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Role of disorder-order transformation in consolidation of ceramics

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The ordering of stacking-disordered silicon carbide prepared from the elements by high energy ball milling was investigated during sintering. A sharp increase in density in the temperature region 1700–1800°C was associated with a decrease in the disorder. Samples which had low disorder density showed a more continuous sintering behavior with temperature. Highly dense (up to 99% relative density) SiC can be obtained at 1900°C under a pressure of 70 MPa with no hold time. Similar results were observed for structurally disordered carbon with 10 at% of boron. The sintering behavior exhibited an abrupt density increase in the narrow temperature region of 1450–1600°C and was associated with disorder-order transformation.

1. Introduction

Present and potential technological structural applications of silicon carbide are the consequence of its unusual properties which include low density, chemical stability, and high strength at high temperatures. In addition, silicon carbide has recently been considered for device applications because of its attractive electronic properties [1–5]. As a wide-gap semiconductor, it has received considerable attention as a material for high-power devices, including radar and microwave applications under extreme conditions. Its high temperature strength, high thermal conductivity, and low nuclear activation, make it attractive for these applications [6–10]. Carbon has also been the focus of investigations because of its excellent properties, including high heat resistance, high corrosion resistance, and high electrical and thermal conductivities [11–16]. Dense, fiber-reinforced carbon has also been investigated for aerospace turbine engines [17].

However, because of the covalent nature of their bonding, carbon and silicon carbide, are difficult to fully consolidate without the use of additives. For silicon carbide, consolidation has been typically achieved by liquid phase sintering [18] (where additives are required) or by solid-state sintering [19, 20] (where high pressures and additives have been used). Carbon has been often consolidated by compacting the carbon powder with binding reagents such as coke, or petroleum pitch, and then carbonization under a reducing atmosphere [11, 21–23].

Recent investigations have shown that structural changes occurring during sintering can aid the densification process, making it possible to sinter such materials as nanostructured SiC to relatively high densities (98%) without the use of additives or exceptionally high pressures [24–27]. A related study on the synthesis and densification of B_4C from the elements showed a direct correspondence of the rate of consolidation with the annealing out of twins [28]. In this paper we describe disorder/order transformation-driven sintering of silicon carbide and carbon.

2. Experimental

2.1. Preparation of stacking disordered SiC

The reactants used in this study were elemental powders of Si (ca. 1.0 μm, >99% pure, Kojundo Chemical Co. Ltd., Japan) and C (ca. 10.0 μm, >99.9% pure, Tokai Carbon Co. Ltd., Japan). For the synthesis of SiC, the powders were blended in a 1:1 stoichiometric ratio and then ball-milled in a Fritsch planetary mill. Milling was done in two systems, one with zirconia balls (10 mm diameter) and vial and the other with silicon nitride ball and vials. The vials had an inside diameter of 75 mm

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and a height of 70 mm. A charge ratio (ball-to-powder mass ratio, B/P) of 40:1 was used with 7.5 g of the mixed reactants. To minimize powder contamination from the balls and vial, reactant mixtures were first milled for 12 h so that the balls and vial were covered with a thin layer of powder. The ball and vial were then used in this condition for subsequent milling. Powder mixtures were milled for 24 h. All transfers of powders to and from the vials were done in a glove box. The glove box was evacuated and back-filled three times with pure (99.99%) argon. The vials were sealed and transferred to a Fritsch Pulverisette P5/2 planetary mill. The revolution speed of the milling was 300 rpm and the rotation speed of vial was 375 rpm. After each milling cycle, a small amount of the powder was removed for X-ray diffraction (XRD) analysis. For comparison we also used a commercial nano-SiC powder made by plasma CVD [19] (CM-SiC with 3.5 wt% of C, ca. 30 nm, Sumitomo-Osaka Cement Co., Tokyo, Japan).

2.2. Preparation of disordered carbon

The powders used were elemental carbon (ca. 10.0 μm, >99.9%, Tokai Carbon Co. Ltd., Japan), and boron as additive (−300 mesh, >99.6% Furuuchi Chemical Co., Japan). The carbon powder was milled with 0 and 10 at% boron as additive. Milling was done using silicon nitride balls (10 mm-diameter) and vials (inside diameter = 75 mm and height = 70 mm) in a Fritsch P6 planetary mill for 5 h. The revolution speed of milling was 560 rpm and the rotation speed of the vial was 700 rpm. A charge ratio (ball-to powder mass ratio) of 40:1 was used with 7.5 g of the mixed powders. All powder transfers to and from the vials were also done in an inert atmosphere of Ar gas, as described above.

