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Microstructure of spark plasma sintered silicon carbide with Al-B-C

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Densification of SiC powder with total amounts of 2, 4, 8 wt% Al-B-C additive was carried out by spark plasma sintering (SPS). The unique features of the process are the possibilities of a very fast heating rate and a short soaking time to obtain fully-dense materials. The heating rate and applied pressure were kept at 100 K \cdot minute⁻¹ and 40 MPa, while the sintering temperature and soaking time varied from 1,700-1,800 °C for 10-40 minutes, respectively. The SPS-sintered SiC at 1,800 °C with different amounts of Al-B-C reached near-theoretical density. The sintered SiC ceramics were predominantly composed of 6H polytype with 15R and 4H polytype as minor phases. The microstructure of SiC sintered up to 1,750 °C consisted of equiaxed grains. In contrast, the growth of large elongated SiC grains in small matrix grains was shown in sintered bodies at 1800 °C, and a plate-like grains interlocking microstructure had been developed by increasing the soaking time at 1800 °C. The grain growth rate decreases with increasing amounts of Al-B-C in SiC, however, the volume fraction and the aspect ratio of large elongated SiC grains in the sintered bodies increased.

Key words: SiC, Al-B-C additive, Spark plasma sintering, Microstructure.

Introduction

Silicon carbide is a very interesting ceramic material due to its superior properties like high hardness, low bulk density and high oxidation resistance, which make SiC useful for a wide range of industrial applications [1-4]. The crucial requirement for the effective applications of polycrystalline silicon carbide is a high degree of densification. The sintering process and densification mechanism of covalent SiC materials are different from those of ionic ceramics because of the low diffusivity of atoms and high energy of grain boundaries. For this reason, densification of silicon carbide ceramics always needs sintering additives or pressure. Depending on the types of doped sintering additives, SiC may be densified to a high density by solidstate or liquid-phase sintering mechanism. Solid-state sintering usually requires sintering temperatures of more than 2,100 °C and easily results in exaggerated grain growth, which is detrimental to the mechanical properties [5]. The sintering additives help to reach a high density through a reduction of the grain boundary energy (boron) and reaction with residual silica (carbon) present on the SiC particle surfaces [6-8]. In contrast, the liquid-phase sintering process can be carried out at temperatures between 1,850 and 2,000 °C.

A wide variety of oxides, usually in combination with

a rare-earth oxide, CaO, Al₂O₃, Y₂O₃ may be used as sintering additives for SiC to accomplish a liquid phase sintering process, in which the oxides form a liquid phase at a low temperature or react with the SiO₂ present in the form of a thin surface layer on commercial SiC powders to form a liquid at even lower temperatures [9-13] Besides the oxides, Al-B-C nonoxide system additives can serve as sintering aids for the low temperature sintering of SiC. Additions of Al compared to the case with only B and C as sintering additives in SiC materials have been known to facilitate liquid phase sintering of SiC, to lower the densification temperature, to induce the phase transformations among SiC polytypes, to promote anisotropic growth of SiC grains, to form amorphous grain boundary films, and to produce various secondary phases in junctions [14-20].

Among the pressure sintering techniques, spark plasma sintering (SPS) developed in the 1990s, is a type of solid compaction sintering. SPS makes very rapid sintering possible to obtain fully-densified ceramics [21-30]. In SPS and hot pressing (HP) processing, the sample preparation procedure, such as die setting, the powder loading into the graphite mould, and the application of mechanical pressure, is almost the same, as shown in Fig. 1. Whereas only mechanical pressure is applied in the HP process, spark impact pressure (P_s) as well as mechanical pressure (P_m) exerts additional influences on the densification of materials in the SPS process. In conventional hot pressing, the main forces promoting the densification are the Joule heating and the applied pressure, i.e., the sample is heated by an external source, which implies that the rate of densification is strongly constrained by the rate of heat

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Fig. 1. Heating procedure in pressure sintering: (a) external heating type of hot pressing and (b) internal heating type of spark plasma sintering.

transfer to the specimen located in the pressure die.

The purpose of this study is to examine the microstructural changes in SiC ceramics by spark plasma sintering with Al-B-C additives. The microstructure of spark plasma sintered SiC containing three different amounts of Al-B-C additives is quantitatively characterized by image analysis. The quantitative analysis is conducted on the grain size, aspect ratio and grain size distribution of SiC.

