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$_3$B$_2$N$_4$, was newly formed when melted Mg reacted with hexagonal BN (hBN) solid above 1150 °C and formed the eutectic with Mg and hBN at 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$_3$B$_2$N$_4$–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$_3$BN$_2$ 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$_3$BN$_2$ is closely related to the lower temperature limit of cBN formation in the system Li$_3$N–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; 4Mg + 2 BN = Mg$_3$N$_2$ + MgB$_2$(or MgB$_6$). However, it is almost certain that Mg$_3$N$_2$ 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$_3$N$_2$ 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.
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, \( \alpha \)-Al\(_2\)O\(_3\) was used throughout. The temperature of the sample (\( T \)) and the difference in temperature (\( \Delta T \)) between \( \alpha \)-Al\(_2\)O\(_3\) 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, \( \alpha \)-Al\(_2\)O\(_3\) and the sample could not be placed in the isothermal section of the carbon heater. The thermocouple junction of \( \alpha \)-Al\(_2\)O\(_3\) 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 \( \Delta T \) 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