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Phase transformation between diamond and graphite in preparation of diamonds by pulsed-laser induced liquid–solid interface reaction

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Abstract. The phase transformation between diamond and graphite in preparation of diamond by pulsed-laser-induced liquid–solid interface reaction (PLIIR) was studied by calculating the probability of phase transition of the carbon atoms over a potential barrier in the pressure–temperature (P – T) phase diagram of carbon. It is found that the probability of phase transition from graphite to diamond is as high as 10^{-3} – 10^{-4} in the C pressure–temperature region where the pressure and temperature are in the range of 10 GPa to 15 GPa and 4000 K to 5000 K, respectively, in the pressure–temperature phase diagram. The distribution of the probability of the phase transformation from graphite to diamond was obtained in the corresponding pressure–temperature region, in which diamonds are prepared by PLIIR. In addition, the dependence of the probability for the transformation of graphite to diamond on temperature was investigated and found to be in agreement with the Arrhenius rule.

1. Introduction

There is great interest in the preparation of diamond material because of diamond's unique physical and chemical properties; many methods have been developed to prepare diamond since the 1950s when diamond crystals were first synthesized by a high temperature and high pressure (HTHP) method [1]. In recent years, the direct deposition of diamond films from the vapour phase has been demonstrated at very low pressure and has become a widely used method to obtain diamonds for technological use [2, 3]. Detonation has been used to prepare ultra-disperse diamonds [4, 5], but there are many impurities existing with the ultrafine diamonds. In order to understand the physical and chemical mechanism of diamond formation in varied preparations, Zhang *et al* studied the thermodynamic transformation between graphite and diamond of an HTHP method in the pressure–temperature phase diagram [6]; however, the thermodynamic mechanism of preparing diamonds by the two methods, i.e., vapour phase deposition and detonation, so far, has not been well understood. Very recently, Yang *et al* developed a unique method to prepare nano-crystalline diamonds, i.e., pulsed-laser-induced liquid–solid interface reaction (PLIIR), and obtained nano-crystalline diamonds with cubic and hexagonal structure [7]. To give a better understanding of the physical mechanism of the nano-crystalline diamond formation during PLIIR in this paper, based on Zhang's thermodynamic models, we mainly study the thermodynamic phase transformation between graphite and diamond, i.e.,

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the probability of phase transition from graphite to diamond, taking place in the corresponding pressure–temperature region of the phase diagram.

2. Thermodynamic models

Based on the understanding from experimental observations until 1994, Bundy provided a new pressure–temperature phase diagram of carbon [8] as shown in figure 1. The solid lines represent equilibrium phase boundaries, and the solid line from low temperature and low pressure to the triple point (12 GPa–5000 K) of diamond, graphite and liquid carbon is the so-called Berman–Simon line (B–S line) in the phase diagram. From the phase diagram one can see that diamond is in the metastable state in the region above the Berman–Simon line. The A region is the pressure–temperature region utilized for the HTHP commercial preparation of diamond from graphite. The dashed line, B–F–G, in figure 1 marks the threshold of very fast (i.e. ms– μ s) transition of highly compressed graphite, or its low temperature derivatives, to cubic-type diamond. The B region on the dashed line B–F–G marks the temperature–pressure threshold of very fast (<1 ms) and complete solid–solid transformation of graphite to diamond. This transition always yields cubic-type diamond. Experimentally, it is done by pressurizing graphite above 12 GPa and heating the sample with a pulse of electric current or laser radiation. From the studies of the effect of a high power laser irradiating the surface of a solid graphite target by Venkatesan *et al* [9], the pressure dependence of the temperature of the carbon cluster in the preparation of diamonds by PLIIR [7] can be determined by $T = -0.1163P^2 + 15.66P + 4000$, with T in kelvin and P in kilobars. In previous experimental studies, the range of the temperature was deduced to be above 4000 K [9]. Thus, the

