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Mechanical Properties of β-SiC Fabricated by Spark Plasma Sintering

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The consolidation of SiC nanopowder synthesized by the mechanical alloying method was subsequently accomplished by spark plasma sintering of 1700 °C for 10 min under an applied pressure of 40 MPa. The SiC sintered compact with relative density of 98% consisted of nano-sized particles smaller than 100 nm. This phenomenon resulted in the ordering process of stacking disordered structure formed by mechanical alloying. In this work, the effect of grain size and relative density on the mechanical properties were studied. The mechanical properties of sintered compacts were evaluated and compared with the reference samples fabricated from the commercial SiC powder (β-SiC, 0.3 μm, IBIDEN Co., Gifu, Japan) with sintering additive (B-C mixture). The Vickers hardness and bending strength of those sintered compacts increased with the increment of the density. However, the mechanical properties were lower than those of reference samples in case of lower density, even though the mechanical property was close to that of reference sample in case of higher density. This phenomenon was considered for the difference of bond strength between grains because those sintered compacts were fabricated without any sintering additives, while those reference samples were fabricated by accelerating the grain bonding with a sintering additive of B-C mixture. In other words, those results indicated that the effect of sintering additive affected on mechanical properties directly.

Keywords bending strength, hardness, mechanical alloying, silicon carbide, spark plasma sintering

1. Introduction

Silicon carbide (SiC) is a promising materials candidate for high-temperature structural components due to its many excellent properties, including strength retention, oxidation resistance at high temperature, and others (Ref 1, 2). It is difficult to consolidate SiC while preventing grain growth because it is sintered at temperatures higher than 2000 °C. Usually, sintering additives are used for reducing the sintering temperature and preventing grain growth. The correlation between mechanical properties and grain size of SiC sintered compact has already been studied with consideration of the Hall-Petch relation (Ref 3). However, those SiC sintered compacts can be regarded as a composite material, and its correlation considered according to the rule of mixtures depending on the situation. Therefore, there are hardly any investigations of the correlation between mechanical properties and grain size without any sintering additives.

Mechanical alloying (MA) and mechanical grinding (MG) processes are well known for synthesizing nanocomposite materials, nanopowders, quasicrystalline, and metastable phases (Ref 4-8). MA nano-powders synthesized by ball milling have a grain size smaller than 10 nm or amorphous phase (Ref 9). Furthermore, by increasing the powder specific surface area and accumulating lattice defects and strain into the MA powder, it is possible to sinter them at lower temperatures and for shorter times (Ref 10-12). The MA method can be performed in different ways. In particilar, MA performed by planetary ball milling makes it possible to synthesize the compound from elemental powders at shorter times. In the previous work, consolidation of SiC nanopowder synthesized by MA method was subsequently accomplished by spark plasma sintering (SPS) without any sintering additives (Ref 13-15). SPS has been developed based on the idea of using an electric discharge machine for sintering metals and ceramics (Ref 16-18). This SiC sintered compact had the relative density of 98%, a mean grain size of 50 nm and a single phase (βSiC). The sintering temperature was approximately 1700 °C, which was much lower than the conventional value. It was concluded that this high density was obtained due to the enhanced volume diffusion resulting from the disordered structure formed during MA the process.

In this work, the SiC sintered compacts with various densities and grain sizes were fabricated by controlling the conditions of SPS. Their correlation with mechanical properties were discussed, with comparison to SiC sintered compact fabricated from commercial powder with sintering additives. These results are discussed with respect to the Hall-Petch relation.

