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High-pressure synthesis of cubic BN using Fe–Mo–Al and Co–Mo–Al alloy solvents

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ABSTRACT

The pressure and temperature regions of cubic BN formation were determined using Fe–Mo–Al and Co–Mo–Al ternary alloys as synthetic solvents of cubic BN. The alloy compositions employed in the present study were (in weight percent) Fe60.14–Mo36.86–Al3 and Co57.6–Mo38.4–Al4. The cubic BN was successfully synthesized at minimum pressure of about 4.4 GPa and temperature of about 1250 °C. Pressure and temperature of cubic BN synthesis were decreased drastically by small amount of Al addition into Fe–Mo or Co–Mo alloy solvents. The growth of cubic BN was started at the interface between the molten alloy and the source hexagonal BN. In the present study, we proposed that Fe–Mo and Co–Mo work as solvent of B and N atoms and Al acts as a nucleation agent of cubic BN.

1. Introduction

Cubic BN (cBN), second hardest material next to diamond, is produced as an abrasive material of grinding wheels and as starting powder of polycrystalline cutting tools for ferrous work materials. Industrial abrasive grains of cBN are normally synthesized using alkali or alkali-earth boron nitride solvents (such as Li_3BN_2) at high pressure and high temperature (HPHT) [1–3].

It has been reported that some elements such as Sb, Sn and Si or Fe–Al alloy are available for synthesizing solvents of cBN [4–6]. Wentorf [7] and DeVries and Fleischer [8] reported alloy solvents of the transition metals (Cr, Mn, Co, Ni) containing small amount of Al. They examined cBN formation using (in weight percent) Fe46–Ni32–Cr21–Al1, Ni39.2–Mn58.8–Al2, Ni49–Cr49–Al2, Fe8–Ni43–Cr47–Al2 and Fe39.2–Mn58.8–Al2 alloy solvents at pressures in the 5–5.5 GPa range and temperatures in the1400–1500 °C range [8]. Recently, Co, Ni, Ni–Mo and Ni_3Al were investigated as the growth solvents of cBN crystal [9–12]. Metal solvents for cBN synthesis are interesting because they are stable and are easy to handle. It is well known that alkali and alkali-earth boron nitride solvents (such as Li_3BN_2) react with moisture in air. Alloy solvents for cBN growth provide basic knowledge of cBN-metal polycrystalline system to develop new polycrystalline cutting tolls (PCBN). They are interesting also as new solvents for hBN and cBN at HPHT and at normal pressure [13].

Metal alloy having some amount of solubility for nitrogen and boron makes it a good candidate for growth solvents of cBN. Molten transition metals, such as Fe, Co and Ni are good solvent of boron (about 4–5 wt%) [14], but they can dissolve very small amount of nitrogen (about 0.05 wt%) [15]. Liquid Mo dissolves nitrogen up to about 4 wt%. Addition of Mo into Fe, Co, Ni is expected to increase the solubility of nitrogen in the alloy system. Liquid formation temperature of Fe62–Mo38 (in weight percent) is about 1450 °C and for Co60–Mo40 (in weight percent) is about 1350 °C at normal pressure. These liquid formation temperatures are about 100–150 °C lower than that of pure Fe or Co. As already reported in the literature, minimum temperature of cBN growth was greatly decreased using Ni–Mo solvent due to decrease of liquid formation temperature [11].

However, minimum pressure of cBN growth in the Ni–Mo alloy solvent was not obviously decreased to the minimum formation pressure of cBN in the Ni solvent. Minimum pressures of cBN formation were in the 5–5.5 GPa range for both Ni and Ni–Mo alloy solvents.

In the present report, we used the ternary alloys (in weight percent) Fe60.14–Mo36.86–Al3 and Co57.6–Mo38.4–Al4 for the synthetic solvent of cBN at HPHT. We expected that small amount of Al addition into the Fe–Mo or Co–Mo alloys was effective to decrease synthesizing pressure of cBN due to increase nucleation density of cBN. We propose the composition of alloy solvents of cBN synthesis based on the scope of nitrogen and boron solubility and enhancement of cBN nucleation in the molten alloys.

