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PROCEEDINGS OF THE SYMPOSIUM ON SPARK PLASMA SYNTHESIS AND SINTERING

Consolidation of SiC/BN composite through MA-SPS method

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Abstract Hexagonal-BN has been selected as a second phase for SiC/BN composite to improve SiC's machinability and thermal shock resistance. In this research, nanometric SiC/BN was prepared through mechanical alloying (MA) from Si + C + BN powder and then consolidated by SPS without any sintering aids. XRD results after MA revealed the absence of sharp peaks corresponding to SiC and BN. The density and the intensity of the SiC and BN peaks on XRD increased with temperature during SPS. The final density of the composite reached approximately 90–99% with 50/50 of SiC/BN to 100/0. During the consolidation process, crystallization, phase separation, and ordering were observed simultaneously. This phenomenon could accelerate the mass transfer for the consolidation and the preparation of bulk SiC/BN composite without any sintering aids. In a 50/50 SiC/BN ratio, the Vickers hardness of the nano-structured reference sample prepared by the conventional method with sintering aids could not be measured due to high porosity. However, the well-consolidated sample prepared in our research showed a hardness of approximately 3 GPa.

Introduction

Silicon carbide (SiC) has been considered for present and potential technological applications in many fields based on its attractive properties, which include low density, chemical stability, low nuclear activation, and high strength at high temperatures [1–4]. However, the brittleness of SiC materials is a major impediment for engineering applications, which also increases the difficulty of machining and cost. Also, SiC has low thermal shock resistance, which leads to a deterioration of its potential. There are several ways to improve these disadvantageous properties of SiC ceramics. Combining with other materials to form a hybrid structure can improve the fracture toughness and the thermal shock resistance of the ceramic materials. For adjusting the elastic modulus, making porous materials with different porosity and composites by adding phases with low elastic modulus are the main approaches. Thus, one valid method for improving the disadvantageous properties of SiC ceramics is making a composite with ceramics. Among ceramics, hexagonal-boron nitride (h-BN) is one top candidate material as a second phase, which has the lowest elastic modulus and corrosion resistance and excellent thermal shock resistance [5, 6].

However, preparing SiC/BN composites is difficult due to the low sinterability of both SiC and h-BN [6, 7]. Adding sintering aids such as a B–C system and a rare-earth oxide with Al_2O_3 is an indispensable condition to prepare dense SiC; even nano-sized powder is used [8, 9]. The existence of B_2O_3 impurity in the raw BN powder and/or adding B_2O_3 is required for dense BN [10]. Also the effectual improvement of properties is only achieved by homogeneous microstructure and isotropical distribution of fine h-BN flakes located at the grain boundaries of SiC. For instance, the fracture strength of composites has been

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reported to remarkably decrease with increasing h-BN addition due to inhomogeneous dispersion [11]. Since dispersing fine h-BN particles into the matrix homogeneously by the conventional mixing of commercial h-BN powders is difficult, many researchers with various methods have studied incorporating h-BN into SiC. Zhang et al. [12–14] prepared SiC/BN composites by an in situ reaction system using $Si_3N_4 + B_4C + C$ and $Si_3N_4 + B_2O_3 + C$. Wang et al. presented the synthesis of the composites by the chemical reaction of boric acid (H_3BO_3) and urea ($CO(NH_2)_2$) under a nitrogen atmosphere [15, 16]. In both cases, using sintering aids is unavoidable due to low sinterability. However, such sintering aids as $Al_2O_3 + Y_2O_3$ (by which the mechanical properties and chemical stability at high temperatures are possibly decreased) are necessary to consolidate the composites due to the low sinterability mentioned above [17].

The authors previously reported an innovative consolidation method for SiC via mechanical alloying-spark plasma sintering (MA-SPS) technique. With this technique, stacking disordered SiC was prepared from the elements by high-energy ball milling and then consolidated by SPS. Without any sintering aids, highly dense SiC (up to 99% relative density) was successfully obtained at 1900 °C under a pressure of 70 MPa. During the process, a sharp increase in density in the temperature region of 1700–1800 °C was associated with a decrease in the disorder [18–21]. The same method was applied to a BN system in which h-BN was consolidated to have over 90% relative density without sintering aids by simultaneous structural ordering from t-BN; it was prepared by mechanical grinding of h-BN and obtained densification above 1500 °C [22].

