height of 5 and a diameter of 6 mm were pressed from the diamond powder into a steel mold under a pressure of 500 MPa and then were placed in a container with a heater for the subsequent thermobaric treatment.

#### The production of diamond-based materials by compacting nanoscale diamond powders under high static pressures

**The synthesis of nanostructured polycrystals from purified diamond powders.** In the first version, the powders were sintered in the state of supply (after chemical cleaning from impurities and non-diamond forms of carbon) under conditions of high pressures and temperatures, both in the stability and metastability areas of diamond (Fig. 3, 4).

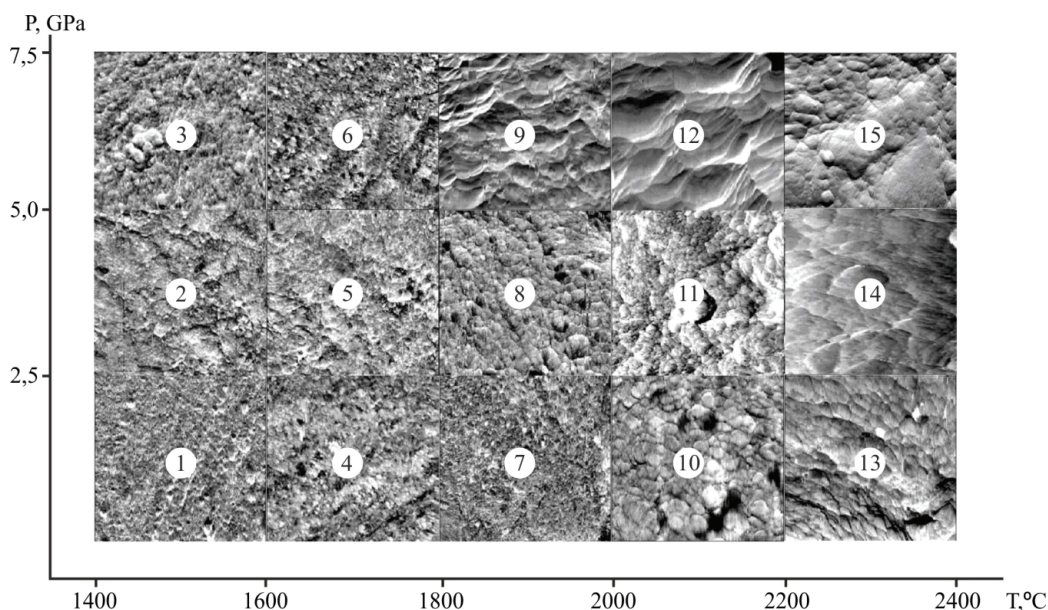
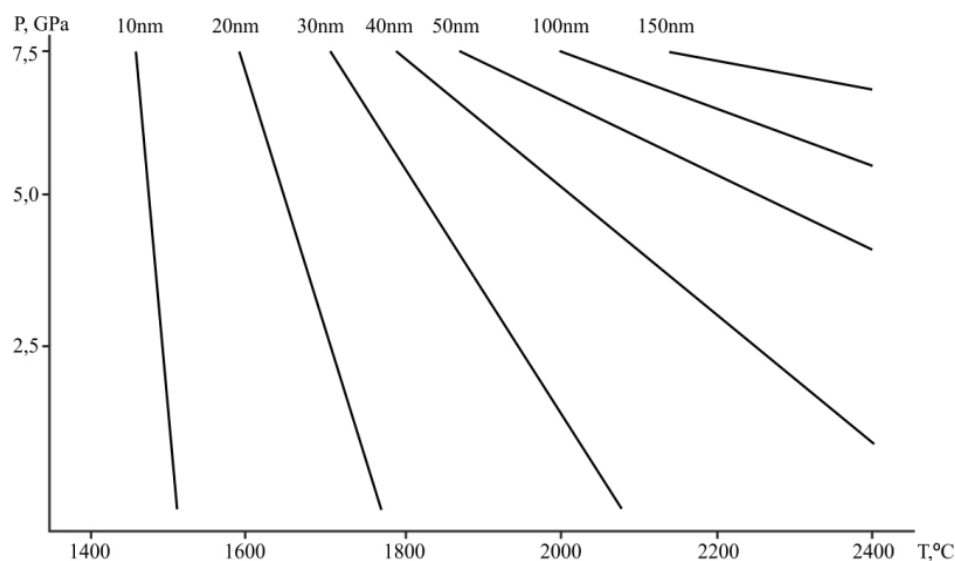
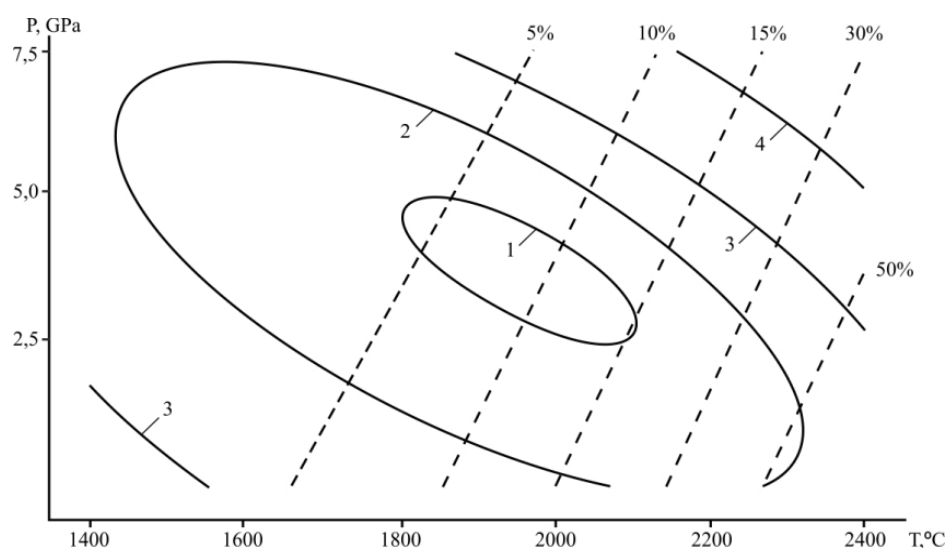