2. Experimental

We used Fe (99%), Co (99.9%), Mo (99.9%) and Al (99.99%) powders as starting materials of the solvents. In this paper we denoted for the (in weight percent) Fe60.14–Mo36.86–Al3 alloy as FMA3 and for the Co57.6–Mo38.4–Al4 alloy as CMA4. Similarly, we denoted for the (in weight percent) Fe97–Al3 alloy as FA3 and for the Co96–Al4 alloy as CA4.

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The solvent was prepared by mixing metal powders in an ethanol. Hot-pressed hBN (N-1 type, Denka, Japan) was used as a starting BN source. The hBN rods of 7 mm in diameter and about 3 mm thickness were machined from hBN block.

The FB25H modified belt type high pressure apparatus [16] was used for HPHT experiments. The furnace cell of FB25H was 21 mm of outer diameter and 17.6 mm in length. Graphite sleeve (12 mm o.d., 10 mm i.d. and 17.6 mm in length) was used for heating element. In the heater, “salt” (NaCl + 10 wt% Y_2O_3-stabilized ZrO_2) sleeve of 7 mm of inner diameter and 7.6 mm in length was used for the sample container. The solvent powder was packed between the hBN disks (7 mm of diameter and 3 mm of the thickness) in the inner “salt” sleeve. Laminated hBN/alloy solvent/hBN samples were covered with 0.05-mm-thick Mo foil.

The HPHT runs were conducted with pressure increase at room temperature and then temperature increase. At about 750 °C, temperature was kept for 10–30 min to homogenized Al melt and Fe–Mo or Co–Mo powders. After keeping for 20–120 min at designed temperature, current supply to the heater was quickly decreased and then press load was decreased slowly. Recovered samples were analyzed by optical microscope, scanning electron microscope (SEM) and X-ray powder diffraction (XRD).

3. Results and discussion

3.1. Pressure–temperature region of cBN formation

In Fig. 1, we plotted the *P–T* region of the cBN growth using FMA3 solvent. We illustrated the results of the growth region of cBN using FA3 catalyst as a reference. In Fig. 2, we also plotted results of cBN growth region using CMA4 alloy and CA4 alloy solvents. In these figures, we denoted *P–T* points of cBN obtained by solid circles. Identification of cBN is normally easy by observing yellow cBN crystals having 0.1–0.3 mm in size under optical microscope. The XRD of the samples mainly showed strong cBN (111) peak, weak hBN (002) peak and extra diffraction peaks due to alloy components. It must be noted that the solid circle marks denoted cBN formation in the figures contained some amount of the residual hBN starting material. As noted later, formation reaction of cBN was started from the interface between metallic solvent and starting hBN. Amount of the hBN residue was increased by increasing the distance from the interface. Minimum pressures and temperature of cBN growth were about 4.4–4.5 GPa and 1200–1300 °C for both FMA3 and CMA4 solvents.

As shown in Figs. 1 and 2, in contrast to the growth region of cBN using FA3 and CA4 alloy solvents, minimum pressure of cBN synthesis was decreased drastically by the use of FMA3 and CMA4 solvents. The cBN growth regions for FMA3 and CMA4 were about 1.3 GPa decreased from the results of FA3 or CA4. These results suggested that FA(Fe–Al) and CA(Co–Al) alloys can dissolve very small amount of nitrogen into the melts and no cBN was synthesized at lower than about 5.5 GPa. We employed HPHT experiments using Fe–Mo, Co–Mo, Fe–Al and Co–Mo as synthesizing solvents of cBN, but no cBN formation was detected below

