Effect of AlN additive on densification, microstructure and strength of liquid-phase sintered SiC ceramics by spark plasma sintering

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SiC ceramics were prepared from β -SiC starting powder with AlN and Y_2O_3 sintering additives by spark plasma sintering. Densification, microstructure and flexural strength of the liquid-phase sintered SiC ceramics were investigated. The relative density of SiC sintered bodies reached over 95% at total amount of 10 vol% AlN and Y_2O_3 additives and at 1900°C for 600 s in N_2 at 30 MPa. When the content of AlN additive increased, the size of SiC grains decreased. The SiC body almost without the grain growth was successfully prepared using 95 mol% AlN and 5 mol% Y_2O_3 additives. The flexural strength of the SiC body was 1150 MPa.

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1. Introduction

Silicon carbide (SiC) ceramics have many attractive properties such as high hardness, excellent mechanical strength at high temperature, good corrosion resistance and oxidation resistance. However, it is difficult to densify pure SiC powder without sintering additives because of its strong covalent bonding. The conventional densification technique of SiC is solid-phase sintering with B and C additives,¹⁾ or liquid-phase sintering with metal oxides additives such as Al_2O_3 and Y_2O_3 .^{2),3)} The advantage of liquid-phase sintered SiC ceramics is that fine-grained microstructure can be formed compared with solid-state sintering because of the lower sintering temperatures and the presence of liquid phase.⁴⁾ The oxides additives react with SiO_2 derived from the surface oxide of SiC particle to form a liquid phase during sintering process, and the liquid promotes densification and microstructural development. The SiC ceramics sintered via liquid-phase sintering with AlN and rare-earth oxides have showed significant improvement of high-temperature strength and oxidation resistance.^{5)–8)} Some researchers have reported that the advancement of these properties would be caused by decrease in glassy phase at grain boundary owing to formation of SiC–AlN solid solution and increase in heat resistance of glassy phase due to addition of AlN and rare-earth oxide additives.^{9),10)}

Spark plasma sintering (SPS) technique can be used to heat specimens rapidly because the pulsed direct current used in this technique can pass through the graphite die and punch rods.¹¹⁾ Hence, the whole sintering process can be completed in a short time. In addition, low-sinterability materials can be densified at moderate temperature due to inhibition of grain growth. Consequently, fully dense materials having fine-grained microstructure are expected to produce by using the SPS. The SPS technique is

sometimes called as pulse electric current sintering (PECS)^{12),13)} and field-assisted sintering technique (FAST).¹⁴⁾ Low-sinterable oxides, nitrides and carbides, which are either difficult or impossible to densify by conventional sintering techniques, have been fabricated as fully dense materials by the SPS techniques.^{12)–17)}

In this work, SiC ceramics were prepared using SPS from high-purity β -SiC powder with AlN and Y_2O_3 sintering additives, and the effect of AlN additive on the densification, crystalline phase, microstructure and flexural strength of the SiC ceramics was investigated.

2. Experimental procedure

High-purity β -SiC (Bridgestone Co., free carbon content: 0.3 mass%, total oxygen content: 1.1 mass%, average particle size: 0.9 μm) powder was used as starting material in order to elucidate effect of sintering additives on densification, crystalline phase, microstructure and mechanical strength of SiC body prepared through liquid phase sintering. The typical morphology of the β -SiC starting powder was shown in Fig. 1. AlN (Dow

Fig. 1. SEM micrograph of SiC starting powder.

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Table 1. Relative Density and Flexural Strength of SiC Bodies Sintered with Different Compositions of AlN–Y₂O₃ Additives and with 2 mass% Al₂O₃ Additive at 1900°C for 600 s

Sample designation	Additive composition (mol%)		Relative density (%)	Flexural strength (MPa)
	AlN	Y ₂ O ₃		
0AN	0	100	97.2	710 ± 90
10AN	10	90	95.0	780 ± 70
30AN	30	70	95.6	640 ± 60
50AN	50	50	97.0	900 ± 40
70AN	70	30	97.6	880 ± 130
90AN	90	10	99.3	1050 ± 120
95AN	95	5	99.1	1150 ± 210
100AN	100	0	75.7	–
2AO	2 mass% Al ₂ O ₃		98.8	780 ± 130

