Nucleation of Cubic Boron Nitride in the Non-metallic and Metallic Solvents

O. Fukunaga, S. Takeuchi
Dept. Mechanical Engineering, Nippon Institute of Technology,
Miyashiro-cho, Saitama 345-8501 Japan

Abstract Non-metallic and metallic solvents for growth of cubic BN at high pressure and high temperature were studied. When we used non-metallic MxByNz solvents such as Li$_3$BN$_2$, P-T region of cubic BN growth was separated into two regions namely rapid nucleation above 5 GPa and slow nucleation below about 5 GPa. In the slow nucleation region, cubic BN crystals were precipitated in the re-crystallized hBN matrix. When we use metallic solvents, (Fe,Co,Ni)-(Mo,Cr,V)-Al alloys, nucleation of cubic BN showed strong pressure dependent nature. It was found that B and N solubility can be controlled to select proper content of (Fe,Co,Ni)-(Mo,Cr,V) alloy system. Small amount of Al addition into the alloy system showed distinct increase the rate of nucleation of cubic BN.

1. Introduction

Since pioneer work by Wentorf [1], many research efforts on the synthetic solvents of cBN growth under high pressure and high temperature (HPHT) have been stimulated. Alkali or alkali earth metal -boron-nitrogen compounds (MxByNz), were studied by many researchers. Metallic solvents including transition metal such as Fe-Al system for cBN growth, were also reported by the several authors.[2-4]

However, growth P-T region of cBN using hBN-solvent system were not well established. The authors reported different nucleation regime of cBN in the system hBN-Ca$_3$B$_2$N$_4$ solvent. [5] The results suggested that higher pressure of above 5GPa, rapid cBN nucleation was dominant but below 5GPa, nucleation rate of cBN was

1. To whom any correspondence to (o-fukunaga@mva.biglobe.ne.jp)
decreased and meta-stable re-crystallized hBN (RC-hBN) formed rapidly and after several hours cBN crystals were precipitated in the RC-hBN matrix. Nucleation mechanism of cBN growth in the slow nucleation region was interesting to control growth stage of cBN crystals.

Growth P-T regions of cBN in the metallic solvent and hBN were not well documented in the previous reports. In this paper, we intended to present results of cBN grow P-T region using both nonmetallic MxByNz solvents and metallic (Fe,Co,Ni)-(Mo,Cr,V)-Al solvents.

2. Growth P-T region of cBN using nonmetallic MxByNz solvents

The HPHT experiments were conducted using modified type belt apparatus having a 25 mm cylinder bore diameter. [6] The powder MxByNz solvent of 7mm in diameter and 1.6 mm of the thickness was sandwiched by the two hBN disks of 7mm in diameter and 3mm of thickness. The samples were placed in a Mo lined NaCl sleeve. The graphite heater having 12mm o.d., 10mm i.d. and 17.6 mm length was used for heating elements. Pressure was increased at room temperature and then temperature was kept for designed period (0.5-11h) and then temperature was decreased quickly (within 1 min.). Recovered samples were examined using optical microscope and XRD analysis. When cBN crystals were existed in the sample, normally they showed brown colored various shaped crystals.

As shown in Fig1 and 2, growth P-T regions of cBN were roughly classified into the two regimes, namely rapid nucleation region (RNR) and slow nucleation region (SNR). In the previous reports, only rapid nucleation regimes in which cBN grew within several minuets were described. In the slow nucleation region, cBN precipitation was detected more than several hours to keep at given P-T condition. We showed examples of cBN growth P-T region for Li3BN2 and Mg3BN3 solvent in Fig. 1 and Fig.2. In the two figures, boundary pressure between RNS and SNR was located roughly at 5 GPa. When we use other solvents, Ca3B2N4 and LiCaBN2, similar pressure boundary between RNS and SNR was exhibited at 5 GPa.[5]

In Fig. 3, a photograph of the sample reacted at 4GPa 1390 C for 5h using Li3BN2 as solvent was shown. Small amount of cBN crystals of brown in color were precipitated in the hBN matrix. The hBN crystals shown in the figure reflect distinct grain growth, although they reacted in the cBN stable P-T condition. We deduced that initial stage of the reaction, meta-stable hBN crystal (RC-hBN) grow in the SNR and successively cBN crystals were precipitated. Rate of cBN nucleation was different with different of P-T condition. When the P-T condition was close to the hBN/cBN
equilibrium boundary [7], rate of cBN nucleation was decreased obviously.

Fig. 1 Rapid and slow nucleation regions of cBN using Li$_3$BN$_2$ as solvent.

Fig. 2 Rapid and slow nucleation regions of cBN using Mg$_3$BN$_3$ solvent. P-T points of the cBN formation in RNR are taken from previous reports.

