J Mater Sci (2006) 41:8352–8355
DOI 10.1007/s10853-006-1078-4

Synthesis of B–C–N nanocrystalline particle by mechanical alloying and spark plasma sintering

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Received: 4 September 2006 / Accepted: 28 September 2006 / Published online: 18 November 2006
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Abstract B–C–N nanocrystalline particles have been synthesized by Spark plasma sintering (SPS) from the amorphous BC_2N (a-BC_2N) precursor, which were prepared by the mechanical alloying (MA) method from a mixture of graphite and hexagonal boron nitride (h-BN). The syntheses have been performed in the temperature range from 1200 to 1900 °C at the heating rate of about 300 °C min^{-1} with loads of 30 MPa. The obtained product has been checked by X-ray diffraction (XRD), transmission electron microscopy (TEM), and electron energy loss spectrum (EELS). It has been found that the B–C–N nanocrystalline particles can be synthesized at the temperature of 1600 °C with the grain size less than 50 nm, and at the temperature of 1900 °C, the a-BC_2N is decomposed into graphite and h-BN.

Recently, ternary B–C–N compounds have attracted much attention because they may have some special properties such as semiconducting and adjustable band gap. The semiconducting property of the hexagonal B–C–N compounds is expected to come from their structures, which are similar to the semimetallic graphite and insulating hexagonal boron nitride (h-BN). The composition, the interlayer stacking sequences, and the intralayer atomic distributions in the hexagonal B–C–N compounds are expected to lead to the adjustable band gaps [1]. Furthermore, hexagonal B–C–N compounds can be used to synthesize cubic B–C–N phases just like the synthesis of diamond from graphite [2]. So far, hexagonal B–C–N materials have been investigated both theoretically [3–5] and experimentally [6–8], and various methods have been used to the synthesis of the graphite-like B–C–N compounds, such as nitriding of solid-phase at high temperatures [9], chemical vapor deposition (CVD) [10, 11], solvothermal method [12], chemical process [13], etc. In general, phase separation to graphite and h-BN has prevented the synthesis of well crystallized hexagonal B–C–N compound.

Mechanical alloying (MA) is a solid-state processing technique that can synthesize a variety of non-equilibrium materials [14], including amorphous C–N compounds [15] and amorphous B–C–N compounds [16–18]. Spark plasma sintering (SPS) is another technique that can produce materials under non-equilibrium conditions. As it is known, the SPS process can concentrate high energy pulses at the point of intergranular bonding utilizing ON-OFF DC pulse energizing, producing several effects such as spark plasma, spark impact pressure, Joule heating, surface current, and electrical field diffusion, etc. Thus, the SPS process can offer significant improvements over conventional hot-press and hot isostatic press sintering. One of the important advantages of the SPS process is the high sintering speed, which can effectively restrain the grain

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growth and allows the formation of nanocrystalline materials in a short time. Therefore, in combination with MA, SPS can be used to recrystallize the amorphous B–C–N materials to the B–C–N nano materials, preventing the phase separation through the high speed sintering. In this letter, amorphous BC_2N (a-BC_2N) powder has been made by high-energy mechanically alloying method, and then the amorphous powder has been recrystallized by the SPS processing as an attempt to synthesize B–C–N nanocrystalline particles.

The graphite (99.9995%) powders and h-BN (99.5%) powders with the molar ratio of 2:1 were loaded into a stainless steel vial with stainless balls. The ball-to-powder weight ratio (BPR) was 30:1, and the stainless vials were sealed with rubber O-rings inside an Ar-filled glovebox. The dry-MA processing was performed to produce the a-BC_2N precursor. Spark plasma sintering was performed on the a-BC_2N precursor in vacuum (2–3 Pa) using a DR.SINTER SPS-3.20MK-IV apparatus. The precursor powder of 4 g was put into a graphite die of a 30 mm diameter. The punch pressure was set to 30 MPa. Different sintering temperatures from 1200 to 1900 °C were tried, and the heating rate was set to be about 300 °C min^{-1}. The temperature was monitored by an optical pyrometer focused on the graphite die surface. After getting to the desired temperature, the electric current was stopped and the pressure was released. The final product was then cooled down in the vacuum to the room temperature.

