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Synthesis and grain size control of cubic BN using Co–Cr–Al base alloy solvents under high pressure

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ABSTRACT

Cubic boron nitride (cBN)-metal composites were synthesized from hexagonal boron nitride (hBN) using Co–Cr–Al base alloy as infiltration solvents under high pressures and high temperatures. To control the grain size of the cBN crystals, Mo or V was used as a substitute of Cr in the base alloy. The pressure–temperature region of the cBN formation under Co–(Cr, Mo)–Al and Co–(Cr, V)–Al systems was determined at pressure between 4 and 6 GPa and temperature up to 1700 °C. It was confirmed that cBN was obtained at pressures above 4.4 GPa and temperatures above 1290 °C. The grain size of cBN synthesized using Co–(Cr, V)–Al solvent was relatively finer comparing with the ones synthesized with Co–Cr–(Mo)–Al alloy solvent. Under the Co–(Cr, V)–Al alloy solvent system where both Cr and V exist, the grain size of the synthesized cBN could be controlled by changing the composition of Cr and V in the solvent.

1. Introduction

Hexagonal boron nitride (hBN) and cubic boron nitride (cBN) are the representative crystal structures of boron nitride (BN), which is the simplest III-nitride compound. The former is chemically and thermally stable and has been widely used as an electrical insulator and heat-resistant material in industry. The latter, which is a high-density phase, is an ultra-hard material close to diamonds in hardness [1].

A conventional but efficient synthesis process for cBN is the solvent process under high pressure and high temperature (HP–HT). Typical solvents for conversion from starting hexagonal BN (hBN) into cBN are boron nitrogen compounds of alkali and alkali-earth elements such as Li_3BN_2 and $Ca_3B_2N_4$ [2–4]. Although such alkali-based solvents are effective for synthesizing cBN, attention must be paid to the quality of the solvents because they are hygroscopic and oxidize easily in air.

Metallic solvents including transition metal such as (Cr, Mn, Co, Ni)–Al system for cBN growth were also reported by several authors. Wentorf et al. and DeVries et al. used (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 [5,6].

Recently, Kubota et al. has investigated Co, Ni, Ni–Cr, Ni–Mo and Ni_3Al as the growth solvents of cBN crystal. They successfully reduced the minimum temperature for the cBN growth down to 1350 °C at the pressure range of 5–5.5 GPa [7–10].

Fukunaga et al. concluded in their report that Fe–Mo and Co–Mo work as solvent of B and N atoms and Al acts as a nucleation agent of cubic BN. By using the (in weight percent) Co57.6–Mo38.4–Al4 ternary alloy, they successfully synthesized the cubic BN at minimum pressure of about 4.4 GPa and temperature of about 1250 °C [11].

The addition of Mo in the Ni solvent improves the extremely low solubility of nitrogen in molten Ni. Moreover, the addition of Cr to Ni solvent, which can better enhance the nitrogen solubility in molten Ni than Mo, resulted in further increasing the crystal size [12]. The same as Mo, vanadium was also reported by Wada et al. to be effective in increasing the solubility of the nitrogen in the Fe–V and Fe–Cr–Ni–V system [13].

In the present report, we employed Co–Cr–Al base solvent and we exchanged Cr with Mo or V in the solvent to control the grain size of cBN crystals. We studied the effect of V addition into the Co–Al and Co–Cr–Al in comparison with Co–Cr–Mo–Al metal solvent during cBN synthetic process. The P–T region of the cBN growth was determined by both Co–(Cr, Mo)–Al and Co–(Cr, V)–Al alloys as the synthetic solvent. We showed that Mo addition into the Co–Cr–Al alloys promotes the grain growth of cBN crystals and obtained more than 400 μm size cBN crystals. On the other hand V addition into the Co–Cr–Al system grain size of cBN was decreased to about 10 μm. We also changed the ratio of Cr and V under Co–Cr–V–Al solvent system to compare the

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cBN growth rate and its morphology between Co–V–Al and Co–Cr–Al solvent system.

2. Experimental methods

We used Co, Cr, V, Mo, Al metal powders (Rare Metallic, 99.9%) as the solvents. The solvents were pre-mixed before pressed to form the green compact. The hexagonal BN source was hot-pressed hBN disk from Denka Co. (type N1).

High pressure and high temperature experiments were carried out by using a modified belt-type HP apparatus at pressures between 4 and 6 GPa and temperatures between 1200 and 1700 °C for 60 min with a conventional quenching method. [14].

The heating cell was 21 mm of outer diameter and 17.6 mm in length. Graphite sleeve of 12 mm o.d, 10 mm i.d. was used for heating element. In the graphite heater, 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 pressure was calibrated at high temperature by determining the minimum P–T condition of diamond precipitation using Ni, Co and invar solvent [14]. Temperature was estimated from the relation between the input power and the temperature, which had been obtained in advance by measuring the temperature with Pt–Pt13%Rh thermocouples. The pressure effect on the electromotive force of the thermocouple was not corrected.

