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Effect of initial particle size on microstructure of liquid-phase sintered α-silicon carbide

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Abstract

Three α-SiC powders of different particle sizes (~0.42, ~0.50 and ~0.71 μm), containing 7.2 wt% $Y_3Al_5O_{12}$ (YAG) and 4.8 wt% SiO_2 as sintering aids, were hot-pressed at 1850°C and subsequently annealed at 1950°C to initiate grain growth. All the hot-pressed specimens consisted of equiaxed grains and showed unimodal grain size distribution. The smaller the starting powder the finer the microstructure was developed. After annealing, the fine (~0.7 μm) and the medium (~1.1 μm) grain-sized specimens showed self-reinforced microstructures whereas the large (~1.5 μm) grain-sized specimen maintained an unimodal grain size distribution. These results suggest that the abnormal grain growth of α-SiC grains during annealing is critically dependent on the average grain size of sintered materials, which in turn depends on initial particle size. The fracture toughnesses (5.6 and 6.1 MPa $m^{1/2}$) of the annealed specimens with self-reinforced microstructures were higher than for the specimen with an unimodal grain size distribution (5.0 MPa $m^{1/2}$).

Keywords: Grain growth; Grain size; Hot-pressing; Microstructure-final; SiC

1. Introduction

In liquid-phase sintered silicon carbide ceramics, the control of abnormal grain growth during sintering or annealing is one of primary concerns in processing because the "in situ-toughened or self-reinforced SiC ceramics" with a microstructure containing abnormally grown SiC grains are known to exhibit high fracture toughness.[1–5] Several attempts to introduce the abnormally grown SiC grains into the microstructure have been reported, including the control of initial α-SiC content in the starting powder,[6] the seeding for favoring preferential grain growth,[7,8] the incorporation of α-SiC platelets[9] and the heat treatment for controlled grain growth.[3,10]

A self-reinforced microstructure containing abnormally grown elongated grains has been usually obtained by using β-SiC starting powders.[3–6] However, β-SiC containing α-SiC seeds[1,2] has also been used to take advantage of β→α phase transformation at high temperatures. Recently, a self-reinforced microstructure has also been obtained from α-SiC starting powders.[8,11] Concerning the microstructure of a sintered body resulting from α-SiC powders, two different suggestions have been made; one is that α-SiC starting powders lead to the equiaxed microstructure[12–14] and the other is that α-SiC starting powders can lead to the self-reinforced microstructure.[11] Such a disagreement may arise from an incomplete understanding of anisotropic or abnormal grain coarsening in specimens prepared from α-SiC starting powders.

Recently, Park et al.[15] have shown that the abnormal grain growth of faceted grains occurs by two-dimensional (2-D) nucleation. The 2-D nucleation theory predicts that there is a threshold initial grain size for the abnormal grain growth. In this study, the effect of α-SiC starting particle size on the microstructure has been investigated. The specimens were liquid-phase sintered and subsequently annealed. Three kinds of starting powders of α-forms with different particle sizes (~0.42, ~0.50, and ~0.71 μm) have been used for this study.

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2. Experimental procedure

The characteristics of α-SiC starting powders are listed in Table 1. Commercially available YAG (99.99% pure, High Purity Chemicals, Osaka, Japan) and SiO_2 (reagent grade, Kanto Chemical Co., Inc., Tokyo, Japan) powders were used as sintering additives. Three batches of powder were mixed, each containing 88 wt% α-SiC, 7.2 wt% YAG and 4.8 wt% SiO_2. The SiO_2 contained in the starting SiC powders was considered in the preparation of the batches. All batches were milled separately in ethanol for 24 h using SiC grinding balls. The milled slurry was dried and hot-pressed at 1850°C for 1 h under a pressure of 25 MPa in an argon atmosphere. For further annealing at high temperature, the load was removed and the temperature was continuously increased to 1950°C. Annealing has been carried out for 4 h under an atmospheric pressure of Ar.

