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Effect of Additive Amount on Microstructure and Fracture Toughness of SiC-TiC Composites

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Powder mixtures of β-SiC-TiC in a weight ratio of 2:1 containing 5-20 wt% additives (Al_2O_3+Y_2O_3) were liquid-phase sintered at 1830°C for 1 h by hot-pressing and subsequently annealed at 1950°C for 6 h to enhance grain growth. The annealed specimens revealed a microstructure of "*in situ*-toughened composite" as a result of the β→α phase transformation of SiC during annealing. The increase of the content of additives accelerated the growth of elongated α-SiC grains with higher aspect ratio and improved fracture toughness. The fracture toughness of SiC-TiC composite containing 20 wt% additive was 6.2 MPa·$m^{1/2}$.

Key words: Silicon carbide-titanium carbide composite, Microstructure, Fracture toughness, Additive

I. Introduction

Densification of SiC-based composites such as SiC-TiB_2 and SiC-TiC without the aid of high pressure or sintering additives is very difficult owing to the covalently bonded nature of SiC and the presence of an inert second phase (TiC). Therefore, sintering additives such as metals or oxides are usually added to densify the composites.[1-3] SiC-TiC composites, consisting of finely dispersed TiC grains in a SiC matrix, can be fabricated by hot-pressing with the aid of Al or Al compound and C to a nearly full density at 2000°C[4,5] or with the aid of Al_2O_3 and Y_2O_3 at 1850°C.[6] The role of additives during the sintering of non-oxide ceramics can be regarded as not only densification aids but also key elements for microstructural development since the mechanical properties of the ceramics are influenced by the microstructure, the type and the amount of additives.[7-9]

Several studies have been reported on *in situ*-toughened SiC-TiC composites with a microstructure consisting of elongated SiC grains and matrix-like TiC grains: the fabrication of SiC-TiC nanocomposites with needle-like microstructure by chemical vapor deposition;[10,11] the addition of Cr_3C_2 for transient liquid-phase sintering;[12] the addition of liquid-forming additives (Al_2O_3-Y_2O_3) and subsequent heat-treatment for controlled grain growth.[13,14] A fracture toughness of 6.2 MPa·$m^{1/2}$ was reported in SiC-30 wt% TiC composites sintered with a Cr_3C_2 additive[12] and a higher fracture toughness of 6.9 MPa·$m^{1/2}$ was achieved in SiC-30 wt% TiC composites prepared with Al_2O_3-Y_2O_3 additives.[13]

In this study, the influence of additive amount on microstructure and fracture toughness of SiC-TiC composites containing Al_2O_3-Y_2O_3 sintering additives is investigated. The Al_2O_3-Y_2O_3 mixture (7:3 in weight ratio) is selected because of its effectiveness, compared to other additives, since it decreases the softening temperature and viscosity of the secondary phase during liquid-phase sintering of SiC ceramics.[15]

II. Experimental Procedure

Commercially available β-SiC (Ultrafine grade, Ibiden Co., Ltd, Nagoya, Japan), TiC (Grade C.A.S, H. C. Starck, Berlin, Germany), Al_2O_3 (AKP-30, Sumitomo Chemicals, Tokyo, Japan) and Y_2O_3 (Grade Fine, H. C. Starck, Berlin, Germany) powders were used as starting powders. Three batches of powders were mixed, containing 5, 10 and 20 wt% of additive (Al_2O_3:Y_2O_3 in a weight ratio of 7:3), respectively. All batches were milled in ethanol for 24 h in a polyethylene jar using SiC balls. The weight ratio of SiC to TiC in each batch was fixed as 2:1. The batch compositions and the sample designations are given in Table 1. The milled slurry was dried, sieved and hot-pressed at 1830°C for 1 h under a pressure of 25 MPa in an argon atmosphere. The heating rate was 20°C/min and the cooling rate was ~50°C/min at temperatures from 1800°C to 1200°C. The hot-pressed SiC-TiC composites were subsequently heat-treated at 1950°C for 6 h under argon to enhance the grain growth and the β→α phase transformation of SiC.

