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Microstructure stability of fine-grained silicon carbide ceramics during annealing

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Fine-grained silicon carbide ceramics with an average grain size of ~140 nm or smaller were prepared by low-temperature hot-pressing of very fine β-SiC powders using Al_2O_3-Y_2O_3-CaO (AYC) or Y-Mg-Si-Al-O-N glass (ON) as sintering additives. The microstructure stability of the resulting fine-grained SiC ceramics was investigated by annealing at 1850°C and by evaluating quantitatively the grain growth behavior using image analysis. The $\beta \rightarrow \alpha$ phase transformation of SiC in AYC-SiC was responsible for the accelerated abnormal grain growth of platelet-shaped grains. In contrast, the $\beta \rightarrow \alpha$ phase transformation in ON-SiC was suppressed, which resulted in a very stable microstructure.

1. Introduction

Silicon carbide is difficult to densify without sintering additives because of its low self-diffusion coefficients and the covalent nature of the Si—C bond. Therefore, sintering additives are commonly used to attain full densification. Densification is achieved in solid-state sintering by using B and C additives, and in liquid-phase sintering by using metal oxide additives. The interest in liquid-phase sintered SiC has grown continually during recent years because such materials are easier to process and seem to have superior mechanical properties than solid-state sintered SiC [1–4]. The development of platelet grains into fine matrix grains during sintering or annealing is advantageous in the toughening of ceramics. These platelet grains can act as reinforcing agents that promote crack bridging and deflection, which result in improved toughness [1, 5]. Thus, many attempts have been made to develop the composite-type microstructures during sintering and/or annealing [6–8]. The evolution of the bimodal microstructure has been attributed to the $\beta \rightarrow \alpha$ phase transformation of SiC and/or the accelerated solution-reprecipitation by seeding during liquid-phase sintering [1, 6, 8]. Optimization of mechanical properties has been conducted through microstructure control [7, 8].

It has also been shown that the SiC ceramics with fine grains (<300 nm) and homogeneous microstructures exhibit superplasticity. The superplasticity of SiC was reported in both the solid-state-sintered β-SiC with a grain size of 200 nm (~140% elongation) [9] and the liquid-phase-sintered β-SiC with a grain size of 230 nm (~150% elongation) [10]. A fine initial grain size and a low grain-growth rate are especially important for superplastic deformation. It has been suggested that both grain size and grain size distribution are important parameters for obtaining superplasticity because dynamic grain growth is responsible for strain-hardening in ceramics during superplastic deformation [10, 11]. Thus, it is important to evaluate microstructural stability by investigating grain growth behavior during annealing. Although the effects of processing parameters on microstructural development have been studied extensively [6, 12, 13], the evaluation of microstructure stability with respect to sintering additive composition has received less attention. Nader *et al.* [6] reported that pure α-SiC and β-SiC do not transform with an Y_2O_3-AlN additive system, and thus result in a stable microstructure. They also showed that the $\beta \rightarrow \alpha$ phase transformation rate decreases with an increasing β-content in the starting powder as well as in the presence of nitrogen. Ortiz *et al.* [14] found that the presence of nitrogen stabilizes the β-phase, which also correspondingly generates stable microstructures.

In this work, the fabrication of fine-grained SiC ceramics have been attempted by starting from very fine (~30 nm) β-SiC powder with an Al_2O_3-Y_2O_3-CaO (AYC) or a Y-Mg-Si-Al-O-N glass (ON) as sintering additives. The microstructure stability of the fine-grained SiC ceramics was investigated by annealing the ceramics for up to 12 h at 1850°C, followed by an observation of the resulting microstructures using scanning electron microscopy (SEM). The SEM images were then characterized using image analysis.

