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Microstructure and Mechanical Properties of Self-Reinforced Alpha–Silicon Carbide

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Abstract: Fine (0.46μm) α-SiC powders with or without large (2μm) α-SiC particles (seeds) added were pressureless-sintered at 1900°C for 1, 4, and 8 h with addition of yttrium aluminum garnet (YAG). The introduction of larger seeds into fine α-SiC accelerated the grain growth of some α-SiC grains and resulted in self-reinforced microstructure consisted of large elongated grains and small equiaxed grains. In contrast, the material without seeds had a relatively equiaxed grain structure. Development of self-reinforced microstructure results in significant improvements in toughness. However, the improved toughness is offset by a significant reduction in strength. The fracture toughness of the 8-h sintered materials without or with seeds was 4.6 and 6.2 MPa m$^{1/2}$, respectively. © 1998 Elsevier Science Limited and Techna S.r.l.

1 INTRODUCTION

Since the first successful sintering of SiC with small additions of boron and carbon in the 1970s,[1] silicon carbide has attracted much attention as one of the promising candidates for high-temperature structural applications due to their excellent high-temperature strength, creep and wear resistance, and chemical stability. However, application of this ceramic as a structural material has been limited by the low fracture toughness, typically of 2.5 to 4 MPa m$^{1/2}$, despite their other superior properties. A number of attempts have been made to improve the fracture toughness of SiC, with toughness values reported as high as 5 to 8 MPa m$^{1/2}$.[2–12] These efforts include toughening by heterophase dispersion,[2–5] by incorporation of α-SiC platelets in a β-SiC matrix,[6] and by introduction of both elongated α-SiC grains and weak interface in microstructure,[7–12] in which grain bridging and crack deflection are promoted by the presence of weak interface. The latter efforts were achieved by liquid phase sintering with the addition of oxide additives, such as Al_2O_3 and Y_2O_3, and subsequent annealing for grain growth of elongated α-SiC grains. This provided self-reinforced material with duplex microstructure, akin to that of tough Si_3N_4.[13] The development of elongated α-SiC grains has been achieved through the $\beta \rightarrow \alpha$ phase transformation. Hence, a raw powder of β-SiC and sintering or heat-treatment at a temperature as high as 2000°C were usually used for the phase transformation and microstructural control.[7–12]

Recently, self-reinforced SiC with duplex microstructure has been fabricated at a temperature as low as 1850°C without appreciable $\beta \rightarrow \alpha$ phase transformation.[14,15] This suggested that a small difference in grain size gave a sufficient driving force for the abnormal grain growth of some grains and a self-reinforced microstructure might be developed without phase transformation as in β-Si_3N_4.[16,17]

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Development of self-reinforced microstructure has not been reported when a raw powder of α-SiC is liquid-phase sintered with oxide additives. A wide particle size distribution in starting α-SiC powder may give enough driving force for abnormal grain growth of some α-SiC grains and result in a self-reinforced microstructure. The wide particle size distribution of starting powder has been obtained through the addition of large α-SiC seeds into a raw powder of fine α-SiC in this study.

The objectives of this study were to develop self-reinforced α-SiC with duplex microstructure using α-SiC powder and to investigate the effect of addition of large α-SiC seeds on the microstructure and mechanical properties of sintered α-SiC.