Fig. 3. Structures of polycrystalline material fractures sintered from purified diamond powder after thermobaric treatment for 10 s



**Fig. 4. Dimensions (in nanometers) of diamond crystallites after the thermobaric treatment of purified nanodiamond powder**



**Fig. 5. Fractal characteristics of the polycrystalline material structures sintered from purified diamond powder under various conditions of the thermo-pressure treatment (see Table 3)**  
(The degree of graphitization for the obtained material is presented in percent)

The formation of the material in this case occurs by the diffusion mechanism [27].

The fractal characteristics of polycrystalline material structures based on purified nanodiamond powder after the thermobaric treatment shown in Fig. 3, with diamond crystallite sizes shown in Fig. 4, were determined using the MFRDrom image processing program [17] and presented in Fig. 5 and in Table 3.

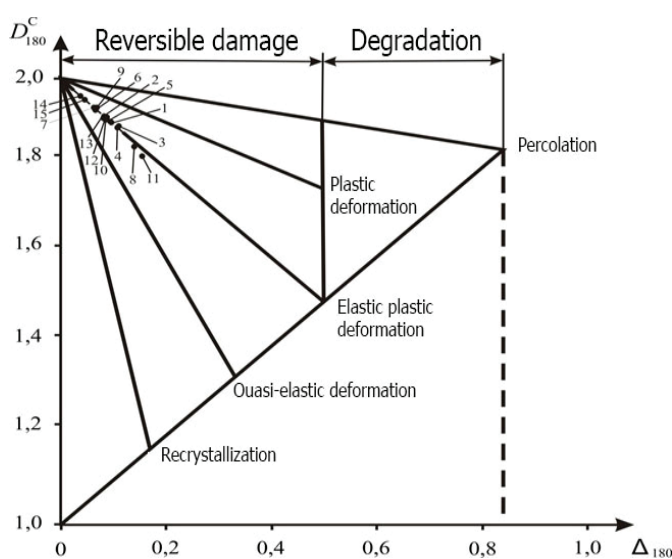
The comparison of the lines determining crystallite sizes (Fig. 4) with the lines of the fractal characteristics of equal level (Fig. 5 and Table 3) shows that the growth of diamond crystallites significantly depends on pressure only at high temperatures ( $> 2000\text{ }^{\circ}\text{C}$ ), while

the fractal characteristics are more dependent on pressure. If we consider the lines of ellipses with maximum diameters, which distinguish the levels of the fractal characteristics, they are almost perpendicular (in the low-temperature area) to the lines of the crystallite size. This suggests that the synthesis of nanostructured materials in addition to the crystallite growth, which is determined by temperature, is accompanied by a multi-level branching of their boundaries. This process may be due to the fragmentation of nanoscale diamond clusters with increasing pressure of the thermobaric treatment.