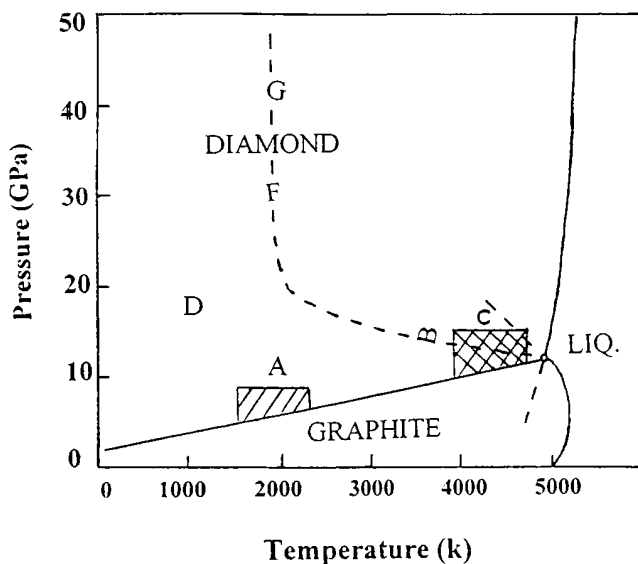


Figure 1. P , T phase and transition diagram of carbon established by F P Bundy. Solid lines represent equilibrium phase boundaries. A: commercial synthesis of diamond from graphite by catalysis; B: P/T threshold of very fast (less than 1 ms) solid–solid transformation of graphite to diamond; C: P , T region of synthesis of diamond by PLIIR; D: single crystal hexagonal graphite transforms to retrievable hexagonal-type diamond; B,F,G: threshold of fast P/T cycles, however generated, that convert either type of graphite or hexagonal diamond into cubic-type diamond.

range of the pressure was deduced to be within 10 GPa to 15 GPa. Therefore, in this study, we focus attention on calculating the probability of phase transition of the carbon atoms over a potential barrier in the C region, in which the formation of diamond by PLIIR takes place. The D region delineates the general area in which single crystal hexagonal graphite transforms gradually to retrievable hexagonal structural diamond.

The Gibbs free energy is an adaptable measure of the energy of a state in phase transformation among the competing phases. For the given pressure–temperature condition, both diamond and graphite phases can co-exist, but only one of the two phases is stable, with minimal free energy, and the other must be metastable and may transform into the stable state. Thermodynamically, the phase transformation is promoted by the difference of the free energies; the phase transformation is therefore determined quantitatively by the probability of the carbon atoms crossing a potential barrier of intermediate state [6]. Generally, the Gibbs free energy $G_{T,P}$ of a phase can be expressed as a function of the pressure–temperature condition, and determined by a general coordinate or reaction coordinate r . The probability of the phase transformation from the metastable phase to the stable phase is determined not only by the Gibbs free energy difference $\Delta G_{T,P}$, but also by an activation energy ($E_a - \Delta G_{T,P}$), which is necessary for the transition. When the two phases are at the equilibrium condition, i.e., $\Delta G_{T,P} = 0$, E_a is the maximum potential energy for both sides with respect to the general coordinate r .

The general expression of the probability f of the phase transformation from the initial states to final states is

$$f = \exp[-(E_a - \Delta G_{T,P})/RT] - \exp[-(E_a/RT)] \quad (1)$$

where R is the gas constant. In our case, for the phase transformation from graphite to diamond, $f = f_d$ and $\Delta G_{T,P}^d = G_{T,P}^g(\text{graphite}) - G_{T,P}^d(\text{diamond})$, and $(E_a - \Delta G_{T,P}^d)$ is the activation energy of the graphite to diamond transition; f_d can be therefore given by relations (1). Instead, for the phase transformation from diamond to graphite, $f = f_g$ and $\Delta G_{T,P}^g = G_{T,P}^d(\text{diamond}) - G_{T,P}^g(\text{graphite})$, f_g should be expressed by

$$f_g = \exp[-(E_a/RT)] - \exp[-(E_a - \Delta G_{T,P}^g)/RT]. \quad (2)$$

According to thermodynamics, we obtain $(\partial \Delta G_{T,P} / \partial P)_T = \Delta V$, then we have:

$$\Delta G_{T,P} = \Delta G_T^0 + \int_0^P \Delta V \, dP \quad (3)$$

where ΔV is the volume difference between graphite and diamond, and ΔG_T^0 is the mole Gibbs free energy difference at zero pressure. When the conditions are on the diamond–graphite equilibrium line of Berman and Simon and its extrapolation (i.e., $\Delta G_{T,P} = 0$), P and T satisfy the relation $P = 2.73 \times 10^6 T + 7.23 \times 10^8$ (Pa). Bundy's experimental results showed that ΔV remains approximately constant with pressure–temperature condition, i.e., $\Delta V = 1.77 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$ [10]. Thus, $\Delta G_{T,P}^d$ for the graphite-to-diamond transition in a unit volume can be given by

$$\Delta G_{T,P}^d = 1.77 \times 10^{-6} (P - 2.73 \times 10^6 T + 7.23 \times 10^8). \quad (4)$$

