

Investigation on the Action Effect of Catalyst in the Cubic Boron Nitride Nucleation

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Abstract We suggest a new hypothesis on the effect of catalyst action in cBN synthesis by the catalyst method under the super high pressure and high temperature. And on the basis of this hypothesis we theoretically found cBN nucleus formation region in P - T phase diagram and compared with the results of the experiment. And we showed that the hypothesis suggested in the paper is appropriate.

Key words cubic boron nitride, nucleation, diffusion mechanism, activation energy

Introduction

After the first discovering of the cubic boron nitride synthesis method many studies on the cubic boron nitride synthesis were progressed but the mechanism of hBN-cBN transition by super high pressure is still under discussion [5–7].

In the study [7] by using the synchrotron radiation for energy dispersive X-ray diffraction cBN synthesis process was observed *in situ*. It is found that cBN grows directly from an amorphous matrix and not from different BN polymorphs as previously proposed in the case of direct transition without the catalyst from hBN to cBN. This is the evidence that cBN formation is carried out by the diffusion mechanism. In the study [1] the diffusion mechanism of cBN synthesis theoretically was studied on the basis of these experimental facts and theoretically determined the cBN synthesis region in the P - T state diagram.

The various catalyst solvent materials are used to decrease the pressure and temperature required for cBN synthesis. In the case of cBN synthesis by the catalyst the catalytic action effect is also still under discussion. In the preceding paper[4] was suggested the colloid theory by which the catalyst material first forms intermediate products by reacting with a part of hBN under the super high pressure and high temperature, then the intermediate product liquid forms the hBN colloid solution and in this liquid hBN colloid particles have transformed to cBN. However this colloid theory was not showed microscopic mechanism how hBN colloid particle have transformed to cBN.

In this paper the catalyst action effect in cBN synthesis by catalyst method was also studied on the basis of the diffusion mechanism.

1. The Hypothesis of Catalyst Action in the cBN Crystal Nucleation and Diffusion Activation Energy

Here we suggested following hypothesis.

If hBN surface was contacted mutually each other under the super high pressure and high temperature with the catalyst liquid and then eutectic compound solvent will be formed in the contact boundary surface [9]. The amorphous component of hBN dissolved in this solvent as an atom state and hBN crystal particles dissolved as the colloid particle to the solvent so that these finally will become the colloid solution. In this time many vacant defect will form in hBN colloid particle surface. Since this vacant defects go into hBN colloid particle by the diffusion (in other words the atoms situated in hBN colloid particle interior go out to the vacant site formed in the boundary surface by diffusion), in hBN colloid particle inner part many vacant defect will be occurred. With the passage of time the vacant defect density in the colloid particle interior obviously will increase suddenly.

Let us calculate the activity energy of cBN crystal nucleation in hBN colloid particle on the basis of this mechanism.

It can be carried out any moment that the one among of hBN three sp^2 bond was turned into a vacant in the hBN colloid particle inner part. In this state we determine the activity energy of cBN crystal nucleus formation. The activity energy of cBN crystal nucleus formation was determined as the work done for removing the B atom and the N atom vertically on hBN (002) plane by distance in which bond with surrounding atoms fully break off.

The energy U_0 (kJ/mol) which was required for removing one atom vertically on hBN (002) plane was calculated as follows.

$$U_0 = E - E_0 \quad (1)$$

where E_0 is the cohesion energy of hBN crystal and E is the cohesion energy of hBN crystal state in which an atom of the hBN was removed vertically on (002) plane.

The cohesion energy of hBN crystal was calculated by using the application program which is analyzing the crystal structure by the first principle (ab initio) method in the local density approximation.

And the cohesion energy of hBN crystal with the vacant was calculated in the structure model in which one of hBN three sp^2 joint is emptying.

As shown in Fig. 1 the results of the calculation on the work done for vertically removing B atom and N atom of hBN on (002) plane to the distance d .

The simulation showed that the B atom or the N atom of the hBN fully break off coupling with surrounding atoms and turn to the isolation atom state if it is moving from (002) plane to

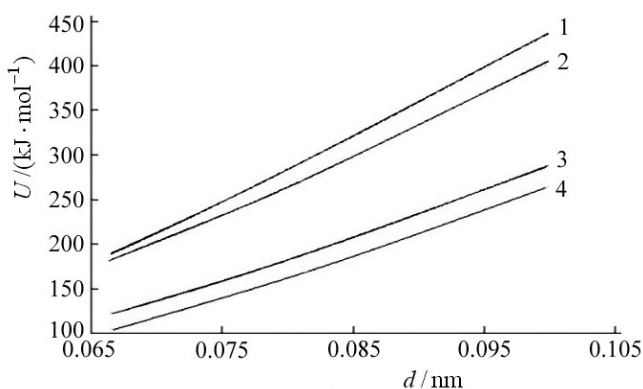


Fig. 1. The energy required for vertical displacement of hBN atom on (002) plane calculated by the first principle method.

- 1, 3—B atom migration energy of the case without the vacant(1) and with the vacant(3);
- 2, 4— N atom migration energy in the case without the vacant(2) and with the vacant(4) moving energy of N atom in the cases with the vacant and without vacant.

the degree of 0.1nm.

As shown in table the energy which are needed to turn to the isolation atom state in the cases with the vacant and without vacant is as follows.