2 EXPERIMENTAL PROCEDURE

Commercially available fine α-SiC powder (Showa Denko, Tokyo, Japan, grade A-1) and relatively coarse α-SiC powder (Lonza-Werke Gmbh, Waldshut-Tiengen, Germany, grade UF-10) were oxidized for 0.5 h at 550°C under air to increase the SiO_2 content and decrease the carbon content. Such treatment increases the sinterability of SiC with oxide additives.[18] The oxidized fine α-SiC (designated as F) and coarse α-SiC (designated as L) powders were used as starting powders. Powder L was added to act as seeds for grain growth. These powders mainly consisted of α-SiC and contained higher SiO_2 content and much lower carbon content than common β-type raw powders, as shown in Table 1. To prepare a powder composition without seeds, 85 wt% powder F and 15 wt% $Y_3Al_5O_{12}$ (yttrium-aluminum garnet, YAG, 99.9% pure, High Purity Chemicals, Chiyoda Sakado, Japan) were ball milled in ethanol with SiC grinding balls for 24 h. To prepare a powder composition containing seeds, 82–84 wt% powder F and 15 wt% $Y_3Al_5O_{12}$ were ball milled in ethanol for 20 h, and then 1 or 3 wt% powder L was added, followed by additional milling for 4 h. About 10% of powder L, i.e. particles larger than 2 μm as shown in Table 1, are considered presumably to act as seeds for grain growth. Hence, 1 and 3 wt% addition of powder L corresponds to 0.1 and 0.3 wt%, respectively, addition of large seed grains. The milled slurry was dried and sieved through 60 mesh screen. Compacts (50×50×10 mm) were then uniaxially pressed at 25 MPa and isostatically pressed at 200 MPa. Sintering was performed in a graphite resistance furnace. The specimens were sintered at a heating rate of 900°C h^{-1} and maintained at 1900°C for 1, 4, and 8 h in an atmosphere of flowing argon. A powder bed with the same composition as the specimens was used to suppress the weight loss of the specimens. The sample designations are given in Table 2.

Table 1. Characteristics of starting powders

Characteristic	Powder F	Powder L
Average particle size (μm)	0.46	0.75
Cumulative mass percent finer		
10 (wt%)	0.22	0.30
50 (wt%)	0.46	0.75
90 (wt%)	1.10	2.10
Specific surface area ($m^2 g^{-1}$)	14.2	9.4
Impurities (wt%)		
SiO_2	4.50	3.08
Free C	0.04	0.02
Phase	α	α

Densities were measured using the Archimedes method. The theoretical density of the specimen, 3359 kg m^{-3}, was calculated according to the rule of mixtures. X-ray diffraction using CuK_α radiation was performed on all ground specimens. The sintered specimens were cut and polished, and then plasma etched by CF_4 containing 7.8% O_2. The microstructures were observed by scanning electron microscopy (SEM). The sintered materials were also cut and machined into 3×4×36 mm bars with an 800 grit diamond wheel for flexural testing. Bend tests were performed at room temperature on 12 specimens for each condition using a 4-point method with outer and inner spans of 30 and 10 mm, respectively, at a crosshead speed of 0.5 mm min^{-1}. The microstructure of fractured surface was observed using SEM. The fracture toughness was estimated by measuring crack lengths generated by a Vickers indenter with a load of 196 N.[19]

3 RESULTS AND DISCUSSION

The characteristics of α-SiC obtained are summarised in Table 3. The relative densities of >98% were achieved by pressureless-sintering with a holding time of 4 h at 1900°C. However, prolonged sintering at 1900°C resulted in a decrease of the relative density independent of the seed addition.

Table 2. Sample designation

Sintering time at 1900°C (h)	Sample designation		
	Material without seeds	Material with 1 wt% seeds	Material with 3 wt% seeds
1	A1	B1	C1
4	A2	B2	C2
8	A3	B3	C3

Table 3. Properties of pressureless-sintered α-SiC materials

*Material	Relative density (%)	Crystalline phase	Flexural strength (MPa)	Fracture toughness (MPa $m^{1/2}$)
A1	98.3	α-SiC	429±54	3.9±0.2
A2	98.8	α-SiC	414±35	4.1±0.3
A3	97.2	α-SiC	346±34	4.6±0.3
B1	96.8	α-SiC	382±42	4.3±0.2
B2	98.9	α-SiC	413±32	4.7±0.2
B3	97.3	α-SiC	346±43	5.0±0.3
C1	94.9	α-SiC	—	4.3±0.4
C2	98.5	α-SiC	411±34	5.4±0.2
C3	97.6	α-SiC	317±38	6.2±0.3

*Refer to Table 2.