Experimental Procedure

This work was conducted using the commercial powders of SiC (Betarundum, Ultrafine, Ibiden Co., Ltd., Japan), Al (99.9% Grade, High Purity Chemicals, Japan), B (Grade HS, Amorphous, H.C. Starck, Germany), and C (99.7% Grade, High Purity Chemicals, Japan). The starting powder mixtures, as given in Table 1, were mixed in a planetary ball mill with silicon carbide milling media for 4 h, and then dried and sieved.

The mixed powders were put into a graphite die (20 mm in diameter) and sintered with the Dr. Sinter 1050 spark plasma sintering system (Sumitomo Coal Mining, Tokyo, Japan) in a flowing Ar atmosphere (500 cc·minute⁻¹). The heating rate was fixed on 100 K·minute⁻¹ and the applied pressure was 40 MPa. The sintering temperature was held at 1,700-1,800 °C for 10 minutes. In the case of sintering at 1,800 °C, specimens with prolonged soaking for 20-40 minutes were also prepared to enhance the grain growth and $\beta \rightarrow \alpha$ transformation.

After sintering, sample surfaces were ground to remove the graphite layer, and then polished by diamond paste. The density of the sintered specimens was measured by the Archimedes method in deionized water as an immersion medium. The theoretical density of the specimens was calculated according to the rule of mixtures. Crystalline

Table 1. Batch compositions of starting powder mixtures for spark plasma sintered SiC with different amount of Al, B and C additives

Nomination	SiC (wt %)	Al (wt %)	B (wt %)	C (wt %)
1ABC-SiC	98.0	1.0	0.5	0.5
2ABC-SiC	96.0	2.0	1.0	1.0
4ABC-SiC	92.0	4.0	2.0	2.0

phases in the sintered specimens were determined by Xray diffraction (Model D5005, Bruker, Germany) using CoK α radiation. The specimens were etched by a plasma of CF₄ containing 8% O₂ for the microstructural observations. The microstructural observations were performed using a scanning electron microscope (Jeol, 6500F, Japan).

Quantitative image analyses on the sintered SiC ceramics were also conducted. The mean diameter and aspect ratio of SiC grains were evaluated. The mean diameter of a SiC grain (d) was the equivalent circle diameter of the SiC grain. The aspect ratio of grain (R) was defined as the ratio of the length and diameter of each grain, which was determined directly from the longest diagonal and the longest dimension perpendicular to the longest diagonal in its two dimensional image. A total of 600-2,000 grains was measured in each specimen. The grain size distribution was evaluated by plotting the fractional grain area versus the grain diameter. Grains deviating from a monomodal grain size distribution are defined as large grains in the present study. The diameter and aspect ratio were evaluated for matrix grains and large grains, respectively, when their microstructures were bimodal.

Results and Discussion

The relative densities of sintered silicon carbide ceramics as a function of sintering temperature are shown in Fig. 2. A relative density of 99.0% was obtained by spark plasma sintering at 1,800 °C, despite a high heating rate and a short soaking time. Such a rapid densification results from the characteristics of SPS. The current passes through both the graphite dies and samples, so that the specimen is heated at the outside and the inside simultaneously resulting in a very rapid heating rate. Thus, these processes promote material transfer and make rapid densification of the powder compact possible at low temperatures and short soaking times (20-30 minutes).



Fig. 2. Density variation of SiC with the amount of Al-B-C, spark plasma sintering temperature and soaking time. The soaking time at 1700 and 1750 °C was 10 minutes.

 Table 2. Identified crystalline phases of 2ABC-SiC by X-ray diffraction

Sintering temperature and soaking time	Major phase	Minor phases		
1,700-10 minutes	3C	6H, 15R		
1,750-10 minutes	6H, 3C	15R, 4H, Graphite		
1,800-10 minutes	6H	15R, 4H, 3C, Graphite		
1,800-40 minutes	6H	4H, 15R, Graphite		

Table 2 lists the contents of polytypes in the sintered 2ABC-SiC materials. The β -SiC starting powder was composed of only the 3C crystalline phase. The specimen sintered at 1,700 °C consisted of 3C as a major phase, and 6H, 15R minor phases, indicating that a small fraction of β -SiC transformed to α -SiC. In contrast, the 1,750 °C sintered specimen consisted of 6H, 3C as major phases, and 15 R, 4H as minor phases. As the temperature and soaking time increased to 1,800 °C for 40 minutes, 3C was essentially transformed to various



Fig. 3. SEM micrographs of the polished surfaces for Al-B-C added SiC ceramics processed by spark plasma sintering: (a) 2ABC-SiC sintered at 1,700 $^{\circ}$ C and (b) 2ABC-SiC sintered at 1,750 $^{\circ}$ C

alpha phases. The initial alpha polytypes detected were 6H and 15R, followed by 4H. The predominant crystalline phase was 6H in this temperature range.