The density of the specimen was determined by the Archimedes method. The theoretical density was calculated according to the rule of mixtures. The hot-pressed and annealed materials were cut and polished, then etched by a plasma of CF_4 containing 7.8% O_2. The microstructures were observed by scanning electron microscopy (SEM). According to the procedure described in previous studies,[7,16] the SEM micrographs of the specimens were analysed by image analysis. X-ray diffraction (XRD) using CuK_α radiation was performed on ground powders.

3. Results and discussion

Relative densities >99% of theoretical were achieved by hot-pressing with a dwell time of 1 h at 1850°C for all the specimens (Table 2). Typical microstructures of the hot-pressed specimens are shown in Fig. 1. As it is shown, the hot-pressed specimens consisted of mostly equiaxed grains regardless of the starting powders.

Table 1
Characteristics of starting α-SiC powers

Powder	Average particle size (μm)	Specific surface area (m^2/g)	Impurities (wt%)		Supplier
			Oxygen	Free carbon	
F	0.42	17.7	0.94	0.95	Lonza-Werke, Waldshut-Tiengen, Germany
M	0.50	15.0	0.71	1.08	Showa Denko, Tokyo, Japan
L	0.71	13.8	0.80	1.00	H.C. Starck, Germany

Phase analysis on hot-pressed specimens by XRD showed that the major phase of all specimens was α-SiC (6H). Specimens F and M contained $Y_2Si_2O_7$ as a trace. In contrast, specimen L contained polytype 15R and $Y_2Si_2O_7$ as traces. Fig. 2 shows the grain size distributions for the specimens: all exhibit the unimodal distribution. The average grain sizes of hot-pressed specimens were 0.7, 1.1 and 1.5 μm for the specimens F, M and L, respectively. In Fig. 2, the largest grains in each specimen are equal to or smaller than twice of each average grain size, indicating normal grain growth. The smaller starting powder led to the finer microstructure because the grain growth during hot-pressing was minimal[17] and the acceleration of grain growth through the β→α phase transformation[6] was avoided by using α-SiC starting powders. These results suggest that the microstructural development of α-SiC ceramics during hot-pressing is critically dependent on the average particle size of the starting powder.

Fig. 3 shows the microstructures of the specimens obtained after annealing at 1950°C for 4 h. As it can be seen, the difference in the microstructures resulting from the particle size became much more distinguishable when they were further annealed. The annealing resulted in a slight decrease of the relative density, probably due to the evaporation of volatile components such as SiO and CO.[18] However, this is not expected to result in the change of grain growth behavior. Phase analysis on annealed specimens by XRD showed the same results with those on hot-pressed specimens, indicating no detectable phase transformation during annealing. Although the grains in all specimens grew during annealing, some selected grains have grown abnormally in specimens F and M. The grain-size distributions of the annealed specimens are shown in Fig. 4. As it is shown, bimodal grain size distributions were obtained in the annealed specimens F and M. The results of image analysis for annealed specimens are summarised in Table 3. The average diameter of matrix grains increased with the starting particle size. The aspect ratios (3.7–4.0) of large grains for specimens F and M

Table 2
Relative density, fracture toughness and polytype of the sintered and the annealed specimens

Specimen		Relative density (%)	Fracture toughness (MPa $m^{1/2}$)	Crystalline phase[a]	
				Major	Trace
Hot-pressed specimen	F	99.8	2.9 ± 0.1	6H	$Y_2Si_2O_7$
	M	99.9	3.2 ± 0.1	6H	$Y_2Si_2O_7$
	L	99.1	3.6 ± 0.2	6H	15R, $Y_2Si_2O_7$
Annealed specimen	F	98.1	5.6 ± 0.4	6H	$Y_2Si_2O_7$
	M	98.2	6.1 ± 0.3	6H	$Y_2Si_2O_7$
	L	97.5	5.0 ± 0.3	6H	15R, $Y_2Si_2O_7$

