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Synthesis of coarse-grain-dispersed nano-polycrystalline cubic boron nitride by direct transformation under ultrahigh pressure

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ABSTRACT

Using a turbostratic pyrolytic boron nitride produced by a chemical vapor deposition process as a starting material, we conducted experiments for synthesizing polycrystalline cubic boron nitride (PcBN) at a temperature of 1600–2600 °C and pressure of 25 GPa with a multi-anvil high-pressure apparatus. Moreover, we evaluated the microstructure and hardness characteristics of the synthesized PcBN. The results showed that a complete single-phase PcBN without residual wurtzite BN was produced at 1900 °C or higher and a nano-polycrystalline cBN (NPcBN) having a mean grain size smaller than 100 nm could be synthesized at a temperature of 1950 °C or lower under a pressure of 25 GPa. Furthermore, we found that a single-phase NPcBN (CGD-NPcBN) having a characteristic microstructure of dispersed relatively coarse grains in a fine polycrystalline structure, which was harder than 53.5 GPa in Knoop hardness, was produced at a temperature range of 1900–1950 °C. In particular, at 1950 °C, CGD-NPcBN having a Knoop hardness of 54.7 GPa, which is 25% higher than that of the hardest binderless PcBN tool currently in practical use, can be synthesized. In addition, we verified that the Knoop hardness of the single-phase PcBN with a uniform microstructure increased with decreasing mean grain size, which complied with the Hall–Petch relationship.

1. Introduction

Cubic boron nitride (cBN) is the second hardest material after diamond among all engineering materials; moreover, it possesses superior thermo-chemical stability compared with diamond [1,2]. Therefore, cBN is widely used as a tool for machining various ferrous metals such as alloy steels, cast irons, die steels, and high-speed steels [3]. Although cBN tools exhibit a much higher performance than conventional tools, such as a ceramic tool, the development of a cBN tool with higher potential is required because of increasing demands to improve machining efficiency and accuracy across various manufacturing industries [4].

To date, for overcoming the disadvantages of conventional sintered cBN tools containing a binder, many studies for synthesizing polycrystalline cBN without binders (hereafter denoted as PcBN) from hexagonal BN (hBN) using the direct conversion method under high pressure and temperature without catalysts have been conducted [2,5–13]. For instance, using hBN as a starting material, a PcBN having a crystal grain size < 0.5 μm was synthesized using direct conversion under conditions of 7.7 GPa and 2300 °C [10]. This PcBN has a higher hardness, heat resistance, and thermal conductivity than conventional sintered cBN, and cutting tools made using this PcBN exhibit superior performance in high-speed machining of ferrous materials [11]. On the other hand, using pyrolytic BN (pBN) as a starting material, a PcBN having a crystal grain size below 0.5 μm was synthesized by the direct conversion method [12]. This PcBN has higher hardness and fracture strength than conventional PcBN [14]. Therefore, cutting tools and grinding wheels made using this PcBN exhibit excellent performances in cutting and grinding ferrous materials, respectively [15].

In recent years, it was reported that nano-polycrystalline cBN (NPcBN) was synthesized from low-crystallinity pBN at 20 GPa and 1770 K and exhibited a high Vickers hardness value of 85 GPa [16,17]. A recent report described that NPcBN with a Vickers hardness of 108 GPa was produced using onion-like BN as a starting material [18]. However, it has been pointed out that there is a large error in the Vickers hardness values evaluated in these studies, which is caused by the occurrence of cracking at the ends of indentations in the samples and by a large elastic recovery of the indentation profile after unloading [19–22]. In these reports [19,20], hardness measurements on many PcBN samples synthesized from hBN and pBN at 10–20 GPa and 1500–2300 °C have been carefully conducted. The maximum hardness of PcBN obtained in these studies is 48 GPa using the Knoop hardness (Hk) test, which is harder than that of the hardest PcBN tool currently in practical use [8–11].

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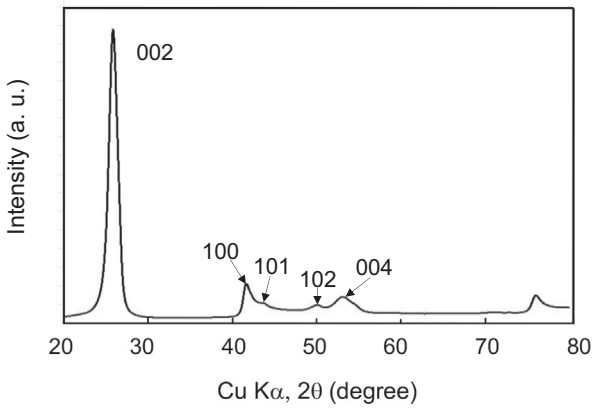

Fig. 1. X-ray diffraction pattern of starting material pBN.

The purpose of this study is to develop a novel type of PcBN harder than 50 GPa in terms of Hk by applying an ultrahigh pressure of 25 GPa, which has not yet been used in previous studies. Using turbostratic pBN produced by a chemical vapor deposition process as a starting material, we conducted a series of synthesis experiments for producing PcBN at a temperature range of 1600–2600 °C with a multi-anvil high-pressure apparatus. Moreover, the microstructures of the produced PcBN samples were analyzed with transmission electron microscopy (TEM) and field-emission scanning electron microscopy (FE-SEM), and their hardness characteristics were accurately evaluated using Hk.

