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Effect of annealing on mechanical properties of self-reinforced alpha-silicon carbide

JAE-YEON KIM, YOUNG-WOOK KIM
Department of Materials Science and Engineering, The University of Seoul,
Seoul 130-743, Korea
E-mail: ywkim@uoscc.uos.ac.kr

JUNE-GUNN LEE
Division of Ceramics, Korea Institute of Science and Technology, Seoul 130-650, Korea

KYEONG-SIK CHO
School of Materials and Metallurgical Engineering, Kumoh National University of
Technology, Kumi 730-701, Korea

Alpha-SIC powder containing 7.2 wt% $Y_3Al_5O_{12}$ (YAG, yttrium aluminum garnet) and 4.8 wt% SiO_2 as sintering aids were hot-pressed (SC0) at 1820 °C for 1 h and subsequently annealed at 1920 °C for 2 h (SC2), 4 h (SC4) and 8 h (SC8). When the annealing time was increased, the microstructure changed from equiaxed to elongated grains and resulted in self-reinforced microstructure consisted of large elongated grains and small equiaxed grains. Development of self-reinforced microstructure, consisted of mostly 6H phase, resulted in significant improvements in toughness. However, the improved toughness was offset by a significant reduction in strength as in the materials consisted of 4H originated from β-SiC. The fracture toughness and strength of the 8-h annealed materials were 5.5 MPa $\cdot$ $m^{1/2}$ and 490 MPa, respectively. © *1999 Kluwer Academic Publishers*

1. Introduction

Silicon carbide can be sintered via solid state sintering with the aid of B and C [1] or liquid phase sintering with the aid of metal oxides, such as Al_2O_3 and Y_2O_3 [2–6]. Due to the very high temperature needed for solid state sintering of SiC and low fracture toughness of resulting ceramics (typically of 2.5 to 4 MPa $\cdot$ $m^{1/2}$), liquid-phase sintered materials have received more attention than solid state sintered ones, recently.

The microstructure of liquid phase sintered SiC can be controlled by using the $\beta \rightarrow \alpha$ phase transformation or controlled grain growth by seeding [7–10]. An equiaxed grain morphology was obtained with high α-content powders, whereas a platelet-shaped morphology resulted from β-SiC or β-SiC containing α-SiC seeds. Hence, β-SiC raw powder is usually used as the starting point for tough materials; β-SiC dissolves in the liquid phase and precipitates at existing α-SiC seeds as α grains with a platelet morphology during sintering or annealing of oxide-doped β-SiC [11]. These materials, consisted of large platelet-shaped grains and the smaller, more-equiaxed matrix grains, are known as "*in-situ* toughened composites" or "self-reinforced materials." The platelet α grains increase the toughness of these materials by crack bridging [3] or crack deflection [9]. Typical self-reinforced SiC ceramics fabricated using β-SiC powder have a fracture toughness in the range 5–8 MPa $\cdot$ $m^{1/2}$ when the powder is densified or annealed at 1900–2000 °C [3, 8].

The microstructure of a self-reinforced materials is also developed when α-SiC starting powder is sintered and subsequently annealed at $\geq$1900 °C [12]. A high β content of the starting powder is not always necessary for the development of self-reinforced materials. The wide size distribution of α-SiC grains is the main factor for selective grain growth of platelet-shaped grains [12]. The self-reinforced microstructure can be obtained with α powder by (1) controlling the initial particle-size distribution, (2) adding a small amount of oxide, and (3) sintering or annealing at high temperatures ($\geq$1900 °C).

Aspect ratio of the platelet-shaped grains approached to 4 irrespective of the crystalline phase of the starting powder [10–13]. However, the polytype of the resulting crystalline materials was different; the polytype of the self-reinforced material originated from β powder was mostly 4H while that of the material from α powder was 6H [14, 15]. The mechanical properties of the self-reinforced material fabricated from β powder have been extensively reported in the literature [7, 13–15]. However, the strength and toughness properties of the self-reinforced material fabricated from α powder have not been comprehensively studied.

