JOURNAL OF MATERIALS SCIENCE 23 (1988) 3254–3257

The kinetics of cubic boron nitride formation in the system BN–Mg_3N_2

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Cubic boron nitride is synthesized using Mg_3N_2 as a catalyst at a pressure of 6.5 GPa in the temperature range $1600 < T < 2200$ K. The temperature variations of growth and net transformation rates are estimated. Above 1650 K the transformation kinetics is well described by a nucleation and growth process. The theoretical description based on the homogeneous nucleation and layer growth mechanism yields reasonable results in comparison with the experimental data. The relevant parameters are estimated and discussed. The effect of the catalyst is suggested to consist in lowering the activation enthalpy for nucleation. Below 1650 K it is shown that the transformation kinetics changes qualitatively and the nucleation and growth mechanism is not the appropriate description. The physics of transformation in this temperature range have hitherto remained unexplained.

1. Introduction

It is well known that under high pressure (HP) and high temperature (HT) conditions the hexagonal boron nitride (hBN) is transformed into the cubic crystal modification (cBN). Some materials called "catalysts" promote the conversion of hBN into cBN under HP–HT conditions.

After Wentorf [1] had carried out the first synthesis of cBN with a catalyst, a number of different catalysts were proposed. Wentorf used the alkali and alkaline earth metals and their nitrides [1, 2] such as lithium, magnesium, calcium, Li_3N, Mg_3N_2 and Ca_3N_2. These catalysts and their influence on the phase transition have been investigated by numerous authors.

By using the binary metal nitride Li_3N, De Vries and Fleischer [3] identified the high-pressure phase of the ternary metal nitride Li_3BN_2 as the active component in the BN–Li_3N system. Li_3BN_2 was formed by the reaction of hBN and Li_3N. Endo *et al.* [4, 5] identified the compound $Mg_3B_2N_4$, and similarly $Ca_3B_2N_4$ [6, 7]. The ternary metal nitrides have a eutectic with BN under high pressure and temperature and hBN is dissolved into the liquid ternary metal nitride. cBN crystallizes from this solution because its solubility is lower than that of hBN. However, the mechanism of nucleation and crystal growth is still a subject of discussion.

On the basis of this background, the present work was undertaken to investigate the kinetics of the phase transition and to discuss the mechanism of nucleation and crystal growth.

2. Experiments

2.1. Starting materials

The sintered body of hexagonal BN powder contained 0.6 wt % oxygen and had a graphitization index of 1.6. Mg_3N_2 was synthesized by heating magnesium metal under a nitrogen stream at 600° C for 4 h, and subsequently at 900° C for 8 h. The Mg_3N_2 had an oxygen content of 0.8 wt %.

The oxygen contents were measured by neutron activation analysis and the graphitization index was determined by X-ray diffraction patterns.

2.2. High pressure and high temperature experiments

The high-pressure experiments were carried out using a belt apparatus. A microprocessor system allowed fully automatic control of force and electric heating power and the storage of all values which were measured in the course of the experiment.

The pressure was calibrated at room temperature at the fixed points for the phase transitions in bismuth (2.55; 7.7 GPa), tantalum (3.68 GPa) and barium (5.5 GPa). The temperature in the reaction cell was determined from the relation between the electric power supplied to the carbon heater and the temperature. The pressure effect of e.m.f. of the thermocouple was not corrected. Fig. 1 shows a typical construction of the cell assemblies for the experiments. The catalyst Mg_3N_2 was placed in the centre of the reaction cell and was surrounded by hBN.

After the HP–HT experiment, the sample was leached with diluted HCl to solve the catalyst. cBN was refined from hBN with molten hydroxides [8]. Recovered samples were examined by X-ray diffraction. The crystal habit and the surface structure of cBN were observed under an optical microscope and a scanning electron microscope (SEM).

3. Results

The conversion rate and the crystal growth rate of cBN were investigated in the temperature range 1600 to 2200 K at a pressure of 6.5 GPa. In all runs the

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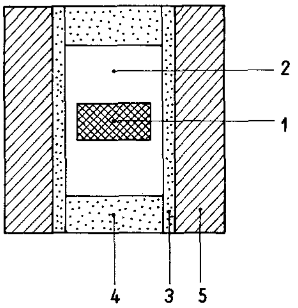

Figure 1 The reaction cell: 1, Mg_3N_2 catalyst; 2, hBN; 3, carbon heater; 4, carbon disc, 5, pyrophyllite.

reaction time was 15 min. After cooling to a temperature lower than 500 K the applied pressure was released. Fig. 2 shows the relative conversion rate plotted against temperature. The conversion rate exhibits two ranges with one maximum each. The morphology and the grain size of cBN are different in both ranges.