Chemical, total oxygen content: 2.0 mass%, average particle size: 1.1 μm) and Y₂O₃ (Shin-Etsu Chemical Co., Ltd., 0.3 μm) powders were added to SiC as sintering additives. The total amount of the additives was fixed at 10 vol% and the AlN content was changed from 0 to 100 mol%. The additive composition was listed in **Table 1**. As a reference, we also used 2 mass% Al₂O₃ (Sumitomo Chemical Co., Ltd., α -phase, 0.5 μm) as sintering additive to prepare SiC sintered body. These powders were mixed with a small amount of ethanol. The mixed slurry was dried and then sieved with a pore-opening size of 300 μm . The mixed powders were filled in a graphite die, and sintered at temperature of 1900°C for 600 s under a uniaxial pressure of 30 MPa in N₂ atmosphere at heating rate of 1.7°C/s using SPS (SPS-515S, SPS SYNTEX Inc.). The temperature on the surface of the die was measured with a radiation thermometer. Linear shrinkage of the powder compacts during the SPS process was continuously monitored by displacement of the punch rod. The densities of the sintered specimens were measured by the Archimedes method. The crystalline phase was identified in sintered form by using X-ray diffractometry (XRD; MiniFlex, Rigaku Co.) with Cu K α radiation. The specimens were polished with 3 μm diamond slurry, cut with diamond wheel, and then etched by plasma in a mixture of CF₄ and O₂ gases. The microstructures were observed by scanning electron microscopy (SEM; S-5200, JEOL Ltd.). Flexural strength was measured using a three-point bending method (Universal testing machine AG5000D, Shimadzu Co.) on test specimens with dimensions of 2 mm × 2 mm × 15 mm at room temperature.

3. Results and discussion

The displacement of specimens during the SPS process was monitored according to the heating schedule. **Figure 2** shows the change in shrinkage of powder compacts with elevating temperature up to 1900°C. The isothermal shrinkage at 1900°C up to 600 s is also shown in Fig. 2. The shrinkage of 0AN sample started at 1520°C. The beginning temperature of shrinkage for 10AN, 50AN and 90AN was lower than that for 0AN, around 1480°C. For 100AN sample, the starting temperature of shrinkage increased to 1650°C. The shrinkage of 90AN finished during holding time of 600 s at 1900°C, while the other samples continued to shrink during the holding.

Table 1 summarizes relative density of SiC bodies prepared

Fig. 2. Effect of sintering temperature on the displacement of SiC compacts containing different compositions of AlN–Y₂O₃ additives at 1200 to 1900°C, and the time dependence of isothermal displacement at 1900°C up to 600 s. **Fig. 3.** XRD patterns of SiC bodies sintered with different compositions of AlN–Y₂O₃ additives and with 2 mass% Al₂O₃ additive at 1900°C for 600 s.

with various compositions of AlN and Y₂O₃ additives and with 2 mass% Al₂O₃ additive at 1900°C for 600 s. The relative density of 0AN sample was 97.2%. The densities of more than 95% were achieved for 10AN to 95AN obtained with AlN and Y₂O₃ additives, and the density increased with increasing AlN additive content. In contrast, the density of 100AN decreased to 75.7%. 2AO sample prepared with Al₂O₃ additive had high density of 98.8%.

The densification of SiC compacts was accelerated by adding 90 to 95 mol% AlN additive to SiC–Y₂O₃ system, as confirmed from the lower starting temperature of shrinkage in Fig. 2 and the higher relative density in Table 1. The eutectic temperature of SiO₂–Y₂O₃ system is 1660°C.¹⁸⁾ By adding Al₂O₃ to the SiO₂–Y₂O₃ system, as known from the phase diagram of SiO₂–Al₂O₃–Y₂O₃ system, the eutectic temperature decreases to less than 1400°C.¹⁹⁾ In this study, a liquid phase of SiO₂–Al₂O₃–Y₂O₃ system derived from surface oxides of SiC and AlN particles may be formed. This could be attributed to the promotion of the densification of SiC compacts with AlN and Y₂O₃ additives.