In this study, a hot-pressed α-SiC material with equiaxed microstructure and three annealed α-SiC materials that possess different microstructures were prepared using α-SiC powder with YAG and SiO_2 as sintering aids. Their room temperature strength and fracture

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toughness properties are presented and correlated with their respective microstructures.

2. Experimental

Alpha-SiC Powder (A-1 grade, Showa Denko, Tokyo, Japan) was oxidized at 600 °C for 0.5 h under air to remove free carbon and hydrofluoric acid-treated to remove SiO_2. The SiO_2 and free C contents in the purified powder were 1.10% and 0.04%, respectively. Commercially available YAG (High Purity Chemicals, 99.99% pure, Osaka, Japan) and SiO_2 (Kanto Chemical Co., Inc., reagent grade, Tokyo, Japan) powders were used as sintering additives. To prepare a powder composition, 88 wt% α-SiC was mixed with 7.2 wt% YAG and 4.8 wt% SiO_2 and then the mixture was milled in ethanol for 24 h using SiC grinding balls. The milled slurry was dried and hot-pressed at 1820 °C for 1 h under a pressure of 25 MPa in an argon atmosphere. The hot-pressed materials (SC0) were heated further at 1920 °C for 2 h (SC2), 4 h (SC4) and 8 h (SC8) under an atmospheric pressure of Ar to enhance grain growth.

Sintered density was measured using the Archimedes' method. The theoretical densities of the specimens, $3.227\ \mathrm{g \cdot cm^{-3}}$, were calculated according to the rule of mixtures. The hot-pressed and annealed materials were cut and polished, then etched by plasma of CF_4 containing 7.8% O_2. The microstructures were observed by scanning electron microscopy (SEM). X-ray diffraction (XRD) using CuK_α radiation was performed on ground powders. The bar samples were cut and polished into $2 \times 1.5 \times 25$ mm bars up to 1 μm finish for flexural testing. Bend tests were performed at room temperature on 7–8 specimens at each condition using a four-point method with outer and inner spans of 10 and 20 mm, respectively, and a crosshead speed of $0.5\ \mathrm{mm \cdot min^{-1}}$. The fracture origin and microstructure of the fractured surface were observed using SEM. The fracture toughness was estimated by measuring crack lengths generated by a Vickers indenter with a load of 196 N [16].

3. Results and discussion

3.1. Microstructure

The characteristics of both the hot-pressed and annealed α-SiC are summarized in Table I. A sample with a relative density of $\geq$99.8% was produced by hot-pressing at 1820 °C with a hold time of 1 h. However, prolonged annealing at 1920 °C resulted in a decrease in the relative density, which is probably due to the formation of volatile components such as Al_2O, SiO, and CO [4, 17]. Fig. 1 illustrates that trend for specimens annealed at 1920 °C.

TABLE I Characteristics of both the hot-pressed and annealed SiC

Sample designation	Annealing time at 1920 °C (h)	Relative density (%)	Crystalline phase	
			Major	Trace
SC0	Hot-pressed	99.8	6H	YAG[a], $Y_2Si_2O_7$, SiO_2
SC2	2	99.7	6H	YAG, $Y_2Si_2O_7$, SiO_2
SC4	4	99.0	6H	YAG, $Y_2Si_2O_7$
SC8	8	98.1	6H	YAG, $Y_2Si_2O_7$

[a] $Al_5Y_3O_{12}$ (yttrium aluminum garnet).

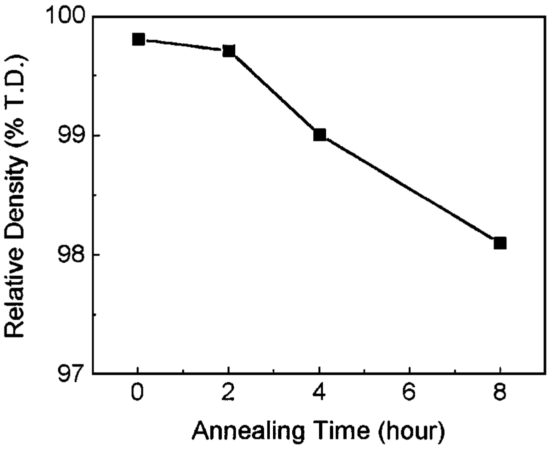

Figure 1 Plot of density versus annealing time at 1920 °C.

