

THERMOMECHANICAL MODEL OF THE GRAPHITE → DIAMOND PHASE TRANSFORMATION

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The authors propose a thermodynamic criterion of the graphite → diamond phase transformation, which allows for the contribution of the potential elastic strain energy to the free energy of the system. The curves of the direct graphite → diamond transformation have been determined, they agree well with the known data. The authors demonstrate a prevailing contribution of the internal stress energy to the value of the excess of the transformation pressure above the equilibrium pressure at a given temperature.

Introduction. The graphite–diamond phase equilibrium is usually calculated by the methods of chemical thermodynamics using the Gibbs energy equality condition for the respective carbon phases: $G_1(T, p) = G_2(T, p)$ (the subscripts 1 and 2 stand for diamond and graphite, respectively). In this case, the graphite–diamond equilibrium criterion takes the final form [1]

$$\Delta G_T^0 + \int_0^{p_{eq}} \Delta V_T dp = 0, \quad (1)$$

where the first term in the left part of the equality is the Gibbs energy variation at atmospheric pressure and a given temperature (or variation in the temperature component of the free energy) and the second term is the system energy variation due to the work of external forces.

The thermodynamic calculation of the pressure dependence of equilibrium temperature for the graphite–diamond system was first performed by Leipunskiy in 1939 [2]. Later on, Berman et al. [3], Vereshchagin et al. [4], and Andreyev et al. [5] confirmed these data and made some refinements. In parallel with theoretical research there have been experimental studies of the carbon phase diagrams. For example, the equilibrium boundary between graphite and diamond, as proposed by C. Kennedy and G. Kennedy [6], is represented by the equation $T = (p - 1.989)/0.0025$, where p is the pressure (GPa), T is the temperature (°C). The carbon phase diagram was most adequately generalized by Bundy et al. [7] in 1996 in the review article where they showed the lines of equilibrium between various carbon phases, a zone of commercial diamond synthesis using metal melts, and threshold conditions for the direct graphite → diamond transformation by static and dynamic synthesis. It is seen that numerous experiments on the direct graphite → diamond transformation confirm that on the p - T plane there is a region which represents a considerable deviation of the real transformation line from the equilibrium one calculated by the methods of chemical thermodynamics. However, the graphite → diamond phase transformation in a metal–graphite mixture can be initiated at a far lower pressure than that of the direct transformation (without a metal).

It is well known that the methods of chemical thermodynamics are generally applicable for liquids and gases where pressure is distributed uniformly. In a solid, where a new phase nucleates

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and has mechanical characteristics which differ from those of the initial phase, the stress state is nonuniform and nonhydrostatic. Additionally, a force of resistance to the phase boundary motion generates in a solid, and this force has a threshold nature. Clearly, during the nucleation of a new phase an elastic strain energy which exists in an initial solid makes an additional contribution to the free energy of the system. Thus, when calculating the p , T conditions of the graphite \rightarrow diamond transformation one should take into account the mechanical component of the free energy which is ignored in the graphite–diamond equilibrium calculations by equation (1). Therefore, from the standpoint of mechanics of materials, there arises a problem to determine the mechanical state of the graphite–diamond system at high pressures and temperatures, choose a phase transformation criterion, and calculate the p , T conditions of the graphite \rightarrow diamond transformation. Thus, one can determine the “mechanical” contribution to the extent of deviation of the transformation pressure from the equilibrium pressure at a given temperature.

Thermodynamic criterion of the graphite \rightarrow diamond phase transformation. We propose the following model of the graphite \rightarrow diamond phase transformation. Let us consider a two-layer sphere of volume V , which consists of a diamond inclusion of radius r_1 and a graphite layer of outer radius r_2 . Pressure p is applied to the outer surface of the sphere S_2 .