These results suggest that prolonged exposure to high temperatures may cause reactions between SiC and YAG and probably result in the formation of volatile components such as AlO, Al_2O, and CO.[20] Fig. 1 shows such a result for a sintering at 1900°C for 8 h. From Fig. 1 it can also be seen that the density decreases with increasing seeds (powder L) content for a sintering of 1900°C for 1 h. The densification behaviour coincided well with the general observation that the relative densification rate of a compact consisting of larger particles was slower than that of a compact consisting of smaller particles.[21]

Figure 2 shows the microstructure of the α-SiC with or without seeds after sintering. Silicon carbide grains were etched away by the CF_4 plasma, so that the microstructures were delineated by the grain-boundary glassy phase. The 1-h sintered materials (A1, B1, and C1) with or without seeds have relatively fine, equiaxed microstructures with the average grain sizes ranging from 0.6 to 0.7 μm. When the holding time was increased, the microstructure changed from equiaxed to elongated grains and the size and aspect ratio of the grains increased as shown in Fig. 2. Elongation of some grains are clearly shown in materials with seeds (B2, B3, C2, and C3). The 8-h sintered materials with seeds (B3 and C3) have duplex microstructure consisted of large elongated grains and relatively fine matrix grains. A kind of self-reinforced microstructure was obtained in α-SiC without $\beta \rightarrow \alpha$-phase transformation. Polytypes of all the sintered materials were mainly 6H (>90%) with trace of 15R. These results suggest that the addition of large α-SiC seeds accelerated the grain growth of some α-SiC grains during sintering and resulted in self-reinforced microstructure. The driving force for the grain growth in materials without seeds was smaller than that in materials with seeds because of their narrow particle size distribution. Grain growth in materials without seeds therefore was slower than in the materials with seeds. For materials with seeds, small number of large α-SiC particles, presumably ~10% of powder L added, i.e. particles larger than 2 μm as shown in Table 1, acted as nuclei for the growth of elongated grains, because the growth of SiC grains was controlled by Ostwald ripening,[22] i.e. the solution of some α-SiC grains that were smaller than the critical size, mass transport by diffusion through the liquid, and reprecipitation onto large α-SiC grains that were larger than the critical size. In contrast, the grain growth of SiC grains in materials without seeds may have resulted from the growth of relatively large number of relatively small α-SiC particles, compared with the materials with seeds contained in the starting powder. Hence, differences in microstructure between materials with seeds and those without seeds may have resulted from the difference in growth behaviour.

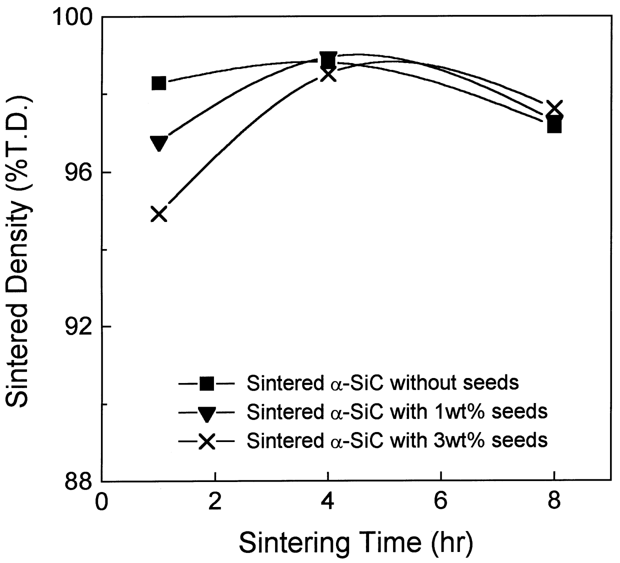

Fig. 1. Plot of sintered density vs sintering time at 1900°C.

The microstructural development of materials with seeds is similar to the in situ formation of platelike or elongated grains during sintering of oxide-doped β-SiC.[7–12] Such kind of a duplex microstructure has been developed only with β-SiC starting powders or β-SiC starting powders containing α-SiC seeds. However, our results suggest that self-reinforced SiC can be fabricated using α-SiC starting powders with wide particle size distribution.