The microstructures of the hot-pressed and annealed materials are shown in Fig. 2a–d. Silicon carbide grains are etched away by the CF_4 plasma, thus these microstructures are delineated by the grain boundary glassy phase. The microstructures of SC0 consisted of fine, equiaxed α-SiC grains. When the annealing time was increased, the microstructure changed from equiaxed to platelet-shaped grains, and the diameter and aspect ratio of the grains increased. As shown in Fig. 2a–d, platelet-shaped grains appeared after 4 h of annealing in the annealed materials, i.e. SC4 and SC8. A kind of "self-reinforced microstructure", consisted of large elongated grains and relatively fine matrix grains, has been developed from α-SiC starting powders. Such a self-reinforced microstructure has been developed only with β-SiC or β-SiC starting powders containing α-SiC seeds [3, 13] or α-SiC starting powders containing large α-SiC seeds [12]. However, present results suggest that a small difference in grain size gives enough driving force for abnormal grain growth of some grains via solution-precipitation and self-reinforced microstructure can be developed without $\beta \rightarrow \alpha$ phase transformation and without seeding.

Phase analysis of the hot-pressed and annealed materials by XRD showed that the major phase in each material was polytype 6H (Table I). These results show that the growth of platelet-shaped grains resulted mainly from the overgrowth of α-SiC on the starting powder (polytype 6H) via solution-precipitation [2]. The self-reinforced materials (SC4 and SC8) have a similar microstructure with self-reinforced materials (mostly 4H) prepared from β-SiC powders [15], but a different polytype of SiC. The SC0 and SC2 materials contained YAG, $Y_2Si_2O_7$, and SiO_2 as the secondary phases. In contrast, the SC4 and SC8 materials contained YAG and $Y_2Si_2O_7$ as the secondary phases.

3.2. Mechanical properties

Fig. 3a–d show SEM micrographs of the fracture surfaces of SiC ceramics with various microstructures. As shown, the fracture mode of SC0 and SC2 was mostly intergranular, which was a result of a weak interface created by the difference between the coefficients of thermal expansion of the liquid and the matrix on cooling