From Fig. 1 and table we can find that the cBN nucleation activity energy is $U_0 = 276.54 \text{ kJ/mol}$. This activation energy U_0 is the value in temperature

Table. The energy needed to turn to the isolation atom state(kJ/mol)

Atom	Case without the vacant	Case with the vacant
B	436.86	288.60
N	406.42	264.48

0K. Therefore we must consider the relationship of the activation energy with temperature.

For this we would use following empirical formula which show temperature dependency of the activation energy $U(T)$ [2].

$$U(T) = U_0 \cdot e^{-f\left(\frac{T}{\theta}\right)} \quad (2)$$

where

$$f\left(\frac{T}{\theta}\right) = \frac{T}{\theta} + c\left(\frac{T}{\theta}\right)^2 + d\left(\frac{T}{\theta}\right)^3 \quad (3)$$

And U_0 is the activation energy value in temperature 0K and θ is a Debye temperature for cBN; $\theta = 710 \text{ K}$ [3]. The c and d as the temperature correction coefficients must determinate by the experimental data. These temperature correction coefficients are determined so that theoretical result of cBN crystal nucleus formation region in P - T state diagram was united with the experimental data in the case of the cBN synthesis without the solvent [1].

2. The Determination of the cBN Crystal Nucleus Formation Region

We will find the cBN formation region in the P - T state diagram by using the following formula.

$$P = a + bT + \frac{3(2 \ln 10)^{1/2} (\sigma kT)^{1/2} e^{\frac{U}{2kT}}}{(\pi \omega \tau)^{1/2} a_0^2 |n_0 \Delta \bar{V}|} \quad (4)$$

where a_0 is radius of the volume space occupied by an atom, $\Delta \bar{V} = V_h - V_c$ is the atomic volume difference between hBN and cBN, the constants a, b are the parameters which determined the phase equilibrium equation of cBN and hBN $P = a + bT$ while it is -1.46 GPa , 0.0031 GPa/K respectively and ω is the oscillation frequency of an atom in the cBN crystal surface, k is Boltzmann constant, p is the pressure, T is the temperature, U is activation energy, τ is cBN crystal nucleus formation time, σ is the surface energy density between cBN crystal nucleus and hBN phase and it can place $\sigma = \sigma_c - \sigma_h$.

For calculation of the activation energy we have used formula (2), (3) and (4).

In this case the activation energy of cBN nucleation in temperature 0K is $U_0 = 276.5 \text{ kJ/mol}$ according to an expression (2). And we chose so that the temperature correction coefficients c

and d were equivalent to case of the direct synthesis [1]. We chose cBN crystal nucleus formation time $\tau=5\text{ms}$, that was same time with a period of the direct synthesis [1].

We choose the other material constants in equation(4).

$$\begin{aligned} a_0 &= 1.12 \cdot 10^{-10} \text{ m}, & V_c &= 5.9 \cdot 10^{-30} \text{ m}^3, \\ V_h &= 9.05 \cdot 10^{-30} \text{ m}^3, & \sigma_c &= 4.72 \text{ J/m}^2, \\ \sigma_h &= 3.40 \text{ J/m}^2, & \omega &\approx 2.0 \cdot 10^{14} / \text{s}. \end{aligned}$$

Then the cBN nucleation region in P - T diagram were theoretically obtained by using the formula (2) – (4) (curve 1 of Fig. 2). This theoretical result is well uniting with the experimental result (curve 2 of Fig. 2 [8]).

This is shown that our hypothesis for crystal nucleus formation in the cBN synthesis by the catalyst method is appropriate.

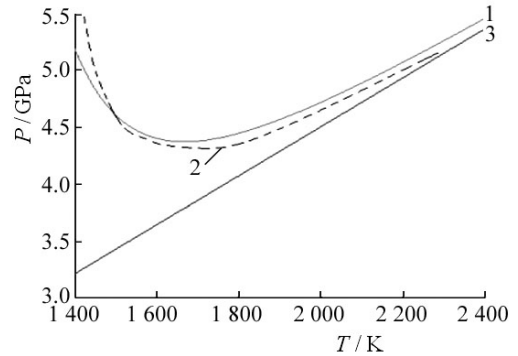


Fig. 2. cBN formation area in P - T phase diagram

1 — theoretical data, 2 — experimental data [8]

Conclusion

In this paper we suggested the new hypothesis on the catalyst action effect in the case of cBN synthesis by the catalyst method under the super high pressure and high temperature.

If hBN surface was contacted mutually under the super high pressure and high temperature with the catalyst liquid, eutectic compound solvent will be formed in the contact boundary surface.

The amorphous component of hBN is dissolved in this solvent as an atom state and hBN crystal particles are dissolved as the colloid particle to the solvent so that they finally will be the colloid solution. In this time many vacant defect will be formed in hBN colloid particle surface.

Since this vacant defects go into hBN colloid particle by the diffusion (in other words the atoms situated in hBN colloid particle interior go out to the vacant site formed in the boundary surface by diffusion), in hBN colloid particle inner part many vacant defects will occur.

With the passage of time the vacant defect density in the colloid particle interior obviously will increase suddenly.

This has been reduced the activation energy of the cBN nucleus formation so that the pressure and temperature for the cBN synthesis has been reduced.

Then on the basis of this hypothesis we find theoretically cBN nucleus formation region in P - T phase diagram and by comparing the result of the theory and the experiment we showed that the hypothesis suggested in this paper is appropriate.

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