

Electrical Resistivity and Fracture Toughness of SiC-ZrB₂

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The mechanical and electrical properties of hot-pressed and annealed β -SiC+39vol.%ZrB₂ electroconductive ceramic composites were investigated as a function of the liquid forming additives of Al₂O₃+Y₂O₃ (6.4wt%). In this microstructures, no reactions and elongated α -SiC grains with equiaxed ZrB₂ grains were observed between β -SiC and ZrB₂. The properties of the β -SiC+39vol.%ZrB₂ composites with 4wt% Al₂O₃+Y₂O₃ at R.T. are as follows: fracture toughness is 6.37 MPa·m^{1/2}, electrical resistivity is $1.51 \times 10^{-4} \Omega \cdot \text{cm}$ and the relative density is 98.6% of the theoretical density. The fracture toughness of the β -SiC+39 vol.%ZrB₂ composites were weakly decreased with increasing amount of Al₂O₃+Y₂O₃ additives. Internal stresses due to the difference of β -SiC and ZrB₂ thermal expansion coefficient and elastic modulus mismatch appeared to contribute to fracture toughening in β -SiC+39 vol.%ZrB₂ electroconductive ceramic composites.

Key words: β -SiC+39 vol.%ZrB₂ composites, Fracture toughness, Electrical resistivity, Internal stresses, Elastic modulus

I. Introduction

SiC semiconducting ceramics have a high temperature strength, high melting point of about 2800 °C, intrinsic resistance to oxidation, high thermal conductivity and also a low thermal expansion coefficient of about $4.36 \times 10^{-6} / ^\circ\text{C}$ at 20-1000 °C.¹⁾

However, since SiC does not have PTCR(positive temperature coefficient resistance) character below 1000°C, it does not control current with increasing temperature.²⁾

Also, the moderate fracture toughness (3 ~4 MPa·m^{1/2}) and expensive cost for machining limit their wide applications under stresses of impact.³⁾

ZrB₂ ceramics have a high melting point of about 3200°C, high hardness, low electrical resistance and excellent corrosion resistance against molten and slag.⁴⁾

Therefore, dispersing particles such as ZrB₂ satisfy the above demerits without losing SiC matrix's original superior characteristics.

SiC-ZrB₂ ceramic composites are one of the most promising candidate materials for heater and ignitors because of its high strength, superior oxidation resistance at high temperature and high electrical conductivity. The first two properties are due to the SiC characteristics and the third is due to ZrB₂ characteristics.⁵⁾

The improvement of fracture toughness was achieved through the development of elongated α -SiC grains.⁶⁻⁷⁾

In this study, the composites were fabricated from 61 vol.% β -SiC and 39 vol.%ZrB₂ powders with the liquid forming additives of Al₂O₃-Y₂O₃ by hot pressing at 1850 °C and subsequent annealing at 1950 °C to develop the grow-

th of elongated α -SiC grains.

The electrical and mechanical properties of the β -SiC+39 vol.%ZrB₂ ceramic composites with Al₂O₃+Y₂O₃ additives were investigated to evaluate the effect of porosity and aspect ratio on the electrical resistivity and fracture toughness of samples.

II. Experimental Procedure

High pure β -SiC(H. C. Starck, Germany, Grade BF12), ZrB₂(H. C. Starck, Germany, Grade B), Al₂O₃(Showa Chemical Inc., Japan) and Y₂O₃(Aldrich Chemical Inc., U.S.A.) were used as starting powders. The powder mixture of β -SiC+39vol.%ZrB₂ containing 4wt% Al₂O₃+Y₂O₃ (6:4 mixture of Al₂O₃ and Y₂O₃, designated as SZ-AY₄), 8wt% (SZ-AY₈) and 12wt% (SZ-AY₁₂) as the liquid forming additives were planetary-ball-milled using a polyurethane jar of diameter 120 mm Φ and height 140 mmL (volume: 1583.4 ml) and a high purity SiC ball of diameter 10 mm Φ , 20 mm Φ (1:1 wt%) in acetone.

The planetary-ball-milled conditions of each batch were as follows: the ratio of starting powder containing acetone: SiC balls was fixed 1:5 charge, milling time 24 h, rotating speed of mill 22 rpm.

The milled slurry was dried at 80°C for 6h and sieved through a 60 mesh screen.