Table 3

**Fractal dimensions, degrees of ordering and measure of material homogeneity depending on the modes of the thermo-pressure treatment**

Modes of the thermo-pressure treatment (see Fig. 5 and 9)	1	2	3	4
Fractal dimensions, $D_0$	1.985	1.990	1.995	1.997
Degrees of ordering, $\Delta_q$	0.015	0.010	0.005	0.003
Measure of homogeneity, $f_q$	3.700	3.200	2.700	2.500



**Fig. 6. Adaptation map of polycrystalline materials sintered from the purified diamond powder after the thermobaric treatment**

(Adaptation mechanisms: re-crystallization, vasi-elastic deformation, elastic-plastic deformation, plastic deformation, percolation.  $D_{180}^C$  is the threshold value of the Renyi entropy;  $\Delta_{180}$  is a degree of the structure ordering. The numbers of points correspond to the numbers of the structures in Fig. 3)

According to Table 3 and Fig. 3 and 5, a map of the structure adaptation to external effects for the synthesized material was constructed (Fig. 6).

When placing the critical values of indicators of the structure ability to adapt in the field of elastic-plastic deformation, the material structure remains in a stable state, and when leaving it or when approaching the line characterizing the transition from the reversible damage to the irreversible one, there is a violation of the system stability accompanied by a change in the adaptation mechanism.

The adaptation of the material structure to external thermo-pressure effects occurs without degradation and

destruction. In general, the adaptation manifests itself in an elastoplastic area at high temperatures and relatively low pressures accompanying the beginning of the graphitization process.

Analyzing the results of multifractal parameterization and critical indicators of the ability of the coating structure to adapt, we can admit that the material, for which there are large values of mechanical properties, in particular hardness, is characterized by the highest values of fractal dimension and the smallest values of the degree of ordering and measure of the structure homogeneity. Such materials are also characterized by the greatest ability to adapt to external loading.

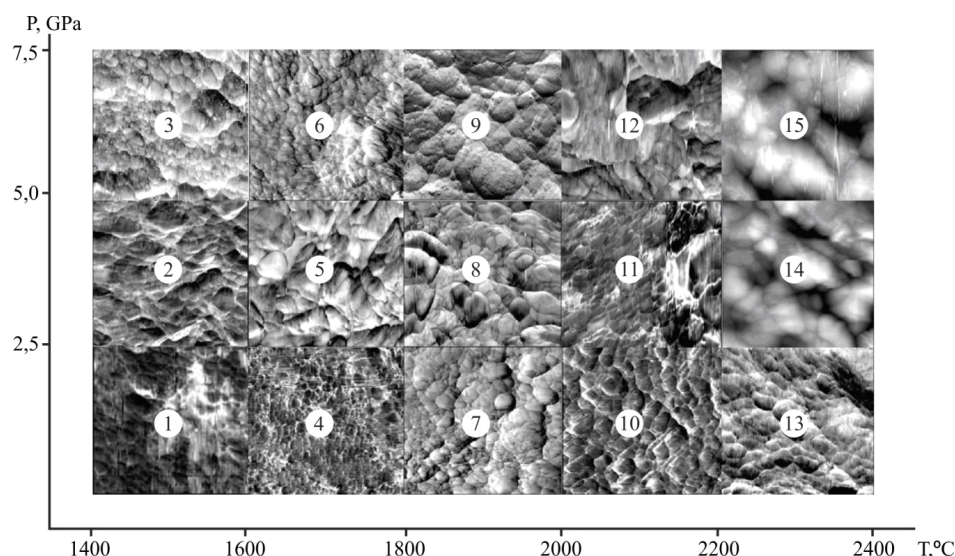
**The synthesis of nanostructured polycrystals from the diamond powders with non-diamond forms of carbon on the particle surface.** In the second variant, the diamond powders with a coating based on non-diamond (graphite-like) carbon with a thickness of about 1 nm, obtained by graphitizing the surface of the diamond particles under the vacuum heat treatment at 900 °C, were sintered under conditions of high pressures and temperatures (Fig. 7, 8). The diamond particle and the surface layer of non-diamond carbon is a metastable system with excess surface energy.