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2. Experimental procedure

Pure, ultrafine β-SiC powder (designated as T1F) was prepared by oxidizing commercially available β-SiC powder (T-1 grade, Sumitomo-Osaka Cement Co., Tokyo, Japan) to eliminate free carbon and by treating it with hydrofluoric acid to remove SiO_2. The particle size, oxygen content, free carbon content and polytype of the T1F powder were 30 nm, 1.83 wt%, 1.75 wt% and β-SiC, respectively. A mixture of SiO_2 (Reagent Grade, Kanto Chemical Co., Inc., Tokyo, Japan), MgO (High-Purity Grade, Wako Pure Chemical Industries, Ltd., Osaka, Japan), Y_2O_3 (99.9% pure, Shin-Etsu Chemical Co., Tokyo, Japan), Al_2O_3 (99.9% pure, Sumitomo Chemical Co., Tokyo, Japan), and AlN (Grade F, Tokuyama Soda Co., Tokyo, Japan) powders was prepared to an oxynitride composition of $Y_{0.124}Mg_{0.160}Si_{0.414}Al_{0.302}O_{1.400}N_{0.151}$ by ball milling in ethanol for 24 h using SiC media and a jar. A combination of 90 wt% T1F with 10 wt% oxynitride glass was milled in ethanol for 24 h using SiC balls and a jar. The powder mixture of ON-SiC was dried and hot-pressed at 1800°C for 1 h under a pressure of 20 MPa in a nitrogen atmosphere. To prepare a powder composition for AYC-SiC, 90 wt% T1F, 7 wt% Al_2O_3, 2 wt% Y_2O_3, and 1 wt% CaO (High Purity Grade, Wako Chemical Co., Osaka, Japan) were ball milled in ethanol for 24 h using SiC balls and a jar. The powder mixture for AYC-SiC was dried and hot-pressed at 1750°C for 30 min under a pressure of 20 MPa in an argon atmosphere. The hot-pressed specimens were heated further at 1850°C for 6 h or 12 h under an atmospheric pressure of argon (AYC-SiC) or nitrogen (ON-SiC) to enhance grain growth.

Sintered density was determined by the Archimedes method. The theoretical densities of the specimens, 3.207 g/cm^3 for ON-SiC and 3.278 g/cm^3 for AYC-SiC, were calculated according to the rule of mixtures (the theoretical density of the oxynitride glass was 3.18 g/cm^3) [15]. The hot-pressed and annealed specimens were cut and polished, then etched by a CF_4 plasma containing 7.8% O_2. The microstructures were observed by SEM. SEM micrographs were quantitatively analyzed using an image analyzer (Image-Pro Plus, Media Cybernetics, USA). The grain diameter was defined by the equivalent diameter of each grain area in the two-dimensional image. The average grain size was determined from the 50% value of the cumulative area curve of grain diameter. The three-dimensional morphology of SiC grain was a hexagonal platelet. The thickness of each grain (t) was determined directly from the smallest grain dimension in its two-dimensional image; the apparent length of each grain (L) was obtained from the largest dimension. The mean value of the 10% highest observed aspect ratio (L/t) was taken to be the mean of the actual values (R_{95}) [16].

3. Results and discussion

Relative densities of >98.0% were achieved by hot-pressing and subsequent annealing for all specimens (Table I). The maximum hot-pressing temperatures of 1750 and 1800°C were high enough for AYC-SiC and ON-SiC, respectively, to successfully yield high-density specimens. The temperature was about 50°C or 100°C lower than that for submicrometer powders. The fine starting powder and low sintering temperature were effective in minimizing grain growth during sintering. The typical microstructures of hot-pressed and annealed specimens are shown in Figs 1 and 2. The microstructures of hot-pressed specimens were very fine and uniform, consisting of equiaxed grains (Figs 1a and 2a). This kind of microstructure had not been attained from submicrometer powders because of the presence of nuclei for abnormal grain growth [17, 18]. The average grain sizes of AYC-SiC and ON-SiC were ~120 and ~140 nm, respectively. The grain growth during the sintering was very small. It was based on the elimination of large nuclei from the starting powder, as well as the narrow distribution of the starting powder.