To determine stresses in the system under study, we write a set of thermoelectricity equations in the spherical coordinates

$$\begin{aligned}\sigma_r &= \frac{E}{(1+\nu)(1-2\nu)} [(1-\nu)\varepsilon_r + 2\nu\varepsilon_\theta] - \frac{E(\alpha T + \varepsilon_f)}{1-2\nu}, \\ \sigma_\theta &= \frac{E}{(1+\nu)(1-2\nu)} (\varepsilon_\theta + \nu\varepsilon_r) - \frac{E(\alpha T + \varepsilon_f)}{1-2\nu}, \\ \frac{d\sigma_r}{dr} + \frac{2}{r}(\sigma_r - \sigma_\theta) &= 0, \quad \varepsilon_r = \frac{du}{dr}, \quad \varepsilon_\theta = \frac{u}{r},\end{aligned}\tag{2}$$

where E , ν , and α are the Young’s modulus, Poissons ratio, and the thermal expansion coefficient (TEC), respectively, ε_r , ε_θ , σ_r , and σ_θ are the radial and tangential strains and stresses, respectively, u is the radial displacement.

We solve the set of equation (2) in terms of displacements and obtain

$$\begin{aligned}u_i &= A_i r + \frac{B_i}{r^2}, \\ \sigma_r^i &= 3K_i [A_i - (\alpha_i T + \varepsilon_f^i)] - 4G_i B_i \frac{1}{r^3}, \\ \sigma_\theta^i &= 3K_i [A_i - (\alpha_i T + \varepsilon_f^i)] - 2G_i B_i \frac{1}{r^3}, \quad i=1, 2,\end{aligned}\tag{3}$$

where u_i , σ_r^i , and σ_θ^i are the displacements and stresses in the i th layer, ε_f^i is the linear phase strain in the i th layer, K_i and G_i are the bulk and shear elastic moduli of the i th layer, A_i and B_i are the constants which are determined from the boundary conditions

$$\begin{aligned}u_1 &= 0 && \text{with } r=0, \\ u_1 &= u_2, \quad \sigma_r^1 = \sigma_r^2 && \text{with } r=r_1, \\ \sigma_r^2 &= p && \text{with } r=r_2.\end{aligned}\tag{4}$$

We solve the set of equations (3) in view of (4) and obtain the following sequence of expressions for the determination of unknown A_i and B_i :

$$B_1 = 0, \quad B_2 = \frac{a_1 d_2 - a_2 d_1}{a_1 b_2 - a_2 b_1}, \quad A_2 = \frac{1}{a_1} (d_1 - B_2 b_1), \quad A_1 = A_2 + B_2 \frac{1}{r_1^3}, \quad (5)$$

where

$$\begin{aligned} a_1 &= 3K_1 - 3K_2, & a_2 &= 3K_2, & b_1 &= \frac{3K_1 + 4G_2}{r_1^3}, & b_2 &= -\frac{4G_2}{r_2^3}, \\ d_1 &= 3K_1(\alpha_1 T + \varepsilon_f^1) - 3K_2(\alpha_2 T + \varepsilon_f^2), \\ d_2 &= p + 3K_2(\alpha_2 T + \varepsilon_f^2). \end{aligned}$$

Using the second law of thermodynamics, we write the graphite \rightarrow diamond transformation condition for a spherical volume loaded with pressure p . In this case, a spherical diamond nucleus forms and grows inside the graphite space (direct transformation). Then,

$$dt \left[\int_{S_2} \dot{u}_2 p dS_2 - \frac{d}{dt} \int_V \psi dV \right] \geq dt \int_{S_1} k \dot{r}_1 dS_1, \quad (6)$$

where S_1 and S_2 are, respectively, surface areas of the diamond nucleus and the graphite layer, \dot{u}_2 and $\frac{d}{dt} \int_V \psi dV$ are, respectively, the velocity of the S_2 surface displacement and the rate of variation of the internal energy of the system which are due to a change in the diamond nucleus radius r_1 , k is the force of resistance to the interface motion. Physical meaning of inequality (6) is as follows: if the work of applied forces (the first term) exceeds the internal energy of the system (the second term) and the energy of resistance to the interface motion (the right-hand part of the inequality), an irreversible change has occurred in the system. In this case, the energy dissipation is due to the graphite \rightarrow diamond phase transformation. The actual phase transformation pressure p applied to graphite is determined from inequality (6) with the known parameters obtained from the solution to the thermoelasticity problem (2).