The study of the chemical state of carbon atoms on the surface of nanodiamond particles by the method of Auger spectroscopy showed that carbon atoms are in the same state as in graphite, i.e. in the  $\sigma_s^1 \sigma_p^2 \pi^1$  state, but with a shifted energy position of the  $\pi$ -zone below the Fermi level by 1 eV [30]. This state determines the activity of nanoscale diamond particles as a catalyst; in particular, it facilitates the transition of  $sp^2$  carbon to the  $sp^3$  state in graphite particles in contact with diamond particles [27]. In this case, the reorganization of chemical bonds starts from the surface of graphite particles, as in the case of using fullerene molecules as a co-catalyst for the synthesis of diamonds [31].

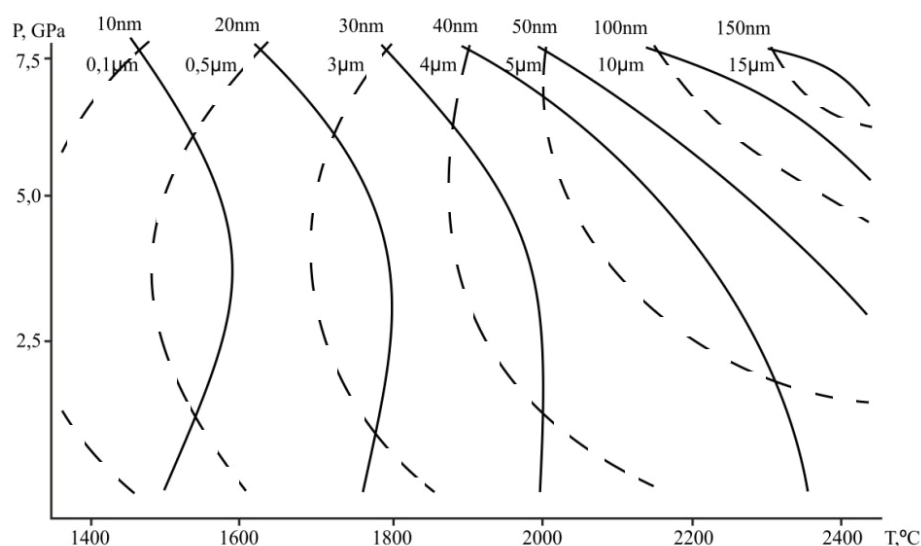
The earlier studies have shown that when processed under conditions of high pressures and temperatures of nanoscale diamond particles with a coating based on non-diamond carbon forms, graphite-like carbon is converted into diamond. Depending on the modes of synthesis, the diamond particles with a size from fractions of a micron to several tens of microns can form [27].

As shown in [32], the formation of the large diamond particles in nanoscale diamond powders can occur as a result of the “self-assembly” of nanodiamonds in the presence of acyclic hydrocarbons or monobasic alcohols.





**Fig. 7. Structures of polycrystalline material fractures sintered from the diamond powders with non-diamond forms of carbon on the surface after the thermobaric treatment for 15 s**



**Fig. 8. Dimensions of diamond crystallites, in nanometers (solid lines) and polycrystalline diamond particles after the thermobaric treatment of the diamond particles with non-diamond forms of carbon on the surface, in micrometers (dashed lines)**