We now report an extension of the MA-SPS method, which is a simplified approach for consolidation without sintering additives, to prepare bulk SiC/BN composites. For making homogeneous SiC–BN powder by high-energy ball milling, Si, C, and h-BN were selected. To discuss the consolidation mechanism of the SiC/BN composite, different kinds of characterizations, such as phase identification, structural observation, and so on, were carried out. The bulk SiC/BN composites were characterized for their density, mechanical properties, and microstructure.

Experimental procedure

Si (ca. 1.0 μm, 99.999% pure, Kojundo Chemical Co. Ltd., Japan), C (TGP-7, ca. 7.0 μm, >99.9% pure, Tokai Carbon Co. Ltd., Japan), and hexagonal-BN (ca. 10 μm, >99% pure, Kojundo Chemical Co. Ltd., Japan) powders were selected as starting materials. They were blended to have a SiC/BN = 100/0–0/100 ratio and then milled using a planetary ball mill (Pulverisette P5/2 Fritsch). Silicon nitride balls (10 mm diameter) and a vial (an inside diameter of 75 mm and a height of 70 mm) were used. The ball-to-powder mass ratio (B/P) was fixed to be 40/1 with 7.5 g of the mixed reactants. The reactants were milled for 24 h. The revolution speed of the vial was 300 rpm with a rotation/revolution ratio of −1.18/1.

To consolidate the SiC/BN composite, a spark plasma sintering (SPS) apparatus (Model 1050, Sumitomo Coal and Mining Co. Japan) was utilized. The milled powders were placed in a cylindrical graphite die. The sample was wrapped in a 0.2-mm thick graphite foil. Graphite plungers were used to apply a uniaxial pressure of 50 or 70 MPa in the SPS. After the system with the sample was evacuated to a pressure of about 10^{-2} Torr, a DC pulsed current was supplied. The pulse cycle of the DC current was 12:2, i.e., 12 pulses of 3.6 ms on and 2 pulses of 3.6 ms off. The sample was heated to selected temperatures at rates of about 100 °C/min and held for 10 min. During the entire process, temperature, average applied voltage and current, and sample linear dimension were recorded in real time.

X-ray diffraction (XRD) analyses were carried out using a RIGAKU RINT2500 (Rigaku Co., Ltd., Japan) diffractometer operated at 200 mA and 40 kV. An infrared absorption spectroscope (FTIR-660 Plus, JASCO, Japan) was used to obtain structural information. Specimens were machined to $24 \times 4 \times 5$ mm^3 and polished for a 3-point bending strength measurement (PL-300, Marubishikagaku, Japan). The span length and crossed speed were 18 mm and 0.2 mm/min, respectively. The strength data were calculated based on the average of three measurements. The hardness was measured by Vickers method (HMV-2000, Shimazu, Japan) with a load of 98 N and a holding time of 15 s. The results of 10 measurements were averaged and used for the hardness data. The fracture surfaces of the sintered specimens were observed using a scanning electron microscope (SEM: JSM-5400, JEOL, Japan). Transmitting electron microscopy (TEM: JEM-4000EX, JEOL, Japan, operated at 400 kV) was used to observe the microstructure of the specimens.

Results and discussion

The elemental and BN powders with different volume ratios were milled using planetary ball milling to prepare the SiC/BN powder. All milling conditions were fixed, such as rotation radius, revolution speed, revolution radius, milling time, and the weight ratio of the milling ball against the powder. Figure 1 shows the influence of the SiC/BN ratio on the X-ray diffraction patterns. When only Si and C were mechanically alloyed (SiC/BN = 100/0: MA-SiC),

