Turbostratic boron nitride consolidated by SPS

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Turbostratic boron nitride (t-BN) powder prepared by mechanical grinding of hexagonal boron nitride (h-BN) under the nitrogen atmosphere with the oxygen concentration less than 1 ppm was consolidated by spark plasma sintering (SPS). The turbostratic structure was maintained after the consolidation, which was characterized by XRD, Raman and IR spectra. The t-BN consolidated without any additives at 1900°C for 10 min under applied pressure of 100 MPa showed a bulk density of 95%. The bending strength, Young’s modulus and Shore hardness of the consolidated t-BN were 72 MPa, 259 GPa and 117 Hs, respectively. They were much higher than those of conventionally consolidated h-BN. On the other hand, the thermal conductivity was 3 W/mK and much lower than the compact of h-BN.

Key-words: Consolidation, Boron nitride, Turbostratic structure, Mechanical grinding, Spark plasma sintering

1. Introduction

Typically, boron nitride (BN) has four crystalline modifications, including cubic (c-BN), hexagonal (h-BN), rhombohedral (r-BN), and wurtzite (w-BN) structures. In addition, the BN also exhibits turbostratic (t-BN) structure as a partially disordered structure based on h-BN in which the stacking hexagonal planes are random and rotated randomly along the c-axis. Only the first two BNs have been applied as engineering materials because the t-BN powder is very difficult to consolidate in the form of the turbostratic structure. The c-BN which is known as an ultra-hard material for cutting and grinding tools is prepared by a high-pressure, high-temperature process. The h-BN is the most common form in the BN series and serves as a soft refractory material with high lubricity and electrical resistance.

On the other hand, t-BN powder can be prepared by the mechanical grinding of h-BN, the thermal decomposition of melamine diborate, and the chemical reaction of a fused urea-boric acid intermediate and ammonia. However, these processes are difficult to completely eliminate the contaminations including oxygen in the t-BN powder as the t-BN powder is significantly reactive with O2 and H2O in air, which made the consolidation of t-BN difficult because even a small amount of O2 in the t-BN powder often leads to the transformation of t-BN to h-BN under annealing temperature above 1500°C in the conventional processes.

In this paper, we describe the consolidation of t-BN without the structural transformation and the mechanical and the thermal properties. The t-BN powder was prepared by the mechanical grinding under the N2 atmosphere with extremely low O2 concentration, and was subsequently consolidated by spark plasma sintering (SPS). Since the SPS process utilized in this work features a very fast heating rate and short holding time for materials consolidation, suppressing the O2 contamination in the powders during consolidation is an advantage.

2. Experimental procedure

The t-BN powders were prepared by planetary ball milling (model: P–6, Fritsch, Japan) of h-BN powders (ca. 10 μm, > 99%, Kojundo Chemical Co. Ltd., Japan) that was performed using 10 mm-diameter silicon nitride balls (Nikkato, Japan) and silicon nitride vials with an inside diameter of 75 mm and a height of 70 mm (250 ml, Fritsch, Japan). A ball-to-powder mass ratio (B/P) of 40/1 was used with 7.5 g of the h-BN powder. Total milling times ranged from 0 to 5 h. The milling speed was 560 rpm, and the rotation speed of the vial was 459 rpm. All transfers of powders to and from the vials were handled in a glove box filled with N2 (O2 concentration < 1 ppm and H2O concentration < 6 ppm) or under air atmosphere. The vials were also covered with stainless pots filled with N2 in the glove box. Residual H2O and O2 were removed from the N2 atmosphere by a recycle purification system during the handling of powders (model: MF–70, UNICO, Japan).

Consolidation of the milled sample was carried out using an SPS apparatus (model: 1050, SPS SYNTEX INC., Japan). The SPS apparatus is an uniaxial 100 kN press combined with a 15 V, 5000 A DC power supply to simultaneously provide pulsed current and pressure to the sample. We used a pulsed cycle of 12 ms on and 2 ms off. The milled powders were placed in a graphite die, and then pressures ranging from 20 to 100 MPa were applied through the top and bottom punches with a diameter of 19.6 mm and a length of 20 mm. The samples were heated at 60°C/min and then held at the consolidating temperature ranging from 1500 to 1900°C for 10 min. The consolidated samples were cooled to room temperature by turning off the power. The temperatures were controlled by an optical pyrometer focused on a hole drilled into the die surface to a depth of 5 mm. The temperature was also measured by a two color pyrometer.

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Structural analysis was performed by X-ray diffractometer (RINT 2500, Cu Kα radiation operated at 100 mA and 40 kV, RIGAKU, Tokyo Japan). The step size was 0.02° in 2θ. Structural characterization was carried out using Raman (NRS–2100, λ = 514.5 nm, JASCO, Japan) and IR spectroscopy (FT-IR 660 plus, JASCO, Japan). Mechanical properties were characterized by Shore hardness (model: Shore D type, SHIMADZU, Japan), bending strength, and Young’s modulus (model: SL–5000, Marubishikagaku, Japan). The fracture surface was observed by scanning electron microscope (JSM–5200, JEOL, Japan). The thermal conductivity was measured by laser flash technique (TC–7000Win, ULVAC–RIKO, Japan) at room temperature.