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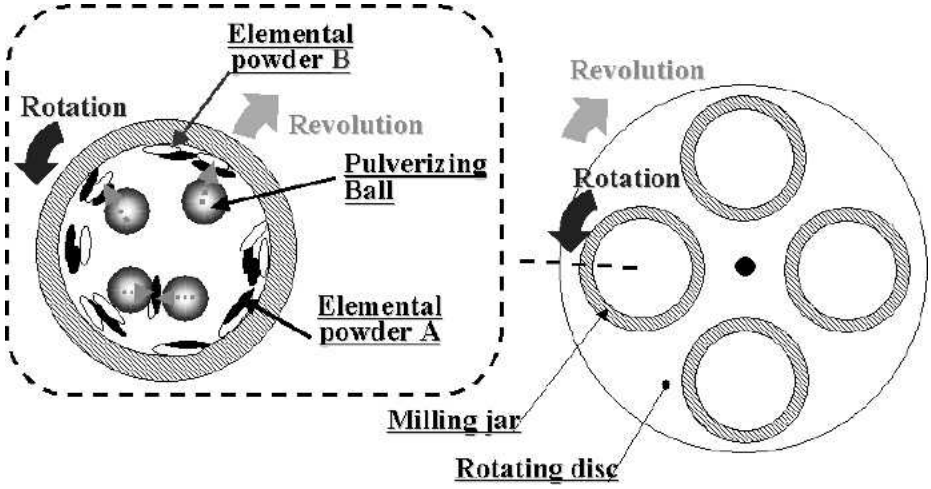

Fig. 1 Schematic illustration of the planetary ball milling machine

2. Experimental Procedure

The reactants used were elemental powders of Si (~1.0 μm, >99%, Kojundo Chemical Co. Ltd., Saitama, Japan) and C (~10.0 μm, >99.9%, Tokai Carbon Co. Ltd., Tokyo, Japan). The powders were blended in a 1:1 stoichiometric ratio and then ball milled in a planetary mill, as shown in Fig. 1. Milling was done using 10 mm diameter zirconia balls and zirconia vials with an inside diameter of 75 mm and height of 70 mm (Fritsch). Those vials and pulverizing balls were coated with silicon carbide by preliminary milling. A ball-to-powder mass ratio (B/P) of 40:1 was used with 7.5 g of the mixed reactants. All powder transfers to and from the vials were done in a glove box filled with Ar gas. The vial was then sealed and transferred to Fritsch Pulverisette P5 planetary mill (Fritsch Japan, Yokohama, Japan). The milling time and revolution speed were 24 h and 300 rpm, and the rotation speed of the vial was 375 rpm. This milling condition was determined based on the previous investigation of Si-C solid-state reaction in a reaction milling process (Ref 15). The reference sintered compact fabricated with the commercial fine SiC powder (average particle size of 300 nm, Ibiden Co. LTD, Gifu, Japan) was used for comparison of the mechanical properties. Because the commercial fine SiC power is hard to consolidate, sintering additives of B-C powder mixture and Al_2O_3 were used in this work.

Synthesis and densification of the milled samples was conducted without any additives in a SPS apparatus (Model 1050, Sumitomo Coal and Mining Co., Tokyo, Japan) under vacuum, as shown in Fig. 2. The SPS apparatus is a uniaxial 100 kN press combined with 15 V, 5000A direct current (dc) power supply to provide simultaneously pulsed current and pressure to the sample. The pulse cycle of the dc current is 12 ms on and 2 ms off. The milled powders were placed into graphite die, and then a 40-70 MPa pressure was applied. The samples were then heated for times ranging from 0 to 10 min at a heating rate of about 180 °C/min. The consolidated sample was cooled to room temperature by turning off the power. The temperature was measured by means of an optical pyrometer focused on the graphite die surface near the center of the sample. The densified cylindrical samples were about 19 or 29 mm in diameter and 5 mm thick.

X-ray diffraction (XRD) analyses were made using a RIGAKU RINT2500 (Rigaku Co., Ltd., Tokyo, Japan) diffractometer with CuK_α radiation operated at 200 mA and 40 kV. The step size was 0.01° in 2θ, and powder weight was kept constant (0.25 g). Microstructural analysis by transmission electron microscopy (TEM; Model JEM-2000EX, JEOL, Tokyo, Japan, operated at 200 kV) was performed in both powder and dense samples. The dense specimen was mechanically strong enough to be ground, dimpled, and thinned by ion milling using Ar ions and was thinned using methods generally used for ceramics. Mechanical properties were evaluated by measuring the bending strength, Young's modulus (Model SL-5000, Marubishikagaku, Tokyo, Japan), fracture toughness (indentation fracture method; IF), and Vickers hardness (10 kg, 10 s, HSV-20, Shimazu, Kyoto, Japan). The reliability of fracture toughness was also confirmed by a single edge precracked beam method (SEPB).