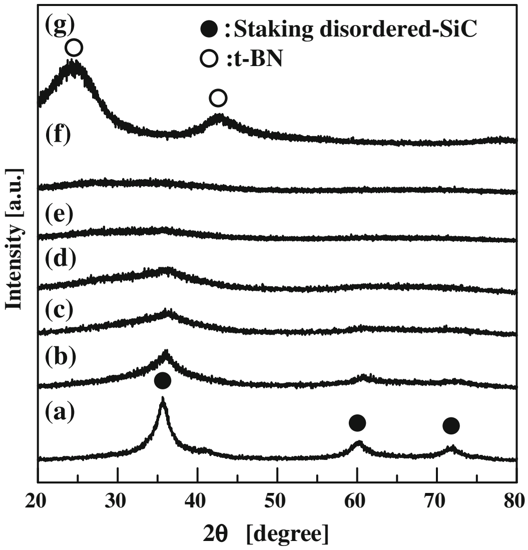

Fig. 1 X-ray diffraction patterns of specimen prepared by MA method. SiC/BN vol ratios are (a): 100/0, (b): 90/10, (c): 80/20, (d): 70/30, (e): 60/40, (f): 50/50, and (g): 0/100

there were three characteristic broad peaks that corresponded to stacking disordered SiC [18]. In contrast, mechanically grinded BN (SiC/BN = 0/100: MG-BN) showed only two broad peaks at 2θ values of about 24° and 42° at which they corresponded to the diffractions from the (002) and (10l) planes of h-BN. This state well agrees with the XRD patterns of turbostratic BN [22], which has 2-dimensional order based on a B–N six-membered ring and its random stacking toward the C-axis instead of the 3-dimensional order for h-BN. Structural disordering was carried out during the MG process with a sliding of the ring plane as a cleavage fracture. With increasing BN ratio, the peak intensities of SiC decreased. However, none of the peaks (appeared at MA-SiC and MG-BN powder) was detected from the specimen with a BN ratio of 40 and higher.

All powders were consolidated by SPS at 1900 °C for 10 min. Figure 2 shows the XRD patterns of the consolidated specimens. MA-SiC with three broad peaks on the XRD pattern was consolidated as beta-SiC with four narrow peaks by ordering from the stacking disordered structure. Also, MG-BN showed three sharp peaks corresponding to h-BN after the consolidation process. The peak intensity ratio of SiC/BN decreased with BN concentration. No peak of the crystal phase was detected except SiC and BN in Fig. 2. Remarkable XRD change was obtained between the milled and consolidated samples, indicating the occurrence of significant structural ordering (disorder–order transformation) in the SiC/BN composite.

Figure 3 shows the relative density of the SiC/BN composite consolidated at 1900 °C for 10 min under applied pressure of 70 MPa. After measuring the specimen size and weight, relative density was calculated from the measured density divided by the theoretical density (3.25 g/cm^3 for SiC and 2.27 for BN). The relative density of the SiC/BN composite increased with SiC concentration. Traditionally, using sintering additives was unavoidable to achieve full consolidation for a SiC/BN composite as well as SiC [12–16]. However, the final relative density of SiC/BN = 100/0 was 99%, even without a sintering aid. The consolidation mechanism of MA-SiC was discussed in references [21]. This consolidation was based on the acceleration of mass transfer and the rearrangement of nano-size grain, which was caused by the diffusion of defects and atoms, while the disordered structure was ordering [19]. Therefore, the consolidation of SiC/BN composite achieved 90% relative density without any

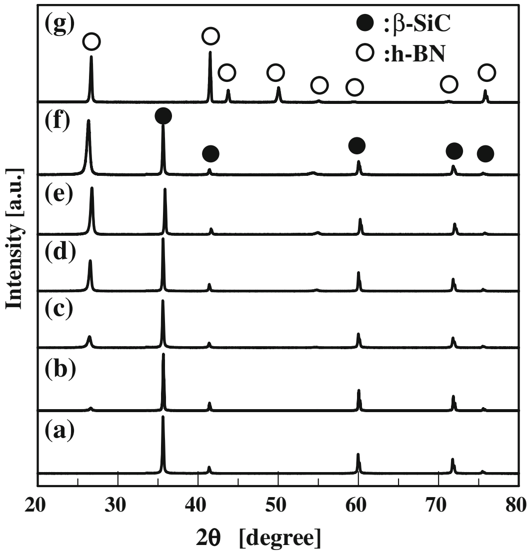

Fig. 2 X-ray diffraction patterns of SiC/BN composite prepared by MA-SPS method. SiC/BN vol ratios are (a): 100/0, (b): 90/10, (c): 80/20, (d): 70/30, (e): 60/40, (f): 50/50, and (g): 0/100