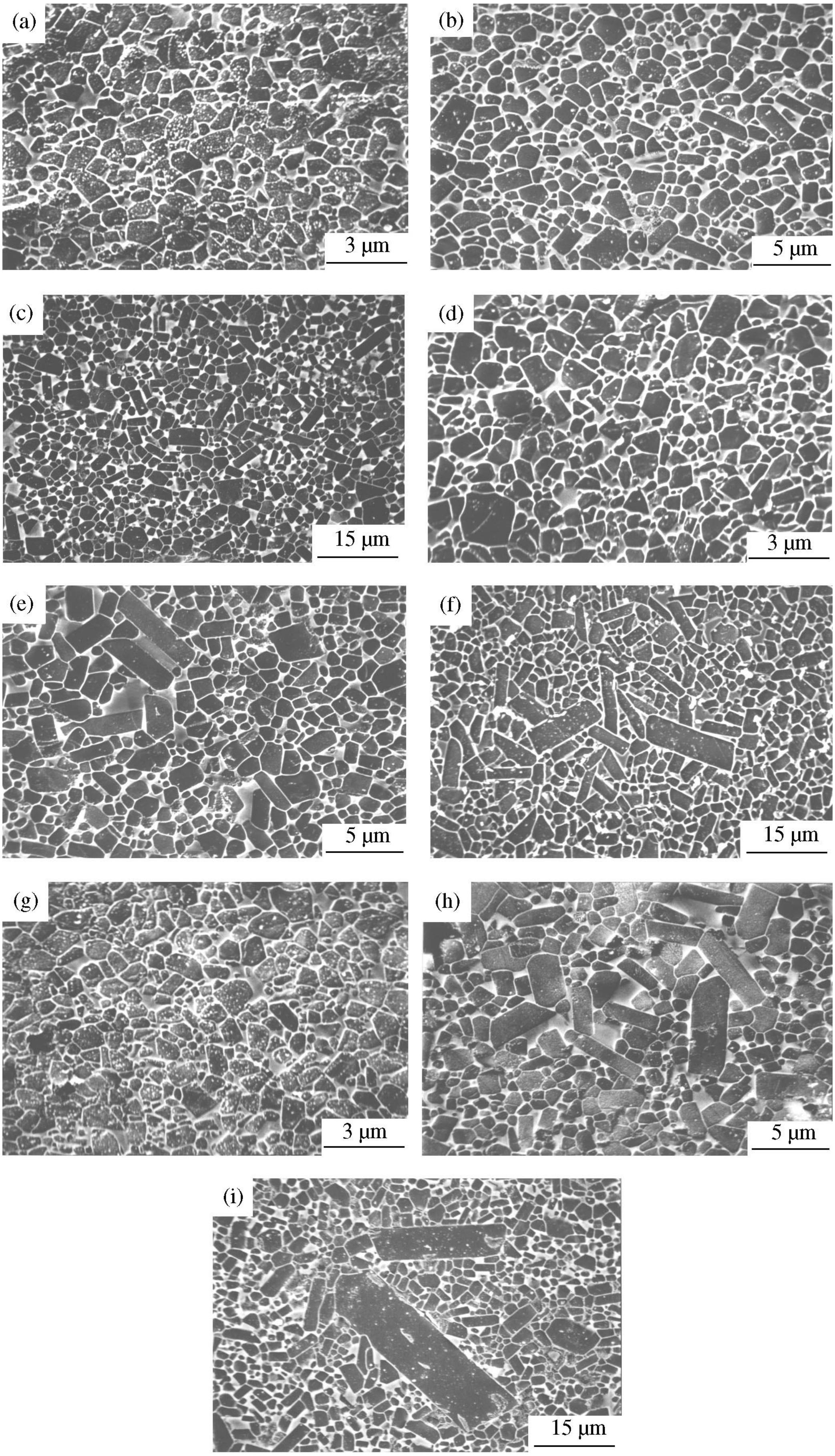

Fig. 2. Microstructures of sintered α-SiC materials: (a) A1, (b) A2, (c) A3, (d) B1, (e) B2, (f) B3, (g) C1, (h) C2, and (i) C3 (refer to Table 2).