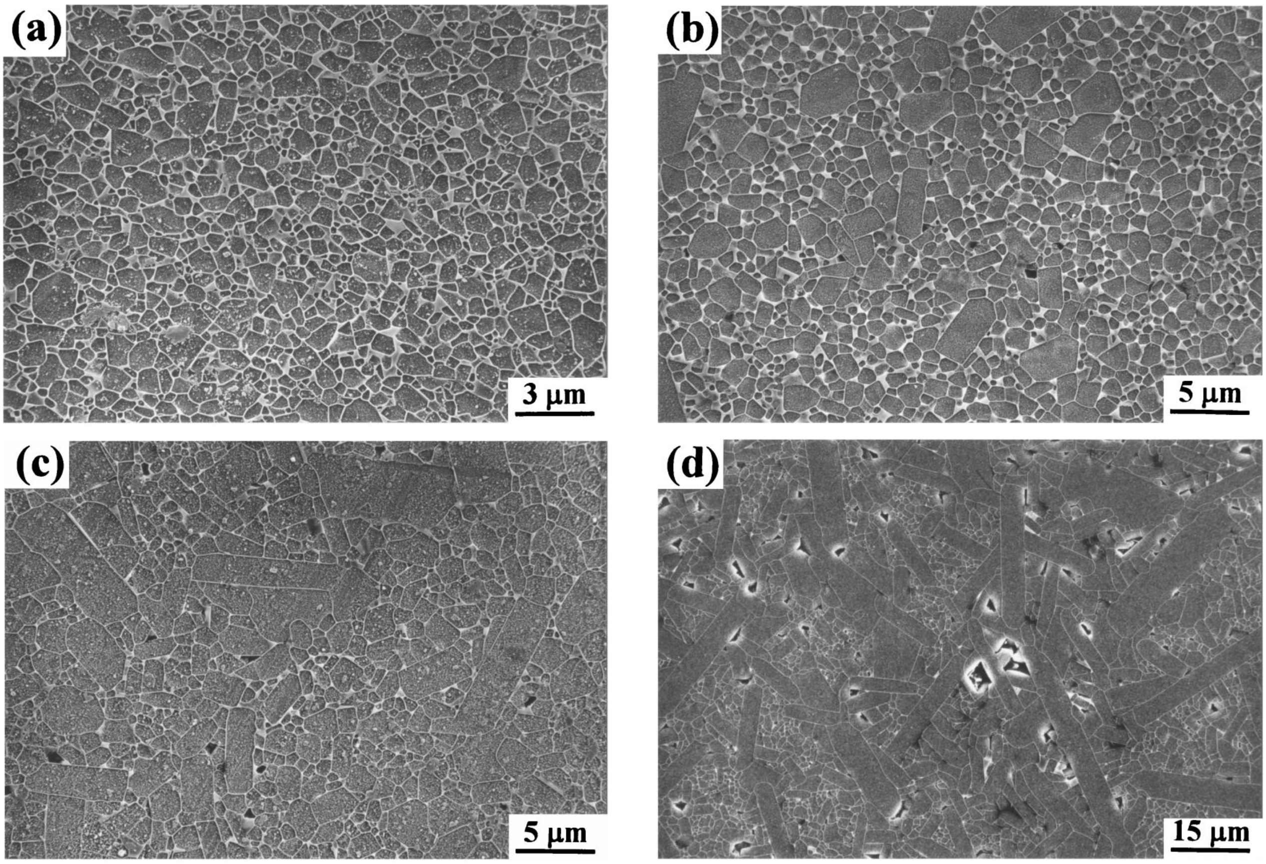

Figure 2 Microstructures of the sintered and annealed materials: (a) SC0, (b) SC2, (c) SC4 and (d) SC8 (refer to Table I).