The sintered density was determined by the Archimedes method. The theoretical densities (3.66 g/cm^3 for A5, 3.68 g/cm^3 for A10 and 3.74 g/cm^3 for A20, see Table 1) of the composites were calculated according to the rule of mixtures. Crystalline phases in the sintered specimens were determined by X-ray diffraction (XRD) using CuKα radiation. The polished and the etched microstructures were observed by scanning electron microscopy (SEM). The length and

Table 1. Relative Density and Polytype of Hot-Pressed and Annealed SiC-TiC Composites

Sample designation*	Composition (wt %)				Relative density (%)	Crystalline phase	
	SiC	TiC	Al_2O_3	Y_2O_3		Major	Minor
H5	63.3	31.7	3.5	1.5	98.5	β-SiC, TiC	
H10	60	30	7	3	98.3	β-SiC, TiC	YAG**
H20	53.3	26.7	14	6	98.4	β-SiC, TiC	YAG
A5	63.3	31.7	3.5	1.5	98.1	α-SiC, TiC	
A10	60	30	7	3	97.0	α-SiC, TiC	YAG
A20	53.3	26.7	14	6	95.1	α-SiC, TiC	YAG

*H and A denote the hot-pressed and the annealed samples, respectively.
**$Y_3Al_5O_{12}$ (yttrium aluminum garnet)

diameter of SiC grains were determined from the longest and the shortest grain diagonals in two-dimensional images, respectively.[16,17] The fracture toughness was estimated by measuring the lengths of cracks that were generated by a Vickers indentor with a load of 196 N.[18]

III. Result and Discussion

The characteristics of both the hot-pressed and the annealed SiC-TiC composites are listed in Table 1. Relative densities of >98% were achieved by hot-pressing with a holding time of 1 h at 1830°C. However, 6 h-annealing at 1950°C resulted in a decrease of the relative density, probably due to the formation of volatile components such as AlO, Al_2O and CO.[19] Densities of the hot-pressed specimens were not affected by the additive amount, but after annealing higher additive concentration resulted in lower relative densities because of increased volatilization of additives during annealing. XRD results of the hot-pressed specimens showed that the major phases of each specimen were β-SiC and TiC (Table 1) and a trace of $Y_3Al_5O_{12}$ (YAG). In contrast, the annealed specimens contained α-SiC and TiC as a major phase and YAG as a trace, indicating the occurrence of the β→α phase transformation of SiC during annealing.

Fig 1. shows the microstructure of the hot pressed (H10) and annealed (A5, A10, A20) SiC-TiC composites with different amount of additives. The bright phase is TiC and the dark phase is SiC. The hot-pressed composite is a two phase particulate composite that consists of randomly distributed TiC grains whose diameters range from 0.4 to 5 μm in the relatively fine and equiaxed SiC matrix. The other hot-pressed specimens showed microstructures similar to Fig. 1(a). After annealing at 1950°C for 6 h, the marked growth of α-SiC is observed because the β→α phase transformation of SiC leads to the in situ growth of elongated α-SiC grains during annealing. The morphology of TiC grains was changed from equiaxed to matrix-like grains during annealing, as shown in Fig. 1. This is due to the brittle-ductile