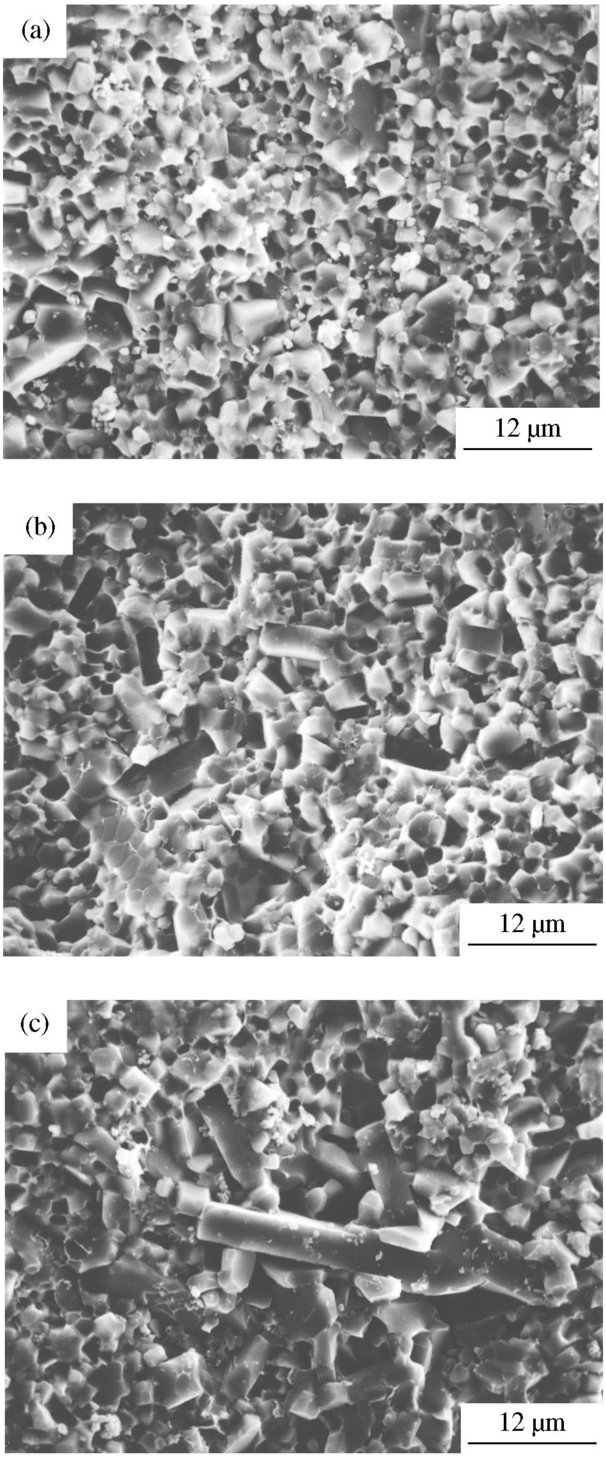

Fig. 3. SEM micrographs of the fracture surfaces of 8-h sintered α-SiC materials: (a) A3, (b) B3, and (c) C3 (refer to Table 2).

It also indicates that a small difference in grain size gives a sufficient driving force for abnormal grain growth of some grains and self-reinforced microstructure can be developed without phase transformation as in β-Si_3N_4.[16,17]

It has been recognised that the boron- and carbon-doped SiC shows transgranular fracture due to a strong grain boundary.[23] In contrast, the fracture mode of α-SiC doped with Al_2O_3 and Y_2O_3 was mostly intergranular, as shown in Fig. 3, due to a weak interface that resulted from the difference in the coefficient of thermal expansion between the glassy grain-boundary and SiC grains on cooling after sintering.[7] However, there is a substantial tendency for relatively large, elongated grains to fracture transgranularly. The true shape of elongated grains is considered as plate-shaped.

Figure 4 shows the strength–fracture toughness relations for the α-SiC ceramics with or without large α-SiC seeds and sintered for 1–8 h, i.e. with different microstructure. Data for 1-h sintered material with 3 wt% seeds (C1) were excluded from the plot because of its relatively low density (94.9%) compared with other materials ($\geq$96.8%). The 1-h sintered materials (A1 and B1), which were composed of relatively fine, equiaxed grains, have relatively low fracture toughness (3.9–4.3 MPa $m^{1/2}$) and relatively high flexural strength (380–430 MPa). In contrast, 8-h sintered materials with seeds (B3 and C3), which were composed of relatively large elongated grains and small matrix grains, have relatively high fracture toughness (5.0–6.2 MPa $m^{1/2}$) and relatively low flexural strength (310–350 MPa). The marked growth of elongated grains with increasing sintering time resulted in the improved fracture toughness and decreased strength. The improvement of fracture toughness was directly related to the microstructure and arose from crack bridging and deflection by elongated grains (Fig. 5). Thus, coarse, self-reinforced microstructure is beneficial to the toughness. On the other hand, fine, equiaxed microstructure is beneficial to the strength. Typical fracture origin were large pores near surface. It is believed that prolonged sintering (8 h) at a temperature as high as 1900°C induced the pore growth as well as the grain growth. From the above results, we can conclude that the improved

