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Processing and microstructure of silicon carbide fiber-reinforced silicon carbide composite by hot-pressing

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Abstract

Continuous 2D woven fiber-reinforced SiC composites were fabricated by hot-pressing in Ar at 1750°C under a pressure of 40 MPa using Al–B–C or Al_2O_3–Y_2O_3–CaO system as sintering additives. In this study, fracture behavior and microstructure of the composites fabricated by this process were investigated. These composites achieved nearly full density in both cases. In the case of the composite with Al–B–C additives, the load-displacement behavior of the composite with non-coated Hi-Nicalon cloths showed completely brittle fracture, whereas that of the composite with BN-coated Hi-Nicalon cloths showed ductile fracture with a lot of fiber pull-out. On the contrary, in the case of the composite with Al_2O_3–Y_2O_3–CaO additives, the load-displacement behavior of the composite with non-coated Hi-Nicalon cloths showed slight ductile fracture with small tails, whereas that of the composite with BN-coated Hi-Nicalon cloths showed completely brittle fracture. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

Continuous SiC fiber-reinforced SiC composite (SiC/SiC_f) is one of the most attractive structural materials for future fusion reactors because of their low atomic number, low activation, good fracture resistance, with potential of good thermal conductivity, excellent high temperature properties and corrosion resistance [1–6]. Furthermore, SiC shows good resistance for high energy neutron irradiation until very high doses [7–11].

There are some processes to fabricate SiC/SiC_f composites, for example, the chemical vapor infiltration (CVI) method and the infiltration of liquid precursor polymers or melt infiltration technique. However, the composites fabricated by these processes usually contain about 10–20 vol% voids, resulting in low mechanical properties [4,12–14].

The hot-pressing method offers the ability to fabricate dense composites. Kamiya et al. [15] hot-pressed SiC/SiC_f composite using AlB_2 as a sintering additive, and Nakano et al. [16] hot-pressed the composite using AlB_2 + TiC. Park et al. [17] reported that SiC/SiC_f composite was hot-pressed at 1750°C and could be densified up to 97% of theoretical density using Al as sintering additive. Recently, Yano et al. [18] fabricated SiC/SiC_f composite using green sheets of SiC with Al–B–C sintering additives obtained by the doctor blade method as the matrix and 2D woven Hi-Nicalon cloths without any coating as the reinforcement by hot-pressing at 1750°C, and could obtain a dense composite.

The aim of this study is to fabricate SiC/SiC_f composite using green sheets with oxides or non-oxides sintering additives and 2D woven Hi-Nicalon cloths with/without BN-coating and to investigate the effects of sintering additives and surface coating of Hi-Nicalon fiber on fracture behavior of composites at room temperature.

2. Experimental procedures

2.1. Fabrication of green sheets

The fabrication process of green sheet is shown in Fig. 1. In this study, Al–B–C system and Al_2O_3–Y_2O_3–CaO system were chosen for the fabrication of SiC/SiC_f composites as sintering additives because of their low densification temperature [19–21].

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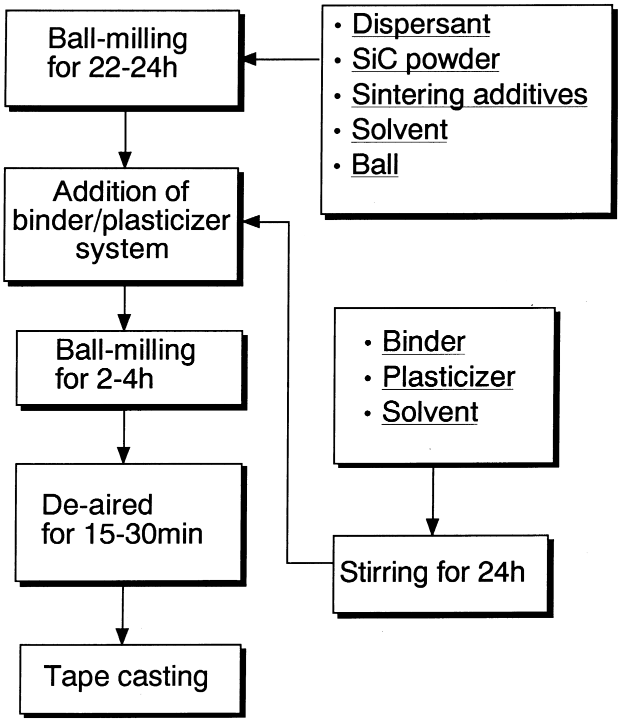

Fig. 1. Fabrication process of green sheets by doctor blade method.

