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Precipitation mechanism of BN in the ternary system of B–Mg–N

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The phase relations in the ternary system B–Mg–N resulting from the reaction between Mg and BN at 2.5 GPa were investigated by means of *in situ* differential thermal analysis (DTA) supported by a conventional quenching technique. One compound, $Mg_3B_2N_4$, was newly formed when melted Mg reacted with hexagonal BN (hBN) solid above 1150° C and formed the eutectic with Mg and hBNat 737 and 1295° C, respectively. It was also confirmed that hBN crystals were precipitated from the liquid above 1300° C. The catalytic mechanism controlling cBN formation in the system Mg–BN was discussed from the experimental results of the present work. The lower temperature limit of cubic BN (cBN) growth region appears to be closely related to the initial formation of liquid phase due to a eutectic of $Mg_3B_2N_4$–BN.

1. Introduction

It is well known that some materials called "catalysts" are of help to the conversion of hBN into cBN. However, little information on the catalytic process controlling cBN formation has been provided except for the data by DeVries and Fleischer [1]. They indicate that the liquid phase of Li_3BN_2 acts as a solvent which dissolves hBN and precipitates cBN by virtue of thermodynamic stable conditions forming cBN at the operating pressure and temperature. This proposal was based on their experimental results that the initial liquid formation temperature in the system BN–Li_3BN_2 is closely related to the lower temperature limit of cBN formation in the system Li_3N–BN.

The present authors [2] have previously reported the growth *P–T* region of cBN in the system Mg–BN using hBN with different contents of oxygen as impurity. As the results, the lower temperature limit of cBN formation was about 1380° C at 6 GPa and was about 350° C higher than the melting temperature of Mg. This implies that eutectic relation between Mg and BN was not present. Probably, some unknown intermediate compound with higher melting temperature may be present in the system B–Mg–N, which forms a eutectic relation with BN.

Filonenko *et al.* [3] reported that the following reaction took place in the system Mg–BN; $4\,Mg + 2\,BN = Mg_3N_2 + MgB_2$(or MgB_6). However, it is almost certain that Mg_3N_2 or Mg-borides do not melt, but decompose at a much higher temperature [4, 5]. If the reaction according to the type described above proceeded, it must be considered that BN crystal dissolves in a solid state Mg_3N_2 and/or Mg-borides.

On the basis of this background, the purpose of this work is to investigate the phase relation in the system B–Mg–N by means of *in situ* differential thermal analysis (DTA) and a conventional quenching method.

2. Experimental details

Hot-pressed hBN, the starting material, was supplied by Denka Co. According to the data measured by neutron activation analysis, it contained 1.9 wt% oxygen. The purity, degrees of crystallinity and grain size have been examined previously [2]. Before use, the hBN was dried at 150° C under 10^{-1} Torr for 20 h in order to eliminate water. Magnesium metal (99.9% purity) was purchased from Furukawa Magnesium Co and used without further purification. It was charged into the capsule which was composed of an hBN tube

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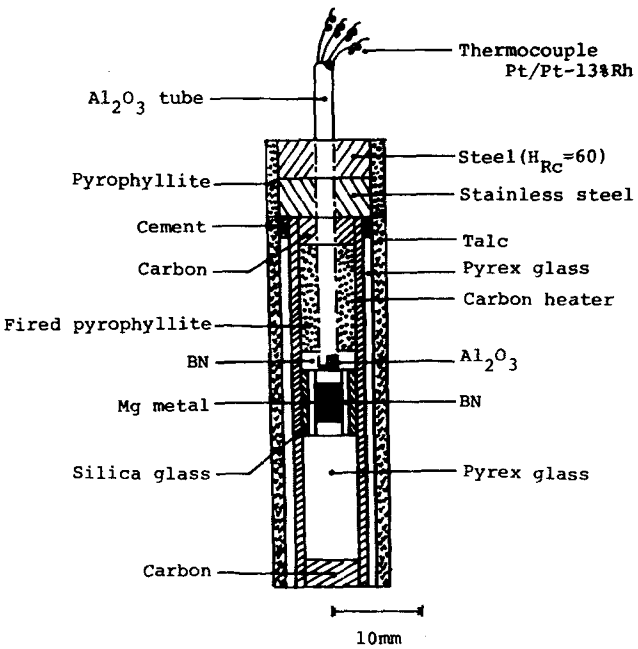

Figure 1 Schematic illustration of the cell arrangement.

with a pair of hBN discs positioned at the top and bottom.