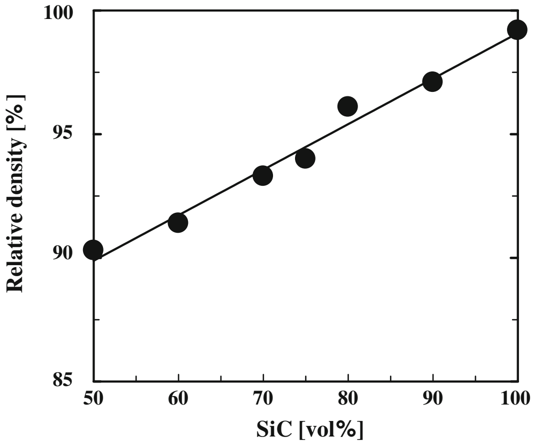

Fig. 3 Influence of SiC concentration on relative density of SiC/BN composite prepared by MA-SPS method

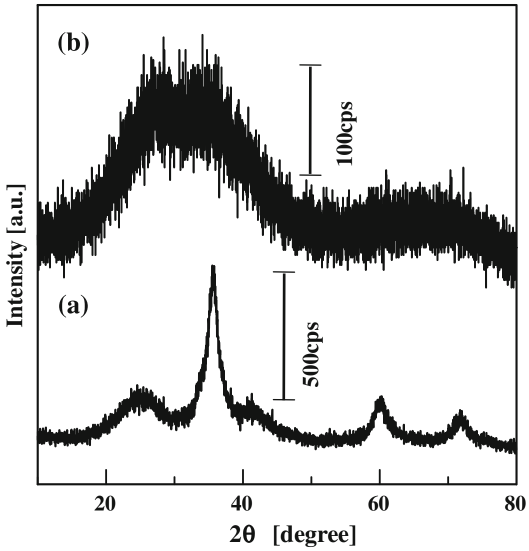

Fig. 4 X-ray diffraction patterns of the sample prepared by MA method. (a): Mixture of MA-SiC and MG-BN powder. (b): SiC/BN = 50/50 composite

sintering aids. However, the consolidation behavior is not clearly discussed in the composite system. To investigate the phenomena of structural change during sintering, the SiC/BN ratio of 50/50 was selected due to the largest change observed from Figs. 1 and 2.

At the beginning, the structure of the SiC/BN = 50/50 composite before sintering was discussed by XRD and IR analysis. Figure 4 compares two powders, both prepared from the same starting materials but in different milling order. To prepare the SiC/BN composite powder, whole powders of Si, C, and BN were milled together (Fig. 4b). In contrast, MA-SiC and MG-BN powders were prepared separately by planetally milling for 24 h and mixed by agate mortar for 5 min (Fig. 4a). The mixture powder clearly exhibited three peaks from stacking disordered SiC and two peaks form turbostratic BN. However, none of the peaks, which appeared in the MA-SiC and MG-BN powders, was detected from the composite specimen (Fig. 4b). These results suggest that effective mixing and milling of Si, C, and h-BN powders was caused by the presence of second phases: BN for SiC and vice versa. Additionally, milling was sufficient to promote the formation of an amorphous-like structure of SiC/BN composite.

IR spectroscopic analysis was carried out to observe the structure of the milled SiC/BM composite powder. Figure 5 compares the IR spectra of the MA-SiC, MG-BN, and SiC/BN composite powder. Typically, SiC has a single peak at 860 cm^{-1} [23], and h-BN shows two peaks at 817 and 1370 cm^{-1} [24, 25] in the range from 600 to 2400 cm^{-1}. However, MA-SiC shows a broad peak at approximately 820 cm^{-1}, which might be affected by the disordered structure. MG-BN showed a broad peak at 1370 cm^{-1}. The existence of a packing defect represents a layer (that is displaced in the six-membered ring plane and in the regular sequence of the hexagonal layers) and broadened the peak at 1370 cm^{-1} [25]. The result of IR spectra indicates that the mixture powder consists of the coexistence of SiC with t-BN in Fig. 5c. However, the SiC/BN composite showed extremely broad peaks ranging from 650 to 1550 cm^{-1} in Fig. 5d. A comparison of the two powders suggests that the composite powder not only had an amorphous-like structure but also Si–C–B–N chemical bonding as the result of planetally ball milling for 24 h with Si, C, and h-BN.

