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Thermodynamics of Diamond Nucleation on the Nanoscale

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Abstract: To have a clear insight into the diamond nucleation upon the hydrothermal synthesis and the reduction of carbide (HSRC), we performed the thermodynamic approach on the nanoscale to elucidate the diamond nucleation taking place in HSRC supercritical-fluid systems taking into account the capillary effect of the nanosized curvature of the diamond critical nuclei, based on the carbon thermodynamic equilibrium phase diagram. These theoretical analyses showed that the nanosize-induced interior pressure of diamond nuclei could drive the metastable phase region of the diamond nucleation in HSRC into the new stable phase region of diamond in the carbon phase diagram. Accordingly, the diamond nucleation is preferable to the graphite phase formation in the competing growth between diamond and graphite upon HSRC. Meanwhile, we predicted that 400 MPa should be the threshold pressure for the diamond synthesis by HSRC in the metastable phase region of diamond, based on the proposed thermodynamic nucleation on the nanoscale.

Introduction

The interest in synthesis of diamond has been motivated by diamond's unique combinations of physical and chemical properties, such as, high physical hardness, high thermal conductivity, excellent chemical corrosion resistance, optical transparency, and others,^{1–4} since diamonds were first time synthesized by the high-pressure and high-temperature process (HPHT) in the 1950s.⁵ Up to date, diamond syntheses include HPHT,⁵ chemical vapor deposition (CVD),⁶ shock-wave method,⁷ pulsed-laser-induced liquid–solid interface reaction (PLIIR),^{8–11} plasma activation,¹² and so on. Recently, the important progress of diamond syntheses was made by HSRC.^{13–20} In detail, by using diamond seeds, Syzmanski et al. synthesized diamonds

by hydrothermal synthesis in the different supercritical-fluid systems in 1995, and Gogotsi et al. almost simultaneously prepared diamonds by using the containing-carbon-element water solution in the hydrothermal synthesis.^{13,14} Following them, a few groups successfully synthesized diamonds by the hydrothermal synthesis without diamond seeds, in which the nondiamond carbon and various carbides with chlorine or supercritical-fluid water solution containing hydrogen were used as raw materials.^{15–17} Furthermore, without chlorine and supercritical-fluid water solution containing hydrogen, Lou et al. synthesized diamonds through the reduction of carbon dioxide and reduction of magnesium carbonate with metallic supercritical-fluid sodium.^{19,20} However, compared with the rapid experimental progress of the diamond synthesis by HSRC, the thermodynamic nucleation of diamonds upon HSRC supercritical-fluid systems still remains much less understood in theory so far. For instance, the phase region, where diamonds are synthesized by HSRC, is in the range of 713 to 1273 K and 0.1 to 200 MPa.^{15,17–20} Then, the phase region is located below the boundary line between diamond and graphite, i.e., the so-called Bundy's line (B line), in the carbon thermodynamic equilibrium phase diagram as shown in Figure 1.²¹ Note that the carbon phase diagram proposed by Bundy has been generally accepted. In other words, the diamond nucleation would not be expected to take place in the phase regions created by HSRC in the carbon phase diagram because the diamond phase is metastable and the graphite phase is stable in the phase region mentioned above. Why would the results of the diamond synthesis in HSRC

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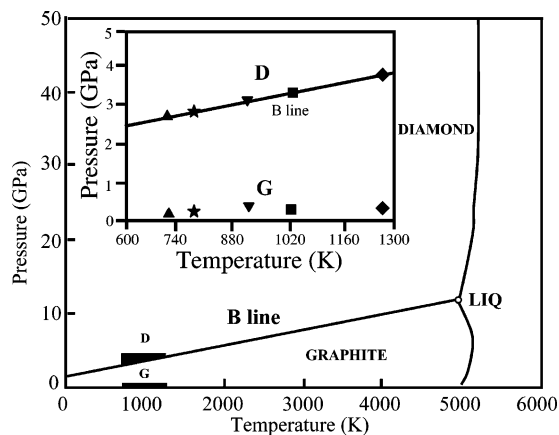


Figure 1. Carbon thermodynamic equilibrium phase diagram based on pressure and temperature. **G** region means a metastable phase region of diamond nucleation; **D** region means a new stable phase region of diamond nucleation by hydrothermal synthesis or reduction of carbide under the nanosize-induced interior pressure conditions. The inset shows the enlarged **G** and **D** region. The data point of the symbols (▲ ★ ▼ ■ ◆) of the **G** region derived from refs 19, 20, 17, 15, and 18, respectively.

systems not be consistent with the prediction of the carbon thermodynamic equilibrium phase diagram? A convincing understanding of this issue has not been reached yet. To our best knowledge, few studies concerning the thermodynamic nucleation of diamonds upon HSRC are found in the literature.