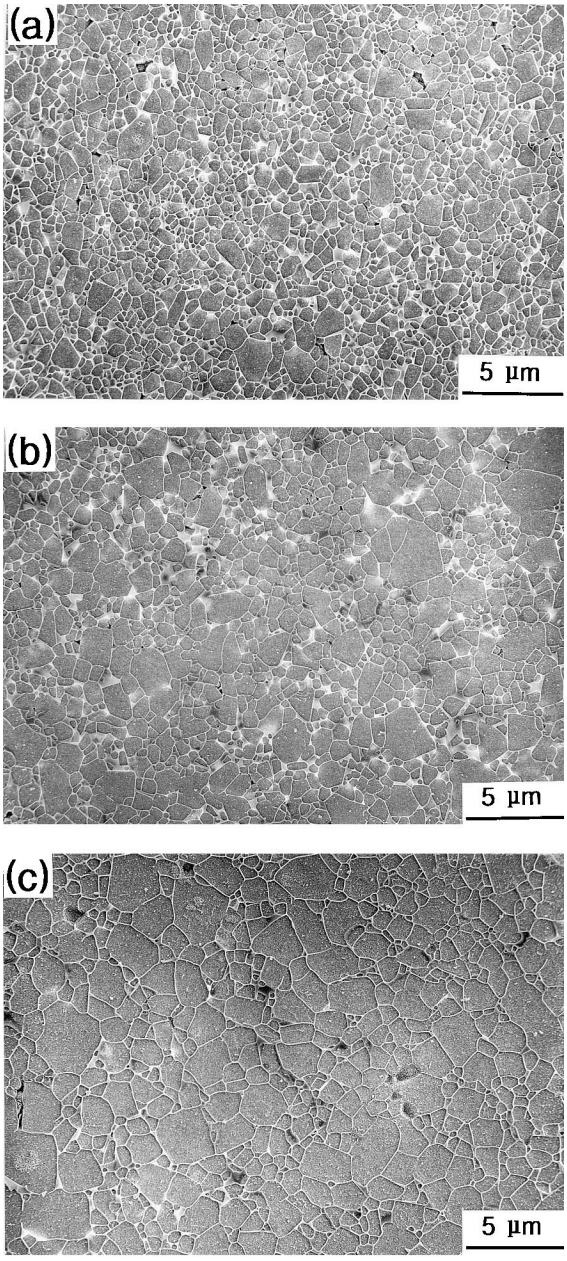

Fig. 1. Microstructures of hot-pressed specimens fabricated from (a) powder F, (b) powder M and (c) powder L (refer to Table 1).

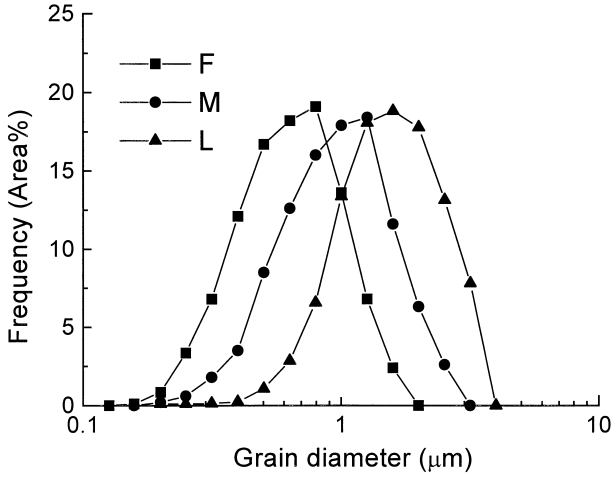

Fig. 2. Grain size distributions revealed by the relation between grain diameter and areal frequency for corresponding specimens in Fig. 1.

were similar to those (3.6–4.0) of the specimens fabricated from β-SiC starting powder, which we reported earlier.[6,7] There was no appreciable difference in the average grain size and aspect ratio of large grains for the specimens F and M. However, the size of matrix grains of the specimen F was finer than that of the specimen M, indicating the higher tendency of the abnormal grain growth in the specimen F.