Powders of submicron β-SiC (Ultrafine, average particle size: 0.28 μm, Ibiden, Japan), two additive systems, using following chemicals; (A) Al (Wako Pure Chemical Industries, Japan), B (Rare Metallic, Japan) and C (Carbon black, Mitsubishi Kasei, Japan), (B) Al_2O_3 (average particle size: 0.18 μm, AKP-50, Sumitomo Chemical, Japan), Y_2O_3 (average particle size: 2–3 μm, 99.9%, High Purity Chemical, Japan) and CaO (99.9%, Kanto Chemical, Japan) and a dispersing agent (SN-7347C, 20%-quaternary ammonium salt solution, San Nopco, Japan) were mixed by ball-milling for 22–24 h in ethanol with Teflon ball or Al_2O_3 ball. Furthermore, polyvinyl butyral (PVB, Sekisui Chemical, Japan) and dioctyl adipate (Wako Pure Chemical Industries, Japan), an organic binder and a plasticizer, respectively, were dissolved into ethanol by magnetic stirrer at 40°C for 24 h. A well-stirred solution of binder/plasticizer system was added to the above solution. This solution was further mixed by ball-milling for 2–4 h, followed de-air process using a rotary pump for 15–30 min to obtain the final slurry for tape casting. The obtained slurry was filled into a laboratory-scale doctor blade equipment (DP150, Tsugawa Seiki, Japan). The blade height and carrier speed of the doctor blade equipment were adjusted in 0.7–1.0 mm and 10 cm/min, respectively. The sheet was dried at room temperature. The thickness of green sheets with Al–B–C sintering additives and with Al_2O_3–Y_2O_3–CaO sintering additives were 340–365 and 220–280 μm, respectively. Composition of SiC powder, sintering additives and organics in the green sheet is listed in Table 1. These green sheets were cut into 35×35 mm^2 square.

2.2. Fabrication and characterization of SiC/SiC$_f$ composite

In this study, Hi-Nicalon (NC-9505, Nippon Carbon, Japan) or BN-coated Hi-Nicalon (Nippon Carbon, Japan) fiber cloth woven in 90° crossing two dimension

Table 1
Composition of SiC powder, sintering additives and organics in the green sheet

Material	A		B
SiC powder	92.5		80
Sintering additives			
Al	4.5	Al_2O_3	14
B	0.9	Y_2O_3	4
C	2.1	CaO	2
Subtotal	100		100
Dispersing agent [a]	7		4
Binder [a]	15		16
Plasticizer [a]	7		11

[a] Amount of dispersing agent, binder and plasticizer added to above powders.

was used as the reinforcement. The thickness of BN-coating was 0.4 μm. These cloths were cut into 35 × 35 mm^2 square and vacuum impregnated with slurry obtained by diluting the slurry for tape casting with ethanol for 15 min. The slurry-impregnated cloths were dried at 50°C. This impregnation-drying process was repeated once again. The green sheets and the cloths were stacked alternately and heat-treated at 300°C for 15–24 h under a pressure of 0.02 MPa. The stacked green body was hot-pressed at 1750°C in Ar under a pressure of 40 MPa. Holding time was 1, 2 and 4 h. Fiber volume fraction of the composites with Al–B–C and with Al_2O_3–Y_2O_3–CaO additives were about 30% and 40%, respectively.

