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Size dependent phase stability of nano-diamond①

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Abstract: The transition between nano-diamond(n-D) and nano-graphite(n-G) were modeled based on the extrapolation of the bulk diamond-graphite equilibrium phase boundary in the temperature-pressure diagram to the nano-size region. It is found that in comparison with n-G, the stability of n-D increases as size and temperature decrease. However, n-D is not the most stable phase in comparison with fullerenes(C60) at the nanoscale by considering the heat of formation.

Key words: solid-solid transition; graphite; diamond; fullerenes
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1 INTRODUCTION

Recently, n-D powder has become a useful engineering material in many fields for its technically important properties, i.e., high hardness, strength, electrical resistivity and magnetoresistivity as well as special optical properties. However, it has been observed that n-D can be obtained at low temperature and pressure although it is well known that the graphite-to-diamond transition occurs at high temperature and pressure[1]. Moreover, n-D that initially formed with grain size (d) below 3 nm transforms into graphite at a larger size[1]. Nuth[2] proposed that n-D could be stable than graphite due to the larger product of surface area and surface energy, and Hwang et al[3, 4] outlined a chemical potential model and a charged cluster model to describe the relative stability of small diamond and graphite clusters in their study of low pressure diamond synthesis. All of the above-mentioned methods predict that n-D is the stable phase of carbon at d less than 6.0 nm. On the other hand, it has been reported that carbon nanoparticles undergo n-D, bucky diamond, carbon onion and fullerence with the reduction of size where n-D will disappear at $d < 2.0$ nm[5]. Moreover, the phase transition of n-D to carbon onions has been observed experimentally with a transformation temperature that is dependent on the size of the particle[6, 7]. If these transformations happen, n-D cannot stably exist. Thus, the stability of n-D is necessary to be considered further.

In this contribution, the stability of n-D is thermodynamically considered in terms of the extrapolation of the bulk diamond-graphite equilibrium phase boundary in the temperature-pressure diagram to the nano-size region and the comparison of the formation heats between n-D and C60.

2 MODEL

According to the phase diagram of carbon[1], the transition pressure function $p(T)$ for the diamond-graphite transition is given as[8, 9]

$$p(T) = 1\,700 + 2.06T \qquad (1)$$

Eqn. (1) is determined by the two linearly connected terminating points of the graphite-diamond phase boundary in the phase diagram of carbon that are (1 700 MPa, 0 K) and (12 000 MPa, 5 000 K)[1], respectively, the latter is the graphite/diamond/liquid triple point[1]. Thus, $dp/dT = (12\,000 - 1\,700)/5\,000 = 2.06$. Eqn. (1) is established by thermodynamic calculations in terms of the measured physical properties of graphite and diamond in the temperature range between 300 and 1 200 K, and by experiments on the graphitization of diamond[1].

In order to estimate the contribution of the size-dependent internal pressure, some assumptions have to be made. Under the assumption of spherical, for quasi-isotropic nanocrystals with a diameter d, the additional curvature-induced internal pressure p_i is given by the Laplace-Young equation as[8, 9]

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$$p_i = 4f/d \tag{2}$$

where f is the surface stress.

Owing to this additional internal pressure p_i, the external pressure p_o necessary for the transition between n-G and n-D decreases by the same amount. Thus, $p_i + p_o = 1\,700 + 2.06T$ is obtained for the size dependent phase boundary. In terms of this expression and considering that during the low-temperature and low-pressure synthesis of diamond, the external pressure can be ignored[3], i. e. $p \approx p_i$. Considering these expressions, there is

$$d = 4f/(1\,700 + 2.06T) \tag{3}$$

The value of f value of a quasi-isotropic nanocrystal can be determined by[8, 9]

$$f = (3Bd_0\gamma_{sl}/8)^{1/2} \tag{4}$$

where γ_{sl} is the bulk solid-liquid interface energy and B is the bulk modulus. d_0 is the critical particle diameter where almost all atoms are located on its surface, which equals $3h$ for a particle or a wire having a curved surface and $2h$ for any kind of low-dimensional crystals with a plane surface (h is the atomic diameter)[8, 9], respectively.