The onset of the $\beta \rightarrow \alpha$ phase transformation has been reported to be approximately at 1,800 °C with Al-B-C additions by hot pressing [31, 32]. In the present







Fig. 4. SEM micrographs of the polished surface for Al-B-C added SiC ceramics processed by spark plasma sintering at 1,800 °C as a function of soaking time: (a) 1ABC-SiC, (b) 2ABC-SiC, (c) 4ABC-SiC for 10 minutes, (d) 1ABC-SiC, (e) 2ABC-SiC, (f) 4ABC-SiC for 20 minutes, and (g) 1ABC-SiC, (h) 2ABC-SiC, (i) 4ABC-SiC for 40 minutes.

SPS process, it was found to profoundly promote the $\beta \rightarrow \alpha$ phase transformation, which results in lowering the onset temperature. Cao et al. [15] found that the 3C to 4H phase transformation was enhanced by the presence of Al together with B and C. Shinozaki et al. [31] reported that the 3C-SiC transformed to 4H-SiC through an intermediate structure of 15R. Williams et al. [32] investigated the transformation of the Al, B and C doped SiC, in which 15R and 4H were initial phases formed with 6H appearing at higher temperatures. Both the 15R and 6H were transitory, and 4H was the dominant high temperature phase. The difference in crystal structures of transformation products was believed to originate from the difference in process conditions, such as the starting β -SiC powders, the final temperature and soaking time, and atmosphere.

Fig. 3 shows the plasma etched surfaces of 2ABC-SiC sintered at 1,700 °C and 1,750 °C for 10 minutes. The microstructure of SiC sintered at 1,700 °C consisted of fine equiaxed grains. When sintered at 1,750 °C, some elongated grains developed, however, equiaxed grains still dominated. In contrast, the growth of large elongated grains having high aspect ratios was shown in sintered bodies at 1,800 °C in Fig. 4. Also the platelike grains interlocking microstructure had been developed by increasing the soaking time at 1,800 °C and by increasing the content of additives. In association with the β to α phase transformation, the SiC grains grew into plate-like shapes. This tendency suggests that the grain growth predominantly proceeded along the direction of the plate, i.e., along the basal planes of the SiC grains. Such an interlocking grain structured SiC exhibited a significant rising R-curve behavior with fracture toughness over 8 MPam1/2, while retaining a high strength of ~660 MPa according to Cao et al. [15].

The sintering of Al, B, and C-doped SiC was believed to be by a liquid phase sintering process reported by Cao et al. [15], similar to that for the Al_2O_3 added SiC described by Suzuki [35]. A likely scenario that could be envisioned was as follows. During heating, metal Al melted, and B, C, and O were presumed to transport into the Al melt and form secondary phases. The liquid phase(s) flowed, filling pores between the nearby SiC particles and engulfing many grains, as observed by TEM [36]. Meanwhile, Al vapor coated the SiC particle surfaces and reacted with native oxide skins on the powder surface and the added C and B to form a liquid grain boundary phase. In the presence of applied pressure, particle rearrangement occurred. A liquid phase sintering mechanism, i.e., a solution-reprecipitation process, caused gradual densification coupled with grain growth. At this stage, corresponding to sintering up to 1700 °C with 3 wt% or more Al addition, a fine grained dense 3C-SiC was obtained. At higher sintering temperatures, SiC transformed from β to α , accompanying the formation and growth of plate-like grains with increasing aspect ratios.



Fig. 5. Grain size distribution of SiC as a function of the amount of Al-B-C, spark plasma sintering temperature and soaking time. The numerical values are mode grain diameter in μ m: (a) 1ABC-SiC, (b) 2ABC-SiC and (c) 4ABC-SiC.

The grain size distributions of the spark plasma sintered SiC as a function of additive content are plotted in Fig. 5 also as a function of sintering temperature and soaking