Hot-pressed specimens were cut into rectangular bars (A : 3.5 mm × 1.8 mm × 34 mm, B : 3.5 mm × 2.6 mm × 34 mm). Bulk density was measured by Archimedes' method. Three-point bending strength measurement was carried out with a crosshead speed of 0.1 mm/min and a span of 30 mm at room temperature. Microstructure of fracture surface was observed by scanning electron microscopy (SEM).

3. Results and discussion

3.1. Density of SiC/SiC$_f$ composite

Silicon carbide is a highly covalent-bonded compound. Therefore, it is difficult to densify SiC without sintering additives. There are a lot of investigations to find effective sintering additives.

Al–B–C system is an effective sintering additive for the densification of SiC at relatively low temperature [19,20]. The mechanism of densification in the Al–B–C system was reported that liquid phase assisted sintering of SiC. The ternary compound $Al_8B_4C_7$, whose melting point is less than 1780°C [22], was reported to be formed in a sintered body. The high temperature eutectic of the oxides based on Si–Al–Y–Ca–O is an effective densification additive for the fine-grained β-SiC at relatively low temperature [21]. In this case, densification also proceeds via liquid phase sintering mechanism.

Fig. 2 shows bulk density of SiC/SiC$_f$ composites hot-pressed for various sintering time. The composites with Al–B–C additives (composite A) and with Al_2O_3–Y_2O_3–CaO additives (composite B) fabricated by this process achieved nearly full density. Bulk density of composite A with BN-coated Hi-Nicalon cloths was lower than with non-coated Hi-Nicalon cloths. The difference in bulk density between these composites is considered to be caused by the presence of BN, which has low-chemically active nature, in the composite. Therefore, BN reduced the sinterability of the composite, resulting in decrease in bulk density. On the contrary, in the case of composite B, bulk density of all composites were nearly the same and not influenced by using BN-coated Hi-Nicalon cloths. The discussion of this result is presented in the next section.

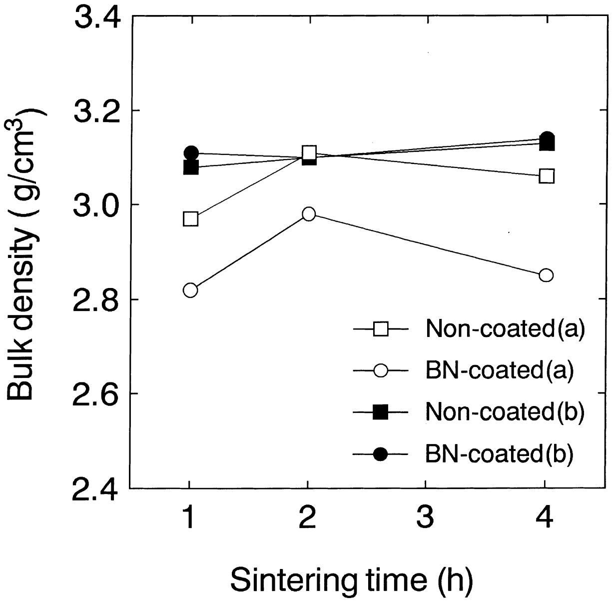

Fig. 2. Bulk density of SiC/SiC$_f$ composite with: (a) Al–B–C and (b) Al_2O_3–Y_2O_3–CaO system as sintering additives fabricated by hot-pressing at 1750°C for various sintering time.

3.2. Fracture behavior and microstructure

Fig. 3 shows load-displacement curves of composite A hot-pressed for 2 h in the three-point bending strength measurement at room temperature. The load-displacement behavior of the composite with non-coated Hi-Nicalon cloths showed brittle fracture, whereas that of the composite with BN-coated Hi-Nicalon cloths showed ductile fracture. The maximum strength of the composite with non-coated and BN-coated Hi-Nicalon cloths were 240 and 168 MPa, respectively. In the case of the composites hot-pressed for 1 and 4 h, the load-displacement curves were similar to that of the composites hot-pressed for 2 h and did not show much difference in maximum strength.