To gain a better understanding of the diamond nucleation upon HSRC supercritical-fluid systems from the point of view of thermodynamics, in this paper, we proposed the thermodynamic analysis taking into account the effect of the nanosize-induced interior pressure on the Gibbs free energy of the diamond critical nuclei based on the thermodynamic nucleation on the nanometer scale. It is noticed that the sizes of diamond critical nuclei are limited in the range of several nanometers upon CVD,^{22–23} and the supercritical-fluid systems were suggested to have liquidlike densities but gaslike properties.²⁴ It is therefore a convincing suggestion that the size of the diamond critical nuclei should be limited within several nanometers in the HSRC supercritical-fluid systems.¹⁷ According to the thermodynamic model, we first calculated the size and the energy of the critical nucleation of diamonds, respectively, in which all data are from the securable literatures about the diamond synthesis in the HSRC supercritical-fluid systems. More importantly, our theoretical results are in excellent agreement with the experiment data and other calculations from the first-principles.^{17, 25–26}

Theory Model

Since the point of the view of nanothermodynamics was bought forward,^{27–30} researchers employed the Laplace–Young

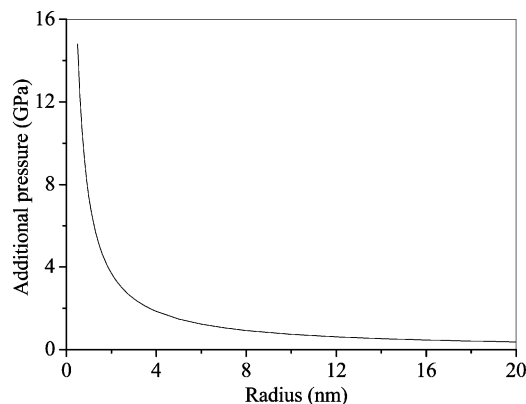


Figure 2. Relationship curve between the nanosize-induced additional pressure and nuclei size based on the Laplace–Young equation: $\Delta P = 2\gamma/r$.

equation ($\Delta P = 2\gamma/r$) to analyze the basic physical and chemical aspects of nucleation and growth of nanocrystals.^{31–35} For example, Tolbert et al. employed the Laplace–Young equation to discuss the elevation of the nanosize-induced interior pressure of semiconductor nanocrystals upon the high-pressure structural transformations.³⁵ Especially, Hwang et al.³⁴ compared the chemical potential of diamond with that of graphite by used the Laplace–Young equation for the stability of the carbon cluster and indicated that the chemical potential of carbon between diamond and graphite is shown to be reversed when the size of the carbon cluster is sufficiently small. Accordingly, that the Laplace–Young equation is used in the diamond nucleation upon HSRC supercritical-fluid systems is reasonable, from the point of the view of thermodynamic nucleation at the nanometer scale. Note that the nanothermodynamics in our model, by taking into account the size dependence of surface tension of nanocrystalline nuclei, definitely differs from the thermodynamics of small systems proposed by Hill. Our thermodynamic theory emphasizes the nanosize effect of surface tension of nanocrystals on the stable and metastable equilibrium state during the microphase growth. Now, we discuss the real influence of the interior pressure of nanocrystals on the phase stability from the Laplace–Young equation in detail. Under the assumptions of spherical and isotropic nanocrystalline diamonds, the nanosize-induced interior pressure ΔP of diamond nanocrystals is given by the Laplace–Young equation: $\Delta P = 2\gamma/r$, where $\gamma = 3.7 \text{ J/m}^2$ is the surface energy of diamond.³⁶ The dependence of the interior pressure ΔP on the size of r is shown in Figure 2. One can see that the interior pressure increases with the crystal particle's size decreasing in Figure 2. Notably, the interior pressure which goes up to 2.0 GPa is marked the **D** region in Figure 1, i.e., the diamond stable region, when the size r is less than 4 nm. In other words, the nanosize-induced interior pressure can drive the metastable region marked the **G** region of the diamond nucleation upon HSRC into the new

