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The binary system of BN–Mg_3N_2 under high pressures and temperatures

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The phase relations in the binary system of BN–Mg_3N_2 were investigated in regions of pressure, *P*, from 3.0 GPa to 8.0 GPa and temperature, *T*, up to 1900 K by means of *in situ* differential thermal analysis (DTA) and X-ray diffraction (XRD) of the quenched products. It was found that the succession in formation of the intermediate compounds Mg_3BN_3 (HP-phase) and $Mg_3B_2N_4$ depends on the molar ratios of hexagonal boron nitride (hBN) and Mg_3N_2 and on the *P–T* conditions. In the *P–T* region of cubic boron nitride (cBN) growth, the system has three metastable eutectics such as Mg_3N_2–hBN, Mg_3BN_3–hBN and $Mg_3B_2N_4$–hBN. It was found that eutectic temperatures are pressure dependent. The difference in the lower-temperature limits of cBN growth regions is explained by cBN crystallization from different eutectic melts.

1. Introduction

It is known that some materials, called "catalysts", promote the conversion of hBN into cBN under high pressure (HP) and high temperature (HT) conditions. One of these catalysts, Mg_3N_2, is commonly used in the practical synthesis of cubic boron nitride (cBN). However there are large differences in the lower temperature limits of the growth *P–T* region of cBN in the BN–Mg_3N_2 system [1, 2, 3]. So, the minimum temperature at 6.5 GPa was equal to 1323 K [1], 1523 K [2] and 1600 K [3]. Lorenz *et al.* [3] reported two temperature limits at 6.5 GPa with different conversion rates of hBN to cBN. By the data of Fukunaga *et al.* [4], the content of Mg_3BN_3 obtained at atmospheric pressure, P_{atm}, and added to hBN influences the temperature and rate of hBN–cBN transformation at 6 GPa. According to Endo *et al.* [5], only a $Mg_3B_2N_4$ compound is formed at 2.5 GPa and 1423 K in the ternary system, Mg–B–N. They found a eutectic point between $Mg_3B_2N_4$ and hBN at 1568 K by DTA. In HT experiments at 6.5 GPa two compounds, such as Mg_3BN_3 and $Mg_3B_2N_4$, were identified from the starting hBN–Mg_3N_2 powder mixture [6].

X-ray data for these compounds differed from the data for the production of Mg_3BN_3 at P_{atm} [7, 8] and $Mg_3B_2N_4$ at 2.5 GPa [5]. This means that an Mg_3BN_3 compound exists in at least two solid states and that a $Mg_3B_2N_4$ compound is formed only at HP–HT conditions. The presence of a chemical reaction between hBN and Mg_3N_2 suggests that cBN crystallization in the BN–Mg_3N_2 system is not limited by one eutectic such as $Mg_3B_2N_4$–hBN.

On the basis of this background the purpose of this work was to investigate the succession of chemical reactions following heating under pressure and their influence on the hBN–cBN phase transition in the BN–Mg_3N_2 system by means of *in situ* DTA followed by a quenching method.

2. Experimental details

HP–HT experiments were carried out using a toroid type apparatus (V_{RZ} was 0.15 cm^3) [9]. The pressure was calibrated at room temperature on the fixed points for phase transitions in bismuth (at 2.55, 2.7 and 7.7 GPa), tallium (3.7 GPa) and barium (5.5 GPa). The reproducibility of these pressure calibrated experiments was estimated as ± 2%. The value of the correction on the elevated temperature was 1.2 MPa K^{-1} [10]. The cell assembly used is shown in Fig. 1, as described in [10]. The pressure was first increased and then the temperature was increased. DTA measurements were made at temperatures up to 1900 K with a thermocouple (Pt/Pt-10%-Rh, 0.3 mm) in the pressure region from 3.0 to 8.0 GPa. No correction was made to allow for the thermocouple's electromotive force being a function of pressure. The sample underwent two heating–cooling cycles at a rate of 1.2 K s^{-1} and all changes in temperature ΔT, were recorded. Then the sample was quenched after the recording of each endothermic peak. More