Since the variations of the graphite surface displacement and the free energy of the system are due to a change in the diamond inclusion radius, we take r_1 as an independent variable and determine the left-hand part of inequality (6) in terms of this variable,

$$\begin{aligned} dt \int_{S_2} \dot{u}_2 p dS_2 &= p \dot{u}_2 S_2 dt = p \frac{\partial u_2}{\partial r_1} \dot{r}_1 S_2 dt, \\ \frac{d}{dt} \int_V \psi dV &= \frac{\partial \int_V \psi dV}{\partial r_1} \dot{r}_1. \end{aligned}$$

Then, inequality (6) is rewritten as

$$p \frac{\partial u_2}{\partial r_1} S_2 - \frac{\partial \int_V \psi dV}{\partial r_1} \geq k S_1,$$

hence the transformation pressure is given by

$$p = \frac{\frac{\partial \int \psi dV}{kS_1 + \frac{V}{\partial r_1}}}{\frac{\partial u_2}{\partial r_1} S_2}. \quad (7)$$

Using the expressions for the determination of displacements (3), we find

$$u_2 = \left(\frac{d_1}{a_1} - \frac{b_1}{a_1} \frac{a_1 d_2 - a_2 d_1}{a_1 b_2 - a_2 b_1} \right) r_2 + \frac{1}{r_2^2} \frac{a_1 d_2 - a_2 d_1}{a_1 b_2 - a_2 b_1}.$$

In view of the $\mathcal{L}_1(r_1)$ function we determine $\frac{\partial u_2}{\partial r_1}$,

$$\frac{\partial u_2}{\partial r_1} = \frac{3b_1(a_1 d_2 - a_2 d_1)}{r_1(a_1 b_2 - a_2 b_1)} \left[\frac{r_2}{a_1} - \frac{a_2(a_1 - b_1 r_2^3)}{a_1 r_2^2(a_1 b_2 - a_2 b_1)} \right]. \quad (8)$$

The free energy in the $\mathcal{A}h$ layer is evaluated as a sum of the elastic resistance energy and the temperature component: $\psi_i = \frac{1}{2} \sigma_i : \varepsilon_i^e + \psi_{0i}$, where $\sigma = \begin{bmatrix} \sigma_r & 0 & 0 \\ 0 & \sigma_\theta & 0 \\ 0 & 0 & \sigma_\theta \end{bmatrix}$ is the stress tensor,

$\varepsilon^e = \begin{bmatrix} \varepsilon_r - \varepsilon^r & 0 & 0 \\ 0 & \varepsilon_\theta - \varepsilon^r & 0 \\ 0 & 0 & \varepsilon_\theta - \varepsilon^r \end{bmatrix}$ is the elastic strain tensor, ε^r is the inelastic strain, ψ_0 is the

temperature component of the free energy. Taking into account that $\varepsilon^r = \varepsilon^f + \varepsilon^s$, where $\varepsilon^f = \alpha T$ is the temperature strain, $\varepsilon^f = \frac{\rho_2 - \rho_1}{3\rho_2}$ is the linear phase strain, ρ_2 and ρ_1 are the densities of graphite and diamond, respectively, we determine the free energy in both the diamond nucleus and the graphite layer,

$$\begin{aligned} \psi_1 &= \frac{9}{2} K_1 (A_1 - \alpha_1 T - \varepsilon_1^f)^2 + \psi_{01}, \\ \psi_2 &= \frac{9}{2} K_2 (A_2 - \alpha_2 T)^2 + 6G_2 B_2^2 \frac{1}{r^6} + \psi_{02}. \end{aligned}$$