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stable region, the **D** region, in the P – T phase diagram of carbon by breaking the **B** line as evidently shown in Figure 1. Consequently, the interior pressures of diamond nuclei in radius of 2–4 nm are enough to drive the **G** region into the **D** region in the carbon phase diagram. These results imply that the diamond nucleation upon HSRC should happen in the **D** region, based on our thermodynamic analysis on the nanoscale. In fact, in 1991, McKenzie et al. pointed out that the surface stress is a vital factor in promoting sp^3 bonding in the diamonds' synthesis by low-pressure and low-temperature methods.³⁷ Namely, the hydrostatic component of the biaxial stress is sufficient to place the growth conditions inside the diamond stable zone at room temperature in the Bundy's carbon phase diagram.²¹ Additionally, a few groups have studied the stability of nanodiamonds from difference aspects.^{25,37} Their research distinctly accounts for the same conclusion that nanodiamonds are more stable than the graphite phase. Especially, Raty's calculations showed that nanodiamonds become more stable on a hydrogenated surface, when they are bare, or terminated surface.³⁷ From these cases above, we deduce that the bare or terminated surface may little affect the surface energy of nanodiamonds. Therefore, we use the surface energy of 3.7 J/m² in our calculations, as the value of surface energy of diamond is assumed to be a constant regardless of a bare or terminated surface.

Generally, the Gibbs free energy of a diamond cluster is expressed as a function of radius r , pressure P , and temperature T under the low-pressure gas phase.³⁸

$$\Delta G(r, P, T) = \left[\frac{4}{3} \pi r^3 \times \Delta g / V_m + 4 \pi r^2 \gamma \right] f(\theta) \quad (1)$$

where r , V_m , γ , and θ are the radius of the spherical cap of the diamond cluster, the molar volume of diamond, the surface energy of diamond, and the contact angle between the spherical cap of diamond clusters and the supercritical-fluid surface, respectively. Moreover, Δg is the molar volume Gibbs free energy depending on the pressure P and temperature T in the phase transition from graphite to diamond, and $f(\theta)$ is the so-called heterogeneous factor in which the value is in the range 0 to 1. According to thermodynamics, we can obtain $(\partial \Delta g_{T,P} / \partial P)_T = \Delta V$. Then, $\Delta g_{T,P} = \Delta g^0_T + \int_0^P \Delta V dP$, where ΔV is the molar volume difference between graphite and diamond and Δg^0_T is the molar Gibbs free energy difference at zero pressure. Bundy's experimental results³⁷ showed that ΔV remains approximately constant with pressure–temperature condition, i.e., $\Delta V = 1.77 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$. According to Figure 1, the **B** line is expressed by $P^e = 2.01 \times 10^6 T + 2.02 \times 10^9$. Note that the external pressure P^e will decrease by the same amount, i.e., $P^e = P^{e*} + 2\gamma/r$, due to the interior pressure ΔP . Thus, we obtain the size-dependent equilibrium phase boundary: $P^{e*} = 2.01 \times 10^6 T + 2.02 \times 10^9 - 2\gamma/r$ (Pa). When the conditions are on the equilibrium line, we have $\Delta g_{T,P} = 0$, the molar volume Gibbs free energy difference is attained as follows

$$\Delta g = \Delta V(P - 2.01 \times 10^6 T - 2.02 \times 10^9 + 2\gamma/r) \quad (2)$$

From eqs 1 and 2, considering the size-induced interior pressure

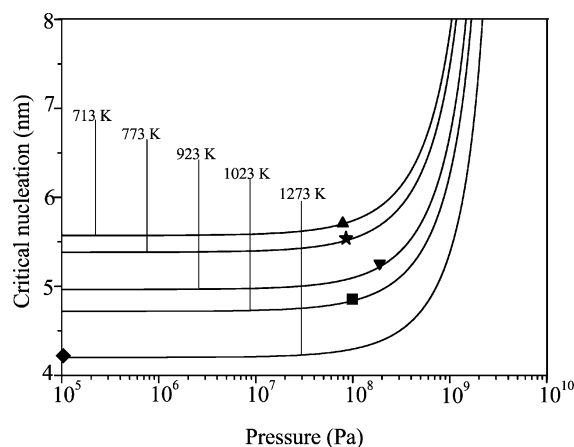


Figure 3. Relationship curves between the size of critical nucleation and the pressure at various temperatures. The data point of the symbols (\blacktriangle \star \blacktriangledown \blacksquare \blacklozenge) derived from refs 19, 20, 17, 15, and 18, respectively.