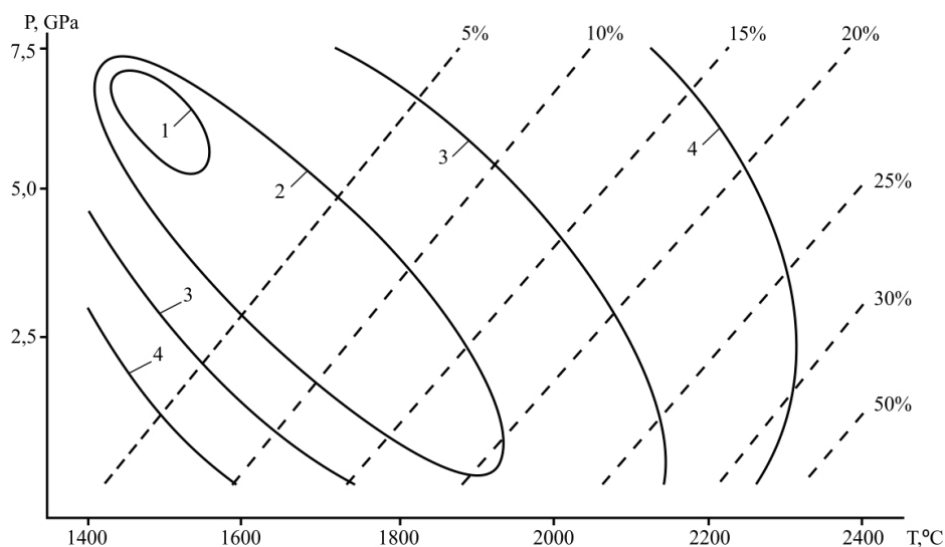
One of the conditions for the formation of nanostructured polycrystalline material from diamond nanopowders with non-diamond forms of carbon is to prevent the growth (re-crystallization) of graphite-like carbon and to keep it in a nanostructured state under conditions of high-temperature heating (according to the graphite – diamond phase diagram in Fig. 2). In this case, it is possible to stimulate the transition of carbon in a graphite-like layer from the  $sp^2$  to  $sp^3$  state by annealing the diamond powders in hydrogen [33, 34] or by doping a layer of graphite-like carbon with boron [35, 36].

In this case, the synthesis of the diamond-based nanostructured material took place in a way more

similar to catalytic using a combination of crystallite and polycrystal growth mechanisms, which resulted in the formation of two subsystems, both due to the diffusion of carbon atoms and the rearrangement of graphite microgroupings into a diamond structure based on the diffusionless (martensitic) mechanism.

The fractal characteristics of polycrystalline material structures based on diamond powders with non-diamond carbon forms on the particle surface after the thermobaric treatment, shown in Fig. 7, with the sizes of nanodiamond crystallites and polycrystalline particles formed from them, shown in Fig. 8, were also determined using the MFRDrom program [17] and presented in Fig. 9 and in Table 3.





**Fig. 9. Fractal characteristics of the polycrystalline material structures sintered from diamond powders with non-diamond forms of carbon on the surface after the thermobaric treatment under different conditions (Table 3)**  
(The degree of graphitization for the sintered material (dotted lines) is presented in percent)

The comparison of the lines determining the sizes of both crystallites and polycrystalline particles (Fig. 8) with the lines of the fractal characteristics (Fig. 9) shows that by averaging the growth of structural components in the two subsystems (nanoscale crystallites and polycrystalline particles based on them) we can make a conclusion about the prevalence of temperature in the processes of growth of the structural components at relatively low temperatures ( $< 1700\text{ }^{\circ}\text{C}$ ) and the most significant effect of pressure on the fractal characteristics of the structures under consideration. The lines of maximum diameters of ellipses, which distinguish the levels of fractal characteristics, are also almost perpendicular to the average between the lines of crystallite and polycrystal sizes.

However, the optimal areas of the fractal characteristics that determine the maximum physico-mechanical characteristics of the material for the powder-sintered diamonds with non-diamond carbon forms on the surface correspond to temperatures ( $\sim 2000\text{ }^{\circ}\text{C}$ ) and at high pressures (7–8 GPa) are almost not associated with the graphitization process.

When the thermobaric treatment of the charge in the *second variant* in a thin surface layer based on non-diamond forms of carbon occurs, they are transferred to diamond (diamond-like carbon), which is stimulated by applied high pressure even at relatively low temperatures of  $1600\text{--}1700\text{ }^{\circ}\text{C}$ .

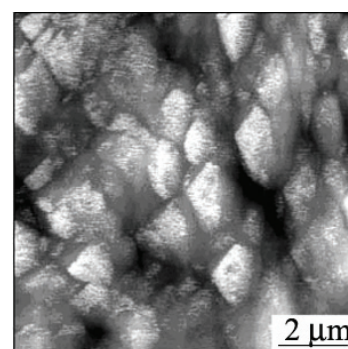
In this case, the initial aggregates of nanoscale diamond particles are combined into larger (polycrystalline) fragments with the preservation of the primary structures. As a result, the formation of particles of submicron and micron size became possible

(Fig. 10) [7]. Using X-ray the diffraction analysis and transmission electron microscopy, it was established that the particles have a substructure characteristic of the initial diamond powders.