SEM photographs of fracture surface of the composite A hot-pressed for 2 h are shown in Fig. 4. In the case of the composite with non-coated Hi-Nicalon cloths (Fig. 4 (a)), fracture surface of the composite is smooth and the cloth layers are not so clear. On the other hand, Fig. 4 (b) shows the fracture surface of the composite with BN-coated Hi-Nicalon cloths, where a lot of fiber pull-out are observed. It was considered that the bonding strength of the composite with BN-coated Hi-Nicalon cloths between matrix and fiber was weaker than that of composite with non-coated Hi-Nicalon cloths.

Fig. 5 shows load-displacement curves of composite B hot-pressed for 2 h. The load-displacement behavior of both composites with non-coated and BN-coated Hi-Nicalon cloths showed brittle fracture and the maximum strength were 277 and 226 MPa, respectively. In the case of the composite with non-coated Hi-Nicalon cloths, the load-displacement curve showed small tails after first matrix-cracking and large drop of load. The composites hot-pressed for 1 and 4 h showed similar fracture behavior as shown in Fig. 5.

SEM photographs of fracture surface of the composite B hot-pressed for 2 h are shown in Fig. 6. In the case of the composite with non-coated Hi-Nicalon cloths, short fiber pull-out were observed (Fig. 6 (a)), whereas the composite with BN-coated Hi-Nicalon cloths was fractured catastrophically without fiber pull-out (Fig. 6 (b)). These results indicate that the bonding strength of the composite with BN-coated Hi-Nicalon cloths between matrix and fiber was stronger than that of the composite with non-coated Hi-Nicalon cloths. It was suggested that the components such as sintering additives in the matrix reacted with BN-coating on the surface of fibers. Shimpo et al. [23] reported that densification of an AlON–BN composite could be promoted by using Y_2O_3 as a sintering additive and the crystalline YAG phase bound both AlON and BN phases strongly. YAG phase was detected in the composite B by the X-ray diffraction. As a result, the sinterability of the composite B with BN-coated Hi-Nicalon cloths was higher than the case of the composite A, and the bulk density of composite B with non-coated and BN-coated Hi-Nicalon cloths showed nearly the same. In order that BN cannot react with the components in the matrix and a lot of fiber pull-out take place, further improvement of

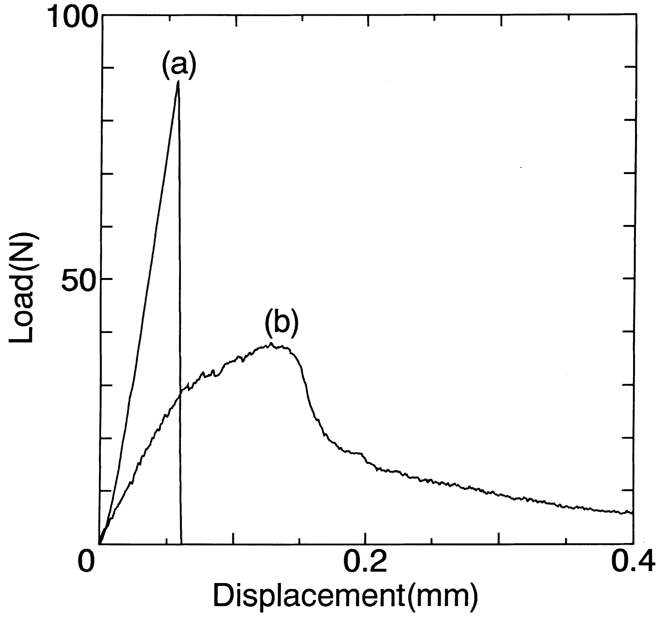

Fig. 3. Load-displacement curves of the composites with Al–B–C additives fabricated by hot-pressing at 1750°C for 2 h. (a) Non-coated and (b) BN-coated Hi-Nicalon cloths were used as the reinforcement.

