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Effect of polycarbosilane addition on mechanical properties of hot-pressed silicon carbide

YOUNG-WOOK KIM, JUNE-GUNN LEE
Structural Ceramics Laboratory, Korea Institute of Science and Technology, PO Box 131, Cheongryang, Seoul, Korea

Silicon carbide ceramics containing 20 wt% polycarbosilane was fabricated by hot-pressing with various additives (B, Al, AlN). The addition of polycarbosilane resulted in a considerable increase in flexural strength up to 1050 MPa for the 1 wt% AlN and 0.5 wt% B-doped specimens and fracture toughness up to 4.0 MPa m$^{1/2}$ for the 1 wt% Al-doped specimen. The improved fracture strength was a result of liquid-phase sintering and the improved toughness was a result of crack deflection along the grain boundaries. Crack branching was also observed in 1 wt% AlN and 0.5 wt% B-doped specimens.

1. Introduction

Silicon carbide is one of the most interesting high-performance ceramic materials due to its excellent strength and oxidation resistance at elevated temperatures [1–3]. Several attempts to improve their strength and reliability have been reported, including grain-boundary oxidation [4], pressure casting [5], preparation of fine-grained materials using polycarbosilane pyrolysis [6], and the use of transient liquids [7].

Recently, organosilicon polymers have attracted considerable attention because they yield very fine crystallites during pyrolysis. Pyrolysis of polycarbosilane yields very fine crystallite sizes of β-SiC in the range 2–100 nm [6]. Furthermore, pyrolysis products of polycarbosilane contain carbon as well as β-SiC. Hence, additional carbon addition as sintering additive will not be necessary for densification.

The objective of the present work was to investigate the effect of polycarbosilane addition on the mechanical properties of hot-pressed silicon carbide. Microstructural observation, X-ray diffraction (XRD), and mechanical property measurements were used to meet this objective.

2. Experimental procedure

The characteristics of the raw materials used in this study are summarized in Table I. Six batches were prepared and their batch compositions are given in Table II.

Polycarbosilane-containing specimens (the PCS series in Table II) were fabricated as follows. Solutions of a polycarbosilane in hexane were prepared. Precalculated amounts of α-SiC powders were then impregnated with these solutions, dried, and pyrolysed at a heating rate of 2 °C min^{-1} under argon with a 1 h hold at 1000 °C. The pyrolysed powders were mixed with various additives in acetone using a WC jar and balls. The mixed slurry was then dried, sieved, and hot-pressed at 1950 °C for 30 min with 35 MPa applied pressure. The SC series batches in Table II were fabricated by a slightly different method. The α-SiC powder was mixed with various additives, dried, sieved, and hot-pressed under the same conditions.

For quantitative chemical analysis, a small amount of polycarbosilane was pyrolysed separately under the same conditions. The silicon content was determined by an inductive coupled plasma method, carbon content by a combustion method, and oxygen content by a carbothermic reduction method. Thermogravimetric analysis (TGA) of polycarbosilane was performed under a continuous argon flow. The pyrolysis residue was analysed using XRD. Crystallite sizes of the pyrolysed powders were determined using the Scherrer equation [8].

Densities were measured using the Archimedes' principle. The volume fraction of SiC polytypes was determined by the relative intensity of certain XRD peaks [9, 10]. The flexural strengths were determined using a three-point rupture test on 3 mm × 4 mm × 25 mm bars whose surfaces and edges were polished with an 800-grit diamond wheel. The fracture toughness was measured using a Vickers indentor with a load of 98 N.

3. Results and discussion

3.1. Polycarbosilane pyrolysis

TGA results for the polycarbosilane are shown in Fig. 1. As shown, the decomposition starts at 300 °C and finishes at 800 °C. The weight residue was 62%. Fig. 2 shows the XRD patterns of polycarbosilane pyrolysed and heat treated at different temperatures.

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TABLE I Characteristics of raw materials

Raw material	Mean particle size (μm)	Supplier	Remarks
B	< 0.1	H. C. Starck, Berlin, Germany	Amorphous
C	20×10^{-3}	Mitsubishi Chemical Industries, Ltd, Tokyo, Japan	Diablack I
Al	< 44	Wako Pure Chemical Industries, Ltd, Tokyo, Japan	Reagent grade
AlN	1.0	H. C. Starck, Berlin, Germany	Grade C
SiC	0.4	Showa Denko, Tokyo, Japan	A-1
Polycarbosilane	Chunk	Nippon Carbon Co. Ltd, Yokohama, Japan	Mean molecular weight 1390