Fig. 1 shows the cell arrangement used in this experiment. All high pressure and high temperature experiments were carried out using a piston-cylinder apparatus of $\frac{1}{2}$in. bore diameter. Pressure generated in the reaction cell was estimated simply from the load operated and the area ratio of piston to hydraulic ram. In the figure, there are many parts composed from silica glass and Pyrex glass as pressure transmitting media. This is based on the idea that the friction acting on the piston is reduced significantly at a high temperature above which the glass softened. The sample is then nearly under hydrostatic pressure at the operating conditions.

Thermometry of the sample was performed using a Pt/Pt–13% Rh thermocouple, the hot junction of which is placed at the upper end of the hBN capsule as shown in Fig. 1. No correction was made to the e.m.f. of the thermocouple as a function of pressure.

2.1. Quenching procedure

A pressure of 2.5 GPa was applied to the cell and the temperature was raised at a rate of 200 to 250° C min^{-1} to a predetermined point in the region 800 to 1600° C at intervals of 50° C. After the sample had been held for 20 min, at the temperature concerned, it was quenched to room temperature within about 30 sec, prior to the release of applied pressure.

Before and after the treatment with dilute HCl, reaction products were examined by optical microscopy, infra-red spectroscopy and X-ray diffraction.

2.2. Differential thermal analysis (DTA)

After the pressure was increased to a fixed point of 2.5 GPa, DTA measurement was made at temperatures up to 1600° C. Temperature change was controlled at a rate of 35 to 40° C min^{-1} on heating or cooling.

As reference material, α-Al_2O_3 was used throughout. The temperature of the sample (T) and the difference in temperature (ΔT) between α-Al_2O_3 and the sample were measured by means of two pairs of Pt/Pt–13% Rh thermocouples. Owing to the limitation of the cell construction as shown in Fig. 1, α-Al_2O_3 and the sample could not be placed in the isothermal section of the carbon heater. The thermocouple junction of α-Al_2O_3 must be located at the distance of 0.7 to 1.0 mm away from that of the sample. In results of the blank test, the change in ΔT depending on thermal arrest was clearly distinguishable from the "basic line" drift. Each sample was submitted to five heating–cooling cycles to check the reproducibility of the results.

3. Results

3.1. Quenching experiments

No visible change was found in the reaction zone below 1100° C, even though Mg did melt. Above

TABLE I X-ray diffraction data of $Mg_3B_2N_4$

d(Å)	I/I_0	d(Å)	I/I_0
7.76	w	1.677	s
3.88	w	1.647	m
3.52	vvw	1.608	vw
3.020	m	1.567	m
2.842	vw	1.552	m
2.692	w	1.493	m
2.585	s	1.456	m
2.437	s	1.386	vw
2.375	w	1.317	w
2.208	vs	1.306	w
2.116	s	1.273	w
1.939	m	1.219	w
1.894	w	1.192	w
1.823	m	1.098	w
1.751	w		

vs = very strong, s = strong, m = medium, w = weak, vw = very weak, vvw = very very weak.

1150° C, on the contrary, it was possible to detect individual lines that might be ascribed to the formation of the corresponding boride such as MgB_6 or MgB_{12} in the X-ray powder diffraction patterns. In addition to these borides, a compound which crystallized in yellow lath-like plates was detected. Chemical analysis of this compound gave Mg, 49.7 to 48.6 wt%; B, 14.5 to 14.1 wt% by means of an atomic absorption analysis. Therefore, the chemical formula was probably $Mg_3B_2N_4$, which is a new compound with an ideal composition (Mg, 48.43 wt%; B, 14.36 wt% and N, 37.21 wt%).

In the infra-red spectra of this compound, remarkable absorptions were exhibited around 1675, 975 and 605 cm^{-1}, which were assignable to the group of $(BN_2)^{3-}$ as shown in [6]. The X-ray diffraction data of this compound were taken by the Debye–Scherrer method with Cu$K\alpha$ radiation, and are shown in Table I.

It was also confirmed that $Mg_3B_2N_4$ could be obtained from a mixture of Mg_3N_2 and hBN in a Ta capsule at under the same P–T conditions as with Mg and hBN. $Mg_3B_2N_4$ was slowly decomposed by water, even if only present in humid air. At higher temperatures, it was easily oxidized to $Mg_3(BO_3)_2$.

Fig. 2 shows the yellow crystals of $Mg_3B_2N_4$ (dark areas) which were formed. Above 1300° C, it could be seen that hBN crystals grew in contact with $Mg_3B_2N_4$. The above observations led to the opinion that $Mg_3B_2N_4$ was formed by the reaction between melted Mg and hBN, which then played the role of a solvent.

