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Pressureless sintering of β-SiC with Al_2O_3 additions

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β-SiC was pressureless sintered to 98% theoretical density using Al_2O_3 as a liquid-phase forming additive. The reaction between SiC and Al_2O_3 which results in gaseous products, was inhibited by using a pressurized CO gas or , alternatively, a sealed crucible. The densification behaviour and microstructural development of this material are described. The microstructure consists of fine elongated α-SiC grains (maximum length $\approx$ 10 μm and width 2–3 μm) in a matrix of fine equi-axed grains (2–3 μm) and plate-like grains (2–5μm). The densification behaviour, composition and phases in the sintered product were studied as a function of the sintering parameters and the initial composition. Typically, 50% of the β-phase was transformed to the α-phase.

1. Introduction

The high percentage of covalent bonding which imparts excellent ambient and high-temperature properties to SiC also makes pressureless sintering impossible without the use of sintering aids. So far, most of the studies on the sintering of SiC have centred on sintering with additions of boron, carbon and aluminium additives [1–3]. Pressureless sintering of β-SiC, in the presence of these additives, takes place by solid state diffusion processes and requires temperatures of over 2100 °C and times of over 1 h. This often results in exaggerated grain growth and in the development of anisotropic α-SiC phase.

More recently, it has been shown that pressureless sintering of SiC can be achieved with liquid-phase forming additives, such as Al_2O_3 [4], Al_2OC [5], (Al_2O_3 + Y_2O_3) [6–8] and (Al_2O_3 + TiO_2) [9]. The reason for using Al_2O_3 as a sintering aid is that it has a reasonably high melting point and superior mechanical properties compared with other oxides. However, a major problem associated with sintering of SiC in the presence of oxide additives is the reaction between SiC and the oxide which results in the formation of volatile components and retardation of densification.

This paper presents studies on the pressureless sintering of SiC with Al_2O_3 addition under small CO gas pressure. Small CO gas pressure (0.105 MPa gauge pressure) was found to inhibit the reaction between SiC and Al_2O_3 and to enhance densification.

2. Experimental procedure

High-purity β-SiC powder produced by the carbothermal reduction of silica with carbon black was used for this study. The characteristics of the powder are given in Table I. Commercially available Al_2O_3 (grade A-16 SG, Alcoa, Bauxite, AR) was used as the additive. Five different compositions were made with Al_2O_3 contents varying from 5–30 wt% (Table II). Mixing was performed by wet attrition milling in methanol using high-purity SiC milling media with a ball to charge ratio of 5 to 1. After subsequent drying and sieving, the powders were compacted by cold uniaxial pressing at a pressure of 35 MPa. The green compacts were then cold-isostatically pressed at a pressure of 210 MPa. The compacts were sintered under three different conditions: (i) open in CO gas at 0.105 MPa gauge pressure, (ii) in flowing argon, (iii) in a closed graphite crucible sealed with graphite foil. The sintering was performed in a graphite resistance furnace. The heating was done at a rate of 35 °C min^{-1} to 1000 °C and at a rate of 10 °C min^{-1} between 1000 °C and the desired sintering temperature.

Phase analysis was performed on an X-ray diffractometer (Miniflex CN2005 X-Ray Diffractometer, Rigaku Corp., Danvers, MA) after removing the as-sintered surface. A plot of relative intensity versus weight per cent Al_2O_3 in SiC was developed, based on the (1 1 3) diffraction line. This was used as a calibration curve for determining the amount of residual Al_2O_3 in the sintered bodies. Based on this composition, the theoretical density of the sintered bodies was calculated. The theoretical density values determined on the basis of X-ray data were checked by determining the volume fraction of porosity using computer-aided image analysis on samples polished to a diamond finish of 1 μm. The amount of α-SiC was determined based on the calibration curve given by Secrist. [10].