TABLE II Batch compositions of SiC samples

Sample designation	Composition (wt %)
PCS1	80% SiC + 20% polycarbosilane + 1% B
PCS2	80% SiC + 20% polycarbosilane + 1.3% Al
PCS3	80% SiC + 20% polycarbosilane + 2% AlN
PCS4	80% SiC + 20% polycarbosilane + 0.5% B + 1% AlN
SC1	100% SiC + 1% B + 2% C
SC2	100% SiC + 1.3% Al + 2% C

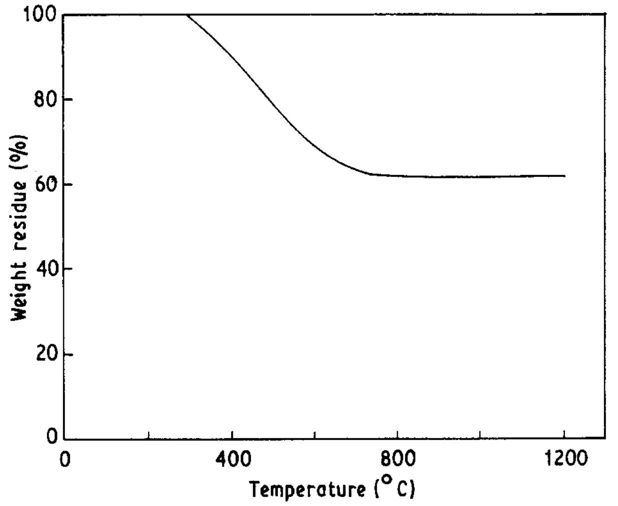

Figure 1 Thermogravimetric analysis of polycarbosilane.

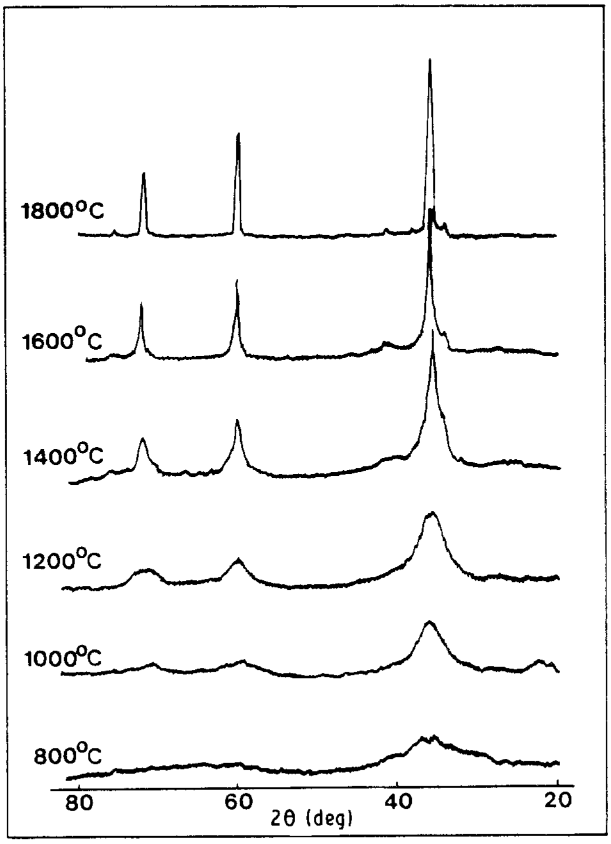

Figure 2 XRD patterns of polycarbosilane pyrolysed and heat treated at different temperatures.

Pyrolysing the polycarbosilane at 1000 °C yields an amorphous powder, crystallization begins above 1200 °C, and the observed broad diffraction peaks can be assigned to β-SiC.

The particle size was calculated using the Scherrer equation

$$t = \frac{0.9\tau}{B \cos \theta_B} \qquad (1)$$

where t is crystallite size, τ is the wavelength, B is the angular width at an intensity equal to half the maximum intensity, and θ_B is the Bragg angle. The results are shown in Table III. As shown, β-SiC crystals grow with increasing temperature and the size range (2–30 nm) was qualitatively consistent with the grain structure observed by scanning electron microscopy (SEM) (Fig. 3).

The chemical analysis results of the pyrolysis residue are shown in Table IV. They indicate that the added polycarbosilane converts to 62% solid residue, which is composed of 80.6% SiC, 4.7% SiO_2, and 12.3% free carbon.