Specimen	Temp. & soaking time (°C-minutes)	Mean diameter (d _M ,µm)	Mean aspect ratio (R _M)	Matrix grains		Large grains		
				Diameter (d _{MG} , µm)	Aspect ratio (R _{MG})	Vol. fraction (%)	Diameter (d _{LG} , µm)	Aspect ratio (R _{LG})
1ABC-SiC	1,700-10	2.56	1.73	2.6	1.73	-	-	-
	1,750-10	3.62	1.77	3.2	1.74	27.0	6.11	1.96
	1,800-10	3.99	1.82	3.5	1.77	31.3	7.44	2.24
	1,800-20	4.10	2.00	3.5	1.95	37.8	7.78	2.26
	1,800-40	5.20	2.07	4.5	2.04	39.4	9.63	2.31
2ABC-SiC	1,700-10	2.52	1.75	2.6	1.75	-	-	-
	1,750-10	2.83	2.03	3.4	2.02	28.1	6.00	2.14
	1,800-10	3.55	2.14	4.2	2.11	33.7	7.43	2.53
	1,800-20	3.77	2.25	4.6	2.14	40.0	7.45	3.03
	1,800-40	5.19	2.44	5.8	2.30	42.9	8.74	3.09
4ABC-SiC	1,700-10	2.49	1.78	2.6	1.78	-	-	-
	1,750-10	2.74	2.16	3.4	2.15	29.1	6.09	2.24
	1,800-10	3.23	2.41	4.2	2.39	35.7	6.10	2.64
	1,800-20	3.60	2.48	4.6	2.32	46.7	7.13	3.53
	1,800-40	4.59	2.98	5.4	2.66	49.6	7.56	4.16

Table 3. Microstructural characteristics of the Al-B-C added SiC ceramics processed by spark plasma sintering

time. Monomodal grain size distributions with a mode grain size of 2.6 µm are clearly shown in all samples sintered at 1,700 °C. A separation between the large grains and the matrix grains, determined from the grain size distributions, is shown in sintered bodies at > 1,750 °C. As a result, the SiC ceramics with Al-B-C had a bimodal grain size distribution in this temperature range. The relative area of the matrix grains and large grains in a bimodal microstructure is directly related to the volume fraction of a certain range of grain size. An increase in the sintering temperature and soaking time shifts the grain size distribution to the larger grain size region while maintaining the bimodal distribution. The maximum mode values of the matrix grains and the large grains in the specimen sintered at 1,800 °C of 40 minutes were 6.6 µm, 9.4 µm for 1ABC-SiC, 5.8 µm, 8.2 µm for 2ABC-SiC and 5.4 µm, 7.8 µm for 4ABC-SiC. The growth behavior coincided well with the general observation that the relative growth rate of small grains was larger than that of the larger grains [37, 38], and experimentally confirmed well with the microstructural observations in Fig. 3 and Fig. 4.

The quantitative image analysis results for grain size (equivalent diameter) and aspect ratio of SiC with Al-B-C are summarized in Table 3. For all the ABC-SiC samples, the average diameter of SiC grains increased gradually as the sintering temperature and soaking time increased. An increase in soaking time at 1,800 °C from 10 to 40 minutes increases the average diameter and the aspect ratio. Moreover, an increase in additive content at each sintering condition results in a lower grain diameter, a higher aspect ratio and a high volume fraction of larger elongated grains. This trend is mirrored as a decrease in volume fraction of matrix grains. It could be postulated that effect of the liquid phase produces a difference in the grain growth rate along the short and long grain axes which increases with more liquid content, and which results in a predominant plate-like grains interlocking microstructure. The total volume fractions of large grains in 1ABC-SiC, 2ABC-SiC and 4ABC-SiC sintered at 1,800 °C for 40 minutes were 0.394, 0.429 and 0.496, respectively.

Summary

The microstructural development of SiC with 2, 4, 8 wt % Al-B-C by spark plasma sintering was characterized. The SPS-sintered SiC at 1,800 °C with different amounts of Al-B-C reached near-theoretical density. The sintered SiC ceramics were predominantly composed of 6H polytype with 15R and 4H polytypes as minor phases. The microstructure of SiC sintered up to 1,750 °C consisted of equiaxed grains. In contrast, the growth of large elongated SiC grains in small matrix grains was shown in sintered bodies at 1,800 °C, and plate-like grains interlocking microstructure was developed by increasing soaking time at 1,800 °C. The grain growth rate decreases with an increase in the amount of Al-B-C in SiC, however, the volume fraction and the aspect ratio of large elongated SiC grains in the sintered bodies increased.

