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Cluster Mechanism of Formation of Micropolycrystalline Diamond Aggregates

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The structure of micropolycrystalline aggregates of the carbonado and ballas types determines their strength properties. The authors of [1, 2, and others] focused attention on the porous structure of natural and synthetic micropolycrystalline diamond aggregates. In some cases, pores can be filled with different phases (syngenetic and/or epigenetic). In other cases, they are empty. The strength characteristics of diamond aggregates can be influenced by a comparatively low dislocation density of diamond crystallites [3] and the second phase (inclusions of crystal-forming medium), which is more elastic than diamond and can play the role of absorber of dynamic loads [4]. This puts forward the problem of investigating the mechanism of formation of micropolycrystalline aggregates based on the example of the graphite + metal-catalyst model system depending on the thermodynamic parameters and physicochemical state of the medium.

In this work, we use the term metal-catalyst (MC) because we consider the role of carbon-dissolving metals, which activate the process in a broad sense: (1) the metal takes part in dissolving graphite with the formation of metastable complexes (carbide complexes); (2) carbide complexes, which possess the elements of graphite, metal, and diamond symmetry, facilitate an increase in carbon diffusion through a metal film into the crystal; (3) carbide complexes change their symmetry during the interaction with crystal phonons in the adsorption boundary layer (saddle point at the potential energy surface) [5, 6]), which leads to the separation of carbon and metal and incorporation of carbon into the metal matrix, while the metal remains in the metal film with subsequent repetition of the physicochemical cycles described above.

Among many factors influencing the structure and properties of diamonds, including carbonado-type formations (and ballases), the thermodynamic and kinetic conditions of their formation should be emphasized first of all [1, 6–8].

The Gibbs thermodynamic potentials of graphite and diamonds are used in the thermodynamic approach [9]. The standard procedure for calculating the Gibbs energy $G(p, T)$ at high pressure implies application of relation

$$G(p, T) = G^0(T) + \int V(p, T)dp, \tag{1}$$

where $G^0(T)$ is the Gibbs potential at normal atmospheric pressure.

Usually, Gibbs energies of graphite and diamond are calculated to determine the P,T parameters of graphite–diamond equilibrium: $G_g(p, T) = G_d(p, T)$. While analyzing the processes occurring far from equilibrium, it is necessary to know the thermodynamic force of the process

$$-\Delta G = G_g(p, T) - G_d(p, T)$$

in a wide range of pressures and temperatures.

The Gibbs energies of graphite and diamonds at different T and P are given in [8, 10, 11] to an accuracy sufficient for the problem considered here.

The difference between the equilibrium temperature in the graphite–diamond system and the melting temperature of MC determines the remoteness of the temperature of the beginning of synthesis from the equilibrium line.

Transformation of graphite to diamond begins at the MC melting temperature found from the formula [12]

$$T_m \approx 37 \cdot 10^{-9} p + 1663. \tag{2}$$

The difference $G_g - G_d$ determined at this temperature characterizes the structure of the polycrystalline part formed at the beginning of the transformation of graphite into diamond. In this work, the difference $G_g(p, T_m) - G_d(p, T_m)$ is calculated at the MC ($Ni_{0.8}Cr_{0.2}$) melting temperature.

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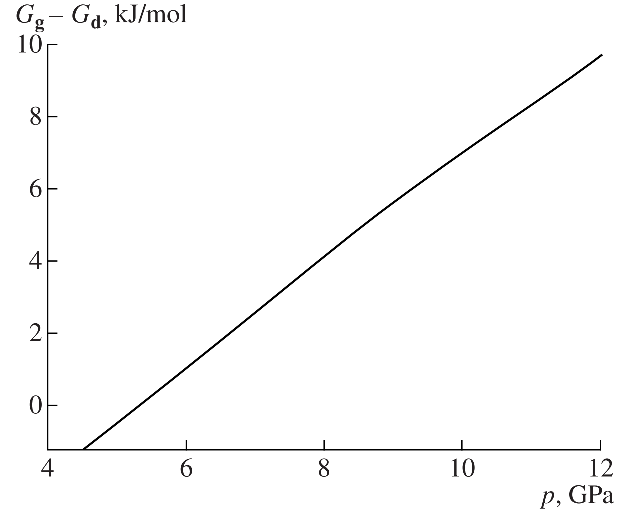

Fig. 1. Pressure dependence of difference of the Gibbs energy of graphite and diamond at the melting temperature of the metal-catalyst [8].