After the SPS treatment, the sample was manually crushed and grinded into powders in an agate mortar. These powders were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), and Electron Energy Loss Spectrum (EELS). XRD spectra were measured on a Rigaku D/Max-Rb diffractometer with Cu-K_a radiation. TEM and EELS analyses were performed with JEOL JEM-2010 at 200 kV equipped with Gatan-ENFINA-776. The EELS spectra were quantified following the Hartree-Slater method.

Mechanical alloying was carried out under an argon atmosphere and with different milling times up to 120 h. XRD measurements were performed on a series of samples obtained at different milling times. Figure 1 shows the variation of full width at half maximum (FWHM) of (002) peak with the milling time. The FWHM increases sharply with the increase of milling time up to 15 h, and above 15 h, the increase of FWHM becomes small, forming a plateau. The mechanically alloying powders at 120 h were characterized by TEM and EELS, indicating that a-BC_2N powders have been prepared, similar to the results of Ref. [18]. Therefore, the mechanically alloying a-BC_2N powders at 120 h were used as the precursor for the synthesis of B–C–N compound.

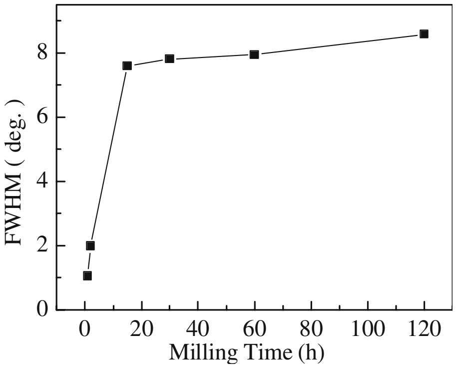

Fig. 1 Plot of the FWHM of (002) peak as a function of milling time

Spark plasma sintering was performed to synthesize the B–C–N nanocrystalline particles. Figure 2 shows the XRD patterns of the samples consolidated by the SPS process at different temperatures in the range from 1200 to 1900 °C. At the temperature of 1200 °C, no obvious (004) peak can be found in the XRD

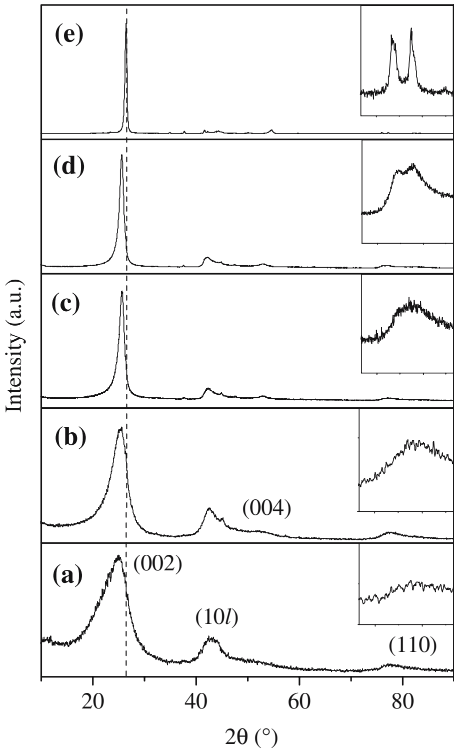

Fig. 2 X-ray diffraction patterns of B–C–N precursor sintered at temperatures of (**a**) 1200 °C, (**b**) 1400 °C, (**c**) 1600 °C, (**d**) 1700 °C, and (**e**) 1900 °C with 30 MPa pressure. The inset of figure are the enlarged (110) peak from the corresponding XRD patterns

pattern. In comparison to that of a-BC_2N precursor, the FWHM of the (002) peak changes from 8.5° to 5.5°. Although some crystalline particles could be formed at this temperature, the XRD pattern still shows the typical amorphous characteristic. The crystalline quality at 1200 °C is obviously no better than the hot-press annealing results [17] at the same temperature. Their difference in the crystalline quality may result from the fact that hot-press treatment time (24 h) is much longer than the SPS treatment time (several minutes). As shown in Fig. 2, with the increase of the SPS temperature, the (002) peak became sharper, and the (004) peak can be observed. When the SPS temperature is increased to the 1900 °C, the precursor is almost recrystallized, and no distinct amorphous peak can be found in the XRD pattern. However, the recrystallized phase is not a single B–C–N phase. From Fig. 2e, it can be well indexed as recrystallized graphite and h-BN, indicating that the temperature 1900 °C is too high to produce B–C–N compounds. For the purpose of synthesizing the B–C–N nanocrystalline particles, the proper SPS temperature can be judged from the change of (110) peak in the relevant XRD patterns. At the temperature of 1900 °C, the (110) peak is separated into the (110) peaks corresponding to graphite and h-BN, respectively. At the lower temperature of 1700 °C, the appearance of two faint peaks can be still observed above the broaden (110) peak. As shown in the Fig. 2, the proper SPS treatment temperature is 1600 °C. At this temperature, the (110) peak does not separate into two peaks corresponding to graphite and h-BN. It should be pointed out that above the temperature of 1600 °C, the minor Fe–B peaks can be observed in the XRD patterns, and at the temperature of 1900 °C, the minor B_4C can be indexed from the XRD patterns. The Fe element should come from the contamination from the MA process.