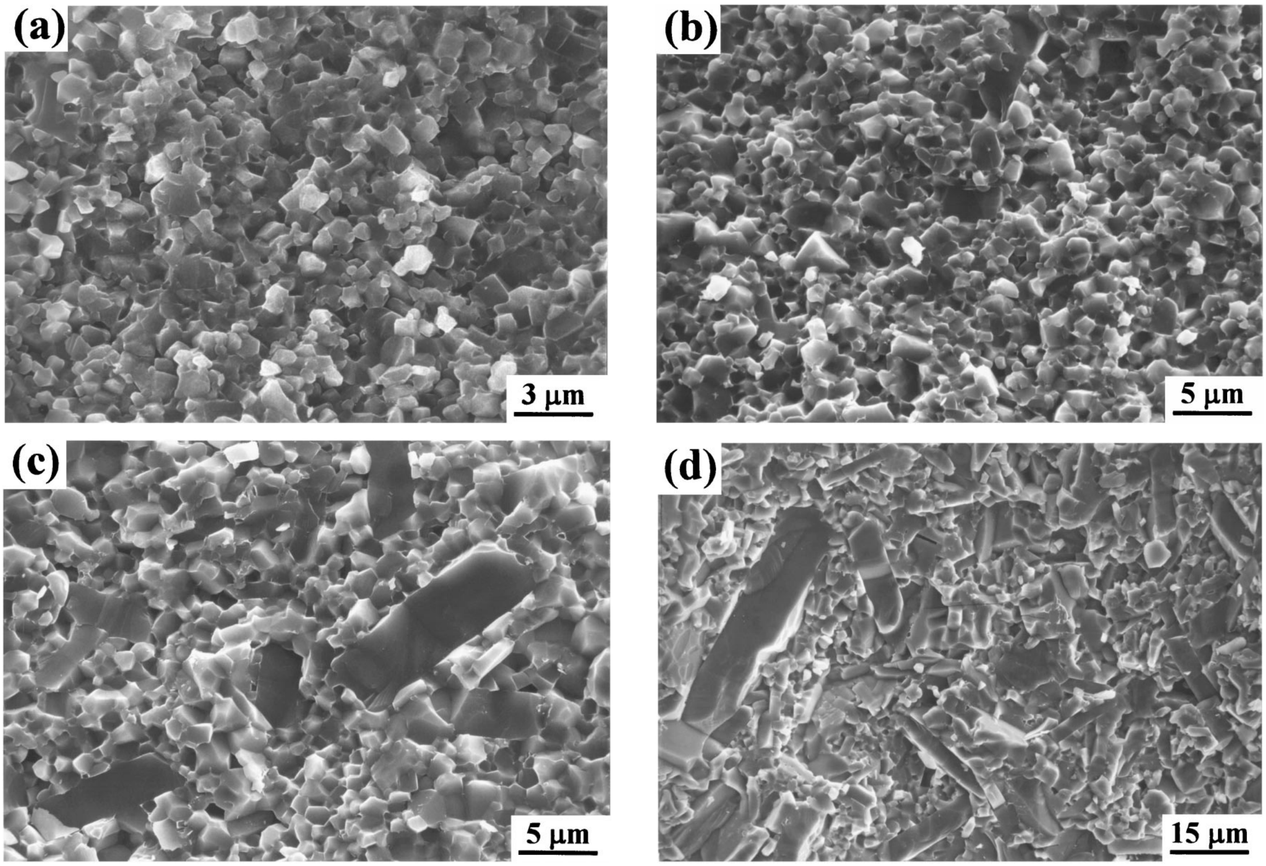

Figure 3 SEM micrographs of the fracture surfaces of hot-pressed and annealed materials: (a) SC0, (b) SC2, (c) SC4 and (d) SC8 (refer to Table I).

after sintering [3]. However, SC4 and SC8 showed a mixed mode of transgranular and intergranular. There was a substantial tendency for relatively large, platelet-shaped grains to fracture transgranular.

Fig. 4 shows the strength-fracture toughness relations for SiC ceramics that have been hot-pressed and subsequently annealed for different times, i.e. they have different microstructures. The hot-pressed material (SC0),

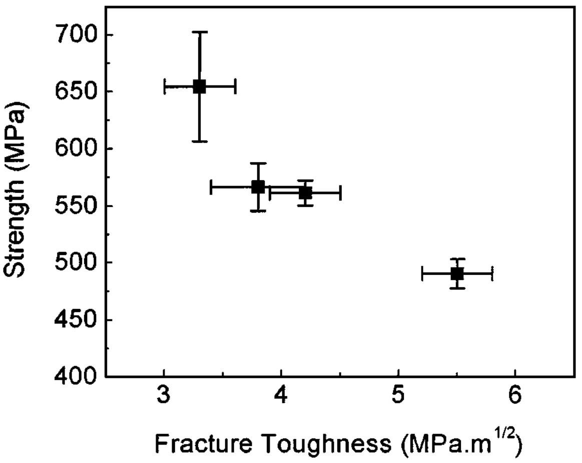

Figure 4 Relation between strength and fracture toughness of hot-pressed and annealed SiC materials.

that is composed of relatively fine, equiaxed grains, have fracture toughness values of 3.2–3.8 MPa · $m^{1/2}$ and a flexural strength of 630–730 MPa. In contrast, the 8 h annealed material (SC8), that is composed of relatively large, platelet-shaped grains and small matrix grains, has relatively high fracture toughness values of 5.2–6.4 MPa · $m^{1/2}$ and a relatively low flexural strength of 480–500 MPa. The marked growth of platelet-shaped grains with increasing annealing time resulted in the improved fracture toughness values and the decreased strength. The improvement in the fracture toughness is directly related to the microstructure and is produced by crack bridging by platelet-shaped SiC grains (Fig. 5b). Thus, coarse, self-reinforced microstructure is beneficial to the toughness. On the other hand, fine, equiaxed microstructure containing a minimal amount of small defects is required to produce