In the temperature interval from 1600 to 1650 K, the conversion rate is large and many crystals grow with a grain size smaller than 1 μm. The crystals tend to form compact agglomerates with a size of a few millimetres (see Fig. 3). The physical mechanism of phase transition is not understood in this range.

Isolated single crystals grow in the temperature interval from 1700 to 2200 K. The conversion rate has a maximum at 1900 K and the amount of conversion is about 30%. The temperature dependence of the conversion rate for a fixed time is determined by the nucleation and growth rates (see the black points in Fig. 4). The crystal growth rate depends on the temperature and includes a maximum at about 1820 K. Crystal growth was only observed in cases where the temperature was more than 300 K below the equilibrium temperature. Therefore, we suggest a layer growth with two-dimensional nucleation as a possible mechanism for the crystal growth. They crystals have a maximum grain size of 200 μm at 1820 K. Predominantly, the cBN crystals show a tetrahedral habit, acute corners and sharp edges. From the grain distribution and the pressure dependence of nucleation observed in the experiments it is concluded that the homogeneous nucleation is the relevant nucleation process. This statement is further supported by the fact that the maxima of the conversion rate and the growth rate appear at different temperatures.

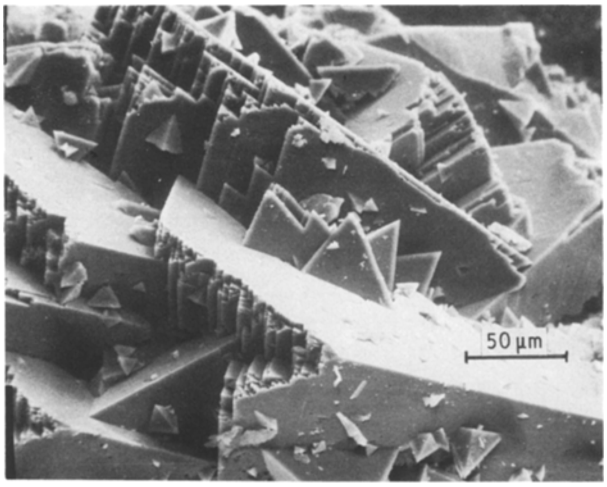

Figure 3 cBN crystals synthesized at about 1600 K and 6.5 GPa

4. Theoretical analysis

The results of the previous section are explained by the kinetics of nucleation and growth [9]. The essential parameters of this process are the mean nucleation rate, I, for homogeneous nucleation and the linear growth velocity, v, which is independent of time for interface-controlled growth. In terms of I and v the relative volume fraction, x_β, of the transformed phase at time t is given in Avrami's equation

$$x_\beta(t) = 1 - \exp\left(-\frac{\pi}{3} I v^3 t^4\right) \qquad (1)$$

The parameters v and I as obtained from thermodynamic considerations are discussed in more detail below.

4.1. Temperature dependence of the growth rate

The qualitative behaviour of the growth rate depends on the growth mechanism which is determined by the shape of the interface [10]. The interfacial structure is characterized by the Jackson factor, $\eta = 4J/kT$, where $J = (\phi_{\alpha\alpha} + \phi_{\beta\beta} - 2\phi_{\alpha\beta})/2$ and $\phi_{\alpha\beta}$ are the microscopic binding energies of growth units of the initial and final phases α and β, respectively. For $\eta < 3.5$ the interface is rough and the growth rate increases linearly with the undercooling below the equilibrium temperature, T_0. However, for $\eta > 3.5$ the interface is microscopically smooth and the process of two-dimensional nucleation is responsible for the crystal growth. In this case the growth rate

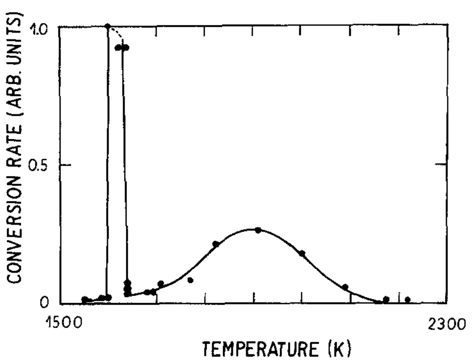

Figure 2 Conversion rate plotted against temperature, for $p = 6.5$ GPa, $t = 15$ min.