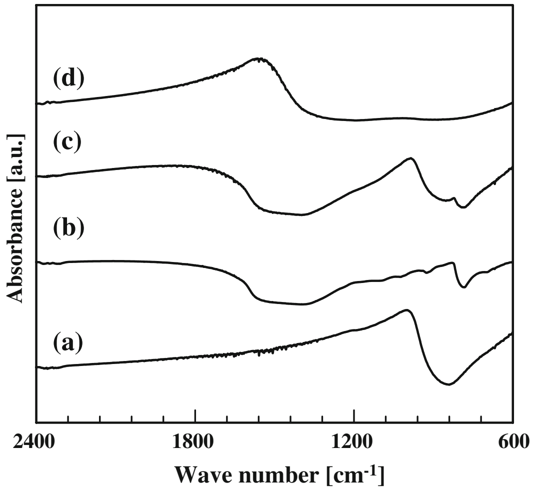

Fig. 5 IR spectra of specimen. (a): MA-SiC powder. (b): MG-BN powder. (c): Mixture of MA-SiC and MGBN powder. (d): SiC/BN = 50/50 composite

Figure 6 shows the influence of holding temperature on the XRD pattern of the SiC/BN composite. The figure's right hand side was magnified in the range from 30° to 45° of the left hand side in Fig. 6. Before the consolidation process, as-milled SiC/BN = 50/50 composite powder did not exhibit any peaks on XRD, as shown above. Also, the formation of h-BN and β-SiC structure did not take place below 1500 °C. The intensity and the width of peaks became simultaneously stronger and narrower with temperature, which can be clearly recognized above 1600 °C. Then the composite, which consolidated at 1900 °C, consisted of well-crystallized h-BN and β-SiC with sharp peaks. Those results suggest that significant crystallization and ordering to form h-BN and β-SiC from as-milled powder with amorphous-like structure was carried out during the consolidation process. Also, small peaks at 33.5° and 38° were detected in the range of 1600–1800 °C. The former peak suggests the existence of α-SiC. Also this peak is the well-known result of the appearance of stacking fault on the β-SiC structure [19, 20]. Due to the existence of stacking fault on the composite consolidated at 1900 °C, a small peak at 33.5° was detected. In contrast, the

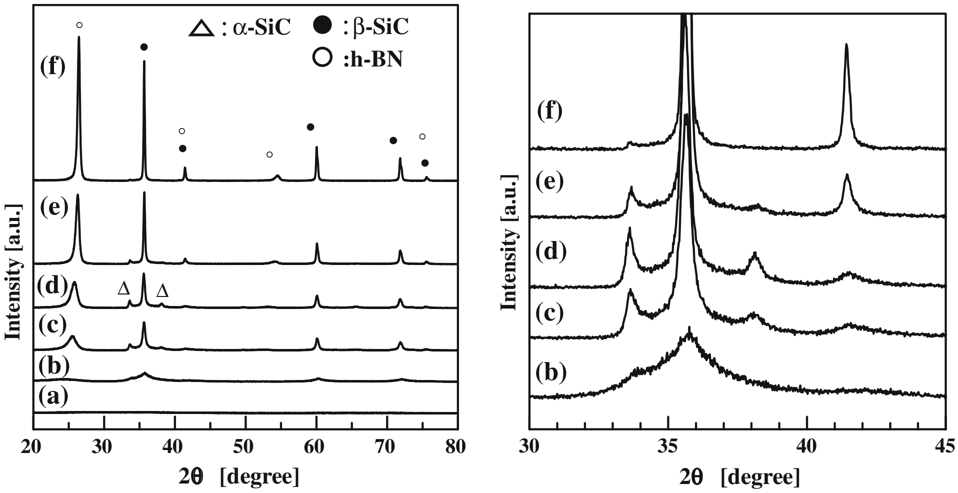

Fig. 6 X-ray diffraction patterns of SiC/BN = 50/50 consolidated by MA-SPS method at various temperatures. (a): MA-powder. (b): The specimen consolidated at 1500 °C, (c): 1600 °C, (d): 1700 °C, (e): 1800 °C, and (f): 1900 °C

