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The influence of hBN crystallinity and additive Lithium hydride on cBN synthesis in Li_3N–hBN system

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Abstract

In this paper, the influence of hBN crystallinity and additive Lithium hydride (LiH) on cBN synthesis with Lithium nitride (Li_3N) as catalyst was investigated under the pressure of 4.5–5 GPa and the temperature of 1500–1700 °C. hBN with different crystallinities was obtained by the same hBN. Some were explored to high pressure and high temperature, and others were subjected to heat treatment with alkali. X-ray diffraction (XRD), Raman spectroscopy and X-ray photoelectronic spectroscopy (XPS) were used to characterize the property of the starting materials. The synthesized samples were observed by optical microscopy (OM). The results indicated that besides the crystallinity of hBN, which is a general parameter for controlling the structural quality of hBN powders, some other factors such as the content of B^+ at the surface of hBN and additive LiH all strongly influence the synthesis of cBN.

Keywords: Crystallinity; Lithium hydride; High pressure and temperature

1. Introduction

Cubic boron nitride (cBN) is a superhard material, next only to diamond, possessing superior mechanical properties for its chemical stability against ferrous alloy at higher temperature, high thermal conductivity and so on. cBN can be synthesized directly under high pressure and high temperature [1–3]. Mostly, hexagonal boron nitride is used as starting material. To reduce the temperature and pressure, the suitable catalysts/solvents were used such as alkali, alkaline earth metals and their nitrides [4–8]. Besides, other catalyst solvents such as Fe–Al and Ag–Cd alloys [9], water, urea and boric acid [10], and a mixture of ammonium fluoride and silicon [11] were also found effective for cBN conversion. hBN plays an important role on the nucleation rate, morphology, properties and formation mechanism of cBN crystal. Therefore the study of the hBN attracts much attention. The effect of hBN crystallinity on cBN synthesis has been studied by many researchers. However, these experiment results and their opinions were different. Some researchers hold that hBN with lower crystallinity is easier to transform into cBN [12,13], while others do not agree because their experimental results show that hBN with high crystallinity is in favor of cBN synthesis [14–17]. In addition, some researchers find other factors such as sp^3 bonding formatted in the balled hBN [18] and nanoarches (half nanotubes) at the edges of the hBN particles [19]. But no uniform disciplinarian is carried out. In this paper, we used hBN with different crystallinities as starting materials to study the influence for cBN synthesis. The

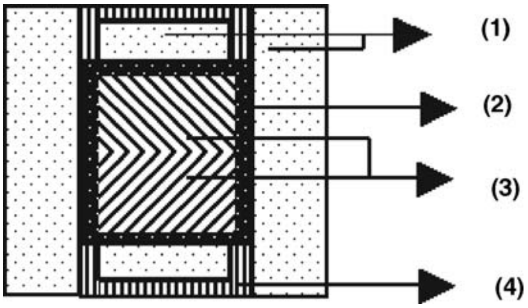

Fig. 1. The assembly for cBN synthesis under HPHT. (1) Pyrophyllite; (2) graphite; (3) sample; (4) steel.

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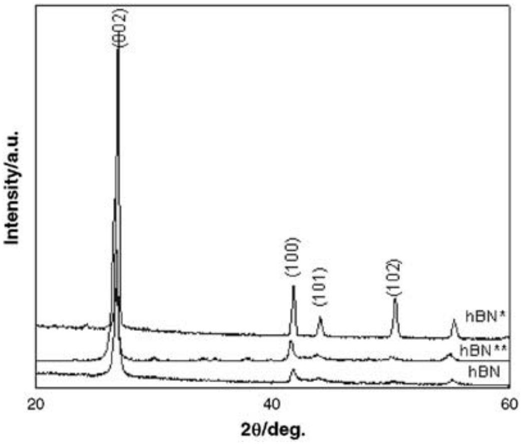

Fig. 2. The X-ray patterns of hBN, hBN* and hBN**.

results showed that the nucleation rate is related not only to the hBN crystallinity, but also to other factors.