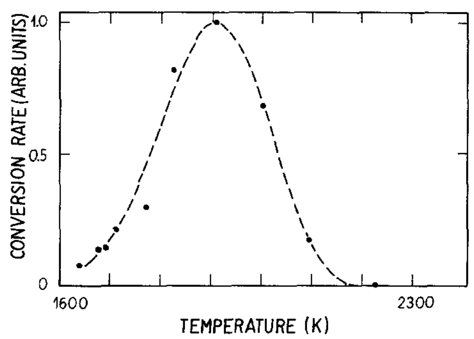

Figure 4 The temperature dependence of the conversion rate for a fixed reaction time: (●) experimental results, (- - -) theoretical analysis.

varies exponentially with temperature for small undercooling, and a measurable growth sets in only for temperatures well below T_0.

The growth velocity estimated at $p_0 = 6.5\,\text{GPa}$ for the cBN synthesis (Section 3) shows a rapid rise at first for temperatures more than 300 K below the equilibrium temperature $T_0 = 2600\,\text{K}$. Therefore, the two-dimensional nucleation is the most probable mechanism for the growth of the cBN cystals under the experimental conditions. The temperature dependence of the growth rate has been studied extensively [11] and is given in the birth-and-spread model as

$$v = C_G \exp(-E_D/kT)\left(\frac{\Delta\mu}{kT}\right)^{5/6} \times \exp\left(-\frac{\pi\gamma^2}{\Delta\mu kT}\right) \qquad (2)$$

where C_G is a temperature independent constant, E_D is the activation energy for the diffusion and γ is the edge free energy of the two-dimensional nucleus. $\Delta\mu$ is the difference of the free enthalpies of both phases and is expanded around the equilibrium point (p_0, T_0)

$$\Delta\mu = (p - p_0)\,\Delta V_0 + (1 - T/T_0)\,\Delta h_0 \qquad (3)$$

ΔV_0 and Δh_0 are the volume change and the heat of transition, respectively, in the point (p_0, T_0). For constant pressure $(p = p_0)$ $\Delta\mu$ is proportional to the undercooling $T_0 - T$.

The interfacial free energy, γ, of the two dimensional nucleus depends on the temperature because the edge of a two-dimensional area is rough and the entropy contribution is considerably large [12, 13]. Using the exact result for the two-dimensional Ising model the edge free energy can be expressed in a good approximation by the binding energy, J, defined above

$$\gamma = J - kT\ln\left(\coth\frac{J}{2kT}\right) \qquad (4)$$

The probability of impingement of growth units to the interface depends on several diffusion processes in the bulk phases. The first exponential factor in Equation 2 takes into account the thermally activated diffusion in the bulk phases with the activation energy, E_D. The temperature dependence of C_G is weak and can be neglected. The growth rate (Equation 2) has a maximum at a temperature T_M given by the implicit equation

$$\tfrac{5}{6}\Delta h_0 - \frac{\pi\gamma^2}{kT_M} + \frac{\pi\Delta h_0\gamma^2}{kT_0\Delta\mu} + 2\pi\gamma\bar{\gamma} = \frac{\Delta\mu}{kT_M}E_D \qquad (5)$$

with

$$\bar{\gamma} = -\ln\left(\coth\frac{J}{2kT_M}\right) - \frac{J}{kT_M}\left(\sinh\frac{J}{kT_M}\right)^{-1}$$

$\Delta\mu$ and γ are the values from Equations 3 and 4, respectively, for $T = T_M$.

The experimental growth rate shows a maximum at about 1820 K. This should be compared with Equation 5 if the relevant parameters are determined. The layer-by-layer growth process observed in the cBN synthesis and discussed above, requires parameter J to be larger than $J_c = 0.87\,kT_0$. For $J \leqslant J_c$ the step free energy (Equation 4) vanishes and the continuous growth of rough interfaces takes place. The heat of transformation, Δh_0, is given by $\Delta h_0 = 3.6\,\text{kcal mol}^{-1}$ [14] corresponding to $\Delta h_0/kT_0 = 0.7$. Comparing the measured growth rates with Equations 2 and 5 we have estimated parameters J and E_D as $J/kT_0 = 1.42$, $E_D/kT_0 = 6.5$. Inserting these values into Equation 2 we get the temperature dependence of v as shown in Fig. 5. At the lower temperatures ($1600\,\text{K} < T < 1650\,\text{K}$) the experimental growth rates are considerably smaller than the theoretical ones. The possible reasons are discussed later.

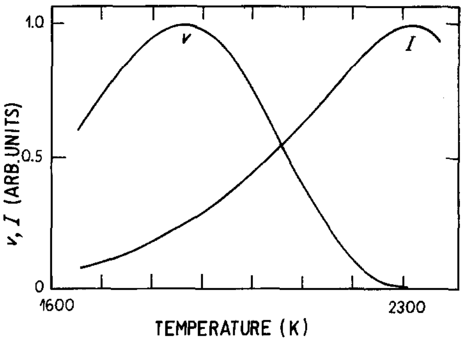

Figure 5 Temperature dependence of the growth (v) and nucleation (I) rates.