Characteristic phases observed on the polished surface were identified by spot analysis using a scanning Auger microprobe (SAM) (Perkin-Elmer Physical Electronics Model PHI-600) after sputtering the surface with a 3 kV Ar^+ ion beam over a 1×1 mm^2 area

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TABLE I SiC powder characteristics

Specific surface area (BET) (m^2g^{-1})	17
Average particle size[a] (μm)	0.4
SiC content (wt %)	> 99.5
β-Phase in SiC (wt %)	> 98.0
Oxygen content (wt %)	< 0.2
Aluminium (wt %)	0.002
Iron (wt %)	< 0.001
Calcium (wt %)	0.002

[a] Sedigraph 5000ET, Micromeritics, Norcross, GA, USA.

for 2 min. The atomic percentage of the element of interest, A_i, was calculated by using the formula

$$A_i = \frac{P_i/S_i}{\sum(P_i/S_i)} \times 100 \qquad (1)$$

where P_i is the peak to peak height for the element of interest, and S_i is the sensitivity factor of the element at the beam voltage.

The polished samples were etched by boiling in Murakami's reagent for 10 min. The average aspect ratio of the elongated grains was calculated after measuring the length and width of 20–30 grains.

3. Results and discussion

Fig. 1 shows the variation of density and weight loss with Al_2O_3 content for the samples sintered in CO gas at 0.105 MPa gauge pressure and those sintered in flowing argon. The decrease in density with increasing Al_2O_3 content for the samples sintered in flowing argon as well as under CO pressure is believed to be associated with the increase in weight loss due to reaction between SiC and Al_2O_3. Owing to the higher affinity of carbon for oxygen than for silicon at elevated temperatures, Al_2O_3 reacts with SiC to liberate CO gas according to the reactions

$$SiC + Al_2O_3 \rightarrow SiO + Al_2O + CO \qquad (2)$$

$$2SiC + Al_2O_3 \rightarrow 2Si + Al_2O + 2CO \qquad (3)$$

$$3SiC + Al_2O_3 \rightarrow 3Si + 2Al + 3CO \qquad (4)$$

The weight loss occurs through volatilization of SiO, Al_2O, CO, and possibly aluminium and silicon which are expected to have high vapour pressures at temperatures above 1850 °C.

As was recognised by Terwilliger and Lange [11] in the sintering of Si_3N_4 with MgO, the pressure developed in the pores and pore-channels by the decomposing gases may greatly neutralize the capillary pressure and thus reduce densification. Therefore, any factor that limits the amount of reaction gases will have positive effect on densification. For example, in the case of SiC-Al_2O_3 system, the maximum densities for samples sintered at 2000 °C for 30 min in argon are less than 90% of theoretical (Fig. 1), whereas samples sintered in pressurized CO had densities of over 95% of theoretical. The reason for the enhanced densification in the presence of CO gas pressure is believed to be the inhibition of the reactions between SiC and Al_2O_3. This view is supported by the fact that considerably smaller weight losses were observed in samples sintered in CO than in samples sintered in argon. Inspection of Fig. 1 suggests that the volume of materials lost from the sample per unit time in flowing argon exceeds the rate of densification for all additions of Al_2O_3 above 5–10 wt%. Similar densities were obtained for the samples sintered in the closed crucible.

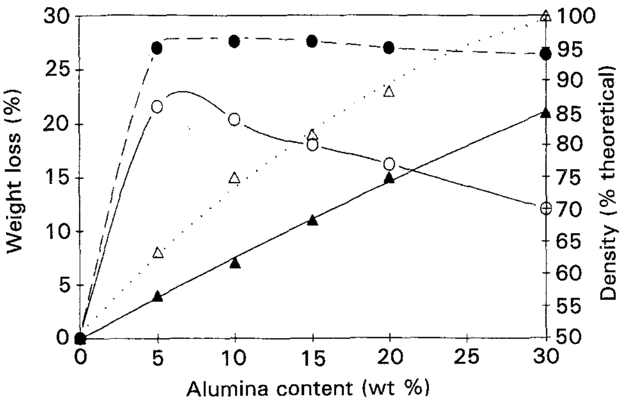

Figure 1 Variation of (△, ▲) weight loss and (●, ○) density with Al_2O_3 content in SiC samples sintered at 2000 °C for 30 min in flowing (△, ○) Argon or (▲, ●) CO atmospheres.

