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PHYSICOCHEMICAL ANALYSIS OF THE PROCESSES OF FORMATION OF NANODIAMOND-BASED POLYCRYSTALLINE MATERIALS

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Based on the physicochemical analysis of the carbon phase diagram, thermodynamic conditions for diamond formation are studied. The possibility and probability of various mechanisms of synthesis of diamond nanostructured materials under nonequilibrium conditions are considered. It is shown that nanodiamonds possess catalytic properties and can act as activators of the phase transformation of graphite into diamond under high pressures and temperatures. Process parameters for obtaining of diamond polycrystalline materials from detonation nanodiamond powders are defined.

Keywords: polycrystalline materials, nanodiamonds, the phase diagram of carbon, physicochemical system, topological model, synthesis

Introduction

It is possible to investigate structures and phases of materials formed during synthesis and to determine their amounts by making physicochemical analysis of diagrams, which are geometric images of system property-to- structure ratios [1]. The bases for the analysis of physicochemical diagrams are formulated by N.S. Kurnakov two principles, continuity and consistency [2], as well as the third principle, the compatibility proposed by Y.G. Goroshchenko [3].

Due to non-equilibrium of high-speed processes of material synthesis, their phase diagrams are metastable [4]. The phase diagrams analysis is complicated by the fact that the processes run in short periods of time in very limited quantities at high temperature and pressure gradients, in the presence of active impurities, often acting as catalysts [5]. Therefore, it is necessary to extend the basic principles of analysis of physicochemical diagrams to study non-equilibrium processes of structure and phase material formation at macro-, meso-, micro- and nanostructure levels [1]. Phase transitions in carbon in view of their diversity in high-speed non-equilibrium or metastable processes of diamond synthesis are insufficiently studied. To actuate them, ultra-high pressures are usually required; this fact increases the cost and complicates the synthesis of diamond materials.

The work objective is to develop new approaches and process solutions with regard to obtaining nanodiamond-based polycrystalline materials using physicochemical analysis of the carbon phase diagram.

1. The phase diagram of carbon

From the viewpoint of thermodynamics of non-equilibrium open systems based on the principles of self-organization of physicochemical systems [6, 7], we consider the processes of synthesis of superhard materials [8] through the example of carbon phase diagrams. The synthesis of diamond from graphite (Fig. 1 a) at high static pressures (greater than 4.0 GPa) and temperatures (in excess of 1400 K) is carried out in the presence of catalysts, such metals as Ni, Fe, Co, etc. used

as carbon-solvents [9]. However, the determination of the mechanism of diamond formation in the presence of transition metals and their alloys at high static pressures was one of the most difficult problems for a long time.

The study of various physicochemical systems Me-C at high pressures has shown [9] that the diamonds originate and grow in a supersaturated solution of carbon in a metal, which in a certain period becomes supersaturated with respect to the diamond concentration, but undersaturated with respect to graphite concentration. In the study of diamond formation mechanism is necessary to consider the process of nucleation. In the synthesis of a diamond, a crystal nucleus should have a certain structure, size and surface properties.