In Eqn. (4), γ_{sl} has been deduced according to the Gibbs-Thomson equation[8],

$$\gamma_{sl} = 2hS_{vib}H_m(T)/(3VR) \tag{5}$$

where R is the ideal gas constant, $H_m(T)$ is the temperature-dependent melting enthalpy, S_{vib} is the vibrational part of the overall melting entropy S_m, V is the gram atom volume. Since T concerned here is far lower than the ideal glass transition temperature T_k and $T_k = T_m/2$ for diamond and graphite, $H_m(T) = H_m(T_k) = H_m/4$ is taken in terms of Helmholtz function[8]. Now, γ_{sl} for graphite and diamond can be rewritten as

$$\gamma_{sl} = hS_{vib}H_m/(6VR) \tag{6}$$

Since carbon nanoparticles undergo n-D, bucky diamond, carbon onion and fullerence (C60) with the reduction of size[5], strictly speaking, the lower limit of phase stability of n-D should be determined compared with bucky diamond (even carbon onion) rather than fullerenes. However, the most of thermodynamic parameters of bucky diamond and carbon onion are unavailable, which makes that fullerenes are used for comparison although this treatment will result in some deviations. However, the temperature-pressure equilibrium phase diagram between diamond and fullerences does not exist, the above-mentioned way does not work. To estimate the relative phase stability of n-D and C60, the size-dependent formation heat $\Delta H_f(d)$ is considered, which can be expressed as a function of surface energy γ_{sv}, surface area A, cohesive energy E_{coh}, curvature-induced strain energy $E_{strain} = pV = 4fV/d$. With $A = 6V/d$ for spherical particles, $\Delta H_f(d)$ of n-D or C60 can be written as

$$\Delta H_f(d) = E_{coh} + 6\gamma_{sv}V/d + 4fV/d \tag{7}$$

3 RESULTS AND DISCUSSION

At equilibrium, n-D and n-G should have the same p and f, to avoid the difference between f^D and f^G in terms of Eqn. (4), as a first order approximation, $f = (f^D + f^G)/2$ is taken. Moreover, $S_{vib} \approx 0.19S_m$ for three phases is estimated as a mean value of Si and Ge since they belong to the same IVA group ($S_{vib} \approx 0.22S_m$ for Si and $S_{vib} \approx 0.15S_m$ for Ge)[9]. The prediction in terms of Eqn. (3) is shown in Fig. 1 with the needed parameters in Table 1[10-16]. For comparison, some theoretical and experimental results[8, 9] are also shown. As d and T decrease, the stability of n-D in comparison with n-G increases, and the critical sizes of n-D decrease from about 8.2 nm at 0 K to 3 nm at 1 400 K, which is in agreement with the experimental and theoretical results. According to the Clausius-Clapeyron equation[8],

$$\Delta H = (\mathrm{d}p/\mathrm{d}T)(V^G - V^D)T \tag{8}$$

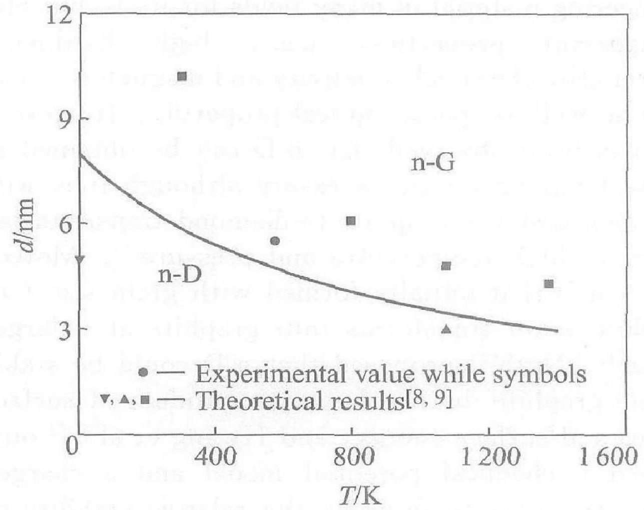

Fig. 1 Size-temperature transition diagram of carbon at zero pressure
(Solid line shows prediction of Eqn. 1)

where ΔH is the transition enthalpy between graphite and diamond, J/mol. Note that $\mathrm{d}p/\mathrm{d}T = 2.06\ \mathrm{J/(cm^3 \cdot K)}$, thus

$$\Delta H = 3.87T \tag{9}$$

and

$$\Delta S = \Delta H/T = 3.87 \tag{10}$$

where ΔS is the corresponding transition entropy, J/(mol·K). This value corresponds to $\Delta S = 3.37$ J/(mol·K) at room temperature and $\Delta S = 4.59$ J/(mol·K) at 1 073 - 1 373 K used by Gammik[17], which contributes partly to the decrease of equilibrium size of the diamond-graphite transition. The mean value of the ΔS is 3.98 J/(mol·K), which is very close to our result. Note that Eqn. (9) implies $\Delta H(T = 0) = 0$, which disagrees with the experimental results of

$\Delta H\,(T=0) = 2.42$ kJ/mol[18]. Thus, the above results are reasonable only when $T > T_D$ where T_D is Debye temperature, or above room temperatures. However, Eqn. (9) indicates indeed that as T increases, specific heat difference of the two phases Δc_p leads to a linear increase of ΔH, or Δc_p is temperature independent at $T > T_D$.