Figure 3a shows a typical TEM image of B–C–N nanocrystalline particles obtained after 1600 °C SPS treatment. The crystalline particles of less than 50 nm in diameter are observed in Fig. 3a. The corresponding SAED pattern shows four diffraction rings (Fig. 3b), matching (002), (10*l*), (004) and (110) planes of the polycrystalline phases, respectively, which is also in consistent with the XRD patterns (Fig. 2c). The composition of the powders was examined by EELS analysis. The EEL spectrum analysis in the same position shows the characteristic boron, carbon and nitrogen K-shell ionization edge, indicating that these polycrystalline phases are composed of B, C and N. In the K-edge of Fig. 4, the sharp peak at 188 eV, 284 eV and 401 eV, can be attributed to the transition from 1*s* to π^* state of the boron, carbon and nitrogen atoms, respectively, indicating that the sp^2 bonds exists among the B, C, and N atoms. Using Hartree-Slater method, the relative atomic ratio of B:C:N is close to the stoichiometric value of 1:2:1.

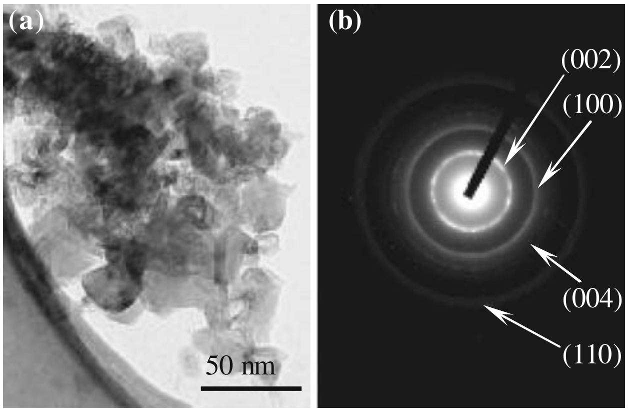

Fig. 3 (**a**) Typical TEM image of the BCN compounds obtained after 1600 °C SPS treatment. (**b**) The corresponding SAED pattern indicating the nanocrystal was synthesized

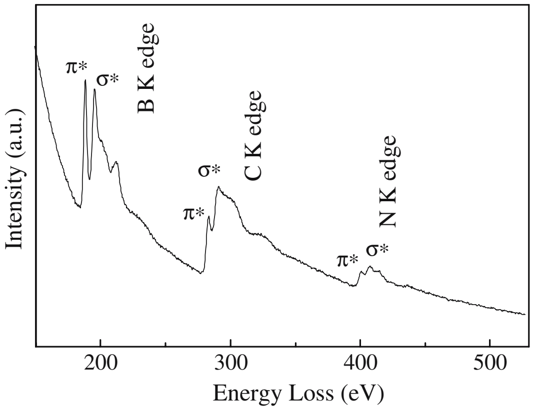

Fig. 4 The EEL spectrum of 1600 °C sintered specimen

In summary, amorphous BC_2N powders were prepared by high energy ball milling of a mixture of graphite and h-BN, and then spark plasma sintering method was used to recrystallize the a-BC_2N precursor at high temperature. The experimental results show that at the high temperature of 1900 °C, the precursor separates into graphite and h-BN. The desirable SPS temperature of synthesizing B–C–N nanocrystalline particles is 1600 °C.

Acknowledgement This work was supported by National Natural Science Foundation of China (Grant No. 50225207, 50372055, 50472051 and 50532020), National Basic Research Program of China (Grant No. 2005CB724400), and the Key Project of Science & Technology Innovation Engineering, the Chinese Ministry of Education (705004).

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