appearance of the latter peak at 38° was basically only based on α-SiC. During the structural change from the amorphous-like structure to h-BN and β-SiC, α-SiC was temporarily formed and transferred to β-SiC. This phenomenon has never been observed in the consolidation of MA-SiC without the addition of BN. However, Shirai et al. [26] reported the same phenomenon during their research on the influence of heating temperature on the structural change of a SiC-AlN solid solution system. They mechanically alloyed Si and C with a small amount of AlN (3 mol%), which was enough to keep the β-SiC structure at 1900 °C, for a MA-SiC-AlN solid solution powder. They showed temporary α-SiC structure characterized by peaks at approximately 34° and 38° when the SiC-AlN solid solution was consolidated ranging from 1700 °C to 1800 °C. The XRD results in Fig. 6 suggest that the existence of Si–C–B–N chemical bonding on the as-milled composite, which was also supported by IR analysis, affected the formation of the temporal α-SiC structure during the consolidation process for a SiC/BN composite system.

For a SiC/BN composite system during the consolidation process (as seen in Figs. 1, 2, and 6), crystallization, phase separation, and ordering were simultaneously observed. This phenomenon might accelerate mass transfer for consolidation and achieves the preparation of bulk SiC/BN composite without any sintering aids.

Figure 7 shows the TEM observation result of SiC/BN = 50/50 consolidated at 1900 °C for 10 min. All

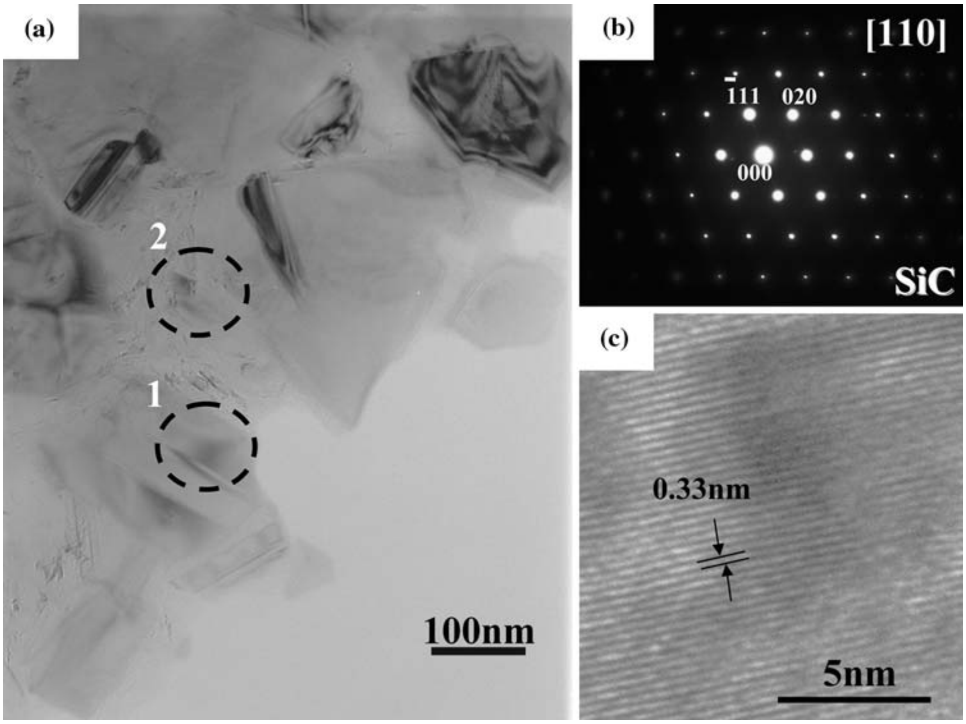

Fig. 7 TEM image of SiC/BN = 50/50 composite prepared by MA MA-SPS method. (**a**): Bright field image. (**b**): Diffraction pattern from the selected area of 1. (**c**): High-resolution image of 2