Since C60 structure can be considered finite two-dimensional analogues of graphite, the values of h and H_m are assumed to be the same as those of graphite. Since n-D and C60 concerned here are nanoparticles, thus $d_0 = 3h$. Moreover, n-D is usually transformed into C60 by annealing n-D at about $T = 2\,000$ K[19], which is larger than T_m of C60, thus $H_m(T) = H_m$ in Eqn. (5), and γ_{sl} for C60 is expressed as

$$\gamma_{sl} = 2hS_{vib}H_m/(3VR) \qquad (11)$$

In terms of Eqn. (7) with the necessary parameters listed in Table 1, the formation heats ΔH_f of n-D and C60 are calculated and shown in Fig. 2. It is known that the phase with smaller ΔH_f will be more stable than one with larger ΔH_f. Thus, it is obvious in Fig. 2 that n-D is not the most stable phase of carbon nanoparticles when the size of particle is lower than 2.1 nm, which is consistent with other theoretical result[5, 10]. Although the lower limit of stability of n-D is made through the comparison of the formation heats between n-D and C60 rather than between n-D and bucky diamond or carbon onions, the deviation is very small. The reason may be the smaller energetic differences among bucky diamond, carbon onions and C60 (as shown in Figs. 2 and 3 in Ref. [5]) and the same sp^2-bonding except that the core of bucky diamond is sp^3-bonding.

Table 1 Thermodynamic parameters of graphite(G), diamond(D) and C60

Material	h/nm	V/(cm^3 · mol^{-1})	H_m/(kJ · mol^{-1})
G	0.142	5.3[9]	115[1]
D	0.154	3.4[9]	118[12]
C60	0.142	7.2[11]	115[1]

Material	T_m/K	S_{vib}/(J · mol^{-1} · K^{-1})	B/GPa
G	3 823[13]	5.8	33.8[16]
D	3 723[14]	6.0	442[16]
C60	1 500[15]	14.6	18.1[11]

Material	f/ (J · m^{-2})	E_{coh}/ (kJ · g^{-1} · atom^{-1})	γ_{sv}/ (J · m^{-2})
G	1.2		
D	5.8	717[10]	3.7[8]
C60	2.8	760[10]	

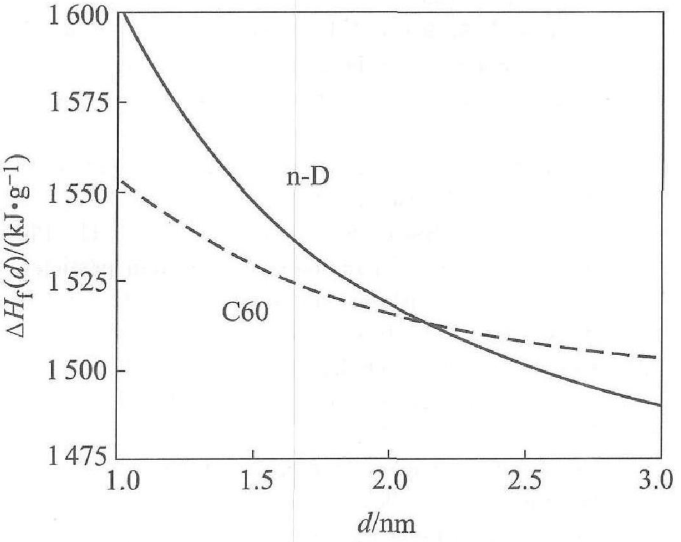

Fig. 2 Calculated formation heat(ΔH_f) as function of particle diameter (d) for n-D(solid line) and C60 (three-point-segment line) in terms of Eqn. (4)

4 CONCLUSIONS

Based on the temperature-pressure phase diagram of carbon and considerations of heat of formation of n-D and C60, the stability of n-D is thermodynamically are determined. It is found that as d and T decrease, the stability of n-D in comparison with n-G increases. However, when $d < 2.1$ nm, C60 is more stable than n-D.

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