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Nanotwinned diamond synthesized from multicore carbon onion

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Dedicated to Prof. Guangtian Zou on the occasion of his 80th birthday

ABSTRACT

Nanopolycrystalline diamond (NPD) and nanotwinned diamond (NtD) were successfully synthesized in a multianvil, high-pressure apparatus at high temperatures by using the precursors of carbon onion. It was found that distinct carbon onions with hollow or multicore microstructures lead to the formation of different diamond products, namely NPD or NtD, respectively. The Vickers hardness of high-quality NtD with an average twin thickness of 6.8 nm reached as high as 180 GPa, which was measured by indentation hardness experiment. The existence of stacking faults other than various defects in the carbon onion was found to be crucial for the formation of twin boundaries in the product. The origin of the extraordinarily high Vickers hardness in the NtD sample is attributable to the high concentration of twin boundaries. Our work directly supports the argument that pursuit of nanotwinned microstructure is an effective strategy to harden materials, which is in good agreement with the well-known Hall-Petch effect.

1. Introduction

Superhard materials with high Vickers hardness (HV) of more than 40 GPa, excellent abradability, and chemical stability are very important for industrial applications [1–3]. Diamond is known to be the hardest material whose Knoop hardness ranges from 80 to 120 GPa [4–6]. It is well known that there is a major challenge to synthesize an alternative superhard material that is harder than diamond. However, the grain boundary is known to impede the dislocation glide to resist the shape deformation and thus is able to promote the material to have a higher hardness. According to the Hall-Petch effect, the mechanical properties of materials can be strengthened by decreasing the grain size [7,8]. Therefore, the fabrication of nanopolycrystalline diamond (NPD) was confirmed as an effective method to enhance the mechanical properties of materials. For example, Koop hardness of NPD is 110–140 GPa when the grain size is 10–30 nm [9]. The HV of NPD with a grain size of 13.4 nm is 147 GPa. When the grain size reduces to 7 nm, the hardness was enhanced to 167 GPa [10]. However, twin boundaries are considered the main factors for the enhanced hardness of nanotwinned diamond (NtD) [10–12]. As a good example, it was reported that the strength of nanotwinned copper improved five times better than that of coarse-grained copper [13,14]. Combining the Hall-Petch effect with twin boundaries, impressively, the Vickers hardness of high-quality NtD reached a remarkable value of 200 GPa, with the twin thickness of ~5 nm. Moreover, the fracture toughness and resistance of oxidation in NtD sample were also dramatically improved [15].

Both NPD and NtD are superior materials that can be categorized into ultrahard materials (HV $\geq$ 80 GPa) [15,16]. High pressure and high temperature (HPHT, P $\geq$ 10 GPa, T $\geq$ 1500 °C) conditions are needed to synthesize both materials, while a proper choice of precursors is also necessary [17–19]. As reported, NPD can be synthesized under HPHT by using polycrystalline graphite, black carbon, quasi-amorphous soot, glassy carbon balls, or pyrolytic graphite [20]. However, the formation of high-quality NtD is strictly confined to the choice of carbon onion as the precursor as reported by a pioneer work that was the first to introduce the nanotwins into the microstructure of diamond [15]. In fact, not all the carbon onions can directly transform into high-quality NtD. For example, the synthesized sample contains a large portion of grain boundary but contains few twin boundaries when the precursor is a regular carbon onion [10]. The witnessed superior mechanical properties of NtD indicate that it is essential to understand the transformation mechanism of carbon onion into NtD in an effort to fabricate high-quality NtD.

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In this work, the precursors hollow carbon onion (HOC) and multicore carbon onion (MOC) were prepared and subsequently pressurized and heated in a large volume press for the synthesis of NtD. The transformation mechanism of carbon onion to NtD was analyzed. The microstructure, morphology, and hardness of the synthesized samples were characterized to optimize the synthesis conditions of high-quality NtD.

2. Experimental

HOC was synthesized using nanodiamond (5 nm, 99.9%) as raw materials using the cubic anvil HPHT apparatus (SPD-6 × 600) under a pressure of 1 GPa, temperature of 1100 °C, and holding time of 15 min. MOC was fabricated from black carbon powders by an impinging streams technology [15]. NPD and NtD were synthesized in a large-volume, multianvil (Walker type), high-pressure apparatus under a pressure of 20 GPa, temperature of 2000–2300 °C, and holding time of 2–30 min. The standard compression 10/4 sample assembly, a Re heater, and a $LaCrO_3$ thermal insulator were used. Temperature was measured using W-Re-type thermocouples, and pressure was estimated from previously obtained calibration curves for the multianvil, high-pressure apparatus. The recovered samples were 1.5 mm in diameter and 1 mm in height, which were then polished for further analysis. Raman spectra were obtained to analyze the precursors and synthesized samples, and the samples were excited using 532-nm laser. A JEM-2200FS transmission electron microscope was used for Transmission Electron Microscope (TEM), high resolution transmission electron microscopy (HRTEM), and selected area electron diffraction (SAED) observations. The Vickers microhardness measurements were made using a Micro-Hardness Tester (HV-1000ZDT), and HV was determined from $HV = 1854.4F/L^2$, where F is the applied load and L is the mean of the two diagonals of the indentation in micrometers (μm). Atomic force microscope using ScanAsyst mode in air (Dimension Icon, Veeco Instruments/Bruker) was used to further confirm the hardness value [21].