From these results, it can be presumed that the abnormal or anisotropic grain growth during high temperature annealing of SiC ceramics is critically dependent on the microstructure after sintering. Since there was no detectable phase transformation during annealing, it is expected that the microstructural evolution observed during the annealing is only related to the microstructure of sintered specimens shown in Fig. 1. The finer the average grain size of the sintered specimen [Fig. 1(a)], the higher the rate of exaggerated grain growth [Fig. 3(a)]. This result can be explained by the growth model based on the 2-D nucleation mechanism, that has already been demonstrated in WC,[15] Sr-hexaferrite,[19] $BaTiO_3$[20] and Si_3N_4.[21]

The grain growth of α-SiC in the presence of a liquid phase is described by solution–reprecipitation[12,13] and the presence of small numbers of large grains is considered to be a prerequisite for abnormal grain growth.[8] Recently, Park et al.[15] claimed that the faceted and flat crystal planes, as observed in the α-SiC grains [Fig. 3(a) and (b)], are the important criterion for abnormal grain growth. They suggested from the atomically smooth interface structure of faceted planes that the abnormal grain growth will proceed by a process similar to 2-D nucleation and growth, for which the growth rate, R, is described by the following equation:

$$R = A_1 \exp\left(\frac{-A_2}{\Delta G}\right)$$

where A_1 and A_2 are constants and ΔG is the driving force for the grain growth. The growth rate will thus remain negligible and increase sharply when ΔG exceeds a certain critical limit. This means that the abnormal grain growth will occur only when the grain size is smaller than a certain critical limit.[21]

Taking into account the above growth mechanism, it is easy to understand the microstructural evolution observed during the annealing at 1950°C. After hot-pressing, the α-SiC grains that are considerably larger than other matrix grains may act as the nuclei for the abnormal grain growth in both specimens F and M. For the specimen L, however, the size of matrix grains is

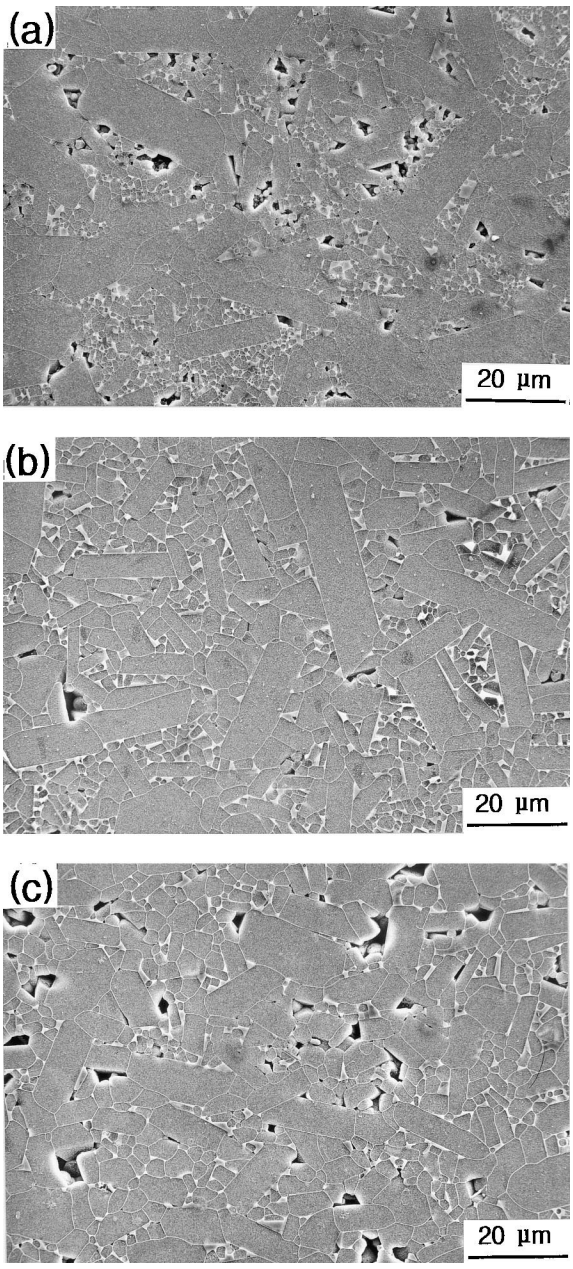

Fig. 3. Microstructures of the hot-pressed and annealed specimens fabricated from (a) powder F, (b) powder M and (c) powder L (refer to Table 1).