4.2. Homogeneous nucleation rate

According to the classical theory of nucleation [9, 15] the nucleation rate, I, is given by

$$I = C_N \exp(-E_D/kT)\exp\left(-\frac{16\pi\sigma^3}{3kT\Delta\mu^2}\right) \qquad (6)$$

where C_N is a temperature independent constant and σ represents the interface free energy of the three-dimensional nucleus. In comparison with the step free energy (Equation 4) the temperature dependence of σ is less essential and can be neglected because in three dimensions there is no roughening transition [12].

The nucleation rate has a maximum at a temperature T_m given by

$$\frac{3T_m - T_0}{(T_0 - T_m)^3} = \frac{3\Delta h_0^2}{16\pi T_0^2\sigma^3}E_D \qquad (7)$$

Experimentally it is verified that the largest crystals are observed at temperatures slightly below the temperature of the maximal transformation rate. Hence, the nucleation rate maximum lies at higher temperatures than the maximum of growth, yielding an upper bound for the interface energy, σ, according to Equation 7, $\sigma/kT_0 < 0.16$.

4.3. Net transformation rate and average grain size

The nucleation rate cannot be measured directly in the high-pressure experiments. Therefore, we fit the temperature dependence of the relative volume fraction, x_β (Equation 1), for a fixed time, t, using Equations 2 and 6. For $\sigma = 0.05\,kT_0$, x_β is shown in Fig. 4. For this value of σ we get a reasonable agreement with the experimental data. The corresponding nucleation rate

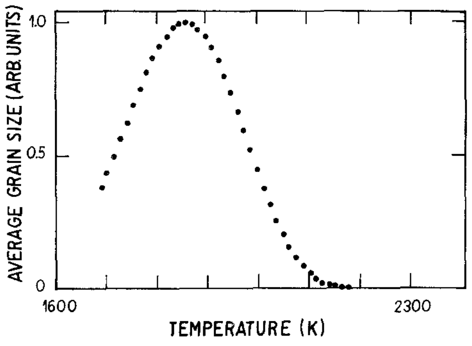

Figure 6 The calculated average grain size plotted against temperature.

is represented in Fig. 5. The maximum I occurs at rather high temperatures and the regime of most effective cBN synthesis is on the low-temperature side of the nucleation rate.

The average grain size, $\bar{x}(t)$, at the time t is calculated from Equation 1 dividing $x_\beta(t)$ by the number of grains

$$\bar{x}(t) = x_\beta(t) \Big/ \int_0^t I x_\beta(t')\,\mathrm{d}t' \qquad (8)$$

and is shown in Fig. 6. In coincidence with the experimental results the grain size has a maximum for temperatures slightly below the maximum of the transformation rate.

The most striking differences of the theoretical and experimental results appear below 1650 K. A careful consideration of this temperature regime seems necessary. Calculating the size of the critical nucleus with the parameters determined above it turns out that below 1650 K the critical size becomes very small. In this case the theory of nucleation and growth is not appropriate and the kinetics of the transformation is determined by different physical mechanisms. The latter statement is confirmed by the qualitative differences in the microstructure of cBN obtained at 1600 K and at higher temperatures. The deviation of the experimental growth rates from the calculated ones at lower temperatures could be due to this qualitative change of the transformation kinetics.

With regard to the parameters estimated above the variation of an order of magnitude between the edge free energy for growth, γ, and the interface free energy for nucleation, σ, is an unexpected result. It can be explained by the influence of the catalyst to consist in the promotion of nucleation and the reduction of the correspoding activation enthalpy.

5. Conclusions

From the systematic investigation of the temperature variation of growth and transformation rates in the cBN systhesis under HP–HT conditions the following conclusions are derived.

1. The catalytic high pressure–high temperature synthesis of cBN is based on the nucleation and growth mechanism. The experimental results are well described by the classical theory of homogeneous nucleation and growth.
2. At very low temperatures ($T < 1650$ K at 6.5 GPa pressure) the transformation kinetics changes qualitatively.
3. The main effect of the catalyst consists in the lowering of the activation enthalpy for nucleation.

Further investigations, especially on the pressure dependence of the transformation kinetics, should be explained within the formalism derived in Section 4. The corresponding experimental and theoretical work is in progress.

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Received 14 September
and accepted 10 December 1987