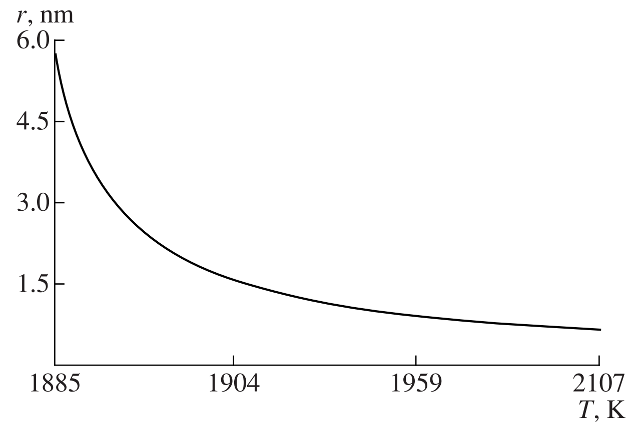

Fig. 2. Dependence of the size of the critical nucleus on temperature at different pressures [8].

The pressure dependence of the driving power of the graphite–diamond transformation in the presence of MC is shown in Fig. 1.

We shall limit ourselves to the model of a spherical nucleus, in which the radius r^* and energy δG of the critical nucleus are written as

$$r^* = 2\sigma V_d(G_g - G_d)^{-1}, \tag{3}$$

$$\delta G = \frac{16}{3}\pi V_d^2\sigma^3(G_g - G_d)^{-2}, \tag{4}$$

where V_d is the volume of a diamond mole, σ is specific surface energy at the graphite–diamond boundary ($\sigma \approx$ 1–10 J/m^2 [7]), $-\Delta G = G_g - G_d$ is the mole difference of free Gibbs energies of graphite and diamonds.

According to Eq. (3), Fig. 2 shows the dependence of the critical radius of the nucleus (r) on temperature ($T \geq T_m$) at different temperatures and pressures, which are determined by Eq. (2).

Thus, nuclei of diamonds are spontaneously formed in graphite and MC as a result of the interaction between carbon atoms under certain PT conditions. It is seen from Fig. 2 that the radius of the critical nucleus decreases with increasing temperature.

The probability of formation of a critical diamond nucleus is determined by the following relation [13]:

$$W_d \sim \exp\left(-\frac{\delta G}{kT}\right)\exp\left(-\frac{E}{kT}\right), \tag{5}$$

where δG is the variation of free energy of the system when nuclei are formed and E is the activation barrier.

Variation in the system energy (δG) during the formation of a critical nucleus of carbonado is approximately 10–100 times smaller than that during the formation of ballas. According to (5), the relative probability of the formation of the carbonado nucleus is much greater than that of the ballas nucleus.

The probability of the formation of a critical nucleus at T_m and fixed pressure sharply decreases with increasing temperature [8]. This means that the critical nucleus forms only during the melting of MC.

Spontaneous formation of critical nuclei in the graphite–MC system is governed by the regularities of percolation theory [14]. In the melted MC–carbon system, each cell of the spatial grid ($r \sim r_{cr}$) corresponds with certain probability to the formation of a critical nucleus.

The probability of formation of a critical nucleus at pressures 8–12 GPa and corresponding temperatures of MC melting is approximately equal to ~0.1 [7]. As a result, according to (5), mass formation of critical nuclei with radii $r \approx 10^{-8}$–10^{-9} m occurs in the melted MC–carbon system. According to the percolation theory, mass formation of clusters of finite size occurs at the corresponding probabilities of formation of the critical nucleus with account of the anisotropy of the diamond crystal containing 10^2–10^3 nuclei. Formation of clusters is a random process. Therefore, their sizes can differ from the mean size but with a smaller probability [8]. The mean density of clusters is 10^7 m^{-3}. The clusters formed both in nature and in the experiment can merge into polycrystalline aggregates with a size of 10–100 μm or greater during their further growth. Partly closed volumes (pores) appear between them. Thus, carbonado acquires a block structure.