3.2 Mechanical properties

Fig. 4 shows scanning electron micrographs of the fracture surface of SiC ceramics with various additives. The fracture mode of SiC ceramics is seen to depend to a great extent on the additives added. For Al- or AlN-doped materials (PCS2, PCS3, SC2), the fracture mode was found to be intergranular, while for the B-doped materials, (PCS1, SC1) and B + AlN-doped material (PCS4), the fracture mode was found to be transgranular. For Al- or AlN-doped materials

TABLE III Calculated particle sizes of pyrolysis product of polycarbosiline

Heat-treatment temperature (°C)	Angular width at 1/2 I_{max} B (rad)	Bragg angle, θ_B (deg)	Particle size (nm)
800	0.055 82	17.70	2.61
1000	0.054 95	17.75	2.65
1200	0.054 08	17.76	2.69
1400	0.026 17	17.80	5.56
1600	0.010 47	17.81	13.91
1800	0.006 63	17.84	21.97
2000	0.005 23	17.91	27.86

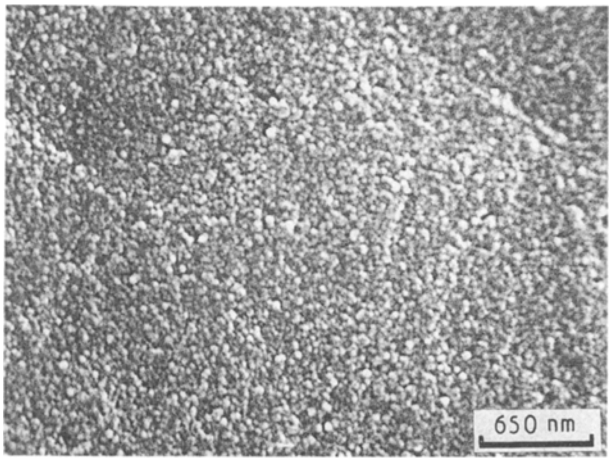

Figure 3 Scanning electron micrograph of pyrolysed polycarbosilane showing grain structure.

TABLE IV Chemical analysis for the pyrolysis residue of polycarbosilane

Ceramic yield (wt %)	Composition (wt %)			SiC content[a] (wt %)
	Carbon	Oxygen	Silicon	
62.0	36.5	2.5	58.6	80.6

[a] Calculated by assigning all oxygen atoms to silicon as silica and residual silicone atoms to carbon as silicon carbide.

(PCS2, PCS3, SC2), the grain boundaries were very clear and the grain shape was equiaxial.

The room and high (1000 °C)-temperature flexural strength and fracture toughness of various samples are summarized in Table V, which shows that polycarbosilane addition has a beneficial effect on the mechanical properties, as expected.

For room-temperature flexural strength, PCS2–PCS4 materials have 30%–50% higher values than SC1 and SC2 materials. The fracture surfaces of strength bars (Fig. 4) indicated that the improved strength was due to both an improvement in density as well as a much finer grain size (1–2 μm) of PCS2–PCS4 materials, as compared to conventionally sintered SiC. It is interesting to note that SC2 material has lower strength than PCS2–PCS4 materials inspite of the almost identical density and grain size with PCS2–PCS4 materials. A major difference between PCS2–PCS4 and SC2 is the content of SiO_2, as shown in Table IV. PCS2–PCS4 materials have much higher content of SiO_2, which is derived from the pyrolysis of polycarbosilane, than SC2 material. It indicates that liquid-phase sintering using the eutectic between Al_2O_3–Al_4C_3 may have occurred, as reported by Jackson *et al.* [7]. Liquid-phase sintering may remove sharp edges which are often the critical stress concentration sites in solid state sintered SiC. Hence, the high strength of PCS2–PCS4 materials may be the direct result of liquid-phase sintering.

For high-temperature flexural strength, no degradation was observed in boron-doped materials (PCS1, SC1) up to 1000 °C, while significant degradation was observed in Al- or AlN-doped materials (PCS2, PCS3, PCS4, SC2). This may be due to the presence of glassy or metallic grain-boundary phases in Al- or AlN-doped materials.

For fracture toughness, Al- or AlN-doped materials (PCS2, PCS3, SC2) have higher values than B-doped materials (PCS1, SC1). As shown in Fig. 4, Al- or AlN-doped materials show intergranular fracture while B-doped materials show transgranular fracture. These

TABLE V Properties of various SiC ceramics

Sample	Density ($g\,cm^{-3}$)	Flexural strength[a]		Fracture toughness[a] ($MPa\,m^{1/2}$)
		RT	1000 °C	
PCS1	3.10	597 ± 55	591 ± 58	2.5 ± 0.2
PCS2	3.21	984 ± 62	575 ± 52	4.0 ± 0.3
PCS3	3.21	1006 ± 73	554 ± 46	3.6 ± 0.2
PCS4	3.21	1050 ± 69	717 ± 55	2.9 ± 0.3
SC1	3.11	623 ± 107	554 ± 90	2.4 ± 0.2
SC2	3.20	752 ± 98	458 ± 79	3.5 ± 0.2

[a] Average of six samples.