3. Results and Discussion

The XRD patterns and TEM image of Si-C powder mixture milled for 24 h are shown in Fig. 3. In previous work, it was confirmed that complete conversion to SiC was accomplished after 24 h of milling at a revolution speed of 300 rpm and B/P weight ratio of 40 (Ref 13-15). The broadening of the SiC peaks is due to refinement of the crystallite size, increase in strain, and presence of structural defects (e.g., stacking faults and twins). From the TEM observation, the product formed after 24 h of milling is seen to be nanostructured. Crystallites with sizes in the range of about 5-20 nm are seen in agglomerates of 50-150 nm. Silicon carbide exhibits considerable polytypism characterized by a one-dimensional (stacking) disorder (Ref 19, 20). The XRD pattern of one-dimensionally disordered SiC is characterized by the presence of only three peaks of (111), (220), and (311) planes, where it is described as a cubic unit. The (111) plane of the cubic unit cell corresponds to the basal plane of the hexagonal unit cell with the *c*-axis of spacing between successive layers. Also, a disordered cubic SiC is characterized by the existence of a diffuse intensity step on the left side of the main (111) peak (Ref 19, 21). Figure 4 shows the displacement diagram with thermal expansion and shrinkage during SPS of this Si-C powder mixture. The decrease and increase in expansion correspond to the shrinkage and expansion, respectively. This displacement does not include the variation of sample but does include the variation of