The mixed powders were hot-pressed (Astro California, U.S.A.) in a graphite die of diameter 30 mm Φ , the inner surfaces of which were coated with high purity graphite foil to prevent sticking of the material to the die walls or between the samples

The hot-pressing was performed at 1850°C for 3 min with an applied pressure of 25 MPa and subsequently annealed at 1950°C for 4 h in flowing argon to enhance the grain growth of ZrB₂ and the elongated grain of α -SiC.

The heating rate was fixed at 10°C/min up to 1950°C and the cooling rate was fixed 12.8°C/min up to 20°C in flowing argon.

Densities were measured using the Archimedes method and the theoretical densities of the β -SiC+39 vol.%ZrB₂ composites with Al₂O₃+Y₂O₃ were calculated according to the rule of mixture (3.217g/cm³ for β -SiC, 6.085 g/cm³ for ZrB₂, 3.978g/cm³ for Al₂O₃ and 5.01 g/cm³ for Y₂O₃).

Phase identifications of the sintered samples were determined by XRD (PW1700 System, Philips, U.S.A.) with CuK α radiation.

The microstructure of the etched surface and crack propagation of the samples were observed by SEM(JSM-840 A, Jeol, Japan).

The polished samples were etched by boiling Murakami's reagent for 20 min.¹⁰

The test samples for fracture toughness measurements were polished using diamond suspension to 0.1 μ m finish.

The fracture toughness were estimated measuring crack lengths generated by Vicker's indenter (Matsuzawa, Model DVK-2, Japan) with a load 20 kgf, load speed 40 μ m/sec and holding time 10 sec.

The fracture toughness K_{IC} was calculated from A.G. Evans & T. R. Wilshaw's equation.¹¹

The grain size and aspect ratio of the grain for the sintered samples were measured using a linear-intercept method.

The test pieces for electrical resistivity measurements were cut using wire-EDM(Electrical Discharge Machining) by the Pauw method.¹²

III. Results and Discussion

The relative densities of $\geq 97.6\%$ of the theoretical densities in all of the samples achieved by hot pressing at 1850°C with an applied pressure of 25 MPa and subsequently annealing at 1950°C for 4 h.

The relative densities decreased (98.6 \rightarrow 98.4 \rightarrow 97.6%) with increased Al₂O₃+Y₂O₃ contents.

The more amounts of Al₂O₃+Y₂O₃ additives increase, the more porosities according to chemical reaction are increase. Therefore, relative densities are affected porosities due to volatile species Al₂O(g), Y₂O(g), SiO(g) and CO(g) with the result of reaction between β -SiC and Al₂O₃+Y₂O₃.

Al₂O₃ and Y₂O₃ additives in the sintering of SiC are known to form liquid phase with the surface SiO₂ of SiC and to promote densification through liquid-phase sintering.^{10,13}

Al₂O₃ and Y₂O₃ additives play an important role in the successful densification of the β -SiC+39vol.%ZrB₂ composites through liquid-phase sintering but porosities are weakly enhanced with increased Al₂O₃+Y₂O₃ contents.

Phase analyses of SZ-AY₁, SZ-AY₈ and SZ-AY₁₂ composites by XRD revealed mostly of α -SiC(6H, 4H), ZrB₂ and weakly β -SiC(15R) phase. It is well documented that the $\beta \rightarrow \alpha$ phase transformation of SiC takes place after annealing at 1950°C for 4h through liquid phase sintering.

β -SiC and ZrB₂ are not solid solution but a two phase particulate composites consisted of equiaxed ZrB₂ grain in the elongated α -SiC matrix.

Fig. 1 shows the microstructure by SEM of the etched surface of the β -SiC+39 vol.%ZrB₂ composites with Al₂O₃+Y₂O₃ contents. The elongated α -SiC and the equiaxed ZrB₂ phases are distinct as shown in Fig. 1: the white phase is the ZrB₂ and the gray phase is the α -SiC matrix.