Fig. 2 shows the change of density with Al_2O_3 addition at five different sintering temperatures. The highest density was obtained for samples sintered at 2050 °C for 30 min. The decrease in density above 2050 °C is thought to be associated with the increase in weight loss due to reaction between SiC and Al_2O_3 (see Fig. 3). On the other hand, poor sintering of the samples with Al_2O_3 additions below 5 wt% is considered to be the consequence of insufficient amount of liquid-phase sintering requires that sufficient amount of liquid phase be present, which in the present system appears to be between 5 and 10 wt%. Although liquid-phase sintering may not be the only mass-transfer process, clearly the dominant mechanism must be the one involving liquid phase. This view is supported by the results in Figs 2 and 4 which show that high densities are achieved very quickly (< 30 min) only at a sintering temperature approaching the melting point of pure Al_2O_3 (i.e. 2050 °C). Soon after the liquid phase was formed (first 30 min of sintering), the rate of shrinkage (Fig. 5) exceeded the rate of reaction between SiC and Al_2O_3, and densification prevailed. Once the densification is completed, further holding (above ≈ 30 min) at sintering temperature resulted in the creation of porosity, which starts first at the surface of the sintered samples and then spreads towards the interior. Although there is continual increase in shrinkage with Al_2O_3 addition (Fig. 5), no significant increase in density was measured for Al_2O_3 addition above 12–15 wt% Al_2O_3, suggesting that the reduction in sample dimensions is entirely due to the loss of volatile components. Evidently, strict control of sintering temperature, time and the level of additions is essential if high density is to be achieved.

Detailed X-ray diffraction analysis (see Table II) shows that approximately 50 wt% added Al_2O_3 was lost as a result of Reactions 2–4. Reactions 3 and 4 also show that the loss of Al_2O_3 is accompanied by the formation of elemental silicon. Based on Reaction 3, it

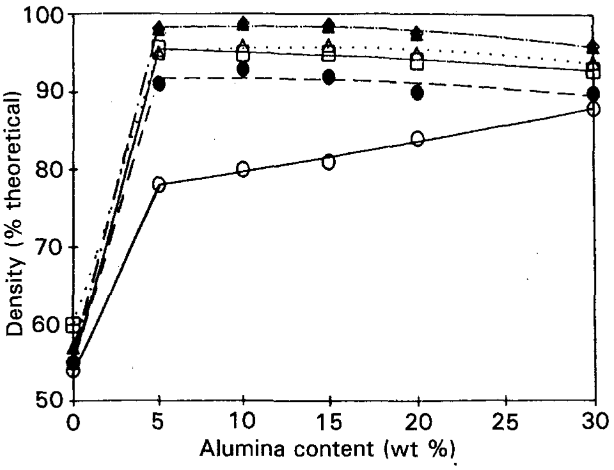

Figure 2 Variation of density with initial added alumina content in SiC samples sintered at various temperatures in CO gas at 0.105 MPa gauge pressure for 30 min. (○) 1900 °C, (●) 1950 °C, (△) 2000 °C, (▲) 2050°C, (□) 2100 °C

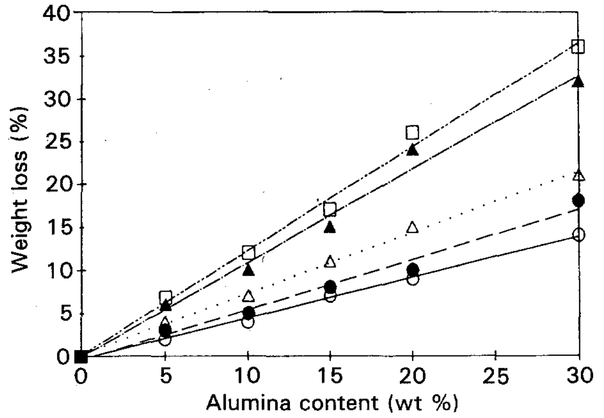

Figure 3 Variation of weight loss with initial added alumina content in SiC samples sintered at various temperatures under CO pressure for 30 min. (○) 1900 °C, (●) 1950 °C, (△) 2000 °C, (▲) 2050°C, (□) 2100 °C.

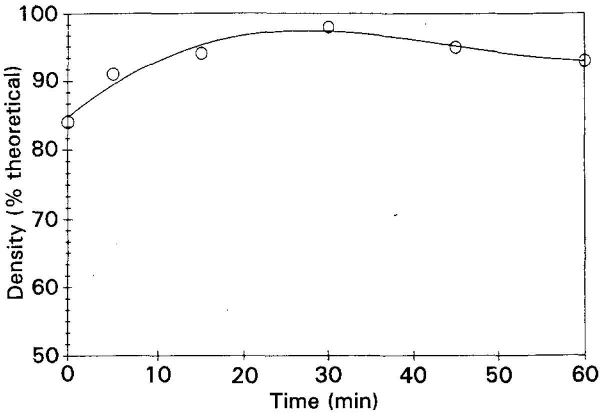

Figure 4 Variation of density with sintering time for SiC sample containing 10 wt% alumina, sintered at 2050 °C under CO pressure, for various times.