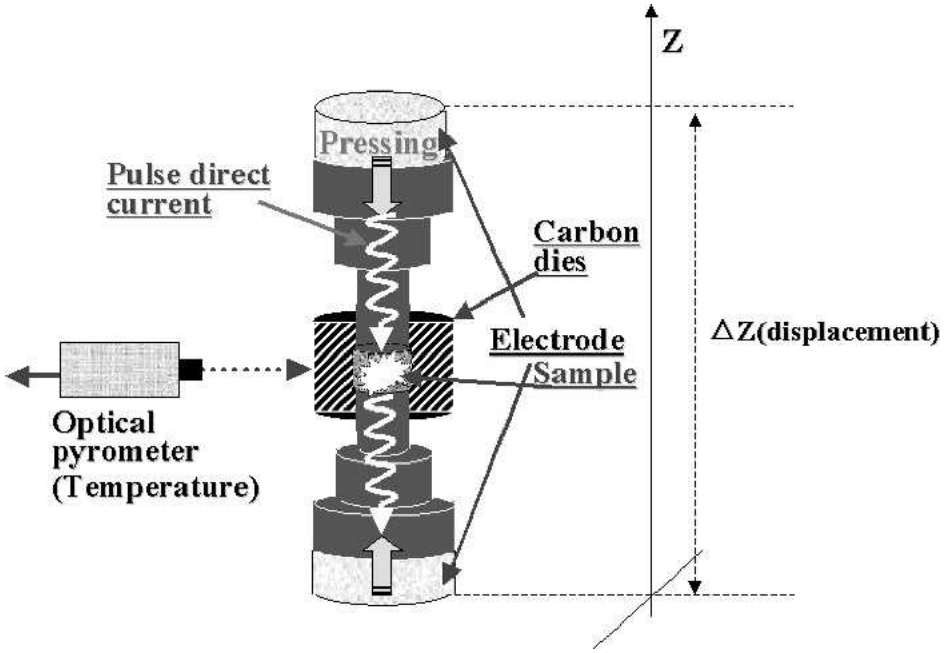

Fig. 2 Schematic illustration of the spark plasma sintering apparatus

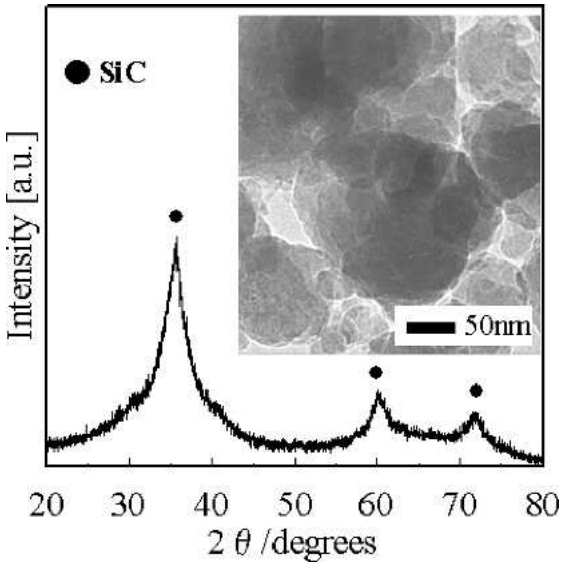

Fig. 3 XRD pattern and TEM image of Si-C powder mixture prepared by planetary ball milling for 24 h

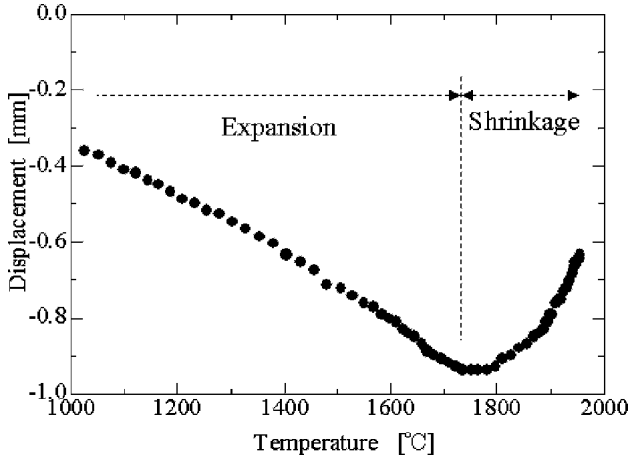

Fig. 4 Displacement diagram of Si-C powder mixture during SPS heating up to 1900 °C under an applied pressure of 70 MPa at a fixed heating rate of 180 °C/min

dies and pistons. On the region of 1000 to 1700 °C in this displacement diagram, the thermal expansions of the piston and sample were mainly investigated. However, the shrinkage increased abruptly when the temperature reached 1700 °C. Therefore, the result in Fig. 4 shows that densification occurred above 1700 °C. Figure 5 shows the changes in the relative density of the consolidated SiC sample with holding time for sintering at 1700 °C. Because it was confirmed that the product phase was only βSiC using XRD analysis, this relative density was calculated on the basis of the theoretical density of 3.21g/cm^3 (βSiC) referred from the crystal structure database (Card No. 29-1129, JCPDS). The relative density increased from 68-98% at holding time ranging from 0 to 10 min, and the grain size also increased from 10 to 50 nm connected with the variation of relative density. It is well known that densification is caused by volume diffusion between particles, and grain growth is possible in the consolidation process. In this work, the grain size of this sample, however, increased slightly even though the relative density increased drastically during densification. Prevention of grain growth was expected because sintering was done without a liquid phase of metal Si and without a phase transformation of SiC. Also, this result suggested that the relative density could be controlled easily by holding time at 1700 °C.

As mentioned above, consolidation can be performed by holding the temperature above 1700 °C and for holding time above 10 min. Thus, controlling the grain size will keep the body dense, the effect of sintering condition on grain size was investigated at holding temperature ranging from 1700 to 1950 °C and for holding time ranging from 0 to 20 min. The grain sizes are averages of more than 100 grains, obtained from the