Figure 3 shows XRD patterns of SiC bodies prepared with various compositions of AlN and Y₂O₃ additives and with 2 mass% Al₂O₃ additive at 1900°C for 600 s. The crystalline phase of the SiC sintered bodies was mainly 3C (β -SiC). 2H phase, which is assigned to AlN or one of α -SiC phases, was identified at a large amount of AlN additive. On the other hand, 4H-SiC (α -SiC) phase was detected when Al₂O₃ was used as sintering additive. Because AlN has 2H structure and is soluble in 2H-SiC, AlN is possible to form solid solution with 2H-SiC.²⁰⁾ In our previous study on SiC–AlN composites, the dissolution of AlN to SiC was revealed to facilitate phase transformation from 3C- to 2H-SiC.^{21),22)} Therefore, the peak of 2H phase observed in this work may indicate the existence of AlN remaining and/or SiC–AlN solid solution in the SiC bodies sintered with AlN additive. When Y₂O₃ only was added to SiC, the peak of Y₂O₃ was detected by XRD after sintering. The XRD peak of Y₂O₃ disappeared by addition of AlN, even at a small AlN content. This means that the AlN addition enhanced the dissolution of Y₂O₃ by forming the SiO₂–Al₂O₃–Y₂O₃ liquid phase. As shown in Fig. 2 and Table 1, the densification of SiC compacts was revealed to promote when the content of AlN additive increased from 10 to 95 mol%. This could be due to the increase in amount of SiO₂–Al₂O₃–Y₂O₃ liquid phase by increasing content of AlN additive.

Figure 4 shows SEM micrographs of the etched surface of SiC sintered bodies prepared with different compositions of AlN and Y₂O₃ additives and with 2 mass% Al₂O₃ additive at 1900°C for 600 s. The size of SiC grains in 10AN to 95AN samples was smaller than that in 0AN. The grain size decreased with increasing amount of AlN additive in 10AN to 95AN. The shape changed from globular to angular grains when the content of AlN additive increased. The morphological change might be caused by the compositional variation of liquid phase of SiO₂–Al₂O₃–Y₂O₃ derived from the surface oxides of SiC and AlN particles. The increase in content of AlN additive might lead to an increase in the viscosity of a liquid by containing nitrogen, which can suppress the grain growth during liquid-phase sintering.²³⁾ The size and morphology of SiC grains for 95AN sample were almost similar to those of SiC starting powder and bimodal microstructure was composed of angular grains with 1 to 2 μ m and less than 0.5 μ m in diameter. This suggests the inhibition of the grain growth during liquid-phase sintering. In 2AO sample obtained using Al₂O₃ additive, on the other hand, the grain growth and elongated grains were clearly observed. The present results demonstrate that densification of SiC powder is successfully achieved without the grain growth during liquid-phase sintering by using AlN additive and SPS technique.

The effect of AlN additive on the formation of microstructure in SiC ceramics prepared through liquid-phase sintering is summarized as follows. A liquid of SiO₂–Al₂O₃–Y₂O₃ system derived from surface oxides of SiC and AlN particles may be formed. When the AlN content increased, a large amount of the liquid could form, resulting in promotion of the densification (Fig. 2 and Table 1). Although a large amount of liquid generally promotes grain growth through solution-precipitation, grain growth was inhibited with increasing AlN content in the present study (Fig. 4). This might be due to increase in the viscosity by formation of a nitrogen-containing liquid with the addition of AlN to SiC. It should be also noted that AlN remained or dissolved into SiC to form the 2H phase. The inclusion of AlN and 2H-SiC in 3C-SiC matrix could be another factor for inhibition of grain growth by pinning effect.

Table 1 also summarizes the flexural strength of SiC sintered

Fig. 4. SEM micrographs of the etched surface of SiC bodies sintered with different compositions of AlN–Y₂O₃ additives and with 2 mass% Al₂O₃ additive at 1900°C for 600 s.

bodies prepared with different compositions of AlN and Y₂O₃ additives and with 2 mass% Al₂O₃ additive at 1900°C for 600 s. The flexural strength of SiC bodies increased with increasing content of AlN additive. This might be caused by small size of fracture origin due to the increase in density of sintered SiC bodies and the inhibition of grain growth. The crack deflection may also be expected due to the bimodal microstructure composed of angular grains, as shown in Fig. 4. The strength of 95AN sample without the grain growth reached high value of 1150 MPa. The strength of 2AO sample was 780 MPa, regardless of the high density of about 99%. Hence, the improvement of strength for SiC bodies would support the fine-grained microstructure. As described here, we achieved the high strength of 1150 MPa in SiC ceramics consisting of fine grains prepared by SPS through liquid-phase sintering. Since AlN forms solid-solution with SiC, a glassy phase consisting of Y–Si–Al–O–N at SiC grain boundary could reduce during densification. This may lead to further improvements in heat and corrosion resistance for liquid-phase sintered SiC ceramics.