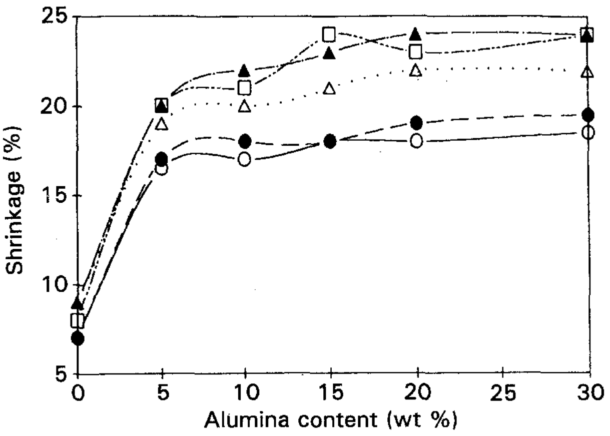

Figure 5 Variation of shrinkage with alumina content in SiC samples sintered at various temperatures for 30 min under CO pressure. (○) 1900 °C, (●) 1950 °C, (△) 2000 °C, (▲) 2050°C, (□) 2100 °C.

TABLE II Compositions and characteristics of green compacts and sintered bodies.

Green compacts Al_2O_3 content (Wt %)	Sintered bodies (2050 °C, 30 min)			
	Al_2O_3 content (wt %)	Silicon content (vol %)	Average aspect ratio	Length (μm) × width (μm)
5	2	0.2	7.5	15 × 2
10	4	0.45	12	12 × 1
15	7	0.6	8	8 × 1
20	11	1.2	6	6 × 1
30	15	1.5	–	–

is calculated that for the samples with 10 wt% Al_2O_3 addition, approximately 3.29 g Si should be formed, resulting in residual silicon of 4.84 vol%. This value is significantly higher than the measured value for residual silicon, which was ≈ 0.45 vol% (see Table II).

The weight loss for this composition (10 wt% Al_2O_3) was calculated to be approximately 7.4%. Comparison of this predicted weight loss and the measured value in Fig. 3 suggests that, in addition to Al_2O and CO, most of the silicon evaporated during the course of sintering.

The evidence for residual silicon in the sintered samples is found in Fig. 6 which shows the polished surface of a sample sintered at 2050 °C for 30 min. The bright areas in Fig. 6 were identified by SAM to be elemental silicon with a small amount of oxygen and carbon (see Fig. 7). Typical scanning Auger analysis is shown in Fig. 8. The size of these residual silicon grains is of the order of 1–2 μm.

The presence of Al_2O_3 had a pronounced effect on the microstructure of SiC. Although the sintered densities of samples with 5 and 10 wt% Al_2O_3 were almost the same, their microstructures were quite different (Fig. 9). The microstructure of the sample with 5 wt% Al_2O_3 was composed of mostly plate-like α-SiC grains, with some amount of elongated grains having an aspect ratio of over 7.5 (Table II). As the concentration of Al_2O_3 increases, the aspect ratio of elongated grains also increases, reaching a maximum value in 10 wt% Al_2O_3 samples (Fig. 9b). The lowest aspect ratio grains were observed with samples containing a maximum amount of Al_2O_3 additive (Fig. 9d). The refinement of microstructure with the addition of

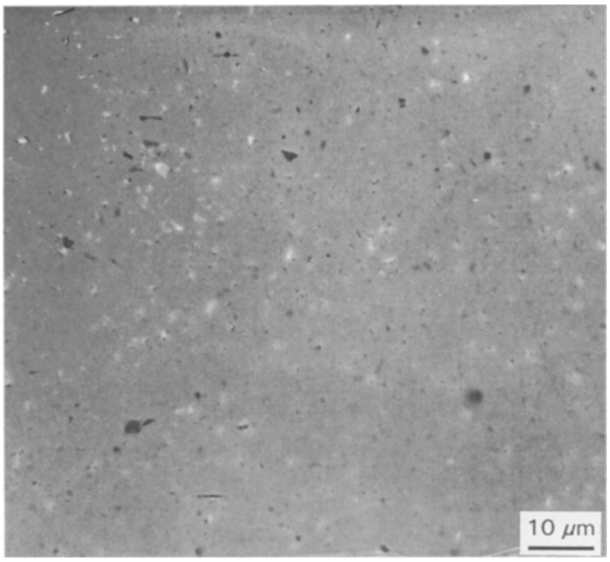

Figure 6 Polished surface of 10 wt% alumina sample, sintered at 2050 °C for 30 min under CO pressure.