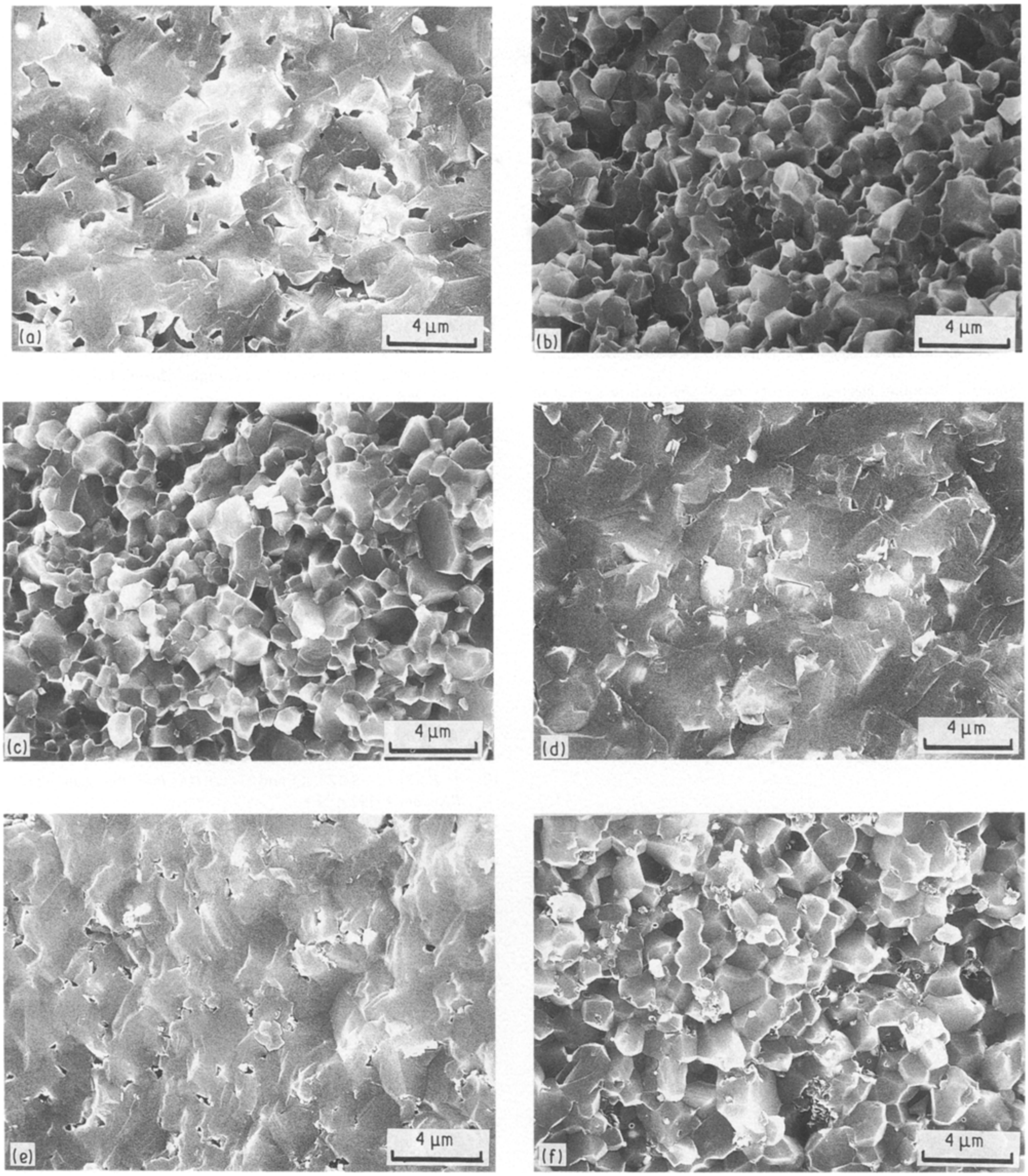

Figure 4 Scanning electron micrographs of the fracture surface of hot-pressed SiC samples: (a) PCS1, (b) PCS2, (c) PCS3, (d) PCS4, (e) SC1, and (f) SC2.

results show that crack deflection along the grain boundaries provided significant toughness increases in Al- or AlN-doped materials. Crack branching was also observed in PCS4 material (Fig. 5).