4. Conclusions

SiC bodies were prepared with AlN and Y₂O₃ sintering additives at sintering temperature of 1900°C for 600 s in N₂ atmosphere at pressure of 30 MPa by SPS. The effect of AlN additive on the densification, crystalline phase, microstructure and flexural strength of SiC bodies was studied. The relative density of sintered SiC bodies was more than 95% at total content of 10 vol% AlN–Y₂O₃ additives. The size of SiC grains decreased

with increasing content of AlN additive. The inhibition of the grain growth was significantly observed for SiC body sintered at additive composition of 95 mol% AlN and 5 mol% Y₂O₃. The flexural strength of the sintered SiC body reached 1150 MPa. The use of SPS is also effective to control the fine microstructure because of the rapid heating and the short time sintering.

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References

- 1) S. Prochazka, "Special Ceramics 6," Ed. by P. Popper, British Ceramic Research Association, Stoke-on-Trent, U.K. (1975) pp. 171–181.
- 2) M. Omori and H. Takei, *J. Am. Ceram. Soc.*, **65**, C-92 (1982).
- 3) M. A. Mulla and V. D. Krstic, *Am. Ceram. Soc. Bull.*, **70**, 439–443 (1991).
- 4) N. P. Padture, *J. Am. Ceram. Soc.*, **77**, 519–523 (1994).
- 5) M. Keppeler, H.-G. Reichert, J. M. Broadley, G. Thurn, I. Wiedmann and F. Aldinger, *J. Eur. Ceram. Soc.*, **18**, 521–526 (1998).
- 6) G. Rixecker, I. Wiedmann, A. Rosinus and F. Aldinger, *J. Eur. Ceram. Soc.*, **21**, 1013–1019 (2001).
- 7) Y.-W. Kim, M. Mitomo and T. Nishimura, *J. Am. Ceram. Soc.*, **85**, 1007–1009 (2002).
- 8) H.-J. Choi, J.-G. Lee and Y.-W. Kim, *J. Am. Ceram. Soc.*, **85**, 2281–2286 (2002).
- 9) Y.-W. Kim, M. Mitomo and T. Nishimura, *J. Am. Ceram. Soc.*, **84**, 2060–2064 (2001).
- 10) K. Suzuki and M. Sasaki, *Ceram. Int.*, **31**, 749–755 (2005).
- 11) M. Tokita, *J. Soc. Powder Technol. Jpn.*, **30**, 790–804 (1993).
- 12) Y. Zhou, K. Hirao, M. Toriyama and H. Tanaka, *J. Am. Ceram. Soc.*, **83**, 654–656 (2000).
- 13) M. Suganuma, Y. Kitagawa, S. Wada and N. Murayama, *J. Am. Ceram. Soc.*, **86**, 387–394 (2003).
- 14) J. R. Groza, J. D. Curtis and M. Krämer, *J. Am. Ceram. Soc.*, **83**, 1281–1283 (2000).
- 15) J. Tatami, M. Iguchi, M. Hotta, C. Zhang, K. Komeya, T. Meguro, M. Omori, T. Hirai, M. E. Brito and Y.-B. Cheng, *Key Engineering Materials*, **237**, 105–110 (2003).
- 16) Z. Shen, M. Johnsson, Z. Zhao and M. Nygren, *J. Am. Ceram. Soc.*, **85**, 1921–1927 (2002).
- 17) M. Hotta and T. Goto, *J. Ceram. Soc. Japan.*, **116**, 744–748 (2008).
- 18) E. M. Levin, C. R. Robbins and H. F. McMurdie, Fig. 2388 "Phase Diagrams for Ceramists," Ed. by M. K. Reser, American Ceramic Society, Columbus, OH (1964).
- 19) E. M. Levin, C. R. Robbins and H. F. McMurdie, Fig. 2586 "Phase Diagrams for Ceramists" Ed. by M. K. Reser, American Ceramic Society, Columbus, OH (1964).
- 20) A. Zangvil and R. Ruh, *J. Am. Ceram. Soc.*, **71**, 884–890 (1988).
- 21) K. Shirouzu, T. Ohkusa, T. Kawamoto, N. Enomoto and J. Hojo, *J. Ceram. Soc. Japan.*, **116**, 781–785 (2008).
- 22) K. Shirouzu, Y. Nonaka, M. Hotta, N. Enomoto and J. Hojo, *Key Engineering Materials*, **352**, 193–196 (2007).
- 23) Y.-W. Kim and M. Mitomo, *J. Am. Ceram. Soc.*, **82**, 2731–2736 (1999).