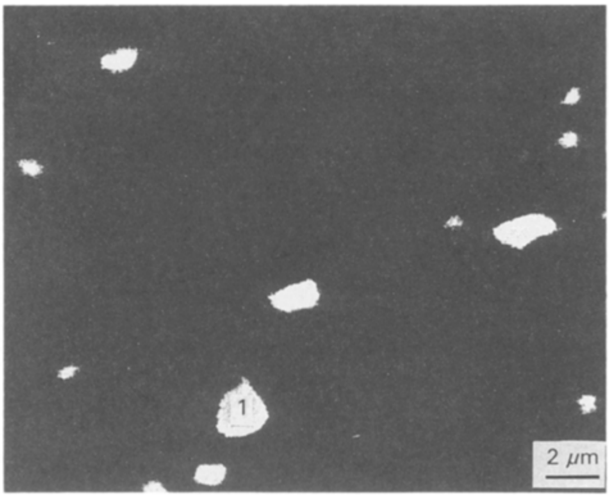

Figure 7 Scanning Auger electron image of 20 wt% alumina sample sintered at 2050 °C for 30 min under CO pressure.

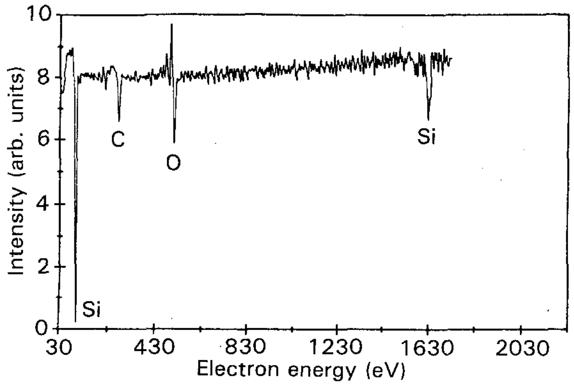

Figure 8 Auger electron spectrum at region 1 in Fig. 7 for sample containing 20 wt% alumina sintered at 2050 °C for 30 min under CO pressure. C, 21.6 at%; O, 18.2 at% Si, 60.2 at%.

Al_2O_3 is quite evident. The increased concentration of Al_2O_3 affects not only the aspect ratio of α grains but also their morphology. The largest number of whisker-like grains and the smallest number of large plate-like grains was found for samples containing 10 wt% Al_2O_3. This type of microstructure showed great promise for toughening and strengthening in SiC [4, 12].

Whilst the Al_2O_3 liquid phase is expected to enhance the $\beta \rightarrow \alpha$ transformation, a systematic quantitative study of the phase transformation was not performed.