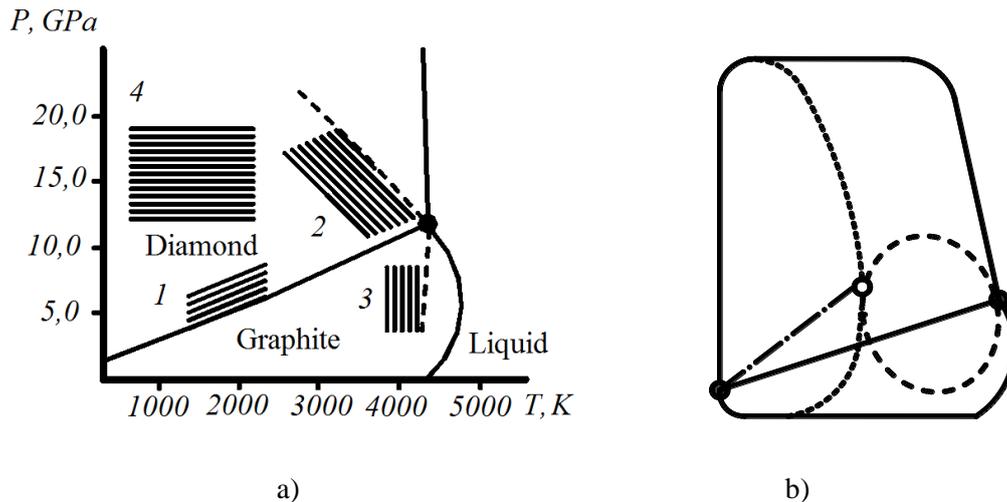


Fig.1. The phase diagram of carbon (a) and the topological model corresponding to the physicochemical system (b): 1 – the area of the catalytic synthesis of diamond from graphite; 2 – the area of the direct transformation of graphite into diamond; 3 – the area of the direct transformation of diamond into graphite; 4 – the area of the direct transformation of graphite into lonsdaleite

When the nucleus emerges, a metastable phase is transformed into a more steady stable phase. Experiments proved [9] that the graphite crystallites are sources of diamond crystallization centers. Crystallites are graphite particles with a high degree of order. Being dissolved by the metals, these particles reach a certain size, and become centers of diamond crystallization.

Therefore, the formation of the diamond at static pressures in the system, dissolving carbon, represents the crystal growth from the oversaturated carbon solution in the molten metal; and the crystal growth is carried out by diffusion of carbon atoms through the molten metal. In this case, graphite crystallites are sources of crystallization centres [10].

At a pressure of greater than 12 GPa and a temperature above 4000 K (Fig. 1a) a direct transformation of martensite-type graphite into diamond takes place. This transition takes place when a graphite lattice transforms into a diamond one without a carbon-solvent metal. It would appear reasonable that under pressures and temperatures lower than those corresponding to conditions for the direct transition, in the presence of carbon solvent, crystal growth is possible due to carbon atoms diffusion and graphite microgroups through the molten metal.

2. The topological model of a nonequilibrium system

Based on the experimental data [5, 9], we consider the topology of the carbon phase diagram (Fig. 1b) according to the model proposed in [10], taking into account the introduction of additional components and the formation of new bonds in the physicochemical system when the number of degrees of freedom, stability and equilibrium of system are changed.

The topological model (Fig. 1 b) was developed on a phase diagram (Fig. 1a), based on the analysis of the number of degrees of freedom of the physicochemical system [10] in metastable states, taking into account the stability of non-equilibrium processes in system evolution to a stationary state.

The analysis of bonds formation in a topological model (Fig. 1b) shows that the addition a loop covering metastable states (indicated by a dashed line) to the (dark) singular point, provides a system by three degrees of freedom and the opportunity of transition to a chaotic state, without the possibility of stabilization of nonequilibrium processes. When introducing an additional component, the stabilization of the limit state (indicated by a dash-dotted line) at one of the points (the light one) is not possible as well. Therefore, only considering the new node (the light point) as the formation of a new chemical compound with the addition of lines that separate it from the solution (dashed lines), it is possible to make a provision for stability of the system in its evolution to the stationary state.

Thus, according to the considered topological model, it is confirmed that the synthesis of diamond proceeds in two ways: direct and catalytic ones; besides, the catalytic and the direct ways can be combined (transition from one to another). Consequently, depending on the conditions of formation of diamond, the synthesis of diamond from graphite can be carried out through various mechanisms:

1) under extreme conditions (conditions of direct transition of graphite into diamond without the use of carbon solvents) the transformation of a graphite lattice into a diamond one takes place (martensite-type transition);

2) in the synthesis of diamond monocrystals (at low supersaturation), crystal growth proceeds due to the diffusion of carbon atoms through a molten metal;

3) in the synthesis of polycrystalline diamonds (at high supersaturation), crystal growth can proceed simultaneously due to diffusion of graphite microgroups and carbon atoms through a molten metal [4, 9].

In the case of graphite and diamond crystallites of small sizes, for which the contribution of the surface energy to the thermodynamic potential is significant, the conditions of graphite-diamond phase equilibrium differ essentially from the predicted by the stated carbon phase diagram. There are assumptions confirmed by calculations [11], according to which, for small size of nanoparticles it is diamond rather than graphite that is a thermodynamically stable form of carbon.

In this case, a diamond stability boundary should be circumscribed by a surface in the "pressure-temperature-crystallite size" space [12].