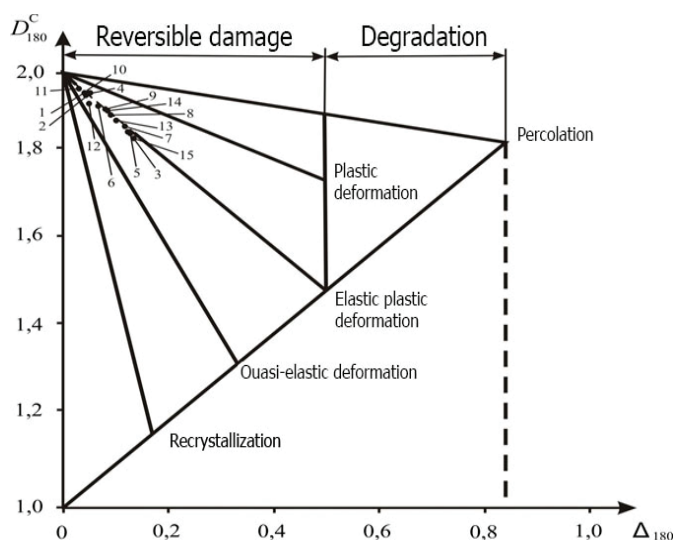
According to Fig. 7 and 9, a map of the adaptation of the synthesized material structures to external influences was constructed (Fig. 11).

The adaptation of the material structure to external effects as well as in the first variant occurs without degradation and destruction. It manifests itself mainly in the elastoplastic area. However, the adaptation is most noticeable at relatively low temperature and high pressure and is associated with the phase transformation of non-diamond forms of carbon into diamond.

Thus, the study of the thermodynamics of non-equilibrium processes for the synthesis of nanostructured materials by compacting nanoscale diamond powders under high pressures and



**Fig. 10. Diamond particles of submicron and micron sizes obtained from nanoscale diamond powders with non-diamond forms of carbon on the surface**



**Fig. 11. Adaptation map of polycrystalline materials sintered from diamond powder with non-diamond forms of carbon on the surface after the thermobaric treatment** (Adaptation mechanisms: re-crystallization, quasi-elastic deformation, elastic-plastic deformation, plastic deformation, percolation.  $D_{180}^C$  is the threshold value of the Renyi entropy;  $\Delta_{180}$  is the degree of the structure ordering. The numbers of points correspond to the numbers of the structures in Fig. 7)

temperatures highlighted two main scenarios of the synthesis due to the diffusion growth of diamond crystallites, stimulated by temperature, and due to the rearrangement of graphite microgroupings into a diamond structure which is activated by applied high pressure.

### Conclusion

In non-equilibrium processes for the synthesis of materials at different structural levels, it is advisable to supplement the basic principles of physico-chemical analysis: *continuity* – by considering the energy dissipation in the formation of structures and phases; *conformity* – fractal representations of geometric images; *compatibility* – the study of possible ways of the system evolution.

The transformation principles for fractal structures in the analysis of synthesized nanostructured materials have shown the feasibility of multifractal parametrization to determine the formation mechanisms of percolation systems.

The transition from metastable to non-equilibrium processes in the analysis of the state diagrams and the corresponding complex topological and fractal models allows to determine the possibility of phase transitions, as well as the mechanisms for their implementation in the synthesis of superhard nanostructured materials.

The findings show that, depending on the surface of the original nanoscale diamond particles, the synthesis of diamond-based polycrystalline materials is implemented in two main scenarios:

- the diffusional growth of diamond crystallites activated at high temperatures;
- the combination of the growth mechanisms of crystallites and polycrystals both due to the diffusion of carbon atoms and due to the diffusion-free (martensitic) transition of non-diamond forms of carbon into diamond realized at high pressures.

The adaptation of the structure of the obtained nanostructured materials to external thermobaric effects occurs without degradation and destruction mainly in the elastoplastic area. For the material based on purified diamond powders, the adaptation of the structure is manifested at high temperatures and relatively low pressures accompanying the beginning of the diamond graphitization process.

For polycrystals formed from diamond powders with non-diamond forms of carbon on the surface of particles, the adaptation of the structure is associated with the phase transformation of non-diamond forms of carbon into diamond and is most noticeable in the low-temperature area at high pressures.

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