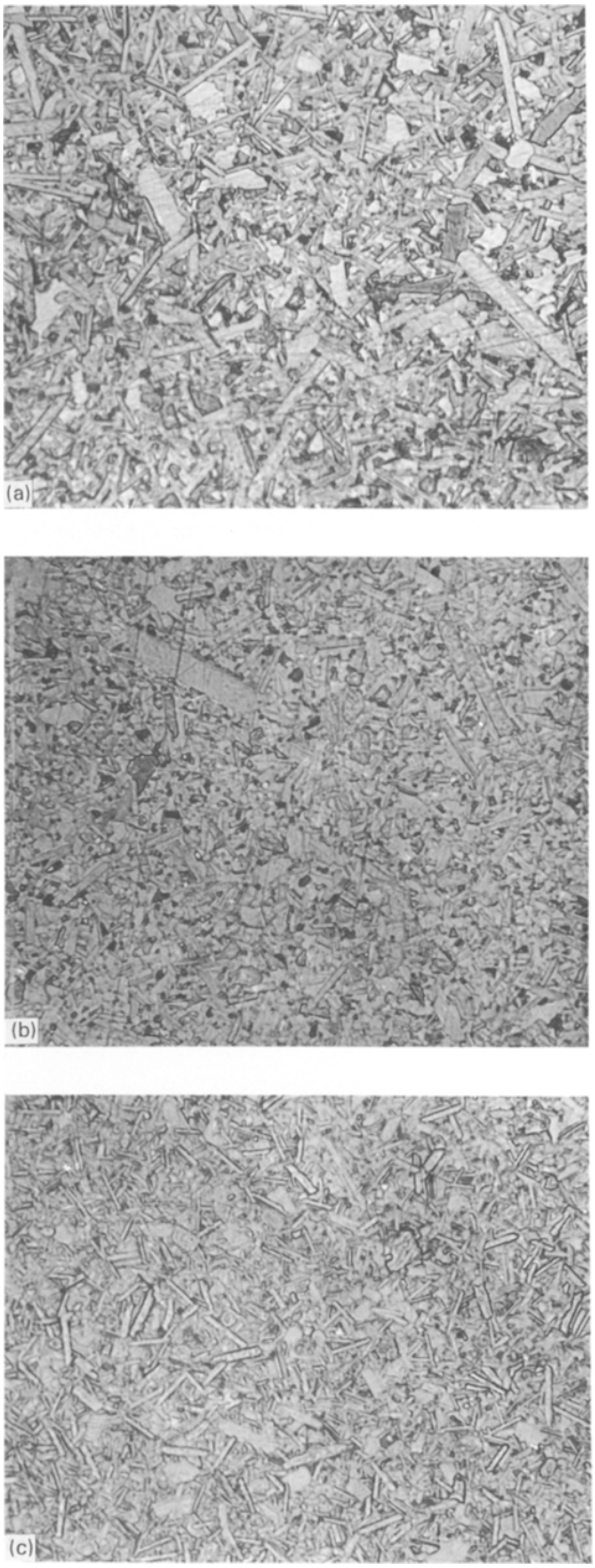

Figure 9 (Continued)

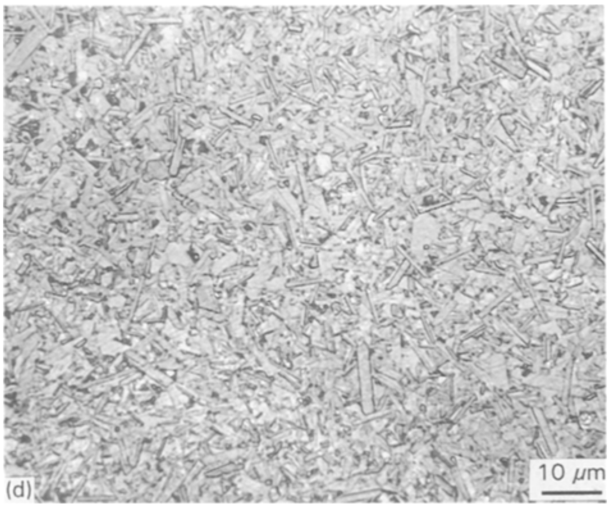

Figure 9 Microstructure of (a) 5 wt% alumina, (b) 10 wt% alumina, (c) 15 wt% alumina, and (d) 20 wt% alumina samples sintered at 2050 °C for 30 min under CO pressure.

4. Conclusions

β-SiC was pressureless sintered with Al_2O_3 additions to 98% theoretical density at 2050 °C for 30 min. The highest density was achieved in samples containing 10 wt% Al_2O_3. Inhibition of the reaction between Al_2O_3 and SiC, using a pressurised CO gas atmosphere was found to be beneficial for achieving high densities. As a consequence, weight losses were reduced to one-half of those without inhibition (i.e. sintering in argon).

The sintering technique is capable of producing a refined grain structure consisting of fine, elongated α-SiC grains in a matrix of β-SiC grains. Analyses by scanning Auger microscope and scanning electron microscope indicated the presence of silicon phase, ≈ 1–2 μm in size. The silicon phase is believed to be formed from the reaction between SiC and Al_2O_3. The grain size of the elongated as well as the equi-axed grains decreases with increasing Al_2O_3 content. This unusual microstructure is expected to have some potential in resisting crack propagation.

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