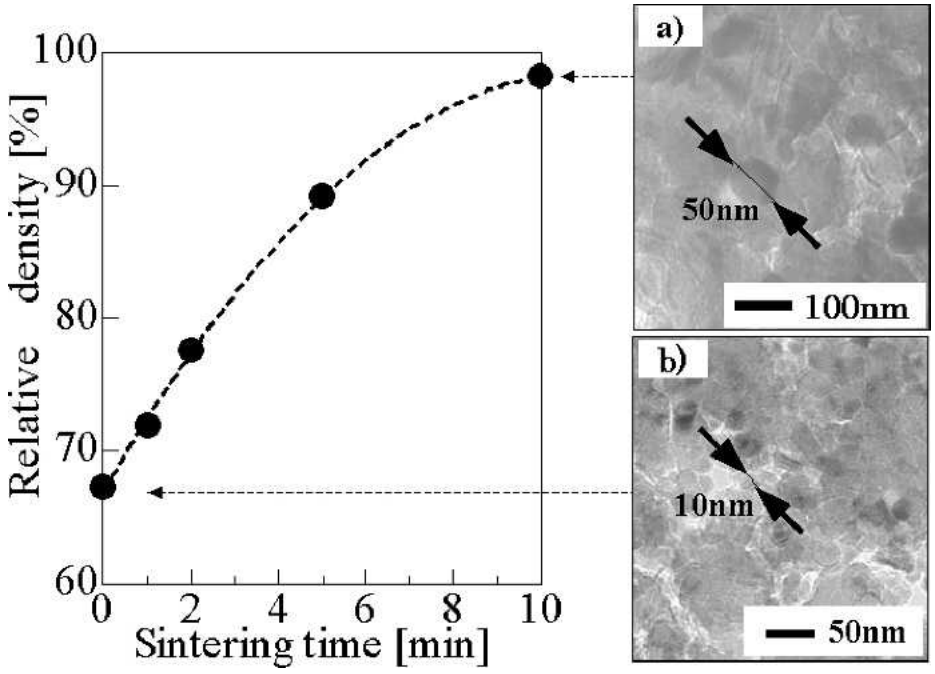

Fig. 5 Change in the relative density of the SiC sintered compact with holding time at 1700 °C and TEM images of SiC sintered compact: (a) dense SiC sintered compact and (b) porous SiC sintered compact

average linear intercept method of the grains in SEM pictures of the fracture surfaces, multiplied by the statistical factor 1.56 (Ref 22). Figure 6 shows SEM images of the fracture surface of samples sintered at 1700 °C for 10 min and 1950 °C for 20 min. As can be seen from the comparison between these SEM images, the holding temperature affected the primary grain size drastically on the basis of diffusion. Thus, the authors controlled the grain size by controlling the holding temperature and time.

The influence of relative density on Vickers hardness and the optical micrograph indentations are shown in Fig. 7. Also, as reference value, Fig. 7 also includes the result of sintered compact prepared from commercial fine SiC powder with the sintering additive of B-C mixture. The optical micrographs of the indentations show clearly a diamond shape that is symmetrical with respect to the origin. In particular, the symmetry was related even if the sample was porous, and thus, it could be verified that those values were reliable. The Vickers hardness increased with the increase of relative density in both cases. However, the values of SPS samples in the current study showed a tendency to be lower than those of the reference sample, even though the relative density of the sample was equivalent to that of the reference sample. Furthermore, a different trend was observed in the variation of bending strength and Young's modulus with relative density, as shown in Fig. 8. Similar to the tendency of Fig. 7, the bending strength of both types of samples increased with the increase of relative density. However, the bending strength of the SPS sample was significantly lower than that of the reference sample when the sintered compact was porous, but those values became almost equal when the relative density was approximately 98%. Although the Young's modulus also increased with the increase of relative density, the values of the SPS samples were slightly lower than those of the reference sample on the whole. Therefore, from the comparison between those results, it was expected easily that the elastic strain of the sample became lower than that of the reference sample when the sintered compacts were porous. The elastic strain and fracture stress (close to the yield stress) are dominated by the condition of grain bonding such as bonding strength, matching extent, existence of precipitates at the grain boundaries, etc. In this work, the sintering additive of B-C mixture, which can accelerate diffusion between particles with a very small quantity of addition, was used to make a highly dense body from commercially fine SiC powder. Therefore, the conclusion drawn is that this difference of bending strength was caused by the difference of bonding strength between grains generated by the sintering additives of B-C mixture.