3. Results and discussion

Figure 1 shows the XRD patterns of the h-BN powder milled for times ranging from 0 to 5 h under an N₂ atmosphere with the concentrations of O₂ < 1 ppm and of H₂O < 6 ppm. The sharp peaks of as-received h-BN powder are shown in Fig. 1(a). The breath of the peaks was broadened even after milling for 1 h and did not change by milling for 3 h or longer. The patterns of the milled powders showed the broadening peak of lattice plane (002) and the defused peaks of lattice planes (101) and (102). The BN has a turbostratic structure without regularity of structure along the a- and b-axes.17–20 This structure has generally been formed by sliding and rotating of the basal plane. We also prepared t-BN from h-BN milled under an air atmosphere (hereafter t-BN-air). Both the t-BN and t-BN-air powders were consolidated using SPS.

Figure 2 shows the time dependence of the displacement and temperature of each specimen during SPS at 1900°C for 10 min under applied pressure of 100 MPa. The inset of Fig. 2 shows the XRD patterns of the sintered compacts. In the profiles, the shrinkage of the specimen was drawn as negative. In SPS, the shrinkage of the punches was conversely drawn as positive. In the profiles, the thermal expansion of the punches has been often observed in the first stage of displacement. When the temperature was below 1000°C, both profiles showed thermal expansion due to the contribution of punches and the specimen. The displacement profile of t-BN-air showed shrinkage behavior above approximately 1000°C. On the other hand, the shrinkage of t-BN initiated when the temperature reached about 1500°C. The structure after the consolidation of t-BN powder was maintained to be turbostratic as shown in the inset (a) of Fig. 2. However, when the conventionally prepared t-BN powder was consolidated above 1500°C, the t-BN often transformed to h-BN during the processes.22–25 Indeed, when all transfers of powders to and from the vials in the planetary ball mill were handled in the glove box filled in N₂ with 0.7% of O₂ and subsequently covered with stainless pots, the XRD pattern of the consolidated compact showed the existence of both h-BN and t-BN. This suggests that a small amount of O₂ impurity in the t-BN powder is enough to transform t-BN into h-BN. Consequently, controlling the O₂ level during the MG process is crucial to prepare the t-BN powder for the t-BN consolidation. On the other hand, as predicted, the consolidated t-BN-air transformed to h-BN with characteristic and clear diffraction peaks of (002), (101), and (102) planes of h-BN at 2θ values of about 26°, 44°, and 50°, respectively. However, the intensity ratio of the diffraction peaks of (002) and (100) in the consolidated t-BN-air was quite different from that of the h-BN powder compact, as shown in Fig. 1(a). Generally, the c-axis of the hexagonal structure in the h-BN compact which was prepared by a hot pressing method was oriented parallel to the pressure direction.21 This non-conventional orientation of the hexagonal plane occurs with the transformation from t-BN to h-BN during SPS as reported previously.22

The local structures of the t-BN powder and the consolidated t-BN compact were characterized by Raman and IR spectra. Figure 3 shows the Raman spectra of (a) h-BN, (b) t-BN powders and (c) consolidated t-BN compact. In Fig. 3, only a single peak at 1370 cm⁻¹ was clearly observed from the Raman spectra of the h-BN powder. However, no peak was detected from the t-BN powder. Basically, h-BN only has a Raman signal of interlayer E₂g vibration at 1370 cm⁻¹.23,24 Therefore, the t-BN prepared herein may be identified as an amorphous rather than the turbostratic structure. On the other hand, the Raman peak of consolidated t-BN showed much lower intensity and broader than the h-BN. The broadening of the peak at 1370 cm⁻¹ comes from many stacking faults between the hexagonal basal planes in h-BN and the structure is identified to be t-BN.23 These results of the Raman spectra of t-BN and the consolidated t-BN also
agree with their XRD patterns.

Figure 4 shows the IR spectra of the (a) h-BN, (b) t-BN powders and (c) the consolidated t-BN compact. In the range of 600 to 1800 cm\(^{-1}\), h-BN has two peaks.\(^{25}\) The peaks at 1370 cm\(^{-1}\) and 817 cm\(^{-1}\) correspond to in-plane and out-of-plane vibrations, respectively.\(^{25}\) Then, the peak at 817 cm\(^{-1}\) shifts to the low-frequency region when h-BN is partially stacking-disordered.\(^{25}\) The peak lower than 817 cm\(^{-1}\) was observed from the IR spectra of the t-BN powder and the compact. These IR spectra supported again that the t-BN powder and the consolidated t-BN compact prepared in this work have also stacking disordered structure. The IR spectra observed in the t-BN powder and the compact also agreed with the reported IR spectra around 817 cm\(^{-1}\) of the t-BN powder.\(^{1,26}\) The peak at 1370 cm\(^{-1}\) corresponding to the in-plane vibration in the t-BN powder and the compact also shifts to the slightly higher frequency region and broadens compared to that of the h-BN. This seems to be something structure-changed in the BN in-plane.