effect, the Gibbs free energy difference of the phase transition is expressed

$$\Delta G(r, P, T) = \left[\frac{4}{3} \pi r^3 \Delta V (P - 2.01 \times 10^6 T - 2.02 \times 10^9 + 2\gamma/r) / V_m + 4 \pi r^2 \gamma \right] f(\theta) \quad (3)$$

When $\partial \Delta G(r) / \partial r = 0$, the critical size of diamond nuclei is obtained as follows

$$r^* = 2\gamma \left(\frac{2}{3} + \frac{V_m}{\Delta V} \right) / (2.01 \times 10^6 T + 2.02 \times 10^9 - P) \quad (4)$$

By substituting eq 4 into eq 3, the nucleation energy of diamond critical nuclei is given by

$$\Delta G(r^*, P, T) = \left[\frac{4}{3} \pi r^{*3} \Delta V (P - 2.01 \times 10^6 T - 2.02 \times 10^9 + 2\gamma/r^*) / V_m + 4 \pi r^{*2} \gamma \right] f(\theta) \quad (5)$$

Results and Discussions

According to eq 4, for the values of ΔV , V_m equaling $3.417 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$ and γ , we show the relationship curves between the size of the critical nucleation and the pressure at various temperatures in Figure 3. It is noticed that the data points of the symbols (\blacktriangle \star \blacktriangledown \blacksquare \blacklozenge) derived from refs 19, 20, 17, 15, and 18, respectively. Clearly, one can see that the size of diamond nuclei increases with the pressure increase at a given temperature and decreases with the temperature increase at a given pressure in Figure 3. In addition, we can see that the sizes of the critical nucleation are close to constant at the pressures below 400 MPa under the condition of a given temperature. Then, the sizes of critical nuclei increase quickly when the pressures exceed 400 MPa. These results thus indicate that 400 MPa seems to be a pressure threshold for the diamond synthesis by HSRC, and the corresponding size of the diamond critical nuclei is about 5 nm. Remarkably, our theoretical results are not only in excellent agreement with Kraft et al. experimental results but also in good agreement with Badziag and Winter's calculations from the first-principle.^{17,25–26} The first-principle calculations suggested that when the size of carbon clusters is

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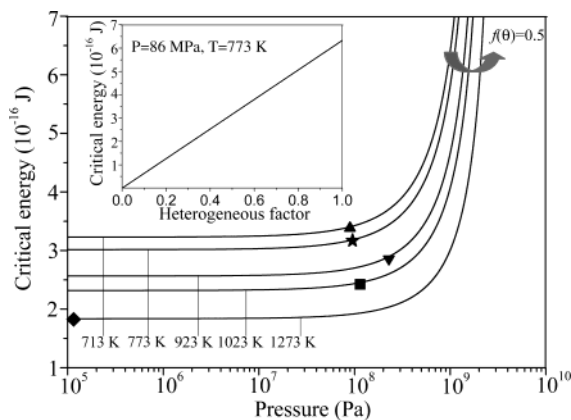


Figure 4. Relationship curves of the critical energy and pressure at various temperatures (the heterogeneous factor is 0.5) considering the nanosize-induced interior pressure condition. The inset shows the relationship curves of the critical energy and heterogeneous factor at given pressure and temperature. The data point of the symbols (\blacktriangle \blacktriangledown \blacksquare \blacklozenge) derived from refs 19, 20, 17, 15, and 18, respectively.

in the range of 3–5 nm, the diamond phase should be thermodynamically more stable than the graphite phase.^{25,26}