2.3. Consolidation

The consolidation of powders of milled SiC and carbon with 10 at% boron was made in a spark plasma sintering (SPS) apparatus (Model 1050, Sumitomo Coal and Mining Co.). The SPS apparatus consisted of a uniaxial 100 kN press combined with a 15 V, 5000 A DC power supply to provide pulsed current during the application of the pressure. The pulse cycle of the DC current was 12:2 i.e., 12 pulses of 3 ms on and 2 pulses of 3 ms off. The milled powders were placed in a cylindrical graphite die which had an inside diameter of 20 mm, an outside diameter of 40 mm, and a height of 40 mm. The sample was wrapped in 0.2 mm thick graphite foil. The applied pressure was in the range 10–70 MPa for the consolidation of SiC and 70 MPa for the consolidation of carbon. The pressure was applied through top and bottom punches, each having a diameter of 19.6 mm and a length of 30 mm. The samples were then heated to the desired temperature at rates of about 180°C·min^{-1} for the case of the SiC samples and about 60°C·min^{-1} for the case of carbon. The consolidation temperatures investigated ranged from 1000 to 1900°C. The samples were held at the selected temperature for 0 to 30 min. The experimental parameters of temperature, applied pressure, current, voltage, and sample displacement (shrinkage) were measured continuously during the consolidation cycle. Temperatures were measured by an optical pyrometer focused on a hole drilled into the die surface to depth of 5 mm. An emissivity of 0.9 was used based on a calibration with a two-color pyrometer. The consolidated samples were cooled to room temperature by turning off the power. The densified samples were in the form of disks about 19 mm in diameter and 5 mm thick.

X-ray diffraction (XRD) analyses were made using RIGAKU RINT2500 diffractometer with CuK$_\alpha$ radiation operated at 200 mA and 40 kV for phase identification. The step size was 0.01° in 2θ.

3. Results and discussion

Fig. 1 shows the X-ray diffraction pattern of SiC which was formed during milling of the Si and C powder mixtures in silicon nitride vial using balls of the same material. Only three broad peaks in the 2θ range of 20–80° were observed. The same pattern was obtained when zirconia vials and balls were used. Silicon carbide exhibits considerable polytypism characterized by a one-dimensional (stacking) disorder [29, 30]. The X-ray pattern of one dimensionally disordered SiC by the stacking sequence is characterized by the presence of only three peaks corresponding to the (111), (220), and (311) planes, where it is described as a cubic unit. The (111) plane of the cubic unit corresponds to a basal plane of a hexagonal unit with 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 (lower 2θ) of the main (111) peak [30–32]. Examination of the patterns of powders milled for 24 h (Fig. 1) reveals that MA-SiC powders have a totally disordered cubic structure [29],

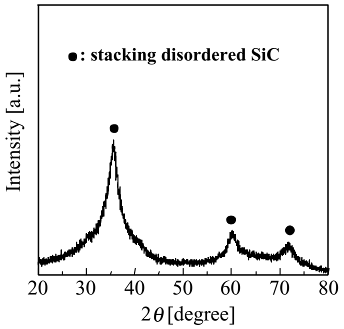

Figure 1 X-ray diffraction pattern of SiC obtained by mechanical alloying of Si and C for 24 h in silicon nitride vial and balls.

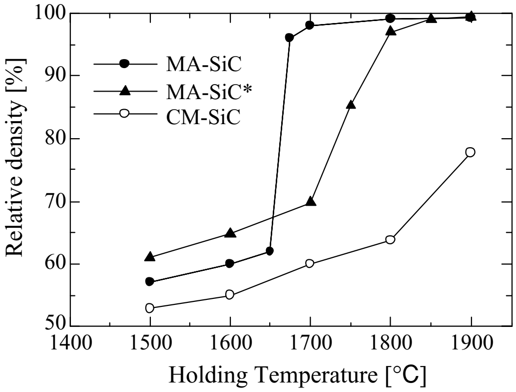

Figure 2 Relative density of MA-SiC, MA-SiC* and CM-SiC sintered at various temperatures for 10 min.

exhibiting only the peaks of (111), (220), and (311) at 2θ values of about 36, 60, and 72°, respectively.