Using ψ_1 and ψ_2 , we arrive at the expression for the free energy in the whole volume \mathcal{V} ,

$$\begin{aligned} \int_{\mathcal{V}} \psi dV &= \pi \left[6K_1 (A_1 - \alpha_1 T - \varepsilon_1^f)^2 - 6K_2 (A_2 - \alpha_2 T)^2 + \frac{4}{3} (\psi_{01} - \psi_{02}) \right] r_1^3 \\ &+ 8\pi G_2 B_2^2 \frac{1}{r_1^3} + 2\pi \left[9K_2 (A_2 - \alpha_2 T)^2 + 2\psi_{02} \right] \frac{r_2^3}{3} - 8\pi G_2 B_2^2 \frac{1}{r_2^3}. \end{aligned}$$

Finally,

$$\frac{\partial}{\partial r_1} \int_{\mathcal{V}} \psi dV = A(a_1 d_2 - a_2 d_1)^2 + B(a_1 d_2 - a_2 d_1) + C, \quad (9)$$

where

$$\begin{aligned}
A &= \frac{6\pi r_1^2}{[a_1 b_2 r_1^3 - a_2 (3K_1 + 4G_2)]^3} \left\{ \frac{8a_2 (3K_1 + 4G_2) G_2 r_1^3}{r_2^3} - \frac{6b_2 K_2 (3K_1 + 4G_2)^2}{a_1} r_2^3 \right. \\
&\quad \left. - \left[3K_1 \left(1 - \frac{3K_1 + 4G_2}{a_1} \right)^2 + 4G_2 - \frac{3K_2 (3K_1 + 4G_2)^2}{a_1^2} \right] [a_1 b_2 r_1^3 + a_2 (3K_1 + 4G_2)] \right\}, \\
B &= \frac{6\pi (3K_1 + 4G_2) r_1^2}{[a_1 b_2 r_1^3 - a_2 (3K_1 + 4G_2)]^2} \left\{ 6b_2 K_2 r_2^3 \left(\frac{d_1}{a_1} - \alpha_2 T \right) \right. \\
&\quad \left. - \alpha_2 \left[6K_1 \left(\frac{d_1}{a_1} - \alpha_1 T - \varepsilon_1^f \right) \left(1 - \frac{3K_1 + 4G_2}{a_1} \right) + 6K_2 \left(\frac{d_1}{a_1} - \alpha_2 T \right) \frac{3K_1 + 4G_2}{a_1} \right] \right\}, \\
C &= 6\pi \left[3K_1 \left(\frac{d_1}{a_1} - \alpha_1 T - \varepsilon_1^f \right)^2 - 3K_2 \left(\frac{d_1}{a_1} - \alpha_2 T \right)^2 + \frac{2}{3} (\Psi_{01} - \Psi_{02}) \right] r_1^2.
\end{aligned} \tag{10}$$

Substitution of (8) and (9) into the phase transformation condition (7) yields a quadratic equation for the transformation pressure

$$Ep^2 + Fp + G = 0, \tag{11}$$

where

$$\begin{aligned}
E &= a_1 (DS_2 + Aa_1), \quad F = (DS_2 + 2a_1 A) (\alpha_2 T a_1 - d_1) a_2 + Ba_1, \\
G &= \alpha_2 T a_1 a_2^2 (\alpha_2 T a_1 - 2d_1) + a_2 B (\alpha_2 T a_1 - d_1) + Aa_2^2 d_1^2 + kS_1 + C, \\
D &= \frac{3b_1}{r_1 (a_1 b_2 - a_2 b_1)} \left[\frac{r_2}{a_1} - \frac{a_2 (a_1 - b_1 r_2^3)}{a_1 r_2^2 (a_1 b_2 - a_2 b_1)} \right].
\end{aligned}$$

Now, to determine the roots of equation (11) we need only to calculate the difference between the temperature components of internal energies of diamond and graphite, which is included in the C constant. This can be done in the assumption that the graphite \rightarrow diamond transformation is fully accomplished at equilibrium pressure and temperature: $p = p_{eq}$, $T = T_{eq}$. Using this condition and taking into consideration that in this case the force of resistance to the interface motion $k = 0$, we can determine the constant $C = C^*$ from equation (11),

$$\begin{aligned}
C^* &= - \left\{ a_1 (DS_2 + Aa_1) p_{eq}^2 + [(DS_2 + 2Aa_1) (\alpha_2 T_{eq} a_1 - d_1) a_2 + Ba_1] p_{eq} \right. \\
&\quad \left. + \alpha_2 T_{eq} Aa_1 a_2^2 (\alpha_2 T_{eq} a_1 - 2d_1) + a_2 B (\alpha_2 T_{eq} a_1 - d_1) + Aa_2^2 d_1^2 \right\}.
\end{aligned}$$