The diameter of each grain (d) was determined directly from the shortest grain diagonal in its two-dimensional

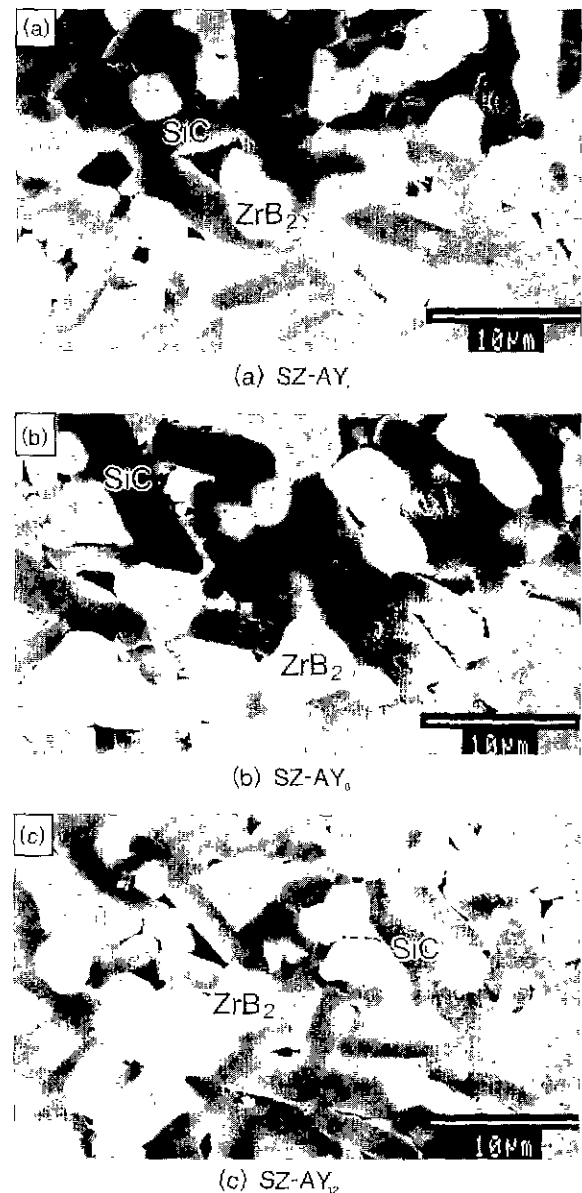
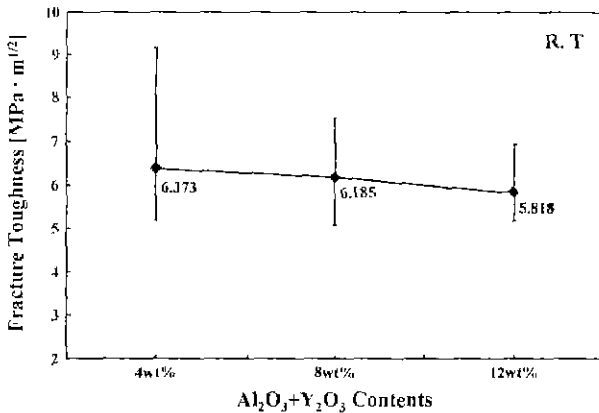


Fig. 1. SEM micrographs of the etched surface of SZ-AY₁ (a), SZ-AY₈ (b) and SZ-AY₁₂ (c).

Table 1. Average Grain Size of α -SiC and ZrB₂

Sample	α -SiC		ZrB ₂ [μ m]
	Aspect Ratio	Length[μ m] \times Diameter[μ m]	
SZ-AY ₄	3.12	7.46 \times 2.39	5.29
SZ-AY ₈	3.39	11.32 \times 3.93	7.10
SZ-AY ₁₂	5.08	11.79 \times 2.32	6.21

**Fig. 2.** Fracture toughness of the β -SiC+39 vol.%ZrB₂ with Al₂O₃+Y₂O₃ contents.

image, the apparent length of each grain (L) was obtained from the longest diagonal. The mean value of the observed aspect ratios (L/d) of about 50% was considered to be the mean of the actual values as shown in Table 1.

The fracture toughness decreased with increased Al₂O₃+Y₂O₃ contents and showed the highest of 6.37 MPa · m^{1/2} for SZ-AY₄ composite as shown in Fig. 2.

The fracture toughness of the β -SiC+39 vol.%ZrB₂ composites with the liquid forming additives Al₂O₃+Y₂O₃ of the annealing at 1950°C for 4 h is $\geq 28\%$ higher than that of hot-pressed composites (4.55 MPa · m^{1/2}).¹⁴

The fracture toughness of SZ-AY₈ and SZ-AY₁₂ were lower than that of SZ-AY₄ composites, although the length and width of α -SiC grains were increased.