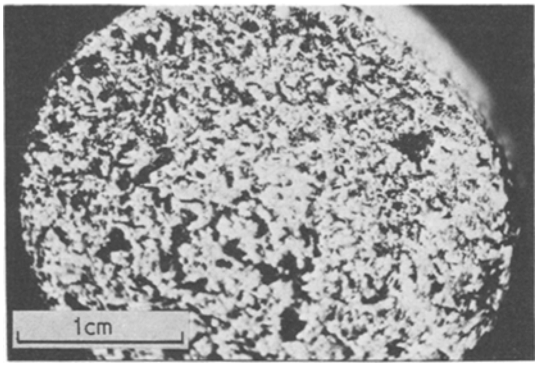

Figure 2 The appearance of $Mg_3B_2N_4$ in the reaction zone.

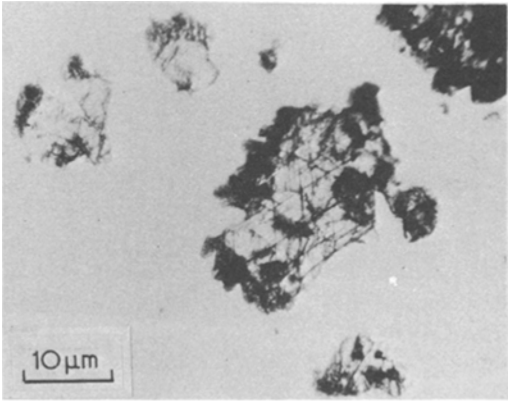

Figure 3 hBN crystals precipitated from the solvent.

Fig. 3 shows some colourless, transparent hBN crystals, 12 to 25 µm in size, grown from $Mg_3B_2N_4$ melt. Because it was difficult to measure quantitatively the total yield of $Mg_3B_2N_4$ in the sample, the solubility data of hBN in $Mg_3B_2N_4$ were scattered and inaccuracy could not be avoided. However, the amount of hBN in the sample varied from 3 to 5 wt%.

3.2. DTA measurements

In order to confirm the results of the quenching experiments, DTA measurements were made in the system Mg–BN.

Fig. 4 shows the successive DTA data of three heating stages. In the first stage, there was one sharp endothermic peak at 800° C and one broad endothermic change near 1100° C (see Fig. 4a). After maintaining the sample at 1250° C (which was the maximum temperature in this stage) for 10 min, it was cooled rapidly to 600° C. DTA signals in the second stage were observed at 737, 800 and 1295° C (see Fig. 4b). The intensity of the

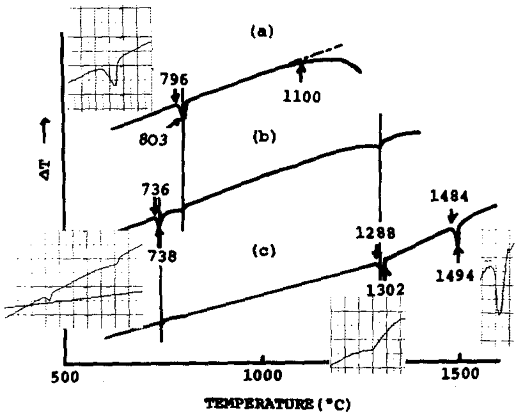

Figure 4 DTA curves at 2.5 GPa.

peak at 800° C decreased remarkably in this stage. The broad peak near 1100° C could not be seen. The maximum temperature in this stage reached about 1400° C. In the third stage, two distinct endothermic peaks were clearly seen at 1295 and 1489° C (see Fig. 4c). The intensity of the signals below 800° C decreased and became almost invisible.

It has been postulated that the peak at 737° C could be assigned to the eutectic in the system Mg–$Mg_3B_2N_4$. An endothermic peak at 800° C, which was found in the first and second stages, was convincingly assigned to the melting point of Mg. This temperature corresponds to the melting data given by Kennedy and Newton at 2.5 GPa [7] within experimental error.

Reactions proceeded in the Mg–BN system during the DTA measurements. Therefore, it must be noted that the system was in a heterogeneous or non-equilibrium state. At first, the interaction of hBN and molten Mg takes place to give $Mg_3B_2N_4$. Once $Mg_3B_2N_4$ is formed, it reacts with the remaining unreacted hBN and Mg. After a few cycles of measurement, the reaction between hBN and $Mg_3B_2N_4$ becomes dominant, because of the nearly complete consumption of Mg to form $Mg_3B_2N_4$.

It is reasonable to assign the peak at 1295° C to the eutectic point in the system BN–$Mg_3B_2N_4$. This conclusion leads to the fact that the lower temperature limit of hBN precipitation in the quenching runs was closely related to the eutectic liquid formation in the system. Sharp and strong features of the endothermic peak at 1489° C suggested assignment to the melting point of $Mg_3B_2N_4$. This is for the following reasons: (1) this peak was reproducible, even if the heating–cooling cycles up to 1600° C were repeated many times, (2) no change was observed in the sample recovered after treatment at 1550° C.