It is noticed that, for the diamond to graphite transition, $\Delta V = -1.77 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$, $\Delta G_{T,P}^g$ for the diamond to graphite transition in a unit volume can be therefore expressed by

$$\Delta G_{T,P}^g = 1.77 \times 10^{-6} (2.73 \times 10^6 T + 7.23 \times 10^8 - P). \quad (5)$$

Bundy *et al* have studied the process of synthesizing diamond in region A in figure 1 [8]. They suggested that, although the process started with solid graphite and ended with solid diamond, it was not a truly solid–solid transition because in this process carbon from the graphite source

dissolved into the ambient catalyst–solvent fluid metal layer and precipitated out on the growing diamond sink, and the activation energy of solution was about 125–160 kJ mol⁻¹. On the other hand, experimentally, Zhang *et al* have studied the diamond growth rate from graphite in region A in figure 1 [11] and found that the diamond growth rates are approximately proportional to $e^{-(E-P\Delta V)/RT}$, which is similar to the factor $e^{-(E_a-\Delta G_{T,P})}$ in equation (1) when $\Delta G_{T,P} \rightarrow P\Delta V$. Moreover, they obtained a value of $E = 120$ kJ mol⁻¹. Since $\Delta V = 1.77 \times 10^{-6}$ m³ mol⁻¹, $P\Delta V$ can be estimated to be about -8 to -13 kJ mol⁻¹ in the A region. Therefore, the activation energy of the graphite to diamond transition in Zhang's experimental studies should be in the range 128–133 kJ mol⁻¹, which is in the range suggested by Bundy. According to Bundy's theory and Zhang's experimental data, we thus use the value of $E_a = 120$ kJ mol⁻¹ in our calculation.

3. Results and discussion

According to equation (1), equation (4) and $E_a = 120$ kJ mol⁻¹, the probabilities of the phase transformation between graphite and diamond can be calculated, and the distribution of the transiting probabilities is shown in figure 2. The f_d constant curves display a 'V'-shape; one side approaches the Berman–Simon line and the other side stands nearly vertical. The distributions of the probabilities f_d and f_g are similar to the experimental results [10]. In addition, f_d increases quickly with the temperature; when the pressure–temperature conditions are in the region of 4 GPa to 10 GPa and 1300 K to 2500 K, in which the HTHP methods are used, f_d is about 10^{-5} . It is noted that the values of f_d are within 10^{-4} to 10^{-3} when the pressure–temperature conditions are in the region of 10 to 15 GPa and 4000 K to 5000 K,

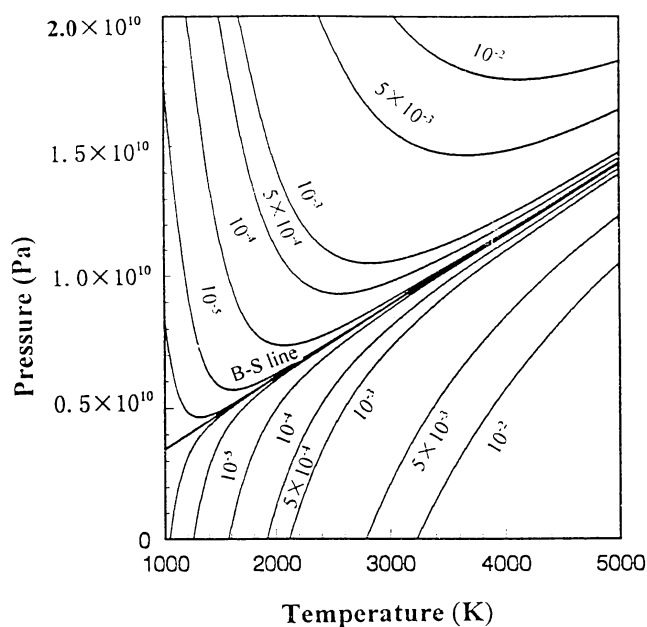


Figure 2. Schematic illustration of the probability of phase transformation in the pressure–temperature diagram. The B–S line is the Berman–Simon line. The curves above and below the B–S line are f_d and f_g , respectively.