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References

- 1. L.J. Schioler, Am. Ceram. Soc. Bull. 64 (1986) 268-294.
- 2. K. Yamad and M. Mori, in "Silicon-Carbide Ceramics"

- C.Greskovich and J.H. Rosolwski, J. Am. Ceram. Soc. 59 (1978) 336-343.
- W.L. Vaushn and H.G. Maaha, J. Am. Ceram. Soc. 73 (1990) 1540-1545.
- 5. S. Prochazk, US Patent 3853566, 10 December 1974.
- 6. E.R. Maddrell, J. Mater. Sci. Lett. 6 (1987) 486-488.
- 7. W. Vanrijswjk and D.J. Shanafield, J. Am. Ceram. Soc. 73 (1990) 148-149.
- 8. R. Hamminger, ibid 72 (1989) 1741-1744.
- 9. N.P. Padture, ibid 77 (1994) 519-523.
- 10. M.A. Mulla and V.D. Kristic, J. Mater Sci. 29 (1994) 934-938.
- Y.W. Kim, H. Tanaka, M. Mitomo and S. Otani, J. Ceram. Soc. Jpn. 103 (1995) 257-261.
- 12. M. Omori and H. Takei, J. Am. Ceram. Soc. 65 (1982) C92.
- 13. Y.W. Kim, M. Mitomo and H. Hiratsuru, ibid 80 (1997) 99-105.
- S. Shinozaki, R.M. Williams, B.N. Juterbock, W.T. Donlon, J. Hangas and C.R. Peter, J. Am. Ceram. Soc. 64 (1985) 1389-1393.
- J.J. Cao, W.J. Moberlychan, L.C. De Jonghe, C.J. Gilbert and R.O. Ritchie, J. Am. Ceram. Soc. 79 (1996) 461-469.
- Y. Zhou, K. Hirao, M. Toriyama and H. Tanaka, J. Mater. Res. 14 (1999) 3363-3369.
- D. Chen, M.E. Sixta, X.F. Zhang, L.C. De Jonghe and R.O. Ritchie, Acta Mater. 48 (2000) 4599-4608.
- X.F. Zhang, M.E. Sixta and L.C. De Jonghe, J. Am. Ceram. Soc. 83 (2000) 2813-2820.
- X.F. Zhang, Q. Yang and L.C. De Jonghe, Acta Mater. 51 (2003) 3849-3860.
- 20. K.S. Cho and K.S. Lee, Key Eng. Mater. 287 (2005) 329-334.
- 21. M. Tokita, J. Soc. Powder Tech. Jpn. 30 (1993) 790-804.
- 22. N. Tamari, T. Tanaka, K. Tanaka, I. Kondoh, M. Kawahara and M. Tokita, J. Ceram. Soc. Jpn. 103 (1995) 740-742.
- 23. D.S. Perera, M. Tokita and S. Moricca, J. Euro. Ceram. Soc. 18 (1998) 401-404.

- L. Gao, H.Z. Wang, J.S. Hong, H. Miyamoto, K. Miyamoto, Y. Nishikawa and S.D. L. Torre, *ibid* 19 (1999) 609-613.
- Y. Zhou, K. Hirao, M. Toriyama and H. Tanaka, J. Mater. Res. 14 (1999) 3363-3369.
- 26. Y. Zhou, K. Hirao, M. Toriyama and H. Tanaka, J. Am. Ceram. Soc. 83 (2000) 654-656.
- 27. E.M. Heian, A. Feng and Z. A. Munir, Acta Mater. 50 (2002) 3331-3346.
- M. Ohyanagi, T. Yamamoto, H. Kitaura, Y. Kodera, T. Ishii and Z.A. Munir, Scripta Mater. 50 (2004) 111-114.
- 29. U. Anselmi-Tamburini, J.E. Garay and Z.A. Munir, *ibid* 54 (2006) 823-828.
- F. Guillard, A. Allemand, J.D. Lulewicz and J. Galy, J. Euro. Ceram. Soc. 27 (2007) 2725-2728.
- S. Shinozaki, J, Hangas, K. Maeda and A. Soeta, in "Silicon Carbide '87" (American Ceramic Society, 1987) p. 113.
- R.M. Williams, B.N. Juterbock, S.S. Shinozaki, C.R. Peters and T.J. Whalen, Am. Ceram. Soc. Bull. 64 (1985) 1385-1389.
- 33. S.K. Lee and C.H. Kim, J. Am. Ceram. Soc. 77 (1994) 1655-1658.
- 34. Y.W. Kim, M. Mitomo and H. Hirotsuru, ibid 80 (1997) 99-105.
- K. Suzuki, in "Silicon Carbide Ceramics-2" (Elsevier Applied Science, 1991) p. 162.
- W.J. Moberlychan, J.J. Cao, M.Y. Niu and L.C. De Jonghe, in "High Performance Composites-Commonalty of Phenomena" (TMS Publication, 1994) p. 219.
- 37. R.M. German, in "Sintering Theory and Practice" (John Wiley & Sons, 1996) p.225.
- 38. Y.W. Kim, S.G. Lee and M. Mitomo, J. Euro. Ceram. Soc. 22 (2002) 1031-1037.