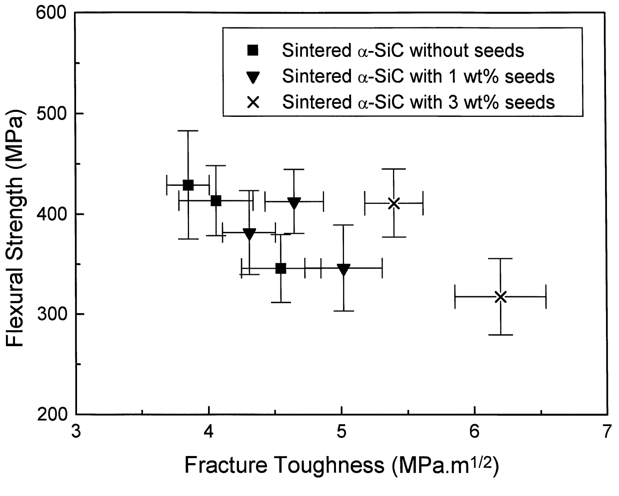

Fig. 4. Relation between strength and fracture toughness of sintered α-SiC materials.

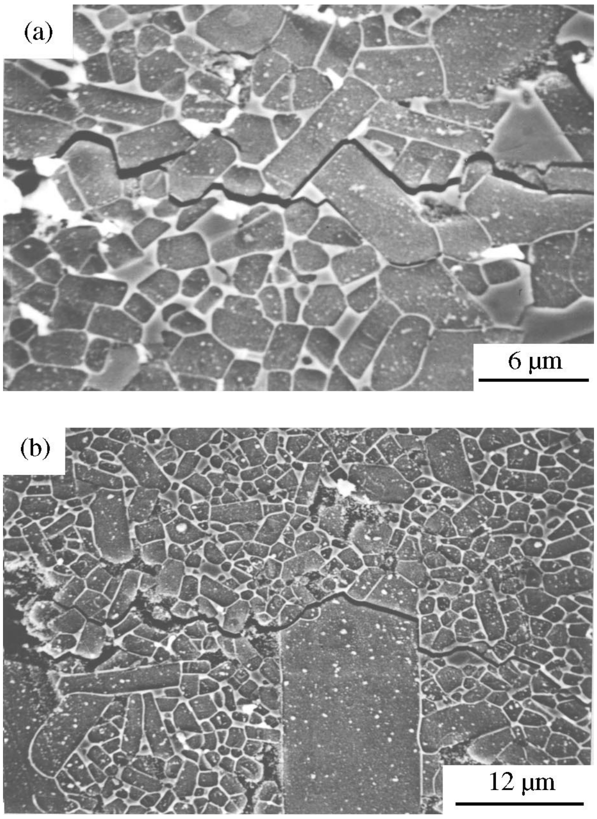

Fig. 5. SEM view of (a) crack bridging and (b) crack deflection by elongated grains in 8-h sintered α-SiC with 3 wt% seeds (C3).

toughness is offset by a significant reduction in strength.

4 CONCLUSIONS

Self-reinforced microstructure consisted of large elongated grains and small matrix grains could be obtained with α-SiC starting powders containing large α-SiC seeds. The result of this study implies that a small difference in grain size gives a sufficient driving force for abnormal grain growth of some grains and in situ formation of self-reinforced microstructure during sintering of SiC is possible without $\beta \rightarrow \alpha$ phase transformation. Development of self-reinforced microstructure results in significant improvements in toughness. However, the improved toughness is offset by a significant reduction in strength. The fracture toughnesses of 8-h sintered materials without or with seeds were 4.6 and 6.2 MPa m$^{1/2}$, respectively.

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