Generally, it is well known that the strength properties are improved on the basis of Hall-Petch relation if the grain size is reduced. Especially, a striking change is observed in the case of fine particles because it is related to $G^{-1/2}$, as shown in the following expression:

$$\sigma_y = \sigma_0 + k \cdot (G)^{-1/2}$$

where σ_y is the yield stress, σ_0 is the material constant, and k and G are factor of stress concentration and grain size, respectively. Figure 9 shows the result of Vickers hardness as a function of the SiC grain size. As reference, Fig. 9 also shows the results with sintering additive of B-C mixture, reported by Vaben et al. (Ref 3) and the SiC sintered compact with sintering additive of Al_2O_3 prepared from commercial fine SiC powder. To exclude the effect of density, the relative density was kept at about 98% by the sintering condition mentioned above. The Vickers hardness of Vaben's sample showed an exponential increase with decrease of grain size, corresponding to the Hall-Petch equation, and thus shows the Hall-Petch relation to be valid on sintering the SiC. However, the Vickers hardness of SPS sintered compact without sintering additive remained a constant with the variation of grain size, and furthermore, the value is approximately the same as the reference sample prepared from commercial fine SiC powder. According to the

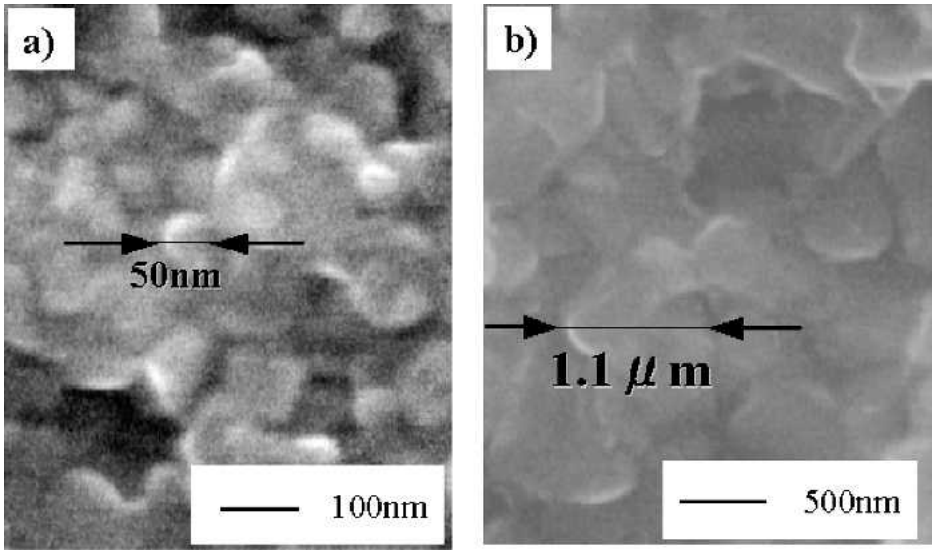

Fig. 6 Fracture surface of nano SiC sintered compact observed by scanning electron microscopy (SEM): (a) sintered at 1700 °C for 10 min and (b) sintered at 1950 °C for 20 min