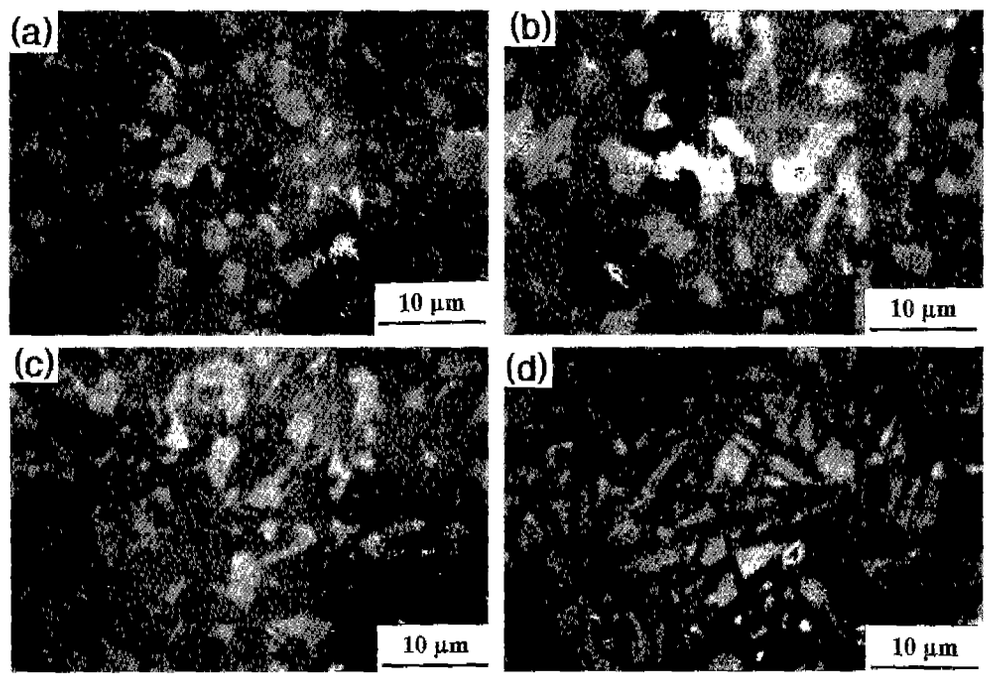

Fig. 1. Microstructures of hot-pressed and annealed specimens: (a) H10, (b) A5, (c) A10 and (d) A20.

Table 2. Grain Diameter and Aspect Ratio of SiC Grains in the Hot-Pressed and Annealed SiC-TiC Composites

Sample designation	Diameter (μm)	Aspect ratio
A5	1.8	5.0
A10	1.1	6.8
A20	0.8	9.0

transition of TiC at ~800°C,[20] yielding to the growth of elongated α-SiC grains. The morphology of α-SiC grains was dependent on the amount of the additive; aspect ratio of SiC grains increased from 5.0 for A5 to 9.0 for A20 with increasing the content of the additive (Table 2), probably due to the reduced impingement of grains at higher additive concentration. The diameter of SiC grains decreased from 1.8 μm for A5 to 0.8 μm for A20 with increasing the amount of the additive.

The fracture mode of SiC-TiC composites containing Al_2O_3-Y_2O_3 additives was mostly intergranular (Fig. 2), as a result of a weak interface caused by the difference between the coefficients of thermal expansion of the liquid and the SiC and/or TiC grains on cooling after annealing. Present results suggest that the Al_2O_3-Y_2O_3 additive is one of the effective additives for *in situ*-toughened SiC-TiC composites due to the formation of a tortuous crack path and intergranular fracture of composites.

The fracture toughness of hot-pressed SiC-TiC composites is shown in Fig. 3 as a function of the additive concentration. The fracture toughness increased as the content of additive increased for both the hot-pressed and the annealed specimens and a maximum value of 6.2 MPa·m$^{1/2}$

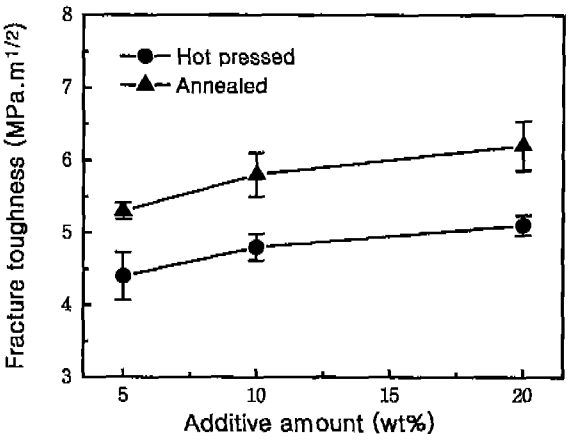

Fig. 3. Fracture toughness of SiC-TiC composites as a function of additive amount.