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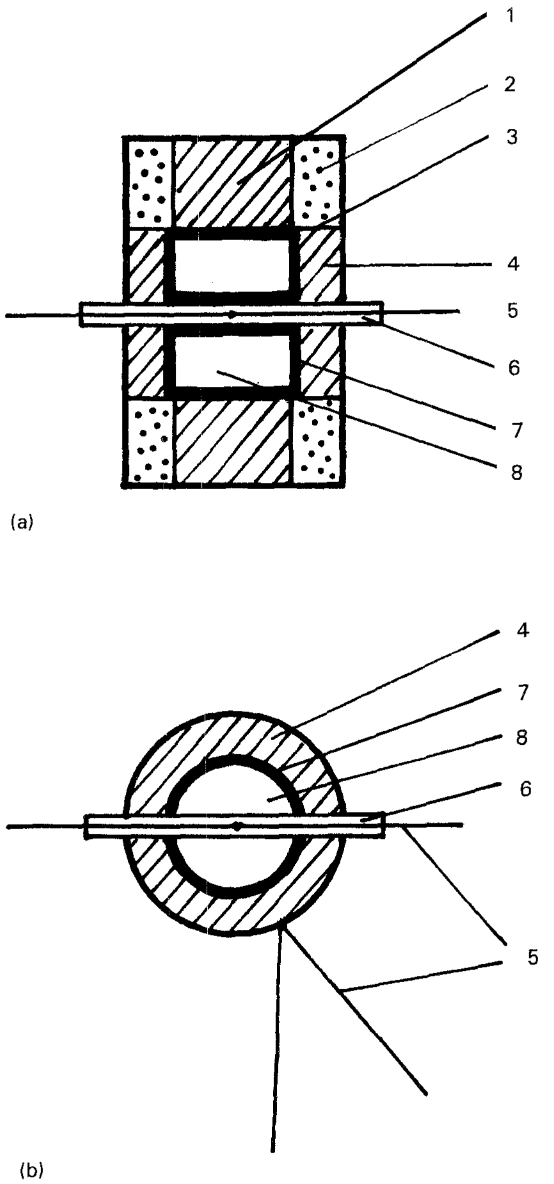

Figure 1 (a) cross-section, and (b) scheme of relative position of the thermocouples of the cell for DTA experiments under pressure: (1) graphite disk, (2) lithographic limestone ring, (3) Mo disc, (4) graphite heater, (5) thermocouples, (6) Al_2O_3 tube, (7) Mo ampoule, and (8) sample.

experimental details of this procedure will be given in [10]. The reproducibility of the temperature results was estimated as ±20 K from the data of three DTA experiments.

Hexagonal graphitic boron nitride (hBN) and magnesium nitride (Mg_3N_2) were used as the starting materials. The hBN powder was purified by a magnesium-thermic method and did not contain more than 0.6 wt % oxygen. A commercial Mg_3N_2 powder (RIEDEL-DE HAEN A.G.) containing a 99.9 wt % base product was used. The powders of hBN and Mg_3N_2 were mixed in the molar ratios: 3:1, 2.5:1, 2:1, 1.5:1, 1:1 and 1:3. All mixtures were prepared in a dry Ar-box and were compacted to a Mo-ampoule directly before the HP–HT experiment.

The samples quenched after DTA measurements were immediately put under a protective film and then were examined by X-ray powder diffraction analysis. The phase composition of the product was estimated by the relative intensity of base reflections from the phases present. The quenched samples contained some MgO as a result of the presence of oxygen in the system. Data from [10] were used to remove the effects of thermal arrests connected with the Mg_3N_2–MgO eutectic.

3. Results

When powder mixtures of hBN and Mg_3N_2 were heated under pressure a series of endothermic peaks were observed by the DTA. The DTA measurements of the samples with different molar ratios of starting materials are shown in Fig. 2. Lines 1, 2 and 3 in Fig. 2 can be attributed to the beginning of endothermic effects. The results of XRD on the samples obtained by quenching under different P–T conditions are shown in Tables I and II. Two systems of reflections corresponding to Mg_3BN_3 (HP phase) and $Mg_3B_2N_4$ compounds were selected on the basis of XRD data in [5, 6]. Table I presents XRD data of samples for two molar ratios of hBN:Mg_3N_2 quenched at 1640 K and 5.0 GPa. At a molar ratio of 1:3, the sample contained Mg_3BN_3 (HP) and a significant portion of non-reacted Mg_3N_2. At a molar ratio of 3:1, the final product consisted of a $Mg_3B_2N_4$ compound and of excess hBN. The results confirm the exact identification of the phases. It can be seen from Table II that a chemical reaction between hBN and Mg_3N_2 leads to the formation of Mg_3BN_3 (HP phase). For an excess of hBN in the mixture, the $Mg_3B_2N_4$ compound was produced in the product at a higher temperature after the formation of the Mg_3BN_3 (HP). The $Mg_3B_2N_4$ compound must be considered to have formed by the reaction between Mg_3BN_3 (HP) and