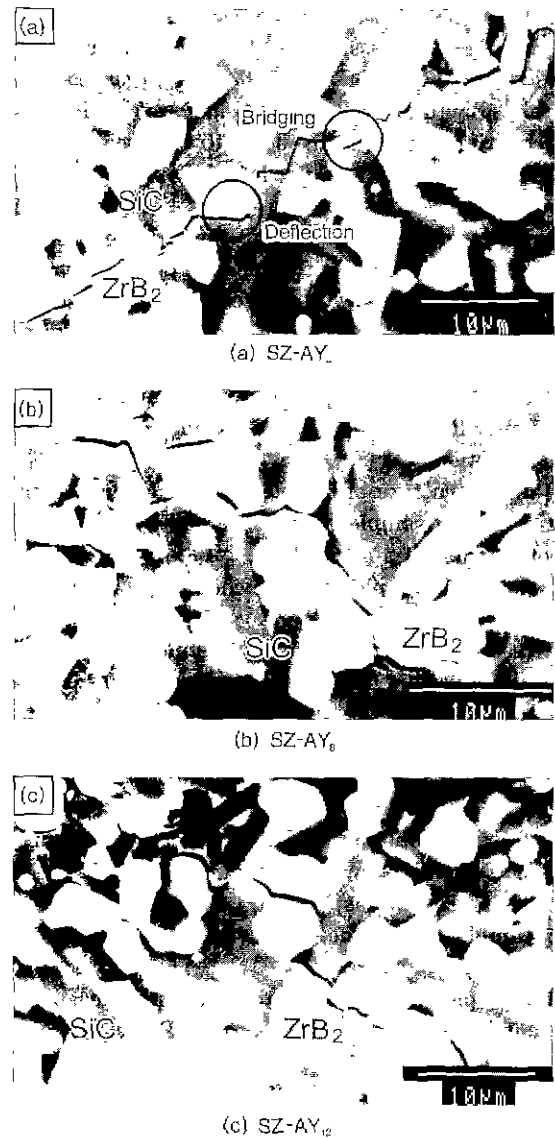
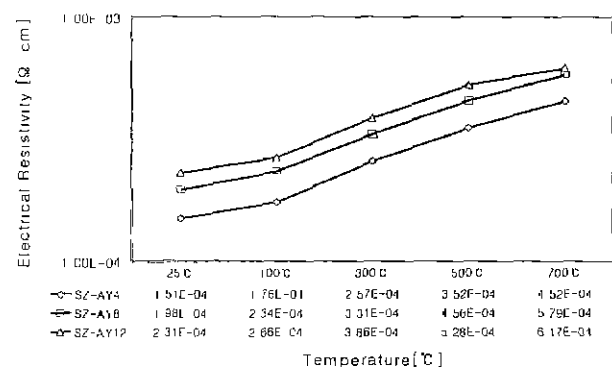
This may be attributed to the increasing tendency of pore formation according to amount of the liquid forming additives Al₂O₃+Y₂O₃.

The improved fracture toughness was attributed to the enhanced bridging and crack deflection by the elongated α -SiC grains as shown in Fig. 3.

Crack deflection around α -SiC particles is likely to be caused by intrinsic residual stresses resulting from differences in thermal expansion coefficient between SiC¹¹($4.36 \times 10^{-6}/^{\circ}\text{C}$ at 20-1000°C) and ZrB₂¹⁵($5.9 \times 10^{-6}/^{\circ}\text{C}$ at 20-1000°C).

Temperature dependence of the electrical resistivity has been investigated by Pauw method¹² for the β -SiC+39 vol.%ZrB₂ composites with the liquid forming additives Al₂O₃+Y₂O₃ as shown in Fig. 4.

The electrical resistivity increased with Al₂O₃+Y₂O₃ contents because of the increasing tendency of pore forma-

**Fig. 3.** Crack propagations of SZ-AY₁ (a), SZ-AY₈ (b) and SZ-AY₁₂ (c)**Fig. 4.** Electrical resistivity of SZ-AY₄, SZ-AY₈ and SZ-AY₁₂.

tion according to amount of liquid forming additives Al₂O₃+Y₂O₃.

The electrical resistivity of SZ-AY₄ composite showed the lowest of $1.51 \times 10^{-4} \Omega \cdot \text{cm}$ among samples at 25°C as shown in Fig. 4, whose electrical resistivity is approximately equal to that of a commercial Ni-Cr heater ($1.11 \times 10^{-4} \Omega \cdot \text{cm}$ at 20°C).