was observed for annealed specimens when 20 wt% of additives were added. The increase in fracture toughness with increasing additive content may be related to the following two factors: (1) microstructure of the composites; when relatively higher amount of additives were added, the SiC grains had higher aspect ratio because the Al_2O_3-Y_2O_3 additive accelerated the growth of elongated SiC grains. The SiC grains with high aspect ratio is beneficial for toughening with the aids of crack deflection and bridging, which is believed to be operated in this system;[13] (2) the increased tendency for intergranular fracture in specimens containing higher extent of additive; when relatively higher content of additives were added, weak interface boundaries due to thermal expansion mismatch between the liquid (Al_2O_3-Y_2O_3-SiO_2 glass) and SiC and/or TiC were maintained after

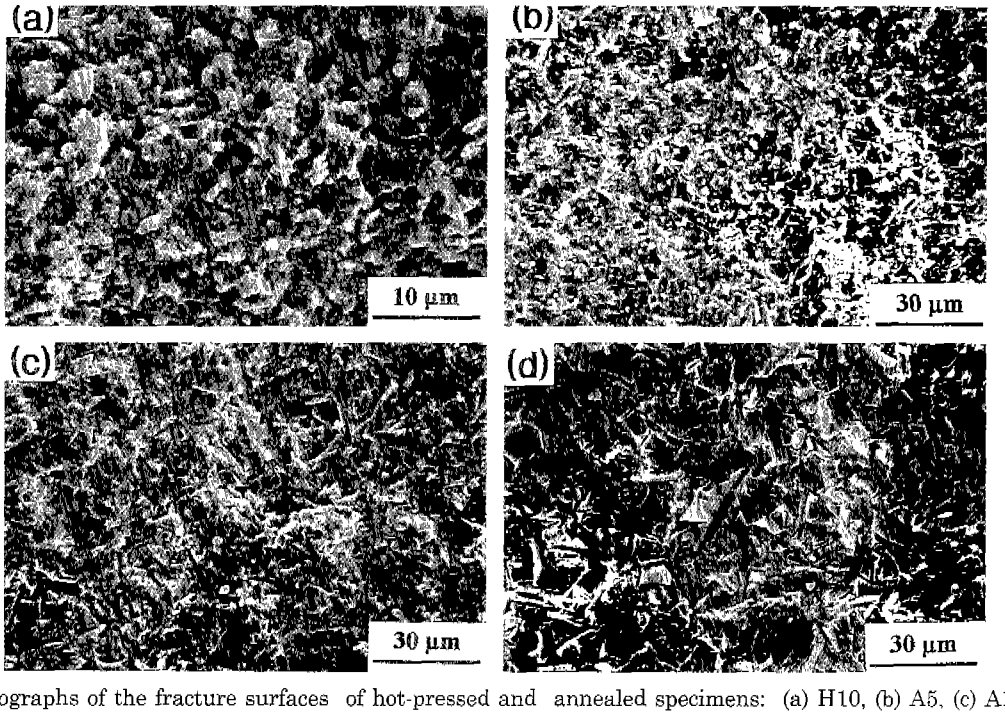

Fig. 2. SEM micrographs of the fracture surfaces of hot-pressed and annealed specimens: (a) H10, (b) A5, (c) A10 and (d) A20.