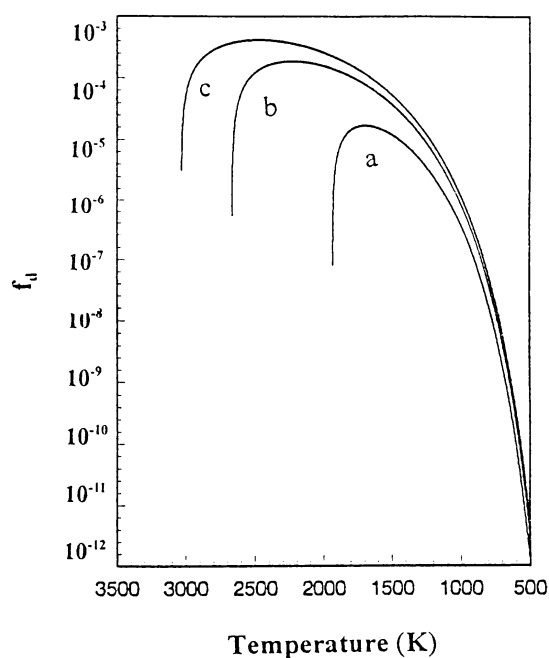


Figure 3. f_d - T curves: (a) $P = 6$ GPa, (b) $P = 8$ GPa, (c) $P = 10$ GPa.

i.e., the C region in figure 1, in which nano-crystalline diamonds are prepared by PLIIR. Therefore, it is interesting that the f_d in the C region is an order of magnitude higher than that in the A region. Thus, the results show that PLIIR is a highly efficient method to prepare diamonds. On the other hand, the temperature dependence of f_d was also calculated based on the above thermodynamic models: the f_d - T curves are shown in figure 3. It is clearly seen that the shape of these curves is similarly to that of the Arrhenius line, i.e., the probability of the graphite-to-diamond phase transition is in agreement with the Arrhenius rule. The formation mechanism of diamonds prepared by detonation is similar to that of PLIIR, and the transformation from graphite to diamond also takes place in the C region. Based on the experimental results [12], the phase transition rate of graphite to diamond was expressed by

$$d\lambda/dt = c(p) \exp[-(E/RT)] \quad (6)$$

where $c(p)$ is a function of P , λ is the percentage of graphite and E is the activation energy. It is noticed that equation (6) is an approximation of equation (1) when $\exp(\Delta G_{T,P}/RT) \rightarrow 1$ and $\Delta G_{T,P} \rightarrow P\Delta V$, where E has a similar value to E_a . In fact, the value of E is also in the range of 125 kJ mol^{-1} to 165 kJ mol^{-1} [8]. Therefore, the rate of the empirical equation (6) is evidently proportional to the probability of phase transition.

From the experimental results [7], the size of nano-crystalline diamonds prepared by PLIIR varies from 40 to 200 nm. According to thermodynamic theory, the size of the diamond grain is related to the difference of the enthalpy of the phase transformation, pressure and temperature. According to the suggested growth mechanism of diamonds by PLIIR two graphite lattices are transformed into two diamond lattices by means of a solid-solid diffusionless transformation in the carbon cluster at the state of high temperature, high pressure and high density, which is followed by the formation of diamond crystal nuclei and the growth of nuclei [7]. Because $\Delta G_{T,P}$ and f_d are very high in the C region, and the frequency of the nucleation of diamonds

increases exponentially with the increase of $\Delta G_{T,P}$ [13], the nucleation rate is so high that the nuclei cannot grow large. In addition to considering the pulse width of the laser, therefore, the size of diamond grains prepared by PLIIR is always on the scale of nanometres. Accordingly, the C region in the Bundy diagram (figure 1) is well suited for preparation of ultrafine diamonds.

4. Conclusions

The probability of the phase transformation between graphite and diamond was calculated in the pressure–temperature phase diagram of carbon based on the thermodynamic models, and the distribution of the probabilities of the graphite-to-diamond phase transition was analysed in the C region of the Bundy diagram, in which nano-crystalline diamonds form upon PLIIR. It is suggested that the C region can be used for efficiently preparing nano-crystalline diamonds.

Acknowledgments

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