When the crystallite size is reduced by less than 10 nm, the phase equilibrium surface deviates considerably from the plane in the direction of low pressures; and when its size is about 1 nm, diamond is stable as well in the absence of external pressure to temperatures of about 2000 K. The size area in which one would expect diamond-structured crystallites to occur at "zero" pressure, is in the range of 0.3-1.5 nm.

3. Catalytic properties of nanodiamonds

Diamond possesses high surface energy, which for different facets is from 3 to 10 J/m² [9, 13]. Estimates show that the value of nanodiamond surface energy is in the range of 1100-3900 kJ/kg. In practice, not individual particles but particle aggregates of nanodiamonds are used, which sizes are larger than 100 nm and can reach 1 micron. The active surface is reduced respectively (for 0.1-0.5 micron particles which are formed during nanodiamonds sintering under high pressures, their surface area is by several times less than that of the initial particles).

Detonation-synthesized nanodiamonds represent one of the most chemically reactive of the known forms of carbon with a highly active surface state with the value of up to 400 m²/g; they can make for breaking π -bonds on the surface of graphite particles under high-pressure conditions. Each

nanodiamond crystallite has a large number of unpaired electrons $(3-7) \cdot 10^{19}$ spin/cm³, and it is a powerful multiradical [13, 14].

After chemical removal of impurities and non-diamond carbon forms, on the surface of nanodiamonds there are 1-2 closed graphene layers [14]. The annealing of nanodiamonds in vacuum results in an increase in the number of graphene layers and the formation of onionated carbon globules of fullerene-like structure. Investigation of chemical state of the carbon atoms on the surface of nanodiamonds using Auger spectroscopy showed that in this case a previously unknown chemical state of carbon atoms localized in a graphene monolayer is realized. A similar state in $\sigma_s^1 \sigma_p^2 \pi^1$ graphite is realized as well, but unlike the graphite in the case of nanodiamonds there is no overlapping of π -states of carbon atoms. The surface state of nanodiamonds determines their catalytic activity and makes for $sp^2 \rightarrow sp^3$ transition in the graphite particles contacting nanodiamond crystallites.

In this context, a promising option of obtaining nanostructured polycrystalline diamond powders is the use of nanodiamonds coated with nanostructured carbon [13]. On the one hand, the nanodiamond particles are ready centers of crystallization in the synthesis of diamond using metal catalysts. On the other hand, nanodiamonds themselves may act as activators making for transformation of graphite particles under high pressures and temperatures.

4. Thermobaric treatment of graphitized surface nanodiamonds

The synthesis scheme when the carbon material is applied directly to the surface of the nanodiamond particles seems the most preferable. In its turn, it makes possible:

- to increase the contact area of nano-dispersed particles of diamond and graphite (graphite-like carbon);
- to create conditions for a coherent intergrowth at the "diamond particle-graphite particle" boundary;
- to provide a direct contact of the surface of the diamond and graphite to increase the probability of diamond nucleation due to autoepitaxy;
- to minimize the amount of impurities in the obtained diamond particles.

Based on the carbon phase diagram, which is established for ideal structures of perfect crystals, conditions of possible mutual transformation of graphite and diamond are defined. Besides thermodynamic conditions of the process probability, the rate of such a transformation is important; and it may be very slow [9-11]. Thus, although at low pressures and temperatures the transformation of diamond into graphite is accompanied by decrease in the free energy, and it is thermodynamically quite possible, this transformation rate is low, and the diamond is remained unchanged for a long time. Direct transformation of macroscopic graphite into diamond proceeds at very high pressures up to 15 GPa. So far as the crystal sizes reduce, the energy of facets, edges and tips makes greater contribution to the total free energy of the system. With fairly small crystallite sizes, the contribution of the surface energy to the total energy becomes very significant.

Thermodynamic calculations show [14, 15] that thin layers of graphite deposited on the surface of diamond crystals are especially easy to transform into diamond due to the decrease in the free energy of the system. Therefore, the use of nanodiamonds coated with thin layers of carbon (graphite) will make for sintering of nanodiamonds accompanied by formation of diamond particles of micron range.