2. Experimental procedure

High-purity turbostratic pyrolytic BN (pBN) synthesized via a chemical vapor deposition process was used as a starting material. This pBN was produced at a temperature over 1800 °C and under a pressure < 10 Torr using the following reaction: $BCl_3 + NH_3 \rightarrow BN + 3HCl$. pBN has an impurity level of 0.001% or less and a density of 2.0 g/cm^3. Fig. 1 shows the X-ray diffraction pattern of this pBN. To evaluate the crystallinity of pBN, the graphitizing index G.I. defined by G.I. = [$Area_{100}$ + $Area_{101}$] / $Area_{102}$ was calculated [23,24]. The value of G.I. determined using this X-ray diffraction pattern was 17.6. Thus, this pBN possesses a low crystallinity [25] because of its random-layer lattice, i.e., its sp^2-bonded turbostratic structure [26]. Fig. 2(a) shows a typical SEM image of the fracture surface of pBN parallel to the c-axis direction. It can be seen that pBN has a layered structure of thin scaly pieces composed of ultrafine crystallites. Fig. 2(b) shows a representative TEM image of the thin pBN specimen cut parallel to the c-axis by focused ion beam (FIB). It is confirmed that the microstructure of the a-plane is mainly composed of nano-crystallites having a grain size smaller than 20 nm.

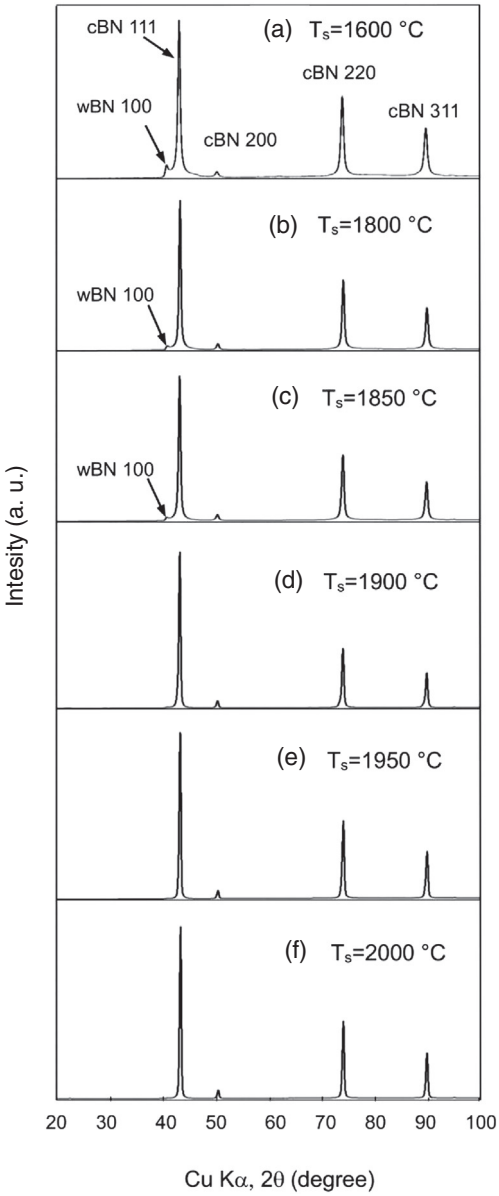

Fig. 3. Typical X-ray diffraction patterns of PcBNs synthesized at (a) 1600 °C, (b) 1800 °C, (c) 1850 °C, (d) 1900 °C, (e) 1950 °C, and (f) 2000 °C.

The pBN starting material was directly converted and sintered to cBN under a pressure of 25 GPa at a temperature of 1600–2600 °C for a holding time of 20 min using a 6–8 Kawai-type multi-anvil high-

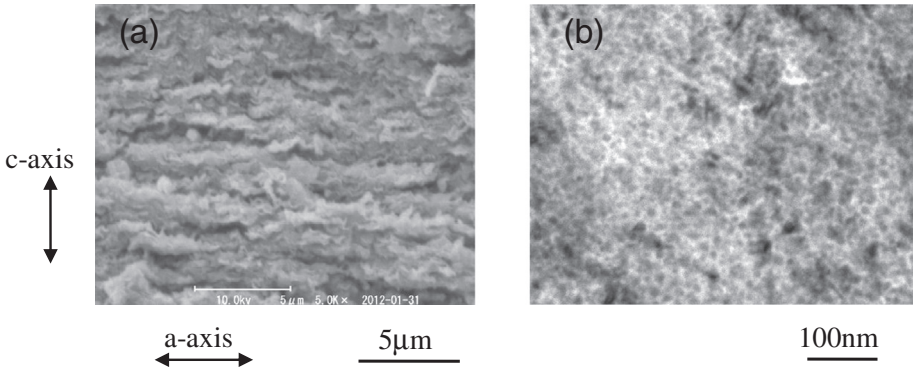

Fig. 2. Microstructure of starting material pBN. (a) SEM image of fracture surface of pBN parallel to the c-axis direction, (b) TEM image of the thin pBN specimen cut parallel to the c-axis by focused ion beam (FIB).