The electrical resistivity of SZ-AY₄, SZ-AY₈ and SZ-AY₁₂ manufactured by hot-pressing at 1850°C with an applied pressure of 25 MPa and subsequently annealing at 1950°C for 4h in order to heat element is all positive temperature coefficient resistance (PTCR) against temperature up to 700°C.

The PTCR of SZ-AY₄, SZ-AY₈ and SZ-AY₁₂ is 4.46×10^{-7} , 5.64×10^{-7} and $5.72 \times 10^{-7} \Omega \cdot \text{cm}/^\circ\text{C}$ in the temperature from 25°C to 700°C respectively.

IV. Conclusion

The composites were fabricated from 61vol.% β-SiC and 39 vol.%ZrB₂ powders with the liquid forming additives of Al₂O₃-Y₂O₃ by hot pressing at 1850°C and subsequent annealing at 1950°C to develop the growth of elongated α-SiC grains.

The fracture toughness decreased with increased Al₂O₃+Y₂O₃ contents and showed the highest of 6.37 MPa·m^{1/2} for composite added with 4 wt% Al₂O₃+Y₂O₃ additives at room temperature. The electrical resistivity increased with increased Al₂O₃+Y₂O₃ contents because of the increasing tendency of pore formation according to amount of liquid forming additives Al₂O₃+Y₂O₃ and showed the lowest of $1.51 \times 10^{-4} \Omega \cdot \text{cm}$ for composite added with 4 wt% Al₂O₃+Y₂O₃ additives at 25°C. The electrical resistivity of composites is all positive temperature coefficient resistance (PTCR) against temperature up to 700°C.

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Reference

1. P. A. Hoffman, "Thermo Elastic Properties of Silicon Carbide-Titanium Diboride Particulate Composites," *M. S. Thesis*, Pennsylvania State University, 1992.

2. H. Hashiguchi and H. Kimugasa, "Electrical Resistivity of α-SiC Ceramics Added with NiO" *J. Ceram. Soc. Japan*, **102**(2), 160-164 (1994).
3. 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).
4. M. Nakamura, I. Shigematsu, K. Kanayama and Y. Hirai, "Surface Damage in ZrB₂-based Composite Ceramics Induced by Electro-Discharge Machining," *J. Mater. Sci.*, **26**, 6078-6082 (1991).
5. K. TakaHashi and R. Jimbou, "Effect of Uniformity on the Electrical Resistivity of SiC-ZrB₂ Ceramic Composites," *J. Am. Ceram. Soc.*, **70**(12), c-369-c-373 (1987).
6. D. L. Jiang, J. H. Wang, Y. L. Li and L. T. Ma, "Studies on the Strengthening of Silicon Carbide-Based Multiphase Ceramics: The SiC-TiC Systems," *Material Science and Engineering*, **109**(A), 401-406 (1989).
7. S. K. Lee and C. H. Kim, "Effect of α-SiC versus β-SiC Starting Powders on Microstructure and Fracture Toughness of SiC Sintered with Al₂O₃-Y₂O₃ Additives," *J. Am. Ceram. Soc.* **77**(6), 1655-1658 (1994).
8. Y. W. Kim, H. Mitomo and H. Hirotsuru, "Grain Growth and Fracture Toughness of Fine-Grained Silicon Carbide Ceramics," *J. Am. Ceram. Soc.*, **78**(11), 3145-3148 (1995).
9. 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).
10. M. A. Mulla and V. D. Kistic, "Pressureless Sintering of β-SiC with Al₂O₃ Additions," *J. Mater. Sci.*, **29**, 934-935 (1994).
11. A. G. Evans and T. R. Wilshaw, "Quasi-Static Solid Particle Damage in Brittle solids-1. Observation Analysis and implication," *Acta Metallurgica.*, **24**, 939-956 (1976).
12. "Philips Research Reports," Philips Res. Repts **13**, 1-9, 1958.
13. T. Grande, H. Sommerset, E. Hagen, K. Wiik and M. A. Einarsrud, "Effect of Weight Loss on Liquid-Phase-Sintered Silicon Carbide," *J. Am. Ceram. Soc.*, **80**(4), 1047-1052 (1997).
14. Y. D. Shin and Y. K. Park, "Properties of Hot-Pressed SiC-ZrB₂ Electro Conductive Ceramic Composites." *Trans. KIEE.*, **46**(4), 566-572 (1997).
15. Y. Kutsukake, "The Development of ZrB₂-Based Cermert," Ceramic Data Book, 687-703, 1987.