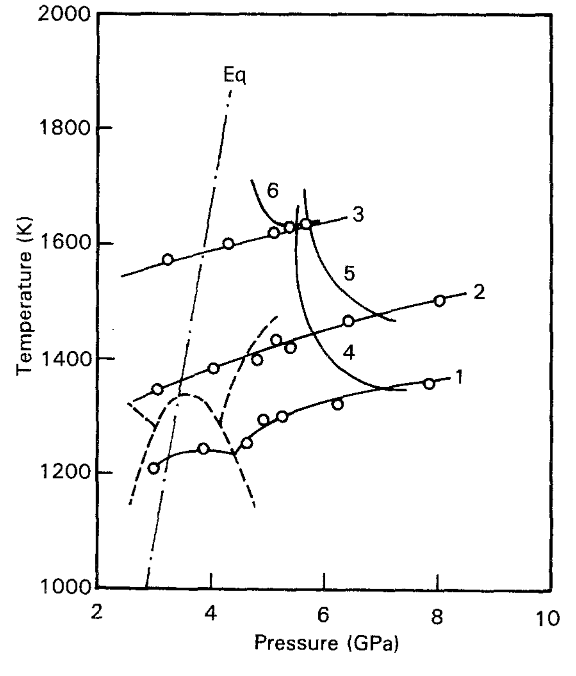

Figure 2 P–T reaction diagram for a BN–Mg_3N_2 binary system. Lines 1, 2 and 3 show Mg_3N_2–hBN, Mg_3BN_3–hBN and $Mg_3B_2N_4$–hBN eutectics, respectively. Curves 4, 5 and 6 represent lower-temperature limits of growth P–T regions of cBN, from Sato *et al.* [1], Fukunaga [2] and Sato *et al.* [7], respectively. The dashed lines show part of the Mg_3N_2 phase diagram [10]. Eq is the equilibrium line between hBN and cBN [11].

TABLE I XRD data of quenched samples at 5 GPa and 1640 K

$hBN:Mg_3N_2 = 1:3$		$hBN:Mg_3N_2 = 3:1$		Mg_3BN_3 [6]		$Mg_3B_2N_4$ [5, 6]	
d (nm)	I/I_0	*d* (nm)	I/I_0	*d* (nm)	I/I_0	*d* (nm)	I/I_0
0.4647	15	–	–	0.465	10	0.4643	3
0.3490	40	–	–	0.3493	25	0.3490	1
0.332**	< 5	0.332**	50	–	–	–	–
0.2688	20	–	–	0.2686	10	0.2690	2
0.2597	30	–	–	0.2605	25	–	–
–	–	0.2573	38	–	–	0.2573	30
–	–	0.2430	60	–	–	0.2414	60
0.2395	20	–	–	0.240	22	–	–
0.2327	15	–	–	0.2332	12	–	–
0.2301	10	–	–	0.2299	5	–	–
–	–	0.2198	100	–	–	0.2195	100
0.2137	100	–	–	0.2137	100	–	–
–	–	0.1927	25	–	–	0.1931	23
0.1885	35	–	–	0.1886	30	–	–
0.1760*	70	–	–	–	–	–	–
0.1737	38	0.1736	10	0.1739	20	0.1745	5
0.1663	30	0.1667	33	0.1663	40	0.1668	20
–	–	0.1571	15	–	–	0.1567	10
0.1552	38	0.1546	20	0.155	25	0.1541	13
–	–	0.1452	30	–	–	0.1447	20

*from Mg_3N_2
**from hBN

TABLE II The results of X-ray phase analysis of some quenched samples in the region 3.0–8.0 GPa

P (GPa)	*T* quench (K)	Molar ratio $hBN:Mg_3N_2$	Phase composition of the product
3.0	1243	3:1	hBN*, Mg_3N_2, Mg_3BN_3
3.0	1438	2.5:1	Mg_3BN_3*, hBN, $Mg_3B_2N_4$
3.2	1613	2.5:1	$Mg_3B_2N_4$*, hBN, Mg_3BN_3
3.9	1243	1.5:1	Mg_3N_2*, hBN, Mg_3BN_3
4.4	1648	1.5:1	Mg_3BN_3*, $Mg_3B_2N_4$
4.9	1290	2.5:1	hBN*, Mg_3N_2, Mg_3BN_3
5.1	1423	2.5:1	Mg_3BN_3*, hBN, $Mg_3B_2N_4$
5.2	1523	3:1	hBN*, $Mg_3B_2N_4$, Mg_3BN_3
5.2	1673	1.5:1	Mg_3BN_3*, $Mg_3B_2N_4$
5.2	1723	2.5:1	$Mg_3B_2N_4$*, hBN, Mg_3BN_3
5.4	1408	1:3	Mg_3N_2*, Mg_3BN_3*
5.4	1643	2.5:1	$Mg_3B_2N_4$, hBN, Mg_3BN_3
5.5	1470	1.5:1	Mg_3BN_3*, $Mg_3B_2N_4$, hBN
5.6	1633	2.5:1	cBN*, $Mg_3B_2N_4$*, Mg_3BN_3
5.6	1673	1:3	Mg_3BN_3*, Mg_3N_2
5.7	1498	2:1	cBN*, Mg_3BN_3*, $Mg_3B_2N_4$, hBN
5.8	1553	3:1	cBN*, Mg_3BN_3*, hBN, $Mg_3B_2N_4$
6.0	1723	1:3	Mg_3BN_3*, Mg_3N_2
6.2	1323	1:1	Mg_3N_2*, hBN, Mg_3BN_3
6.4	1473	1:1	Mg_3BN_3*, Mg_3N_2*, cBN
7.9	1473	1:1	Mg_3N_2*, cBN, Mg_3BN_3
7.9	1473	3:1	cBN*, hBN, Mg_3BN_3