Fig. 2 shows the changes in the density of the consolidated MA-SiC with sintering temperature for a 10-min hold. Also included in this figure are results obtained on commercially available nanostructured SiC formed by plasma CVD. This SiC had a crystallite size of 30 nm and is designated as CM-SiC in the figure. The relative density of the sample synthesized by milling with zirconia balls and vial, designated as MA-SiC in the figure, changed by a small amount (from about 57 to 60%) as the sintering temperature was increased from 1500 to 1650°C. However, the density increased abruptly to 95% when sintering was carried out at 1675°C, and to 98% when sintering was done at 1700°C. We have shown that the consolidation of nanostructured SiC to high relative densities (up to 98%) is due to densification enhanced by a disorder-order transformation [24–27]. On the other hand, for mechanically alloyed SiC prepared with silicon nitride balls and vial, designated as MA-SiC*, showed a different behavior. At holding temperatures below 1700°C, the samples were relatively porous with a 70% or less relative density. At holding temperatures above 1800°C, the relative density of SiC was about 97% or higher. The change in density between 1700 and 1800°C is also relatively abrupt. However, the temperature region providing the sharpest increase in density, 1700 to 1800°C, was higher than that seen for MA-SiC [24–27]. These observations imply that the difference is related to the nature of impurities and their role in the ordering during sintering. However, the nature of the impurities is not known since there is no evidence for their presence in the XRD patterns.

The results in Fig. 2 show that for the MA-SiC and MA-SiC* samples a marked increase in densification occurred within a relatively narrow temperature range. This is in contrast to the results on the commercial sample (CM-SiC) where the increase in densification seems to be relatively smooth with increasing sintering temperature. More importantly, the commercial SiC did not densify to high values, reaching only a density of about 78% at the highest temperature in this work, 1900°C, under the same experimental conditions. This lack of densification of this powder is consistent with previous observations on the consolidation of nano-SiC powders [18].

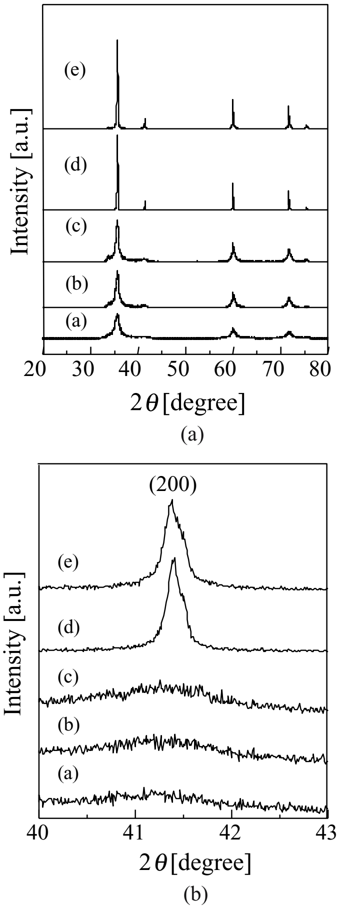

Figure 3 XRD patterns of SiC: (a) In the 2θ range of 20–80°, "a" 1500, "b" 1600, "c" 1700, "d" 1800, and "e" 1900°C. (b) A magnification of diffraction for the range of 40–43° of the sintered MA-SiC*.

Fig. 3a shows typical XRD patterns of the sintered materials of MA-SiC*. When sintered at temperatures below 1600°C, the products were in the totally (stacking) disordered structure, exhibiting only the peaks of (111), (220), and (311) planes at 2θ values of about 36, 60, and 72°, respectively. When the sintering temperature was increased to 1700°C, the product was still disordered (confirmed by the intensity hump at $2\theta \sim 34°$ and by the tiny broad peak at $2\theta \sim 42°$, barely perceptible in Fig. 3a. Fig. 3b shows a magnification of the X-ray diffraction pattern in the 2θ range of 40–43°. The existence of the (200) peak, at $2\theta \sim 41.5°$, is clearly seen and is a feature of cubic SiC. The material sintered at 1800°C and higher temperatures clearly shows the existence of cubic structure of SiC and a higher level of order as seen by the increased symmetry of the main peak (at 2θ of about 35° in Fig. 3a).