Fig. 4 shows cBN yield (volume % of cBN) versus reaction time at 4GPa and 1300 C using Li$_3$BN$_2$ as solvent. The data showed slow cBN nucleation behavior in the SNR P-T region. In the SNR P-T region, rate of cBN nucleation using MxByNz solvents were heterogeneous and normally rate of nucleation was very slow.
Fig. 3 Heterogeneous nucleation of cBN crystals in the RC-hBN matrix. The sample was obtained at 4.2 GPa and 1300°C for 5 h using Li$_3$BN$_2$ as solvent. Background shows 1 mm square.

Fig. 4. Yield of cBN vs reaction time curve at 4 GPa and 1300°C using Li$_3$BN$_2$ solvent. The data showed very slow growth rate in the SNR P-T region.

3. **Growth P-T region of cBN using metallic (Fe,Co,Ni)-(Mo,Cr,V)-Al solvents**

Previous reports on the metallic solvents for cBN growth [2-4] suggested that small amount of Al containing Fe, Co, Ni, Cr or Mn alloy were act as growth solvent of cBN at HPHT. Growth P-T region of cBN using transition metal-Al solvent was not established but minimum formation pressure of cBN was about 5 GPa in the literatures. Recent reports, on the growth P-T region of cBN using Ni or Ni-Mo solvent, resulted similar threshold pressure of 5 GPa. [8-9]

Molten Fe,Co and Ni have several wt % of boron solubility but nitrogen solubility was order of 0.05 wt%. Nitrogen solubility of molten Fe was increased with increase of Cr or V addition.[10] As working hypothesis, we selected alloy system (Fe,Co,Ni)-(Mo,Cr,V) and added small amount of Al as nucleation agent of cBN.

In Fig. 5, we showed growth P-T region of cBN using Co-Mo and Co-Mo-Al alloy as growth solvent of cBN. As shown in the figure, without Al addition threshold pressure of cBN formation was about 6 GPa, but it decreased to about 4 GPa with Al addition. We confirmed that minimum amount of Al addition effectively growth of cBN was about 0.5 wt% into the Co-Mo alloy system.

Similar trend of the effect of Al addition into the Fe-Mo, Ni-Fe-Cr-V and Fe-Ni-Cr
solvents was found. Minimum P-T conditions of cBN growth were about 4 GPa and 1300 C for these alloy solvents. Nucleation of cBN in the metallic (Fe,Co,Ni)-(Mo,Cr,V)-Al solvents was found at the interface between source hBN and molten alloy layer. When yield of cBN was relatively high, the volume of alloy solvent layer was decreased. The molten alloy was penetrated into the source hBN layer with precipitation of cBN crystals.

Fig. 5 Growth P-T region of cBN using Fe50.14-Mo36.86-Al3 wt% as solvent. Solid squares are cBN formed. Solid circles are cBN formed P-T points using Fe-Mo solvent. Solid and open rhombic are cBN and hBN, respectively using Fe-Al solvent.

Fig.6 (left) Volume shrinkage of Fe-Co-Cr-Al solvent reacted at 4.2 GPa and 1340C for 1h. The back ground shows 1 mm square.
Fig.7. (right) Interfacial growth of cBN using Co46.6-Cr31-Mo20-Al2.4(wt%) solvent and reacted at 4.2GPa and 1300 C for 1h Bar shows about 0.5 mm.
Fig. 6 shows an example of volume shrinkage of molten alloy (Fe40-Co20-Cr38-Al2 (wt%) solvent at 4.2 GPa and 1340 °C for 1h reaction). Fig. 7 shows another example of interfacial grain growth of cBN in the sample reacted 4.2 GPa and 1300°C for 1 h using Co46.6-Cr31-Mo20-Al2.4 (wt%) solvent. As shown in the figure, cBN crystals having about 0.5 mm of the diameter were precipitated only at the interface between hBN and solvent.

4. **Comments on the control of cBN nucleation and growth stage of cBN abrasive grains**

Grinding wheel for ferrous materials is major application of cBN grains. Grain size, amount of yield and strength of the cBN are important items to control in the production system of cBN grains at HPHT. As shown in this report, cBN yield was increased with increase reaction pressure, but size of the cBN tended to decrease and crystal morphology was variable. At relatively lower pressure region, nucleation of cBN was heterogeneous and rate of grain growth of cBN was decreased when we use MxByNz non-metallic solvents.

On the other, cBN nucleation and growth stage may possible to control using metallic (Fe,Co,Ni)-(Mo,Cr,V)-Al solvents. We found interfacial nucleation and growth of cBN at lower pressure of about 4 GPa. The rate of cBN nucleation was not slow and it is possible to control grain size and morphology by the accurate control of P-T condition of the reaction. The results of this report may provide new process of cBN abrasive grains.

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