Conditions and regimes of synthesis of diamond polycrystalline materials based on nanodiamond particles modified with non-diamond carbon forms were studied experimentally. Nanodiamonds, the surface of which was coated with a thin layer of non-diamond carbon of about 1 nm thick, were sintered under high pressure and temperature conditions. The coating was formed by annealing purified nanodiamonds in vacuum at 10^{-3} mm of mercury in the temperature range of 900-1100°C. The resulting "nanodiamond-nanographite" composite powder was a metastable system, characterized by excess surface energy. The thermal treatment of the powder under pressure

was carried out both in the diamond and graphite stability areas. When processing the obtained "nanodiamond-nanographite" composite powder under high pressures and temperatures, larger particles of diamond of sub-micron and micron size with retained nanostructure were observed to form (Fig. 2).

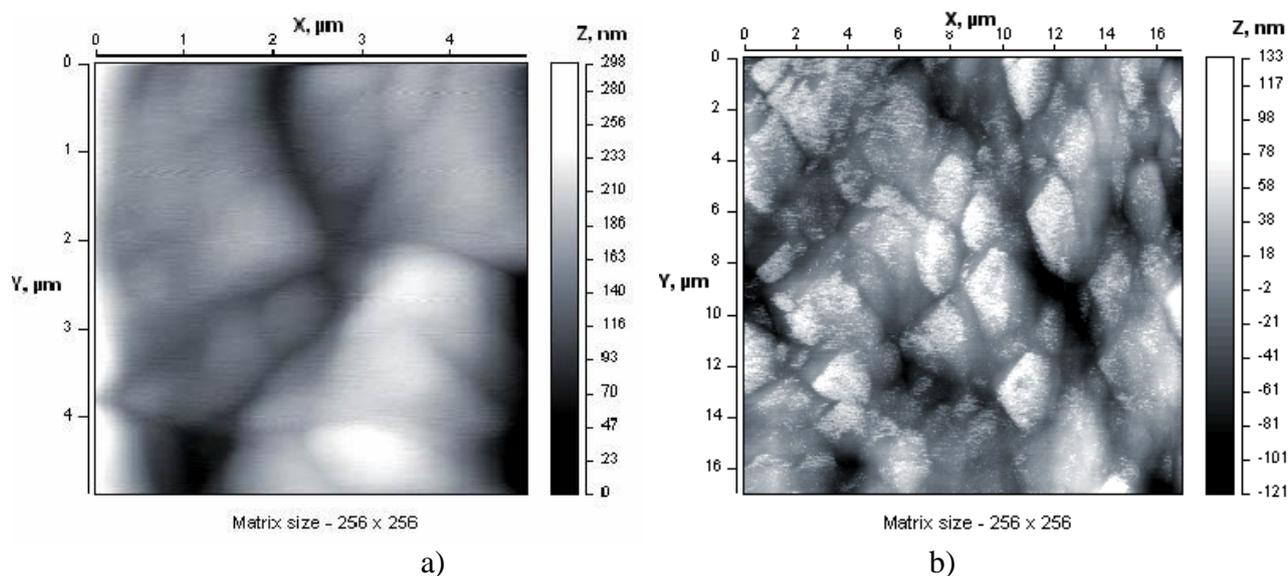


Fig.2. The structure of the polycrystalline nanodiamonds obtained from "nanodiamond-nanographite" composite powder: a) at a pressure of 2 GPa; b) at a pressure of 4 GPa

In the material obtained at a pressure of 2 GPa, diamond crystallite sizes increased slightly compared to the original sizes of the nanodiamond particles and were of 20-30 nm; the polycrystalline particle sizes were 1-1.5 microns (Fig 2a). In polycrystalline samples obtained at pressures up to 4 GPa, polycrystalline diamond particles reached the size of 2-3 microns (Fig. 2b). With increasing temperature up to 2300°C at a pressure of 7 GPa, the formation of polycrystalline diamond particles up to 10 microns and diamond crystallites of up to 150-100 nm sizes was observed.

Conclusion

1. According to the considered topological model, it is confirmed that the synthesis of diamond proceeds in two ways: direct and catalytic ones; besides, the catalytic and the direct ways can be combined (transition from one way to another).

2. In the case of graphite and diamond crystals of small sizes, for which the contribution of the surface energy to the thermodynamic potential is significant, the phase equilibrium conditions graphite-diamond differ essentially from the predicted by the stated carbon phase diagram. The size area of carbon particles in which diamond-structure crystallites are expected to occur at "zero" pressure, is in the range of 0.3-1.5 nm.

3. During processing of nanodiamond-based "nanodiamond-nanographite" composite powder under high pressures and temperatures, nanostructured diamond particles of submicron and micron sizes are formed.

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