Fig. 1 shows the sample assembly used in this study. The pre-mix metal solvent green compact was placed between the hBN disks (7 mm of diameter and 3 mm of the thickness) in the inner NaCl sleeve. Laminated hBN/alloy solvent/hBN samples were covered with 0.05 mm Ta foil. The HPHT runs were conducted with pressure increases at room temperature and then temperature increases. At about 750 °C, temperature was kept for 10 min to homogenized Al melt and Co, Cr, Mo, V powders. After keeping for 1 h at designed temperature, current supply to the heater was quickly decreased and then press load was decreased slowly.

The treated samples were recovered by removing the Ta capsule with a grinding wheel. To get the cross section, the recovered samples were then encapsulated in a hot mounting press before lapped with a diamond disk on the horizontal lapping machine. The samples were examined using the X-ray powder diffraction method (XRD) to confirm the cBN transformation, a scanning electron microscope (SEM) for cBN grain size/morphology observation and an Electron Probe Micro Analyzer (EPMA) for analyzing the infiltration and the distribution of the metal solvent in the BN layer.

3. Result and discussions

3.1. Pressure and temperature region of cBN growth using Co–Cr–Al base alloy systems

When we intended to clear up the cBN grain growth process in the molten alloy solvents, it is important to check the P–T region of cBN growth using various Mo or V content in the Co–Cr–Al base alloy. As described later in Fig. 4, which showed an example of cBN grain growth, the grain size of cBN crystals were different by any different P–T conditions. Normal trend of the cBN grain size was decrease with the increase of the reacted pressure because higher pressure tended to promote nucleation density of cBN. Thus effect of cBN grain size by introducing additional elements to the base alloy must be evaluated under similar P–T conditions.

In these experiments, we checked the cBN growth P–T region using Co65–V25–Al10 wt.% solvent and Co47–(Cr30, Mo20)–Al3 wt.% solvent mainly. The P–T region of cBN formation in the Co–V–Al (C065–V25–Al10 wt.%) solvent is shown in Fig. 2 with the solid line as an estimated minimum pressure and temperature conditions and the squares in the figure indicate the various experimental conditions. The reaction time of each experiment was 1 h. In these figures, we denoted P–T points of cBN obtained by solid marks while the open marks denoted no cBN results. To be noted here, that the solid square marks denoted cBN formation in the figure contained some amount of the residual hBN starting material. The yield of the cBN at each condition will be discussed later. Along with the P–T region of the cBN formation under Co–V–Al, we also plotted the P–T region of cBN formation under Co–Mo–Al (Co58–Mo38–Al4 wt.%) and Co–(Cr, Mo)–Al (Co47–Cr30–Mo20–Al3 wt.%) as comparison.

The double-dot–dashed line in Fig. 2 is an estimated minimum pressure and temperature conditions of cBN formation in the Co–(Cr, Mo)–Al (Co47–Cr30–Mo20–Al3 wt.%) solvent system while the circle marks indicate its various experimental conditions.

The dotted line along with the diamond marks indicate the cBN-formation region in the Co–Mo–Al system obtained from a previous experiment reported by one of the authors while the dashed line along with the triangles indicate the cBN-formation region in the Co–Al system obtained from a previous report [11]. A line representing phase equilibrium between cBN and hBN [15] is also shown in Fig. 2 with dot–dashed lines.

Comparing the P–T region of cBN formation using Co–V–Al solvent system with the minimum pressure and temperature for cBN synthesis

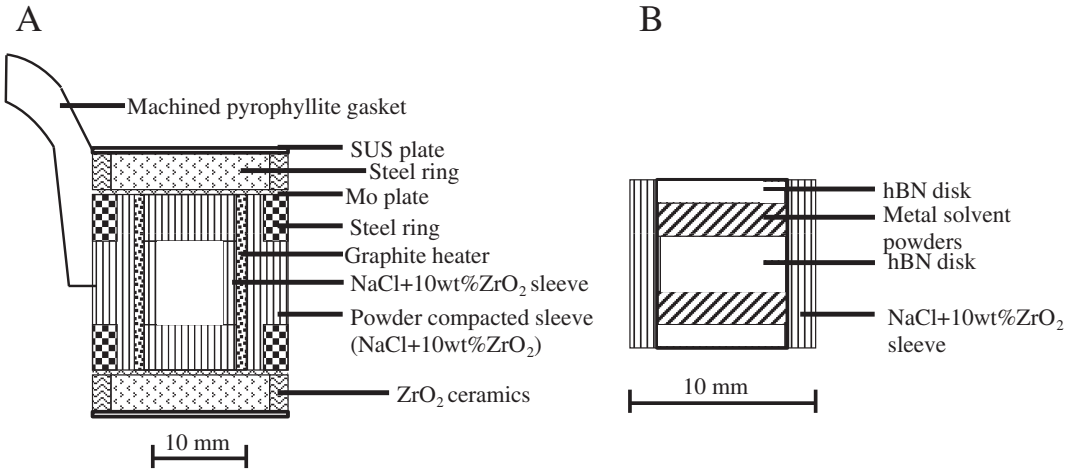

Fig. 1. Sample assembly for high pressure–high temperature (HPHT) synthesis of cBN using metal catalyst. (A) overall view; (B) enlarged view of NaCl + 10 wt.%ZrO_2 sleeve.