Fig. 4 shows the effect of the applied pressure on the relative density of the MA-SiC* sintered at 1900°C. The

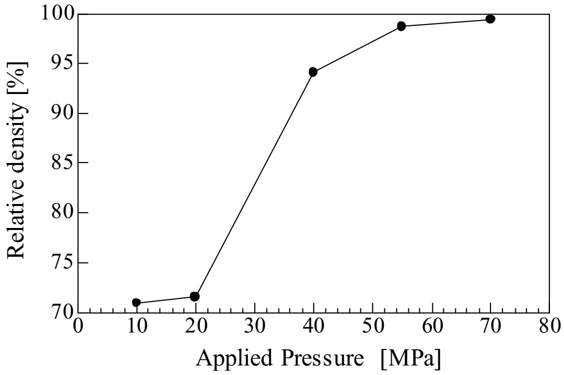

Figure 4 Effect of the applied pressure on the relative density of the MA-SiC* sintered at 1900°C.

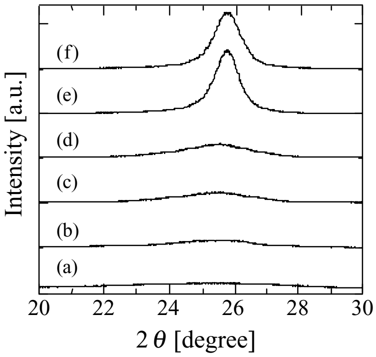

Figure 5 X-ray diffraction patterns of structurally disordered carbon sintered at (a) 1000, (b) 1300, (c) 1450, (d) 1500, (e) 1600 and (f) 1900°C for 10 min under applied pressure of 70 MPa.

density increased markedly with the applied pressure. To achieve a density higher than 98%, 55 MPa pressure is necessary. At all values of applied pressures in the range of 10 to 70 MPa, the sintered SiC had the cubic structure with the characteristic diffraction peak of (200) and a symmetric main peak of (111). To demonstrate the relation between structural ordering and the applied pressure, auxiliary experiments were carried out. MA-SiC* samples were first sintered in the SPS at 1900°C for 10 min under a 10 MPa pressure. The density of these samples was 71% as shown in Fig. 4. When these samples were then heated back to 1800°C and sintered for 10 min at a pressure of 70 MPa (the level used in all of the results reported above), no further densification could be observed. The implication of this is that during the first sintering step (at 10 MPa and 1900°C) structural ordering had taken place, but since the pressure was relatively low, the products densified to only 71%. Subsequent increase in pressure had no effect on the now ordered SiC. It should be recalled that direct sintering at 1800°C under 70 MPa resulted in samples which are 97% dense, Fig. 2.

The observed temperature dependence of sintering leads us to conclude that the rapid densification observed within a narrow temperature range is associated with mass transport enhanced by the structural ordering of SiC. Between 1700 and 1800°C, the cubic structure undergoes significant ordering and the densification exhibits an abrupt increase. Further support for the conclusion that ordering plays a dominant role in the densification comes from observations on the structure and sintering behavior of the commercial SiC powder (CM-SiC). This powder did not exhibit disorder and when sintered, did not show the dramatic change of density with temperature or reach high densities even at 1900°C, Fig. 2. Similar observations on the role of structural defects on consolidation have been recently reported for B_4C [28].

Further demonstrations of the relation between structural ordering and densification come from experiments using carbon. Since graphite has an AB stacking structure of hexagonal basal planes, it is possible to have a stacking disordered structure by a mechanical (milling) process. Moreover, elemental boron has been shown to accelerate the graphitization of lattice plane (002). Its addition has been shown to make possible the synthesis of crystallized carbon with the ordering of lattice plane (002) from carbon black and a phenol formaldehyde resin [33, 34]. In this work, the consolidation of disordered carbon with elemental boron prepared by milling was investigated by the spark plasma sintering method.