* Phases with the highest content in the product

excess hBN against a molar ratio of 1:1. Cubic BN was observed in the samples at 5.6 GPa and 1633 K at molar ratios of more than 2:1. It is evident from Table II that the $Mg_3B_2N_4$ compound is the basis phase coexistent with cBN in these conditions. With the rise in pressure the minimum temperature for cBN crystallization was lowered and the necessary molar ratio of $hBN:Mg_3N_2$ became less than 2:1. The phase composition of the product was also changed. For example, at a molar ratio of 1:1 the base coexistent phases were Mg_3BN_3 (HP) at 5.7–6.5 GPa or Mg_3N_2 at 7.9 GPa.

4. Discussion

The processes in the BN–Mg_3N_2 binary system under HP–HT conditions involve: the formation of intermediate compounds such as Mg_3BN_3 (HP) and $Mg_3B_2N_4$, interaction of the compounds with each other and with hBN, and also polymorphic transitions including the synthesis of cBN. This situation creates difficulties in interpreting the thermal effects observed by DTA. However, the fundamental process taking place in the system at heating under pressure can be selected on the basis of the results of the quenching experiments (Tables I and II).

As a matter of record, the *P–T* boundaries of the interaction of hBN with Mg_3N_2, Mg_3BN_3 (HP) and $Mg_3B_2N_4$ are shown in Fig. 2 by the Lines 1, and 3, respectively. At Line 1 the Mg_3BN_3 compound (HP) begins to form as a result of the interaction of hBN and Mg_3N_2. Line 2 shows *P–T* conditions for the formation of the $Mg_3B_2N_4$ compound from Mg_3BN_3 (HP) and excess hBN. The processes of $Mg_3B_2N_4$ production (Line 2) and the interaction of hBN with $Mg_3B_2N_4$ (Line 3) take place for molar ratios greater than 1:1 and 2:1, respectively.

Each of these interactions was accompanied by cBN crystallization beginning at a definite pressure. Note that the previously reported data on the lower temperature limits of the growth *P–T* regions of cBN (starting from hBN and Mg_3N_2 (Curve 4) [1], Mg_3BN_3

(P_{atm}) (Curve 5) [2], $Mg_3B_2N_4$* (Curve 6)) [7] and also two temperature intervals at 6.5 GPa (with different conversion rates from hBN to cBN [3]) are in good agreement with the boundaries of the interactions of compounds obtained in the present study. Essentially, the formation of cBN at P–T conditions on Line 1 was observed at a molar ratio of 1:1. The noticeable connection of cBN crystallization with the processes mentioned above allows a proposal of the eutectic character of these interactions. In this case, Lines 1–3 illustrate the pressure dependence of the eutectic temperatures. It is clear that the Mg_3N_2–hBN eutectic (Line 1) and Mg_3BN_3–hBN eutectic (Line 2) are metastable. The presence on Line 1 of the break at 4.4 GPa and 1240 K shows the IV–V phase transition in Mg_3N_2. Part of the phase diagram of Mg_3N_2 [10] is shown by the dotted line in Fig. 2. The $Mg_3B_2N_4$–hBN eutectic (Line 3) is metastable in the cBN stable region. We think that the difference in temperatures of stable and metastable $Mg_3B_2N_4$–BN eutectics must be near the hBN–cBN equilibrium line. The pressure dependence of the temperature of the $Mg_3B_2N_4$–hBN eutectic was estimated to about 26.7 K GPa^{-1}. The extrapolation of Line 3 up to 2.5 GPa gives a value of 1550 K which is similar to the results in [5]. The short existence of a metastable liquid phase can serve as a kinetic factor promoting the production of intermediate compounds and recrystallization of BN in HP–HT conditions.

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* On the basis of X-ray data presented in [7] we believe that the starting magnesium boron nitride produced at P_{atm} was Mg_3BN_3 and not $Mg_3B_2N_4$. However, the lower temperature limit of cBN crystal growth was closely connected with the $Mg_3B_2N_4$–hBN eutectic.