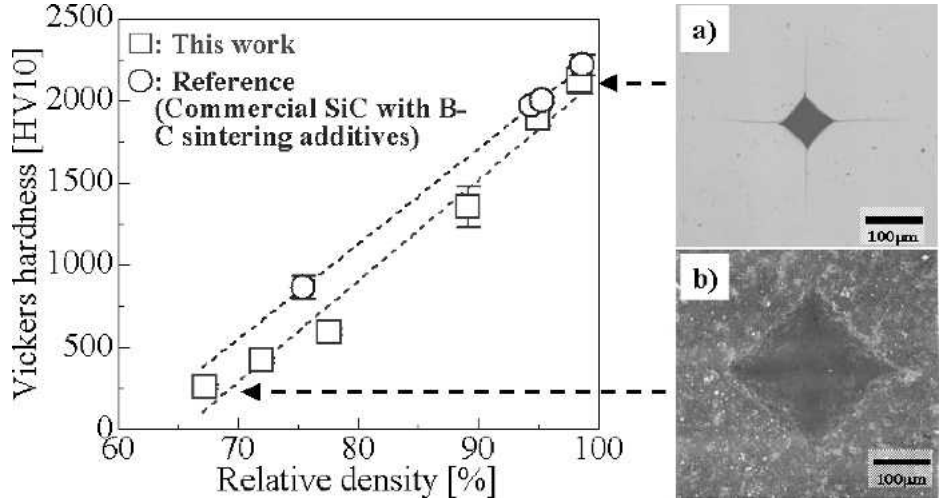

Fig. 7 Influence of relative density on Vickers hardness. The images on the right are the optical micrographs of the Vickers indentations: (a) dense sintered compact and (b) porous sintered compact. This commercial SiC is a fine powder made by IBIDEN Co., Ltd.

Hall-Petch equation, if σ_0 had been equivalent to that of Vaben's sample, k of these samples would have been extremely small. Because k was a factor affected by strength of the grain bonding, it can be concluded that effect of grain size did not appear in the Vickers hardness of SPS sample due to having a weak grain bonding. The bending strength, Young's modulus, and fracture toughness, summarized as a function of the grain size, are shown in Fig. 10. The bending strength and Young's modulus were constant at 520 ± 50 MPa and 380 ± 40 GPa, respectively. Also the fracture toughness was constant at 3.6 ± 0.6 MPa $m^{1/2}$. Even though the valuation of fracture toughness as evaluated by IF definitely indicates an inclination, the absolute value of fracture toughness often includes a systematic error. Therefore, those values of fracture toughness must be compensated by the SEPB method. In this work, the mean value obtained from eight measurements was used. The absolute value obtained by SEPB method was about 3.0 MPa $m^{1/2}$ when the grain size was about 11 μm, and the absolute value was 2.2 MPa $m^{1/2}$ when the grain size was about 150 nm. This

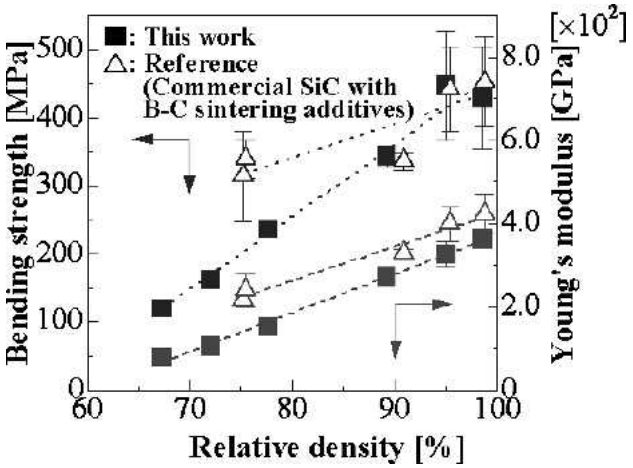

Fig. 8 Variation of bending strength and Young's modulus with relative density. This commercial SiC is a fine powder made by IBIDEN Co., Ltd.

result was similar to the result obtained by the IF method, and it could be confirmed that those results obtained by the IF method indicated definitely an inclination. Thus, the Hall-Petch relation has not been confirmed in the range of these grain sizes of the sintered compact without sintering additive because the grain bonding was not strengthened sufficiently by thermal treatment.

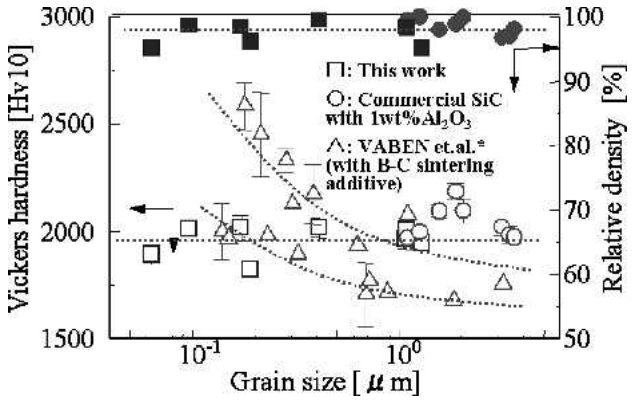

Fig. 9 Variation of Vickers hardness and relative density rearranged with SiC grain size (Ref 3)