2. Experimental

2.1. Preparation of hBN with different crystallinities

Three types of starting hBN have been used. hBN differing in their crystallinity were obtained by the same hBN using different treatments in order to ensure that the result of the cBN synthesis is only related to the hBN crystallinity excluding the effect of other factors. The starting hBN was subjected to high pressure and high temperature in the cBN stable P/T region without catalyst/solvent for 7 min to increase the crystallinity, and the obtained hBN was named hBN*. In preparing the second type of hBN, the same starting hBN was heated with NaOH to reduce the crystallinity, and then the treated hBN was washed with water several times to remove residual NaOH, and then finally treated with ethanol to get rid of the water. The third type of hBN, named as hBN** was obtained. HBN, hBN* and hBN** were mechanically mixed with catalyst/solvent (Li_3N) in a sealed container for 4 h respectively, then the mixed powder was pre-pressed to a cylinder.

2.2. High pressure experiment

In order to observe the effect of hBN with different crystallinities on cBN synthesis, the materials were divided into two groups. One was hBN* and hBN, and the other was hBN** and hBN. Every group was put into one sample cell to ensure that the same pressure and temperature during the synthesis are employed. The sample assembly for cBN synthesis by HPHT is shown in Fig. 1. The experiments were carried out in a cubic anvil high pressure and high temperature apparatus. The samples were subjected to the pressure of 4.5–5 GPa and the temperature of 1500–1700 °C for 7 min. The pressure was estimated by the oil press load, which was calibrated by a curve that was estimated from the phase transition of bismuth, thallium, and barium. The temperature was determined from a relation between temperature and input power, which had calibrated using a Pt6%Rh–Pt30%Rh thermocouple. The product was taken out after the pressure was released and dissected along the longitudinal direction in the middle of the samples. The surface of the cross section was observed by OM to analyze the nucleation and growth of cBN.

Table 1
X-ray diffraction data for GI values

Sample	Lattice planes	Intensity	GI	L_c	L_a
hBN	(100)	4488	3.63	361	737
	(101)	2639			
	(102)	1963			
hBN*	(100)	13,110	1.89	665	1360
	(101)	6103			
	(102)	10,150			
hBN**	(100)	4743	5.43	340	696
	(101)	1838			
	(102)	1211			

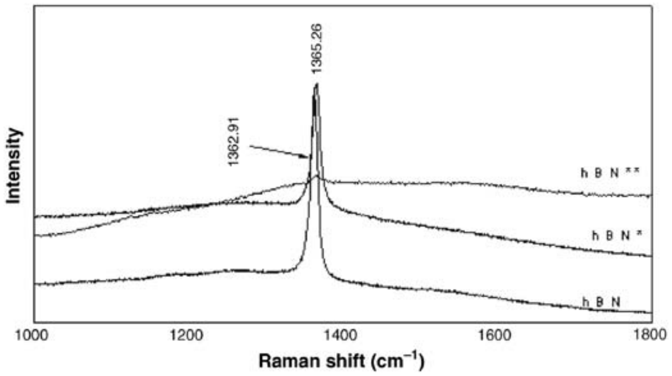

Fig. 3. The Raman spectroscopy of hBN, hBN* and hBN**.

3. Results and discussion

3.1. Starting materials analysis

The properties of the three hBN were characterized by XRD and Raman spectroscopy. We obtained the three types (hBN, hBN*, hBN**) of hBN with different crystallinities from the same hBN, which have the same properties. Fig. 2 showed the X-ray diffraction patterns of hBN, hBN* and hBN**. In Fig. 2, the peaks of hBN* were more obvious and separated in comparison with that of hBN and hBN**, especially the peaks of (103) and (104) which disappeared in the other two. The crystallinities of hBN, hBN* and hBN** were evaluated by the method proposed by Thomas and Wetson using powder X-ray diffractometry [20]. Ref. [20] defined the degree of three-dimensional ordering in terms of the "graphitization-index"(GI) as $GI=[I\ (100)+I\ (101)]/I\ (102)$. The average stack height along the c-direction, L_c, or the mean diameter of the sp^2-layers, L_a, may be determined from the modified Scherrer equation [20] $L=k\lambda/[(B^2-B_1^2)^{1/2}\cdot\cos\theta]$. In this case C_c reads 0.9 while the (100) reflex and $C_a=1.84$ have to be used for L_a. Table 1 shows X-ray diffraction data of hBN, hBN* and hBN**. In Table 1, the result indicated that the crystallinity of hBN* was the highest, hBN took the second place, and hBN** was the lowest