The growth of a nanostructure diamond from the gas phase according to the cluster mechanism was demonstrated experimentally in [2, 15]. Different levels of cluster formation were found: (1) formation of nuclei from atoms; (2) merging of nuclei into clusters; and (3) formation of clusters in crystals from growing nuclei and merging of the final clusters. Black clusters are clusters of empty zones (pores). In carbonado, they take the form of final clusters, which do not form the joining cluster [8].

Thus, pores filled with the second syngenetic phase appear during the formation of clusters as a result of their further growth and merging. Later, a part of the MC–carbon melt localized in pores crystallizes as well-faceted diamond individuals. During oxidation, the melt is substituted by oxide phases with holes, because the density of diamonds is greater than that of the melt. Discrete variation of thermodynamic parameters is possible in the natural formation of diamonds, which is reflected in the probability of nuclei formation, the size of clusters, and finally the textural-structural peculiarities of the newly formed diamond aggregate.

Diamond-forming processes in the systems in the presence of other catalysts (for example, hydrogen) can also be explained within the framework of the model considered here. In this case, hydrogen forms hydrogen–carbon complexes similar to carbide complexes of metals.

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REFERENCES

1. E. N. Yakovlev, V. P. Filonenko, N. F. Borovikov, et al., Sverkhtverd. Materialy, No. 6, 9 (2001).
2. V. A. Petrovsky, I. Karfunkel, M. Martins, et al., Rentgen. Sinkhrotron. Neitron Issled., No. 9, 73 (2004).
3. C. Phaal and G. Zniema, Phil. Mag. **14**, 979 (1966).
4. Yu. S. Genshaft, A. S. Semenova-Tyan-Shanskaya, A. M. Naletov, and G. B. Bokii, Dokl. Akad. Nauk **236**, 1350 (1977).
5. V. A. Petrovsky, A. S. Mal'tsev, and S. A. Troshev, *Role of Oscillatory Symmetry in Self-Organization of the Crystal–Medium System* (Syktyvkar, 1966) [in Russian].
6. V. A. Petrovsky, S. A. Troshev, and A. E. Sukharev, Dokl. Earth Sci. **397**, 703 (2004) [Dokl. Akad. Nauk **397**, 93 (2004)].
7. *Synthesis of Materials* (VNIISIMS, Aleksandrov, 2000), Vol. 3 [in Russian].
8. V. A. Petrovsky, A. E. Sukharev, V. P. Filonenko, and E. N. Yakovlev, in *Proc. Institute of Geology, Komi Scientific Center, Ural Division, Russian Academy of Sciences*, Issue 115 (2005) [in Russian].
9. O. I. Leipunskii, Uspekhi Khimii **10** (8), 40 (1939).
10. L. F. Vereshchagin, E. N. Yakovlev, L. M. Buchnev, and B. K. Dymov, Teplofiz. Vysok. Temperatur **15**, 316 (1977).
11. A. V. Kurdyumov, V. G. Malogolovets, N. V. Novikov, et al., *Polymorphic Modifications of Carbon and Boron Nitride. A Handbook* (Metallurgiya, Moscow, 1994) [in Russian].
12. I. S. Grigor'eva and E. Z. Meilikhova, *Physical Values. A Handbook* (Energoizdat, Moscow, 1991) [in Russian].
13. B. Chalmers, *Principles of Solidification* (Huntington, New York, 1977; Metallurgiya, Moscow, 1994).
14. S. R. Broadbent and J. H. Hammersley, Proc. Cambridge Phil. Soc. **53**, 6292 (1957).
15. V. Melnikova, in *Hydrogen Materials Science and Chemistry of Carbon Nanomaterials* (Kluwer Acad. Publ., 2004), pp. 557–562.