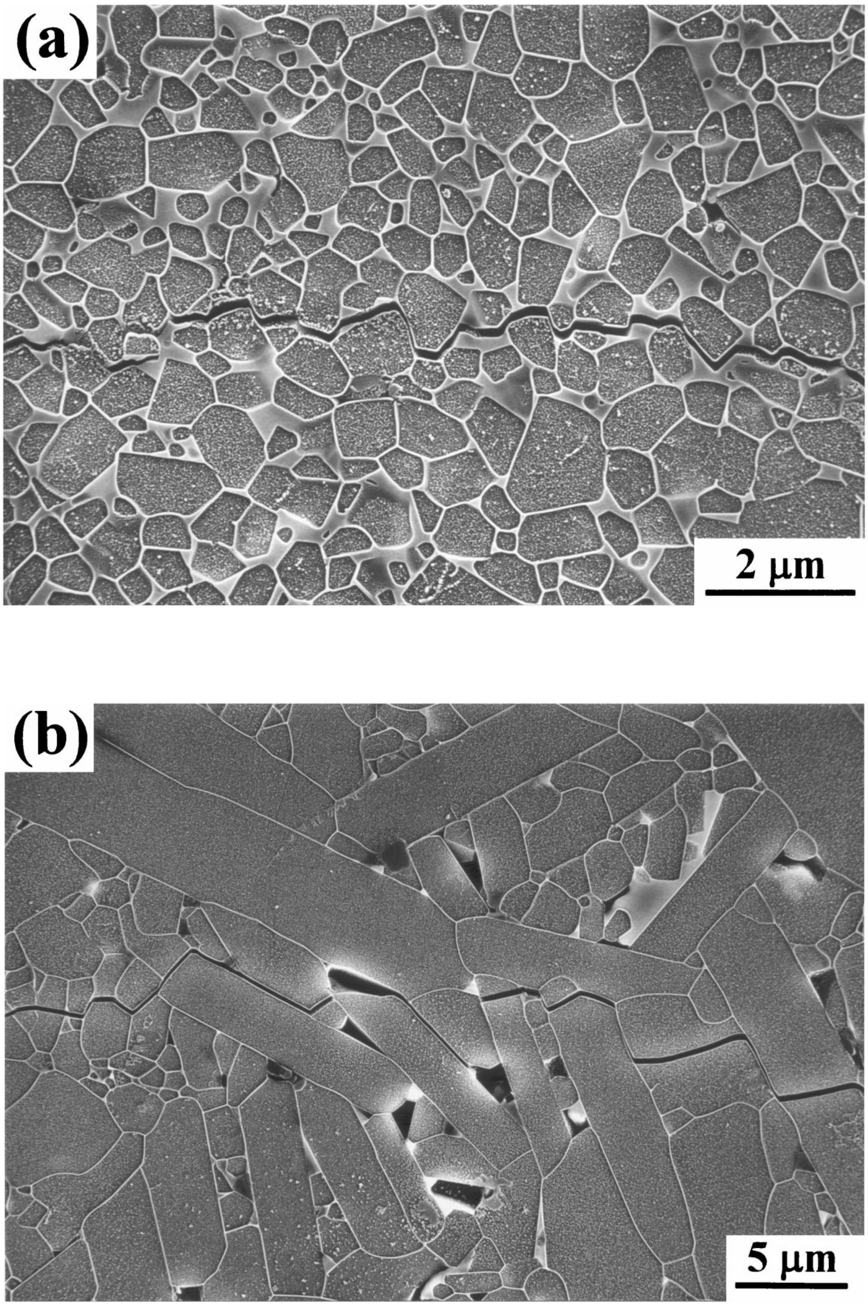

Figure 5 SEM micrographs of crack paths induced by a Vickers indentation in (a) SC0 and (b) SC8 (refer to Table I).