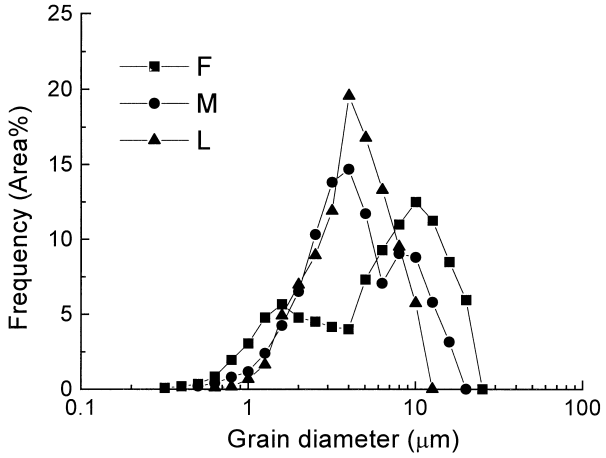

Fig. 4. Grain size distributions revealed by the relation between grain diameter and areal frequency for corresponding specimens in Fig. 3.

Table 3
Microstructural characteristics of the hot-pressed and annealed specimens

Specimen	Matrix grain		Large grain	
	d[a]	R_{95}[b]	d	R_{95}
F	1.8	2.5	10.1	3.7
M	3.2	3.3	9.6	4.0
L	3.6	3.3	–	–

[a] Average diameter.
[b] Aspect ratio (refer to Ref. [7]).

already expected to be larger than the critical size so that the growth rate of those nuclei becomes slow. Development of self-reinforced microstructures without the β→α phase transformation by annealing β-SiC nano-ceramics (average grain size of 110 nm) at 1850°C[16] and by seeding large (~0.45 μm) β-SiC grains into β-SiC nano-ceramics[7] appear to be a strong experimental evidence for the above theory.

The present results suggest that the development of a self-reinforced microstructure from α-SiC starting powders during annealing is critically dependent on the average grain size of sintered specimen as well as its distribution. In turn, the average grain size of sintered specimen is critically dependent on the initial particle size. The critical size for the abnormal grain growth of α-SiC by 2-D nucleation may be ~0.5 μm. Therefore, Padture[1] and other researchers[12,13] were not able to get self-reinforced microstructure from α-SiC starting powders because the particle sizes (~0.7 μm for Padture's work[1] and larger than 0.7 μm for the others[12]) of their starting powders were larger than the critical size for the abnormal grain growth.

The fracture toughnesses of the specimens are also shown in Table 2. The coarser the average grain size of the hot-pressed specimen, the higher the fracture toughness due to the grain coarsening effect of SiC, enhancing the crack-deflection mechanism.[22,23] After annealing, however, the specimens F and M with self-reinforced microstructures showed higher toughness, due to enhanced bridging by elongated grains,[2,16] than specimen L with an unimodal grain-size distribution. Interestingly, the fracture toughness (6.1 MPa $m^{1/2}$) of the annealed specimen M was higher than that (5.6 MPa $m^{1/2}$) of specimen F. This may be due to the difference in the contribution of matrix grains for toughening[24] because the aspect ratio and diameter of large grains were comparable in both materials.

4. Conclusions

We observed that the abnormal growth of α-SiC grains during annealing is critically dependent on the average grain size of sintered materials, which in turn depends on the initial particle size. The abnormal or anisotropic growth of α-SiC grains occurred when the fine α-SiC powders were used. A self-reinforced microstructure, consisting of large elongated grains and relatively fine matrix grains, could be achieved from fine ($\leqslant 0.5$ μm) α-SiC starting powders.

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