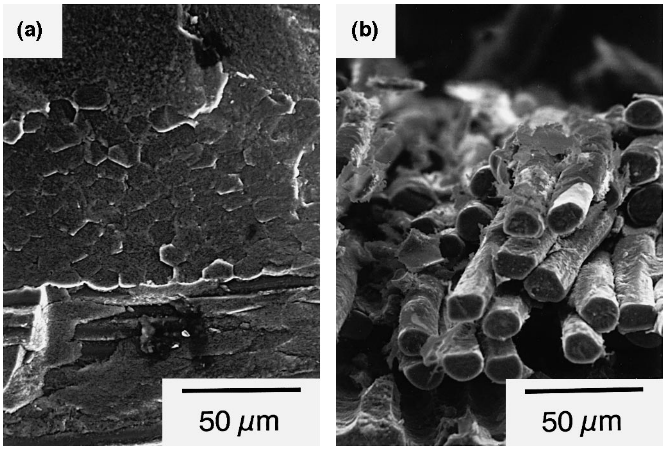

Fig. 4. SEM photographs of fracture surface of the composites with Al–B–C additives fabricated by hot-pressing at 1750°C for 2 h. (a) Non-coated and (b) BN-coated Hi-Nicalon cloths were used as the reinforcement.

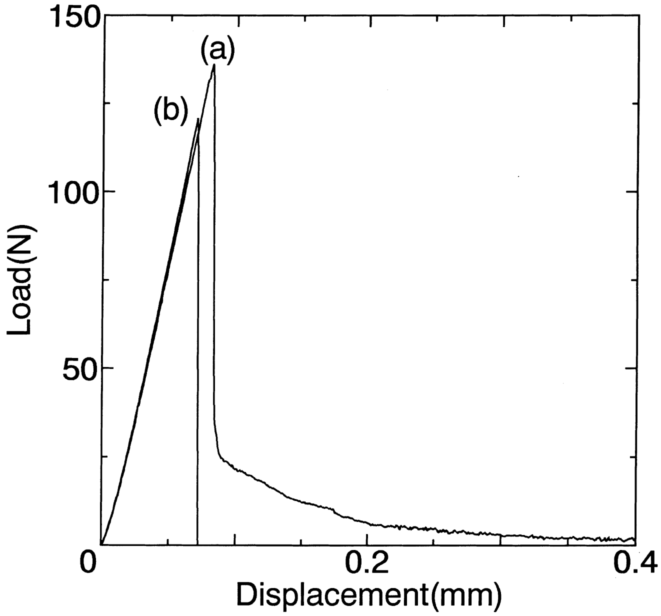

Fig. 5. Load-displacement curves of the composites with Al_2O_3–Y_2O_3–CaO additives fabricated by hot-pressing at 1750°C for 2 h. (a) Non-coated and (b) BN-coated Hi-Nicalon cloths were used as the reinforcement.

the interface between BN-coating on the surface of fibers and the matrix is needed.

4. Conclusion

Continuous 2D woven fiber-reinforced SiC composites were fabricated by hot-pressing in Ar at 1750°C under a pressure of 40 MPa. Using additive system consisted of Al–B–C or Al_2O_3–Y_2O_3–CaO, the composites achieved nearly full density. In the case of the composite with Al–B–C additives, the load-displacement behavior of the composite with non-coated Hi-Nicalon cloths showed completely brittle fracture without fiber pull-out, whereas that of the composite with BN-coated Hi-Nicalon cloths showed ductile fracture and a lot of fiber pull-out were observed.

On the contrary, in the case of the composite with Al_2O_3–Y_2O_3–CaO additives, the load-displacement behavior of the composite with non-coated Hi-Nicalon

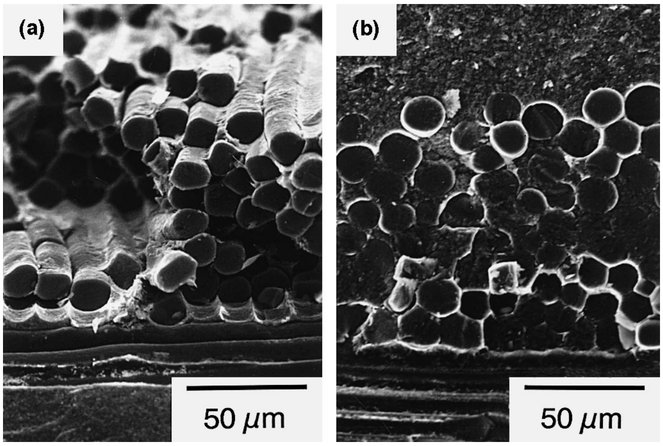

Fig. 6. SEM photographs of fracture surface of the composites with Al_2O_3–Y_2O_3–CaO additives fabricated by hot-pressing at 1750°C for 2 h. (a) Non-coated and (b) BN-coated Hi-Nicalon cloths were used as the reinforcement.