4. Conclusions

The consolidation of SiC nanopowder synthesized by the MA method was subsequently accomplished by SPS at 1700 °C for 10 min under applied pressure of 40 MPa. The relative density increased from 68% to 98% at holding time ranging from 0 to 10 min, and this result suggested that the relative density could be controlled easily by holding time. The Vickers hardness, bending strength, and Young's modulus of the sintered compact without sintering additive synthesised by the MA-SPS method increased with the relative density. However, those values showed the tendency to be lower than those of reference sample with sintering additive of B-C mixture on the whole, although the relative density was equivalent between the sample and the reference sample. Furthermore, these values showed approximately constant values with grain size, although the value of Vaben's sample with sintering additive increased with a decrease of grain size, corresponding to the Hall-Petch relation. Those results were caused by the difference of grain bonding strength, depending on existence of the sintering additive. Thus, the Hall-Petch relation has not been confirmed in the range of these grain sizes in the absence of sintering additive.

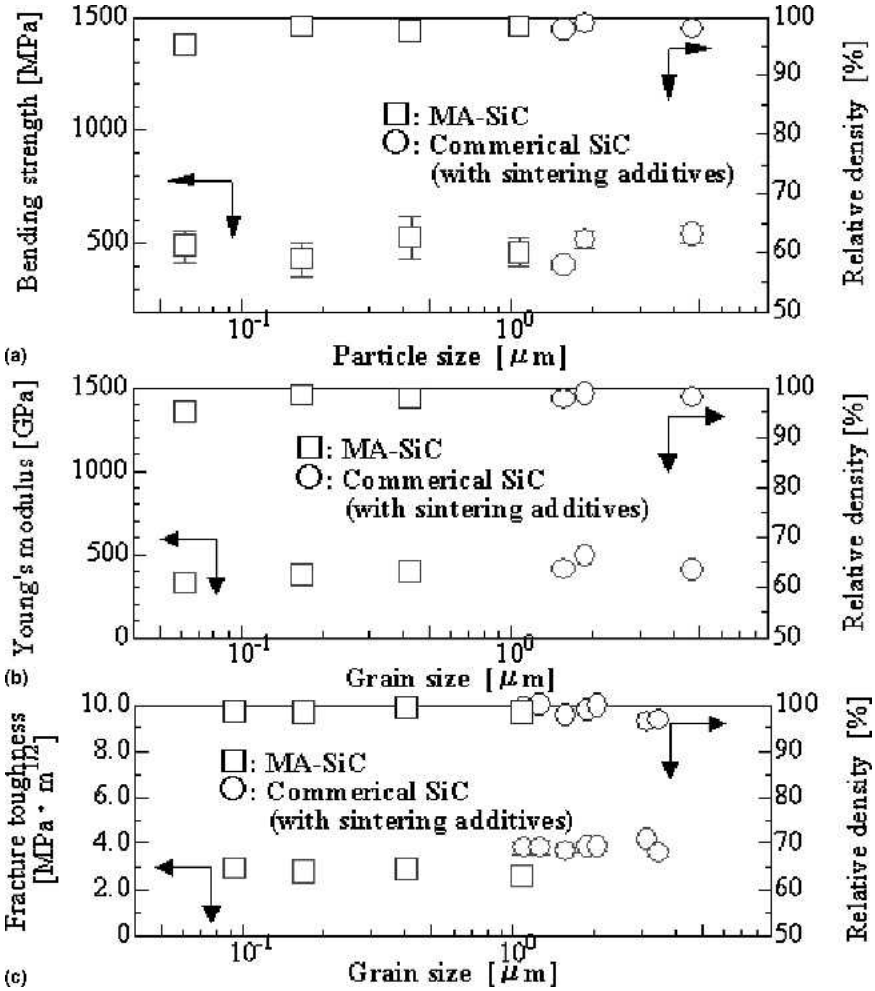

Fig. 10 Variation of mechanical properties with SiC grain size: (a) bending strength, (b) Young's modulus, and (**c**) fracture toughness measured by indentation fracture method

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