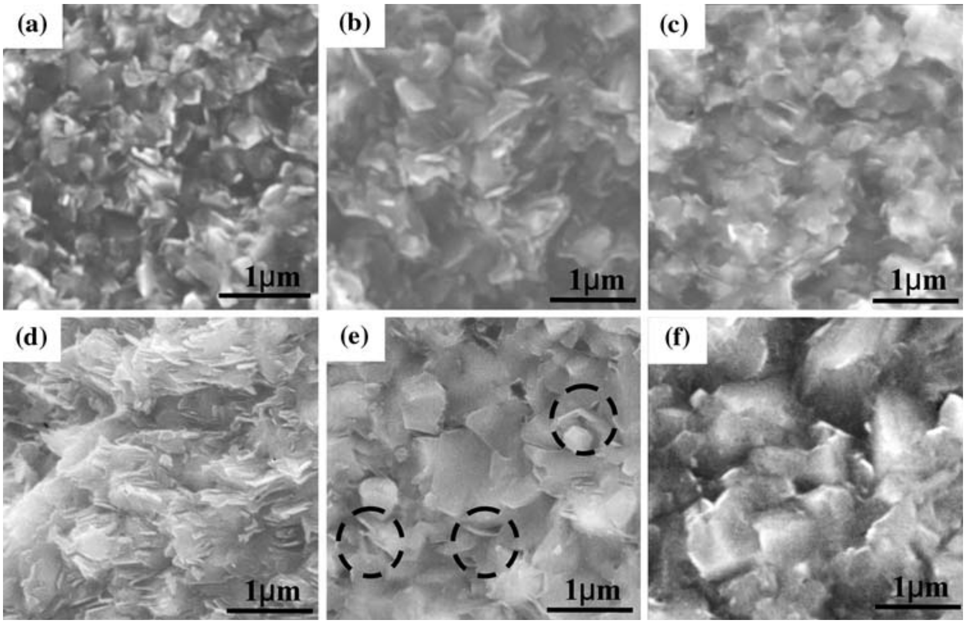

Fig. 8 SEM images of SiC/BN composite prepared by MA MA-SPS method. SiC/BN vol ratios are (**a**): 50/50, (**b**): 60/40, (**c**): 70/30, (**d**): 80/20, (**e**): 90/10, and (**f**): 100/0

particles had a diameter of 100–300 nm, indicating that the composite has nano-metric structure. Diffraction pattern from point 1 in Fig. 7a is shown in Fig. 7b, which was identified as β-SiC structure. The high-resolution image (Fig. 7c) was taken from point 2 in Fig. 7a. The *d*-value of 0.33 nm was measured from the high-resolution image and corresponded to the (002) of the h-BN structure. The nano-size β-SiC particle surrounded by the h-BN particle was observed by TEM.

Figure 8 shows the fracture surface image of the SiC/BN composite consolidated at 1900 °C for 10 min. When 10 vol% BN was added into SiC, flake-like particles were observed, as seen in the dotted circles in Fig. 8e, which were absent for the MA-SiC sample in Fig. 8f. The number of the flake increased with BN concentration. As a consequence, the flakes were h-BN particles less than 1 μm long and 0.1 μm thick. Decreasing mean SiC particle size was also observed with increasing BN concentration. The existence of second phase inhibits grain growth [27]. In contrast, the mean size of h-BN was not increased with the concentration, and h-BN flakes were still fine in the SiC/BN = 50/50 sintered composites. Additionally, an aggregation of flakes was not observed in this study, suggesting that the MA-SPS method can prepare SiC/BN composite with the homogenous dispersion of fine h-BN particles.