Then, from (10) we evaluate $\Psi_{01} - \Psi_{02}$,

$$\Psi_{01} - \Psi_{02} = \frac{3}{2} \left[\frac{C^*}{6\pi r_1^2} - 3K_1 \left(\frac{d_1}{a_1} - \alpha_1 T_{eq} - \varepsilon_1^f \right)^2 + 3K_2 \left(\frac{d_1}{a_1} - \alpha_2 T_{eq} \right)^2 \right].$$

Thus, the phase transformation can be described as follows: (i) by using the physicochemical model (1), we obtain the graphite–diamond equilibrium conditions; (ii) by using the proposed thermomechanical model, we obtain the graphite \rightarrow diamond transformation conditions. Table 1 gives the energy components for these models. It is evident that the work of applied forces and the temperature components of the free energy are present in both approaches; the mechanical component of the free energy and the activation barrier are involved only in the criteria we proposed. If the last-mentioned component of the energy is ignored, the only difference between the proposed model and the conventional model will lie in allowing for the elastic strain energy.

Table 1
Physicochemical and Thermomechanical Criteria of
the Graphite–Diamond Phase State

| State criterion | Work of applied forces | Temperature component of the free energy | Mechanical component of the free energy | Activation barrier | Σ |
|--------------------------|----------------------------------|--|---|-----------------------------------|----------|
| Equilibrium condition | $\int_0^{p_{eq}} \Delta V_T dp$ | $+\Delta G_T^0$ | 0 | 0 | 0 |
| Transformation condition | $dt \int_{S_2} \dot{u}_2 p dS_2$ | $-dt \int_V \dot{\psi}_0 dV$ | $-dt \int_V \frac{1}{2} \dot{\sigma} : \dot{\epsilon}^e dV$ | $-dt \int_{S_1} k \dot{r}_i dS_1$ | 0 |

Calculation of p, T conditions for the direct graphite \rightarrow diamond transformation. Diamond nucleation in a graphite medium leads to a decrease in specific volume. Therefore, when calculating the thermomechanical conditions for the graphite \rightarrow diamond transformation one should take into account the $r_2(r_1)$ function.

Let us write the mass conservation equation for the system under consideration

$$m_{init} = m_1 + m_2, \tag{12}$$

where m_{init} is the graphite mass in the initial state (prior to diamond nucleation), m_1 is the diamond mass, m_2 is the graphite mass after diamond nucleation. Equation (12) can be written as

$$V_{2init} \rho_2 = V_1 \rho_1 + V_2 \rho_2, \tag{13}$$

where V_{2init} is the graphite volume in the initial state, V_1 and V_2 are the diamond and graphite volumes, respectively, ρ_1 and ρ_2 are the densities of diamond and graphite, respectively. From (13) we have

$$V_2 = V_{2init} - V_1 \frac{\rho_1}{\rho_2}$$

or

$$r_2^3 - r_1^3 = r_{2init}^3 - r_1^3 \frac{\rho_1}{\rho_2},$$

where r_{2init} is the outer radius of the graphite layer in the initial state. Finally,

$$r_2 = \sqrt[3]{r_{2init}^3 + \left(1 - \frac{\rho_1}{\rho_2}\right) r_1^3}.$$

Using equation (11) we determine the pressure of the direct graphite \rightarrow diamond transformation for the following physico-mechanical characteristics of diamond and graphite: $K_1 = 590$ GPa, $K_2 = 33.7$ GPa, $\rho_1 = 3.5 \times 10^3$ kg/m³, $\rho_2 = 2.27 \times 10^3$ kg/m³. The shear modulus of graphite depends on temperature: $G = G_0(1 - T/T_{melt})$, where $G_0 = 41$ GPa is the shear modulus at a temperature of $T = 0$ K, $T_{melt} = 5000$ K is the graphite melting temperature. Figure 1 illustrates the temperature dependence of TEC for diamond and graphite.