Fig. 5 shows X-ray diffraction patterns of carbon consolidated by spark plasma sintering at temperatures ranging from 1000 to 1900°C for 10 min under an applied pressure of 70 MPa. The disordered carbon powders were prepared by milling under an inert atmosphere of Ar for 5 h at a revolution speed of 560 rpm and with a charge ratio of 40:1. The peak for the hexagonal basal plane of graphite, at $2\theta \sim 26°$, was not evident or too small to be recognized at sintering temperatures lower than 1500°C, but abruptly increased when sintering was carried out at 1600°C. Structure ordering could be observed when the powder was sintered at temperatures higher than 1600°C. Fig. 6 shows the effect of sintering temperature on the density of the carbon. The density increased relatively steeply at 1600°C, a temperature at which structural ordering occurs as shown in Fig. 5. On the other hand, the

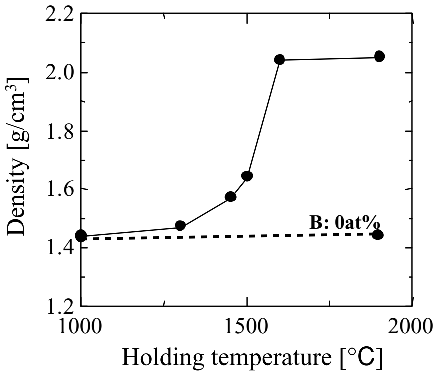

Figure 6 Effect of holding temperature on the density of sintered carbon.

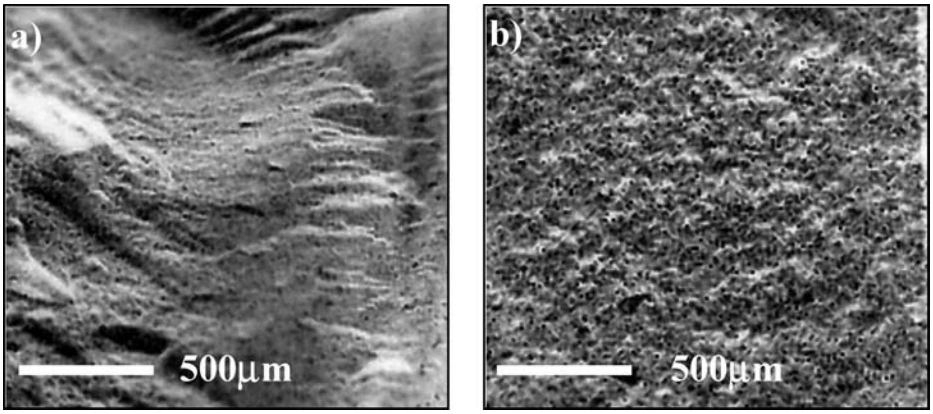

Figure 7 Optical micrographs of fracture surfaces of (a) carbon sintered compact with 10 at% boron and (b) typical commercial carbon block.

density of carbon material consolidated from disordered carbon without the addition of boron did not increase even when sintering was carried out at the highest temperature, 1900°C, as seen in Fig. 6. These results support the proposed conclusion that the ordering of disordered structures plays an important role in the acceleration of densification of silicon carbide and carbon, consistent with the recent observations on boron carbide [28]. Fig. 7 shows optical micrographs of fracture surfaces of (a) sintered carbon compact with 10 at% boron and (b) commercial carbon block with 80% relative density. The surface of the carbon sintered in this study (with 92% relative density) is relatively smooth and depicts a denser material relative to commercial carbon. The bending strength of the material sintered in this work is 210 MPa.

The concept of mass transport enhancement by the ordering of the structure has been observed previously. Seo *et al.* [35] investigated the annealing of stacking faults in beta SiC and reported a significant grain growth occurring during this process. And in a study on the liquid phase sintering of WC, Sommer *et al.* [36] also reported a correlation between grain growth and twin boundaries. Defects, including stacking faults, can play a role in mass transport during sintering [37], but the mechanistic connection between the annihilation of the defects, particularly stacking faults, and the enhanced sintering is not well understood. However, evidence has been provided showing that the shrinkage of stacking faults is related to atomic diffusion [38]. Atomic mobility associated with the annealing of stacking faults is believed to contribute to the observed enhanced sintering.

4. Conclusion

The role of disorder-order transformation in consolidation of silicon carbide and carbon was investigated. It was demonstrated that the transformation is accompanied by a sharp increase in densification. The observations suggest that the atomic mobility associated with the annihilation of the stacking faults also enhances the densification of silicon carbide and carbon.

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