Based on eq 5 and the given value $f(\theta)$, considering the nanosize-induced interior pressure, we display the relationship curves of the nucleation energy of diamond critical nuclei and the pressure at conditions of various temperatures and the heterogeneous factor equaling 0.5 as evidence shown in Figure 4. Similarly, one can see that the nucleation energy of critical nuclei increases with the pressure increase at a given temperature and the heterogeneous factor, and the values of the nucleation energy of critical nuclei decrease with the temperature increase at a given pressure in Figure 4. In addition, we see that the values of the nucleation energy are close to constant at the pressures below 400 MPa under a given temperature. However, the values of the nucleation energy of critical nuclei greatly increase when the pressures exceed 400 MPa. Importantly, these results show that the diamond nucleation upon HSRC does not need a relatively high nucleation energy when the pressure is less than 400 MPa or the size of the critical nuclei is less than 5 nm. Apparently, the low nucleation energy of diamond in HSRC suggests that it is not difficult for the diamond nucleation to take place upon HSRC. Therefore, the diamond nucleation of HSRC seems to happen in the diamond stable region, i.e., the **D** region as shown in Figure 1, based on our theory. As a comparison, we give the relationship curves of the nucleation energy of diamond and the heterogeneous factor at the given pressure and temperature in Figure 4. From the inset, one can see that the nucleation energy increases with the heterogeneous factor increase. Eventually, from Figures 3 and 4, we can predict that 400 MPa should be the threshold pressure for the diamond synthesis by HSRC in the metastable phase region of diamond in the carbon phase diagram. The diamond synthesis would thus hardly take place in a thermodynamic metastable phase region of diamond in the carbon phase diagram when the pressure of HSRC exceeds 400 MPa. In fact, all pressures in the diamond synthesis by HSRC are less than 400 MPa in the present securable literatures.

More recently, it has been reported that various kinds of precursors containing carbon such as SiC, CO₂, and MgCO₃, etc, are used to synthesize diamonds in hydrogen or hydrogen-free systems in the thermodynamic metastable region of

diamond of the carbon phase diagram by HSRC.^{18–20} From these experiments mentioned above, we can deduce that hydrogen is not essential for the diamond nucleation upon HSRC. Similar evidences have existed in CVD diamonds. For example, Yoshimoto et al. synthesized diamond films in the indeed hydrogen-free environment upon CVD.³⁹ On the other hand, the nucleation kinetics of the diamond synthesis from the SiC reduction in HSRC suggests that Si is extracted from SiC resulting in the residual carbon structures forming carbon atoms in sp³ hybridization by kinetic regime. In addition, the diamond formation from CO₂ in HSRC could be deduced from the reductant first combining with oxygen and then carbon atoms forming sp³ hybrid bonds by complicated chemistry and physics processes. Therefore, it should be noted that the diamond nucleation upon HSRC is a relatively complicated chemistry, the physics being similar to that of CVD, and thus, the detailed kinetics has not been understood fully yet.

Following Gleiter,⁴⁰ chemical and physical routes under conditions of moderate not extreme temperatures and pressures are generally used to synthesize nanocrystals with metastable structures. However, the corresponding bulk materials with the same metastable phases are prepared under conditions of high temperatures or high pressures. Definitely, the nanosized effect of nanocrystals should be responsible for the formation of these metastable structures at the nanometer scale. Then, there have not been clear and detailed understandings of which nanosized effect causes the metastable structure formation in moderate environments, in other words, which chemical and physical origins lead to the tendency of metastable phases emerging on the nanoscale. Markedly, the thermodynamic approach on the nanometer scale proposed in this case seems to open a door to insights into the metastable phase generation in microphase growth from the point of view of thermodynamics. Therefore, we expect the nanosized thermodynamic analysis to be a general method for understanding metastable phase formations on the nanoscale.

Conclusion

In summary, aiming at a clear insight into the diamond nucleation upon HSRC supercritical-fluid systems, considering the effect of nanosize-induced interior pressure on the Gibbs free energy of diamond nuclei, we proposed a thermodynamic analysis on the nanometer scale. The theoretical results displayed that the diamond nucleation upon HSRC would happen in the stable phase region of diamond in the thermodynamic equilibrium phase diagram of carbon. Furthermore, the threshold pressure of 400 MPa was predicted for the diamond synthesis by HSRC in the metastable phase region of diamond. Consequently, we expected that the thermodynamic analysis on the nanometer scale above to be a general approach applicable to elucidating the formation of metastable structures taking place in the microphase growth.

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