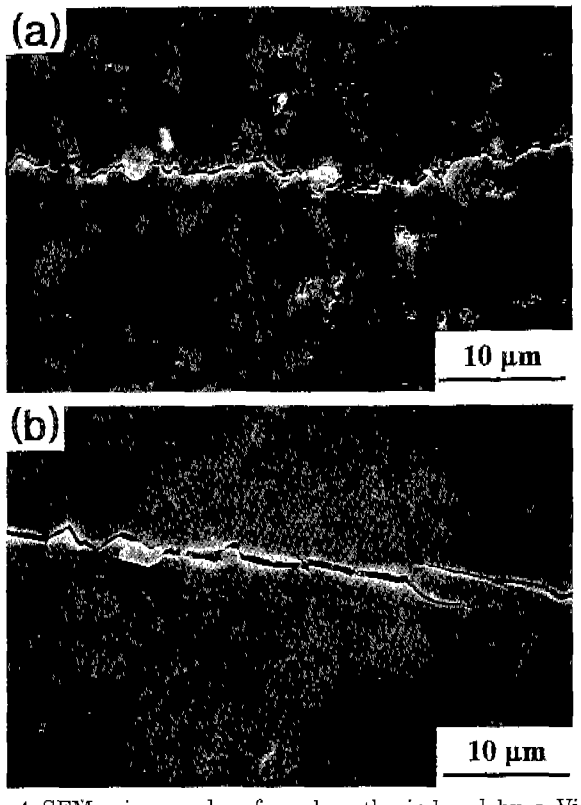

Fig. 4. SEM micrographs of crack paths induced by a Vickers indentor for (a) H10 and (b) A20.

6 h annealing because the sufficient amount of additives is attributed to the enhanced crack bridging and deflection, as observed in Fig. 4. Therefore, it suggests that the optimization of additive amount as well as the additive composition is one of the important parameters for in situ-toughened composites, which was already demonstrated in SiC-TiB^{2}[7]) and SiC-Si_3N_4 composite systems.[21]

IV. Summary

In situ-toughened SiC-TiC composites were fabricated from β-SiC and TiC powders with Al_2O_3-Y_2O_3 additives by hot-pressing and subsequent annealing. The microstructure consisted of uniformly distributed, elongated α-SiC grains and matrix-like TiC grains. The higher extent of additive in the present study accelerated the grain growth of elongated α-SiC grains with higher aspect ratio and maintained the weak interface boundaries after annealing, resulting in the improved fracture toughness. The optimum fracture toughness of SiC-TiC composites containing 20 wt% of Al_2O_3-Y_2O_3 additive was 6.2 MPa·$m^{1/2}$.