3. Results and discussion

NPD and NtD were fabricated from different carbon onions at a pressure of 20 GPa, temperature of 2000–2300 °C, and holding time of 2–30 min. The results of Raman spectra showed that both MOC and HOC precursors transformed to diamond under HPHT (shown in Fig. 1). Despite obtaining the same modes of vibration in the Raman spectra of different synthetic diamond samples, the substructure of NtD (synthesized from MOC) is entirely different from that of NPD (synthesized from HOC). Therefore, the microstructure of the as-synthesized sample was further analyzed by TEM, and the results are shown in Figs. 2–4. NPD synthesized from HOC shows a lamellar structure (Fig. 2). Lamellar structure is also observed in NPD synthesized from isotropic polycrystalline graphite rod [22]. Diamond layers are formed in the lamellar structure during the martensitic process from graphite through the hexagonal diamond phase [23]. Furthermore, partial twin boundaries were found in NPD (shown in Fig. S1). This result is in good agreement with that of previous reports [10]. It is worth noting that TEM images of the sample synthesized from MOC (Figs. 3 and 4) showed that there are many multiple twin boundaries and stacking faults in the structure. The results indicate that the synthesized sample is NtD. Furthermore, most of the multiple twin boundaries are linear, with the parallel twin boundaries in the synthesized samples (NtD) (Fig. S2). Although the twin boundaries present in NPD are mostly nonlinear, the twin boundaries are not parallel. In addition, these twins in NPD start at the surface of grain boundary and terminate at the same point in the grain [20]. The twin thickness of NtD ranged from less than 1 nm to about 25 nm. The average twin thickness was 6.8 nm (Fig. 4 (b)).

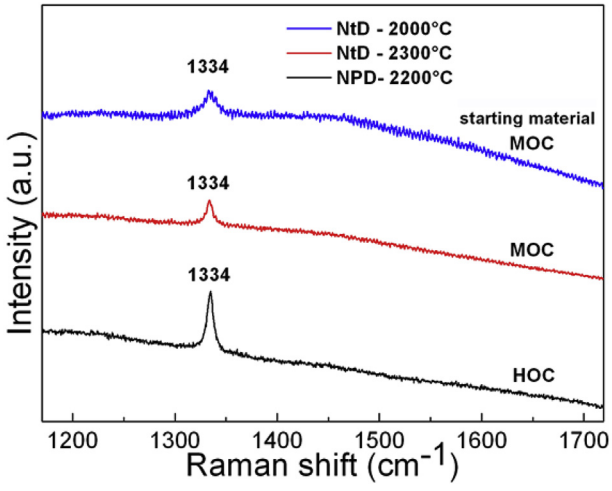

Fig. 1. Raman spectra of synthesized diamond. From top to bottom, the starting material is MOC, MOC, and HOC. (A colour version of this figure can be viewed online.)

The ultrahardness of NPD and NtD are always focused because of its different applications. The Vickers hardness of the synthesized NPD and NtD was determined. The hardness of both NPD and NtD decreased with an increase in the applied load (Fig. 5 (d)). The asymptotic hardness of NPD was 106 GPa, which is consistent with the hardness range of single crystal diamond of 80–120 GPa [4–6]. The hardness of NPD was not obviously enhanced by the grain boundary. This may be because the lamellar substructure in NPD is thin, and the thickness and size of the lamellar substructure is up to micrometer scale. The grain boundary strengthening effect of hardness is from both the thickness and size of the lamellar structure. A lamellar structure with large size results in a lower number of grain boundaries. Therefore, it cannot obviously enhance the hardness of NPD. Moreover, the dislocation can slide along the grain boundary of the lamellar structure and results in the deformation of NPD. Therefore, the hardness of lamellar NPD was lower than that of NPD (147 GPa), which has an average size of 5 nm [10].

The hardness of NtD synthesized from MOC was much higher than that of NPD with lamellar structure (Fig. 5 (d)). The extremely high hardness of 180 GPa was obtained under an applied load of 4.9 N. In this case, the two diagonal lengths of an indentation are determined using an optical microscope. This value is comparable with the previous result [15]. To confirm the extremely high hardness of NtD, atomic force microscopy (AFM), which can determine the diagonal lengths more accurately than optical microscopy, was performed (Fig. 5 (a)) [21]. The diagonal line is 6.31 μm vertically and 6.62 μm horizontally under the indentation with the applied load of 4.9 N; thus, the hardness was reconfirmed as 217 GPa by AFM (Fig. 5 (b) (c)). Obviously, the optical microscopy overestimates the diagonal length, thus providing a conservative measure of the Vickers hardness (underestimated by about 17.0%). This result is in good agreement with that of the previous report [21]. According to the Hall-Petch relation, the higher hardness of NtD is attributed to the small average twin thickness of 6.8 nm, which indicates a high concentration of twin boundaries [15,21,23–26]. These results indicate that the hardness is effectively improved by decreasing the twin thickness. This is an appropriate method to fabricate ultrahard materials.

To understand the mechanism of different products formed from carbon onion under HPHT, analyzing the microtexture of carbon onion is necessary. Carbon onion for synthesizing NtD was fabricated from black carbon powders by an impinging streams