Figure 2 shows the calculated $p(T)$ curves for diamond nucleation by the direct transformation for various values of the force of resistance to the interface motion as well as the straight line of the graphite–diamond phase equilibrium, which was calculated by conventional

chemical thermodynamics methods without regard for nonhydrostatic and nonuniform patterns of stressed-strained state. It is seen that the calculated curve 2 adequately describes the experimental data at $T = 800\text{--}5000\text{ K}$. In this case, the transformation pressure was found to be much higher than the equilibrium pressure. For example, at $T = 1563\text{ K}$ the transformation pressure is 12 GPa, while the equilibrium pressure is 5 GPa. Temperature is another factor that has a considerable effect on the graphite \rightarrow diamond transformation conditions. At lower temperatures the transformation pressure exceeds the equilibrium one by a larger degree. Thus, at $T = 1563\text{ K}$ the pressure of the direct graphite \rightarrow diamond transformation is 7.1 GPa higher than the equilibrium one, while at $T = 3125\text{ K}$ this difference is 3.5 GPa and at $T = T_{melt}$ it is 0.

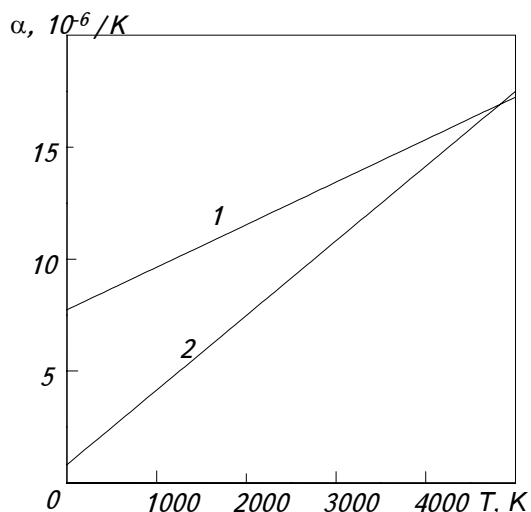


Fig. 1. Temperature dependence of thermal expansion coefficients of graphite (1) and diamond (2) [8].

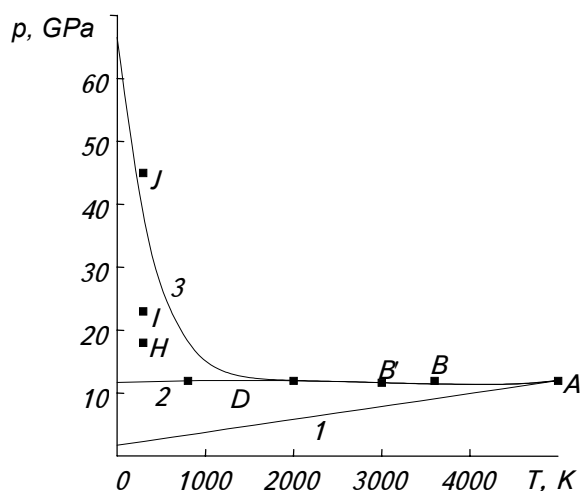


Fig. 2. Graphite–diamond phase diagram: 1 – equilibrium line [7], 2, 3 – calculated curves of the direct transformation under static conditions at $k = 0$ and $k = f(T)$, respectively, A – melting point, B and B' – lower boundaries of the cubic diamond formation at high temperatures [7, 9], D – region of hexagonal diamond (lonsdaleite) formation [7] ($T = 800\text{--}2000\text{ K}$), H (18 GPa), I (23 GPa), J (45 GPa) – points of transformation at room temperature, where graphite acquires diamond properties under hydrostatic compression conditions [7].