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References

1. M. A. Janney, "Microstructural Development and Mechanical Properties of SiC and of SiC-TiC Composites," *Am. Ceram. Soc. Bull.*, **65**(2), 357-362 (1986).
2. Y. Ohya, M. J. Hoffmann and G. Petzow, "Sintering of *In-Situ* Synthesized SiC-TiB_2 Composites with Improved Fracture Toughness," *J. Am. Ceram. Soc.*, **75**(9), 2479-2483 (1992).
3. H. Tanaka and N. Iyi, "Polytypes, Grain Growth and Fracture Toughness of Metal Boride Particulate SiC Composites," *J. Am. Ceram. Soc.*, **78**(5), 1223-1229 (1995).
4. G. C. Wei and P. F. Becher, "Improvements in Mechanical Properties in SiC by the Addition of TiC Particles," *J. Am. Ceram. Soc.*, **67**(8), 571-574 (1984).
5. D. L. Jiang, J. H. Wang, Y. L. Li and L. T. Ma, "Studies on the Strengthening of Silicon Carbide-based Multiphase Ceramics I: The SiC-TiC System," *Mater. Sci. Eng.*, **A109**, 401-406 (1989).
6. K. S. Cho, Y.-W. Kim, H. J. Choi and J. G. Lee, "SiC-TiC and SiC-TiB_2 Composites Densified by Liquid-Phase Sintering," *J. Mater. Sci.*, **31**, 6223-6228 (1996).
7. K. S. Cho, H. J. Choi, J. G. Lee and Y.-W. Kim, "Effects of Additive Amount on Microstructure and Fracture Toughness of SiC-TiB_2 Composites," *Ceram. Int.*, **24**, 299-305 (1998).
8. P. F. Becher, E. Y. Sun, C.-H. Hsueh, K. B. Alexander, S.-L. Hwang, S. B. Waters and C. G. Westmoreland, "Debonding of Interfaces Between β-Silicon Nitride Whiskers and Si-Al-Y Oxynitride Glasses," *Acta Mater.*, **44**(10), 3881-3893 (1996).
9. J. Y. Kim, Y.-W. Kim, M. Mitomo, G. D. Zhan and J. G. Lee, "Microstructure and Mechanical Properties of α-Silicon Carbide Sintered with Yttrium-Aluminum Garnet and Silica," *J. Am. Ceram. Soc.*, **82**(2), 441-444 (1999).
10. F. Gourbilleau, H. Maupas, R. Hillel and J. L. Chermant, "Silicon Carbide-Titanium Carbide Nanocomposites: Microstructural Investigation," *Mater. Res. Bull.*, **29**(6), 673-680 (1994).
11. H. Maupas, J. L. Chermand and R. Hillel, "The Effect of Nanoscale Microstructures on the Mechanical Behavior of Silicon-Carbon-Titanium-Carbon Composites," *Mater. Res. Bull.*, **29**(8), 895-902 (1994).
12. K. W. Chae, K. Niihara and D.-Y. Kim, "Effect of Cr_3C_2 Addition on the Sintering of SiC-TiC Composites," *J. Am. Ceram. Soc.*, **79**(12), 3305-3308 (1996).
13. K. S. Cho, Y.-W. Kim, H. J. Choi and J. G. Lee, "*In Situ*-Toughened Silicon Carbide-Titanium Carbide Composites," *J. Am. Ceram. Soc.*, **79**(6), 1711-1713 (1996).
14. K. S. Cho, H. J. Choi, J. G. Lee and Y.-W. Kim, "Microstructure and Fracture Toughness of *In-Situ* Toughened SiC-TiC Composites," *J. Mater. Sci. Lett.*, **17**, 1081-1084 (1998).
15. N. P. Padture., "*In Situ*-Toughened Silicon Carbide," *J. Am. Ceram. Soc.*, **77**(2), 519-523 (1994).
16. Y.-W. Kim, M. Mitomo and H. Hirotsuru, "Microstructural Development of Silicon Carbide Containing Large Seed Grains," *J. Am. Ceram. Soc.*, **80**(1), 99-105 (1997).
17. Y.-W. Kim, M. Mitomo, H. Emoto and J. G. Lee, "Effect of Initial α-Phase Content on Microstructure and Mechanical

Properties of Sintered Silicon Carbide," *J. Am. Ceram. Soc.*, 81(12), 3136-3140 (1998).
18. G. R. Anstis, P. Chantikul, B. R. Lawn and D. B. Marshall, "A Critical Evaluation of Indentation Techniques for Measuring Fracture Toughness: I, Direct Crack Measurements," *J. Am. Ceram. Soc.*, **64**(9), 533-538 (1981).
19. Y.-W. Kim, H. Tanaka, M. Mitomo and S. Otani, "Influence of Powder Characteristics on Liquid Phase Sintering of Silicon Carbide," *J. Ceram. Soc. Jpn.*, **103**(3), 257-261 (1995).
20. G. Das, K. S. Mazdiyasni and H. A. Lipsitt, "Mechanical Properties of Polycrystalline TiC," *J. Am. Ceram. Soc.*, **65**(2), 104-110 (1982).
21. Y. I. Lee, Y.-W. Kim, H. J. Choi and J. G. Lee, "Effects of Additive Amount on Microstructure and Mechanical Properties of Silicon Carbide-Silicon Nitride Composites," accepted for publication, *J. Mater. Sci.*