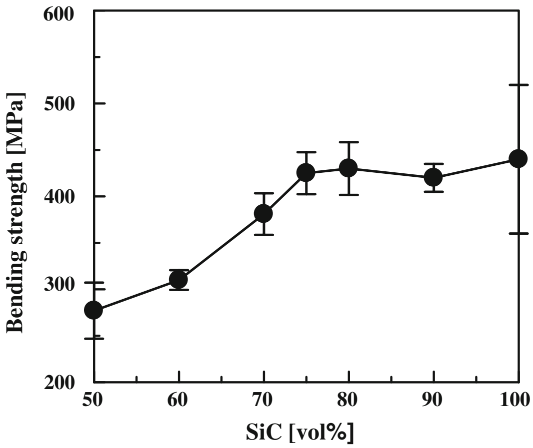

Fig. 9 Bending strength of SiC/BN composites with different SiC ratio

Figure 9 shows the bending strengths of the SiC/BN composite consolidated at 1900 °C for 10 min. The strength decreased with BN concentration, because BN has lower bending strength than SiC and increased porosity (Fig. 3). However, the degradation of the strength was not observed in the range of 0–25% BN, even though the sample porosity decreased from 99% to 93%. Bending strength was possibly improved by the decrease in critical flaw size as a result of the homogeneous distribution of second phase particles with fine size into the matrix. This phenomenon was also obtained for a SiC/BN nano-composite system reported by Kusunose et al. [15, 16]. As without the sintering additive system, bending strength of approximately 275 MPa was obtained in this study at SiC/BN = 50/50, which is a relatively higher value compared with SiC/BN = 46/54 composite consolidated at 2000 °C by conventional and in situ reaction methods with approximately 61 and 56 MPa, respectively [17].

Figure 10 shows the variations of the Vickers hardness of the composite with different SiC/BN ratios. The hardness decreased with BN concentration due to the extremely low hardness of h-BN. However, the composite with SiC/BN 59 = 50 shows Vickers hardness of approximately 3 GPa. In contrast, Vickers hardness measurement for the

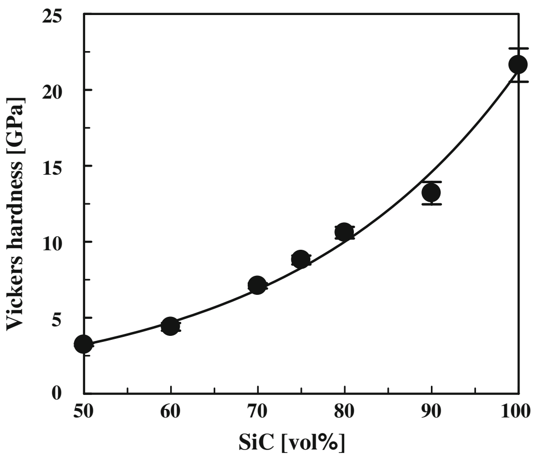

Fig. 10 Influence of SiC concentration on Vickers hardness of SiC/BN composite

SiC/BN = 46/54 composite consolidated at 2000 °C by conventional and in situ reaction without sintering aid failed due to the high porosity of the products [17]. When a sintering additive was used in the in situ reaction system, the Vickers hardness of the samples was 2.7 GPa for SiC/BN = 46/54 and 8.7 GPa for SiC/BN = 75/25[17]. Both values resemble the sample prepared in this research.

From the TEM and SEM results, the composite microstructure was nano-metric with homogeneously dispersed fine h-BN places. All of the mechanical property measurement results suggest that the SiC/BN composite has homogeneous and nano-metric structure.

Conclusion

In this research, nano-metric SiC/BN was prepared by mechanical alloying (MA) from Si + C + BN powder and then consolidated by SPS without any sintering aid. XRD results after MA revealed the absence of sharp peaks corresponding to SiC and BN. The density and the intensity of the SiC and BN peaks on XRD increased with temperature during the consolidation process. The final density of the composite reached approximately 90–99% with 50/50 of the SiC/BN to 100/0. During the consolidation process, crystallization, phase separation, and ordering were simultaneously observed. This phenomenon might accelerate the mass transfer for the consolidation and the preparation of bulk SiC/BN composite without any sintering aids. From the TEM and SEM results, the composite microstructure was nano-metric with homogeneously dispersed fine h-BN places. In the 50/50 of the SiC/BN ratio, the Vickers hardness of the nano-structured reference sample prepared by conventional method with sintering aids could not be measured due to its high porosity. However, the well-consolidated sample prepared in our research showed a hardness of approximately 3 GPa. All mechanical property measurement results suggested that SiC/BN composite has homogeneous and nano-metric structure.

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