Thus, in the case of the direct graphite \rightarrow diamond transformation the stressed-strained state is considerably nonuniform due to a large difference in mechanical properties between graphite and diamond. The transformation pressure depends greatly on temperature: the higher the temperature and the lower the shear modulus of graphite, the smaller excess of pressure over the equilibrium one is needed to enable the graphite \rightarrow diamond transformation. The pressure of the direct graphite \rightarrow diamond transformation allowing for the system strain energy, which is a component of the free energy, is several times higher than the “chemical” equilibrium pressure. This agrees well with the reported experimental data for the high temperature region [7, 9, 10].

Let us compare our results with those reported elsewhere. Andreyev et al. [10–13] showed that at temperatures close to room temperature the pressure of the direct graphite \rightarrow diamond transformation is much higher than that at high temperatures. The same pattern was confirmed by ”undy et al. [7]. This finding can be attributed to the presence of an activation barrier of the graphite \rightarrow diamond transformation, which is due to thermally activated diffusion mechanism of the graphite-to-diamond lattice rearrangement.

In the procedure we propose, the activation energy of the graphite \rightarrow diamond transformation as a function of temperature can be taken into account in terms of a certain force of resistance to the interface motion k in the volume of the diamond being nucleated (see the transition criterion (6)). To determine the $k(T)$ function, which must represent the exponential decreasing of k with increasing temperature, we should have sufficient number of experimental p , T points of the graphite \rightarrow diamond transformation. With the known transformation pressure and temperature at the experimental points given in Fig. 2, we find the k values at these points by equation (7) and approximate them with the $k(T)$ curve (Fig. 3). Using this function, we calculate the transformation curve \mathcal{J} (see Fig. 2) which adequately describes the transformation conditions over the whole temperature range.

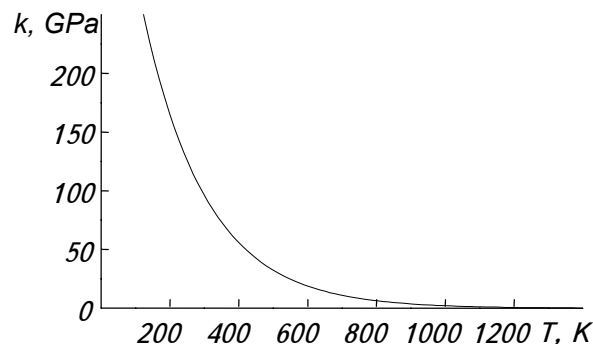


Fig. 3. Temperature dependence of the force of resistance to interface motion, which was calculated from the experimental data [7].

In the regions located below the aforementioned transformation curves the graphite \rightarrow diamond phase transformation is thermodynamically unfavorable.

Analysis of the results suggests that at $T > 800$ K the main factor that restricts diamond nucleation is the elastic strain free energy which makes a prevailing contribution to the fact that the actual transformation pressure exceeds the equilibrium pressure at a given temperature. At $T < 800$ K the activation barrier of the transformation increases abruptly due to a decrease in the energy of thermal fluctuations.

In the case where diamond nucleation occurs in a liquid, which can be qualitatively simulated by assuming the shear modulus of the second layer to be zero, we arrive at hydrostatic distribution of stresses in the system under study and the change in the elastic energy during the transformation becomes equal to zero. In this case, the calculation yields the equilibrium conditions similar to those determined by the physicochemical model. Thus, the addition of a liquid phase reduces the contribution of the mechanical component of the free energy.

Conclusions

A thermomechanical criterion of the graphite → diamond transformation has been put forward which allows for the elastic strain free energy of the medium.

We have proposed a method of taking into account an activation barrier of the transformation in a lower temperature range.

The pressure of the direct graphite → diamond transformation has been calculated. It is several times that of the equilibrium pressure and its value is in good agreement with the available experimental data.

We have demonstrated that the transformation activation barrier in the temperature range from 800 to 0 K is mainly due to a decrease in the energy of thermal fluctuations, while in the range from 800 to 5000 K it is associated with the presence of elastic strain internal energy in the graphite–diamond system.

The addition of a liquid to the reaction mixture substantially decreases the contribution of the internal stress energy and brings the pressure of the diamond crystallization in the liquid phase closer to the equilibrium one.

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