It can be summarized that Al- or AlN-doped materials have higher toughness than boron-doped materials, polycarbosilane-doped materials (except PCS1) have higher strength than elemental carbon-doped materials, and simultaneous addition of boron, AlN, and polycarbosilane leads to the highest strength material in the range of room temperature to 1000 °C.

3.3. Phase transformation

Early studies indicate that while the boron addition preferentially favours the 6H polytype in the SiC ceramics, the aluminium or Al_2O_3 addition enhances the occurrence of the 4H polytype [11, 12]. Table VI shows that polycarbosilane addition suppresses the 3C → 4H phase transformation in spite of aluminium or AlN addition (PCS2, PCS3, PCS4). However, for the SC2 specimen, significant 3C → 4H phase transformation has occurred during hot-pressing. From the above results, we can conclude that polycarbosilane-

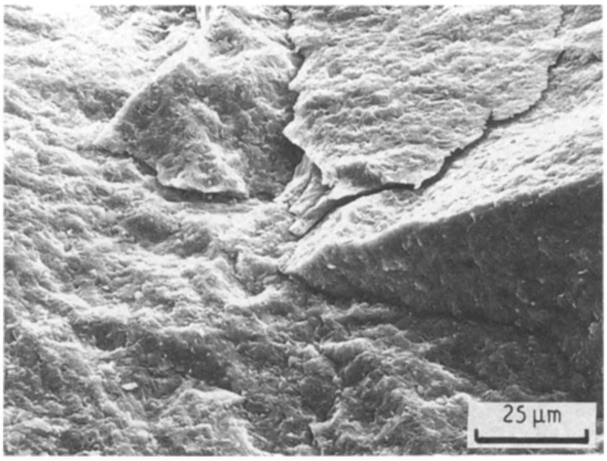

Figure 5 Scanning electron micrograph of the fracture surface of PCS4.

TABLE VI Polytypes in the various specimens

Specimen	3C	4H	6H
Pyrolysed polycarbosilane	92.3	3.0	4.7
A-1	13.0	9.9	77.1
PCS1	21.0	5.3	73.7
PCS2	22.8	7.4	69.7
PCS3	22.4	6.6	71.0
PCS4	21.9	7.8	70.3
SC1	10.2	6.6	83.2
SC2	4.9	24.8	70.3

derived β-SiC does not transform easily during heat treatment.

4. Conclusions

1. Addition of polycarbosilane to SiC resulted in considerable increases in flexural strength and fracture toughness. The strength increase was ascribed to the result of liquid-phase sintering, and the toughness increase was ascribed to crack deflection along the grain boundaries.

2. The fracture mode of SiC ceramics depends to a great extent on additives added: it was intergranular for Al- or AlN-doped materials and transgranular for B-doped materials.

3. Polycarbosilane derived β-SiC does not transform to 4H polytype easily in spite of aluminium or AlN addition.

References

1. J. J. BURKE, A. E. GORUM and R. N. KATZ (eds), "Ceramics for High Performance Applications" (Brook Hill, Chestnut Hill, MA, 1974).
2. J. J. BURKE, E. N. LENOE, and R. N. KATZ (eds), "Ceramics for High Performance Applications II" (Brook Hill, Chestnut Hill, MA, 1977).
3. E. M. LENOE, R. N. KATZ, and J. J. BURKE (eds), "Ceramics for High Performance Applications III" (Plenum Press, Murray Hill, NJ, 1983).
4. W. A. ZDANIEWSKI and H. P. KIRCHNER, *J. Amer. Ceram. Soc.* **70** (1987) 548.
5. J. B. HURST and S. DUTTA, *ibid.* **70** (1987) C303.
6. H. KODAMA and T. MIYOSHI, *Adv. Ceram. Mater.* **3** (1988) 177.
7. T. B. JACKSON, A. C. HURFORD and S. L. BRUNER, in "Silicon Carbide '87", edited by J. D. Cawley and C. E. Semler (The American Ceramic Society, Westerville, OH, 1987) p. 227.
8. B. D. CULLITY, in "Elements of X-Ray Diffraction" (Addison-Wesley, Reading, MA, 1978) p. 99.
9. T. KAWAMURA, *Mineral. J.* **4** (1965) 333.
10. T. HASE, H. SUZUKI and H. UEDA, *Bull. Res. Lab. Nucl. Reactors* **4** (1979) 113.
11. W. BOCKER, H. LANDFERMANN and H. HAUSNER, *Powder Met. Int.* **11** (1979) 83.
12. T. SAKAI and T. AIKAWA, *J. Amer. Ceram. Soc.* **71** (1988) C7.

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