Figure 5 shows the effect of holding temperature on the bulk density of t-BN compact consolidated for 10 min under the applied pressure of 70 MPa. The inset shows the effect of applied pressure on the relative density of t-BN compact consolidated at 1900°C for 10 min.

Fig. 3. Raman spectra of (a) h-BN powder, (b) t-BN powder and (c) t-BN compact consolidated by SPS under 100 MPa for 10-min hold at the holding temperature of 1900°C.

Fig. 4. IR spectra of (a) h-BN powder, (b) t-BN powder and (c) t-BN compact consolidated by SPS under 100 MPa for 10-min hold at the holding temperature of 1900°C.

Fig. 5. Effect of holding temperature on the bulk density of t-BN compact consolidated for 10 min under the applied pressure of 70 MPa. The inset shows the effect of applied pressure on the relative density of t-BN compact consolidated at 1900°C for 10 min.

Fig. 6. XRD patterns of t-BN compact consolidated by SPS under 70 MPa for 10 min-hold at the holding temperature: (a) 1500°C, (b) 1600°C, (c) 1700°C, (d) 1800°C, (e) 1900°C.
increased with applied pressure. Finally the relative density of the t-BN compact reached 95% under applied pressure of 100 MPa.

Figure 6 shows the XRD patterns of t-BN consolidated at a holding temperature ranging from 1500 to 1900 °C. The XRD patterns at each holding temperature show that the turbostratic structure is maintained in the temperature range, but the peak breath of t-BN sharpens with an increase in the holding temperature. This result suggests that the stacking disorder in the t-BN structure gradually reduced with holding temperature. However, the h-BN structure was still never detected from the compact. The O₂ contamination must be suppressed by well-controlled inert atmosphere during the MG process, and subsequent rapid heating and holding for shorter time in SPS.

Figure 7 shows the effect of relative density on the Shore hardness of t-BN compact consolidated at 1900°C for 10 min. The Shore hardness was controlled by the applied pressure (inset of Fig. 5). The Shore hardness increased with density. These values are much higher than the Shore hardness of h-BN compact from t-BN-air, 26 Hs, and also the value of the conventional h-BN compact, 15 Hs. These higher hardness results from the higher density of 95% and the finer grains of t-BN compared to the h-BN compact with a density of 90%. Figure 8 shows SEM photos of t-BN compact (a) and h-BN compact (b) consolidated from t-BN-air. The grains of the t-BN compact are much finer than the h-BN compact. The grain morphologies are also much different in the two compacts.

In Table 1, the Shore hardness, the bending strength, Young’s modulus, and the thermal conductivity of t-BN and the conventional h-BN are listed. The t-BN herein was consolidated at 1900°C for a 10-min hold under applied pressure of 70 MPa. The Shore hardness of t-BN was 117 Hs which is much higher than that of the conventional h-BN compact, 15 Hs. The bending strength and the Young’s modulus of the consolidated t-BN was 72.3 MPa and 259 GPa respectively which were much higher than the 15 MPa and 18 GPa of the conventional h-BN without sintering additives.

The thermal conductivity of the conventional h-BN compact depends on the measured direction due to the preferential orientation of the h-BN crystals. The thermal conductivity of the t-BN compact was measured parallel to the pressure direction. The h-BN compact, prepared using hot pressing, has thermal conductivity of 128 W/m·K and 8 W/m·K when measured in perpendicular and in parallel surfaces of the specimen to the pressing direction, respectively. On the other hand, the t-BN compact exhibits thermal conductivity of 3 W/m·K, which is much lower than conventional h-BN compact because the stacking faults in the t-BN structure scatter the phonon.

### 4. Conclusion

The t-BN powder prepared by a mechanical grinding process from h-BN under a nitrogen atmosphere with an oxygen concentration less than 1 ppm was consolidated by spark plasma sintering without structural transformation. When the t-BN powder was consolidated at 1900°C for 10 min under applied pressure of 100 MPa without any additives, the bulk density was 95%. The local structures of the t-BN powder and the consolidated t-BN compact were characterized by Raman and IR spectra. These spectra supported that the structure after the consolidation of the t-BN powder prepared in this work maintained the turbostratic structure. The bending strength, Shore hardness and Young’s modulus of the consolidated t-BN compact were 72.3 MPa, 117 Hs and 259 GPa, respectively and much higher than those of the h-BN compact. However, the thermal conductivity was 3 W/m·K and much lower than that of h-BN.

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