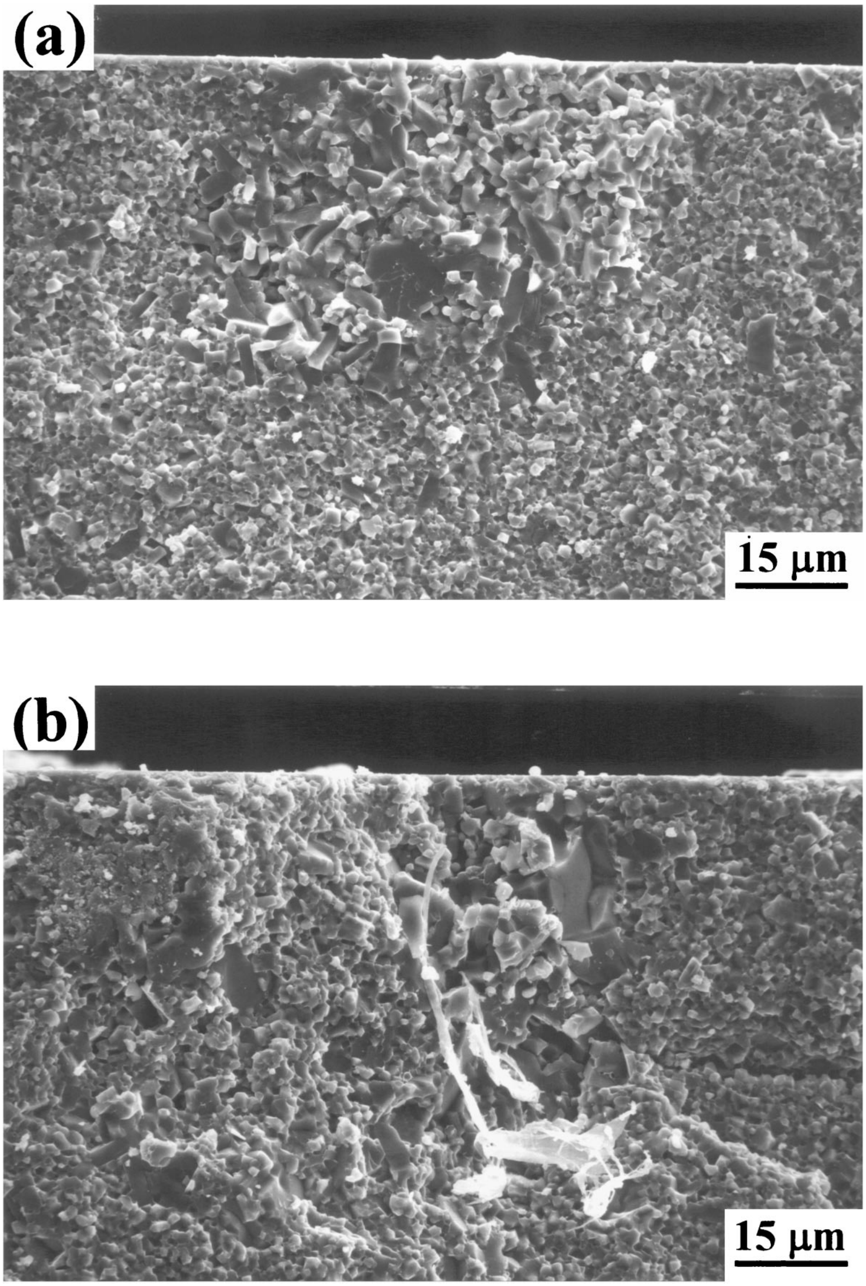

Figure 6 SEM fractography of self-reinforced α-SiC ((a) SC2 and (b) SC4) showing typical fracture origin: clusters of elongated large grains.

improvements in the strength. Typical fracture origins were clusters of large grains near the surface as is shown in Fig. 6a, b. These results indicate that there is a trade-off in improving both the fracture toughness and strength. Thus it appears difficult to simultaneously achieve both a high fracture toughness and strength, as in self-reinforced materials fabricated from β-SiC [15].

4. Conclusions

Annealing of hot-pressed α-SiC ceramics, fabricated from α-SiC starting powders containing YAG and SiO_2 as sintering aids, led to the self-reinforced α-SiC materials consisted of mostly polytype 6H.

The room temperature strengths of the annealed materials decreased as the grain size whereas the fracture toughness increased as the grain size, owing to the crack bridging by platelet-shaped α-SiC grains. There is a trade-off in improving both the fracture toughness and strength, as in self-reinforced materials (mostly 4H) fabricated from β-SiC starting powders. The fracture toughness and strength of the 8 h annealed materials were 5.5 $\mathrm{MPa} \cdot \mathrm{m}^{1/2}$ and 490 MPa, respectively.

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