cloths showed slight ductile fracture with small tails and short fiber pull-out, whereas that of the composite with BN-coated Hi-Nicalon cloths showed completely brittle fracture. It was considered that the components such as sintering additives in the matrix reacted with BN-coating on the surface of fibers and this reaction made bonding between the matrix and the fiber so strong. In order that BN cannot react with the components in the matrix, further improvement of the interfacial structure is needed.

Acknowledgements

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References

[1] G.R. Hopkins, R.J. Price, Nucl. Eng. Design/Fusion 2 (1985) 111.
[2] R.H. Jones, C.H. Henger Jr., G.W. Hollenberg, J. Nucl. Mater. 191–194 (1992) 75.
[3] L.L. Snead, S.J. Zinkle, and, D. Steiner, J. Nucl. Mater. 191–194 (1992) 560.
[4] P. Fenici, H.W. Scholz, J. Nucl. Mater. 212–215 (1994) 60.
[5] H.W. Scholz, M. Zucchetti, K. Casteleyn, C. Adelhelm, J. Nucl. Mater. 212–215 (1994) 655.
[6] L.L. Snead, R.H. Jones, A. Kohyama, P. Fenici, J. Nucl. Mater. 233–237 (1996) 26.
[7] S.D. Harrison, J.C. Corelli, J. Nucl. Mater. 122&123 (1984) 833.
[8] J.C. Corelli, J. Hoole, J. Lazzaro, C.W. Lee, J. Am. Ceram. Soc. 66 (1983) 529.
[9] R.J. Price, Nucl. Technol. 35 (1977) 320.
[10] C.H. Wu, J.P. Bonal, B. Kryger, J. Nucl. Mater. 208 (1994) 1.
[11] T. Suzuki, T. Yano, T. Mori, H. Miyazaki, T. Iseki, Fusion Technol. 27 (1995) 314.
[12] P.J. Lamicq, G.A. Bernhart, M.M. Dauchier, J.G. Mace, Am. Ceram. Soc. Bul. 65 (1986) 336.
[13] E. Fitzer, R. Gadow, Am. Ceram. Soc. Bull. 65 (1986) 326.
[14] T.M. Besmann, Ceram. Trans. 58 (1995) 1.
[15] A. Kamiya, K. Nakano, N. Terazawa, Y. Nishino, H. Ichikawa, J. Ceram. Soc. Japan 103 (1995) 191.
[16] K. Nakano, K. Sasaki, H. Saka, M. Fujikura, H. Ichikawa, Ceram. Trans. 58 (1995) 215.
[17] K. Park, T. Vasilos, J. Mater. Sci. 32 (1997) 295.
[18] T. Yano, Budiyanto, K. Yoshida, T. Iseki, Fusion Eng. Design, to be published.
[19] B.-W. Lin, M. Imai, T. Yano, T. Iseki, J. Am. Ceram. Soc. 69 (1986) C67.
[20] J.J. Cao, W.J. MoberlyChan, L.C. De Jonghe, C.J. Gilbert, R.O. Ritche, J. Am. Ceram. Soc. 79 (1996) 461.
[21] M. Mitomo, Y.W. Kim, H. Hirotsuru, J. Mater. Res. 11 (1996) 1601.
[22] Y. Inomata, H. Tanaka, Z. Inoue, H. Kawabata, J. Ceram. Soc. Japan 88 (1980) 353.
[23] A. Shimpo, H. Ide, M. Ueki, J. Ceram. Soc. Japan 100 (1992) 504.