In addition to the profile described above, upon cooling, two broad exothermic peaks due to the eutectic were produced in the ranges 780 to 740 and 1337 to 1301° C.

DTA measurements of the sample of Mg and hBN powder intimately mixed in various molar portions and charged in the Ta capsule were also carried out by the same operations described above.

The results showed that the intensity of each peak was relatively different, but five distinctive peaks were revealed in the reaction process on heating. In addition to this, a supplementary peak, depending on the change of composition, was also observed. However, it was too small to be distinguishable. Even if the system of powder mixture was applied, it was difficult to evaluate the solidus line in the eutectic system between $Mg_3B_2N_4$ and hBN. This stems from the reason that the reaction between molten Mg and hBN took place in the heterogeneous state due to the large temperature gradient in the sample. A solubility test of hBN in $Mg_3B_2N_4$ solvent is virtually impossible to perform, because of the lack of $Mg_3B_2N_4$ of high purity.

The co-existence of MgO was recognized after repeated DTA measurements or prolonged reaction. However, the usual measurement conditions, such as those described above, appeared to be sufficient to enable one to neglect the effect of oxygen.

4. Discussion

The phase relation in the system B–Mg–N at 2.5 GPa obtained from consideration of the present works is shown in Fig. 5. In this figure, the actual values of temperature obtained from DTA measurements are given, but the eutectic compositions are arbitrary. It is noted that the presence of one phase, $Mg_3B_2N_4$, was recognized when the molten Mg reacted with hBN solid at temperatures above 1150° C. The composition of this phase was not situated on the line joining Mg to hBN, but on the line joining Mg_3N_2 to hBN. This implies that, as the reaction proceeded, the composition of this system deviated from the Mg–hBN line, and moved towards the boron- and nitrogen-rich sides. In fact, a small amount of MgB_6 or MgB_{12} was observed in the recovered samples.

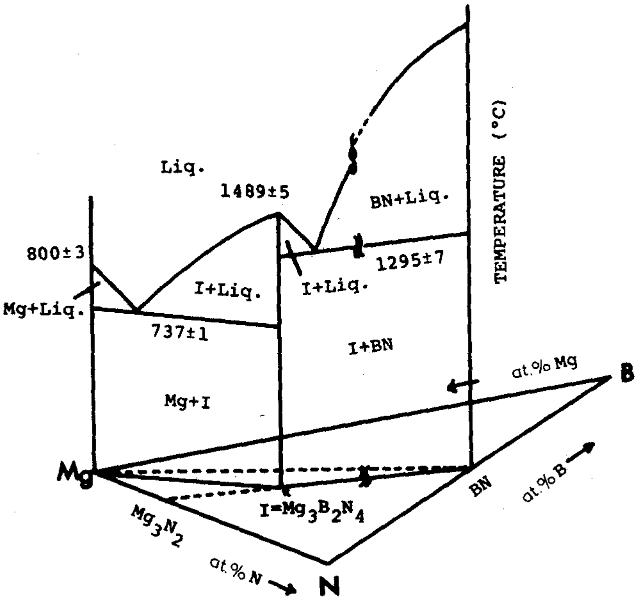

Figure 5 Temperature–composition diagram at 2.5 GPa in the ternary system B–Mg–N.

According to the data of Filonenko *et al.* [3], Mg_3N_2 was formed with MgB_2 and/or MgB_6 as byproducts in the synthesis of cBN. However, in this experiment, it became evident that $Mg_3B_2N_4$ was obtained instead of Mg_3N_2 and had a eutectic with hBN at 1295° C and 2.5 GPa. MgB_2 or higher borides did not melt and decomposed, upon further heating, to liberate the element boron [5]. Therefore, $Mg_3B_2N_4$ was the most probable compound to function as a solvent in the system B–Mg–N.

Previously, the present authors [2] reported the growth *P–T* region of cBN examined in the system Mg–BN, the lower temperature limit of which was about 1380° C at a pressure of 6 to 8 GPa. If the limit has a close connection with the eutectic $Mg_3B_2N_4$–hBN obtained in present work, the initial slope of the temperature versus pressure curve of the eutectic would be estimated to be about 26 to 31° C GPa^{-1}.

On the basis of these considerations it seems most reasonable to conclude that the catalyst mechanism, similar to that indicated by Wentorf [8] and DeVries and Fleischer [1], was founded on the dissolution of excess hBN and precipitation of cBN in the eutectic liquid of $Mg_3B_2N_4$–BN.

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