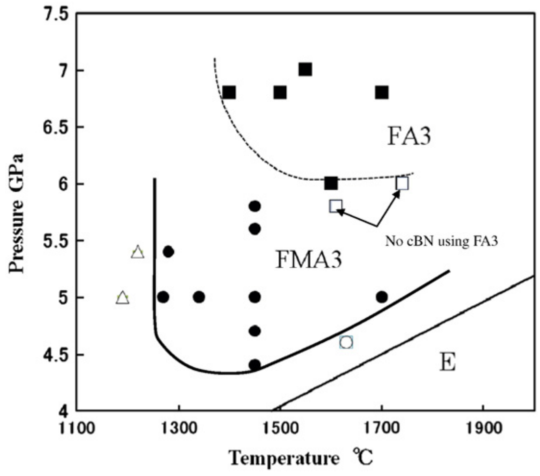

Fig. 1. Pressure–temperature region of cBN using FMA3 solvent. Solid circles denote cBN results. Open triangles and square marks denote no cBN result. Close squares and open squares denote cBN and no cBN results, respectively, using FA3 solvents. The E is equilibrium line between cBN and hBN [17].

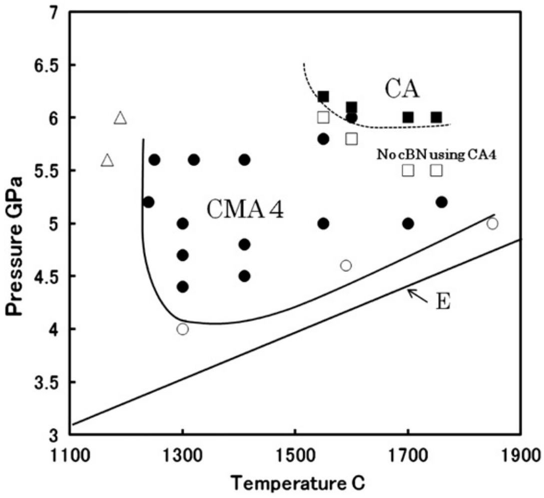

Fig. 2. Pressure–temperature region of cBN growth using CMA4 solvent. Closed circles denote cBN results. Open circles and triangles denote no cBN result. Closed squares and open squares denote cBN and no cBN results, respectively, using CA4 solvent. The E is equilibrium line between cBN and hBN [17].

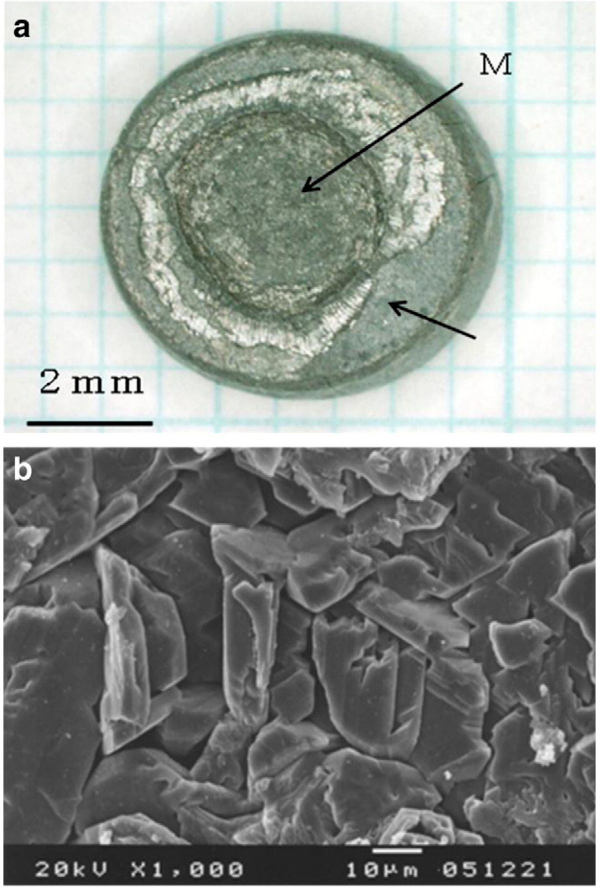

Fig. 3. (a) Residual frozen solvent (M) of the sample treated at 5 GPa and 1300 °C for 1 h using CMA 4 solvent. Arrow mark below denotes cBN zone. (b) Random growth of cBN grains at opposite surface from the solvent.