TABLE I Relative density and polytype of hot-pressed and annealed specimens

Material	Relative density (%)	Crystalline phase	
		Major	Minor
Hot-pressed AYC-SiC	98.9	β-SiC	–
6 h annealed AYC-SiC	98.5	β-SiC	α-SiC
12 h annealed AYC-SiC	98.1	α-SiC	β-SiC
Hot-pressed On-SiC	99.5	β-SiC	–
6 h annealed On-SiC	99.4	β-SiC	–
12 h annealed On-SiC	99.2	β-SiC	–

The microstructure of AYC-SiC after 6 h annealing showed abnormal grain growth in a small number of grains (Fig. 1b). The microstructure of 6 h annealed AYC-SiC consisted of platelet grains and equiaxed grains, and further annealing up to 12 h led to the remarkable growth of platelet grains. In contrast, the microstructures of 6 and 12 h annealed ON-SiC consisted of equiaxed grains only (Fig. 2b and c). The major phase of ON-SiC was β-SiC for both the hot-pressed and the annealed specimens. Previous results [19, 20] have shown that the oxynitride glass maintains β-SiC up to 2000°C and microscopically, β-SiC has an equiaxed morphology in nitrogen-containing liquid. Present results suggest that the microstructure of ON-SiC is more stable than that of AYC-SiC. This effect is also related to the fact that the fine-grained SiC ceramics sintered with oxynitride glass showed no appreciable grain growth during superplastic deformation [10, 21].

The introduction of large grains as seeds results in the different grain size distribution and, thus, different microstructure [7, 8, 22]. The grain size distributions of the hot-pressed and the annealed specimens are shown in Fig. 3. The grain size distributions of both hot-pressed AYC-SiC and hot-pressed ON-SiC are almost the same. In contrast, the bimodal microstructure was

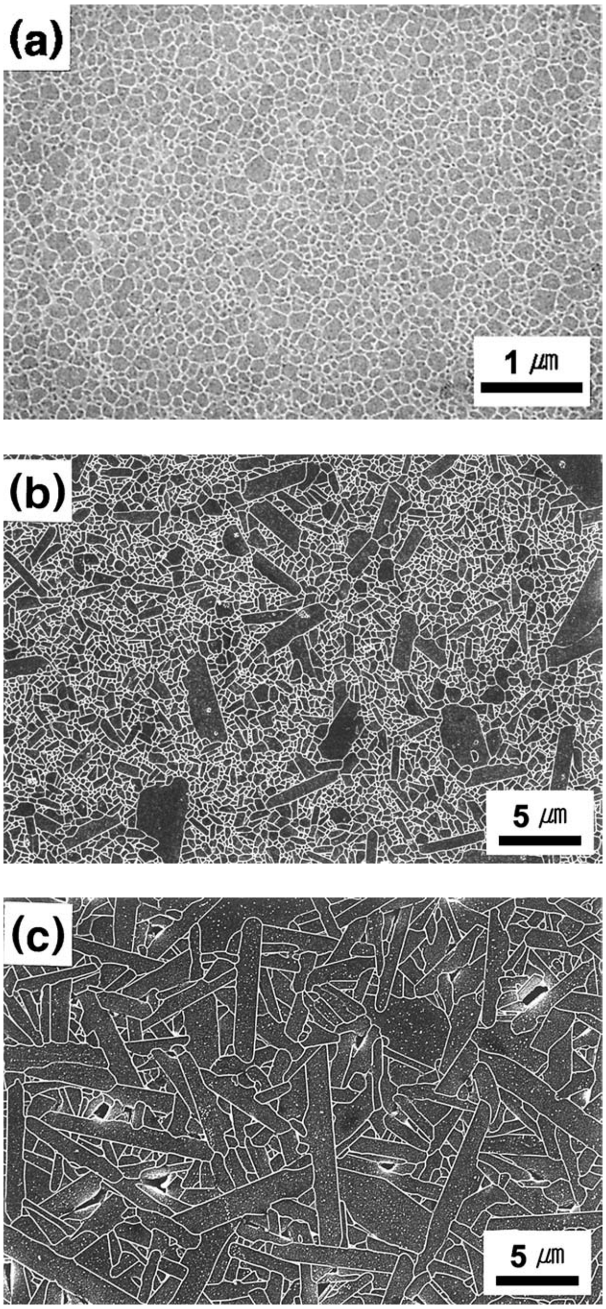

Figure 1 Microstructures of hot-pressed and annealed specimens: (a) hot-pressed AYC-SiC, (b) 6 h annealed AYC-SiC, and (c) 12 h annealed AYC-SiC.

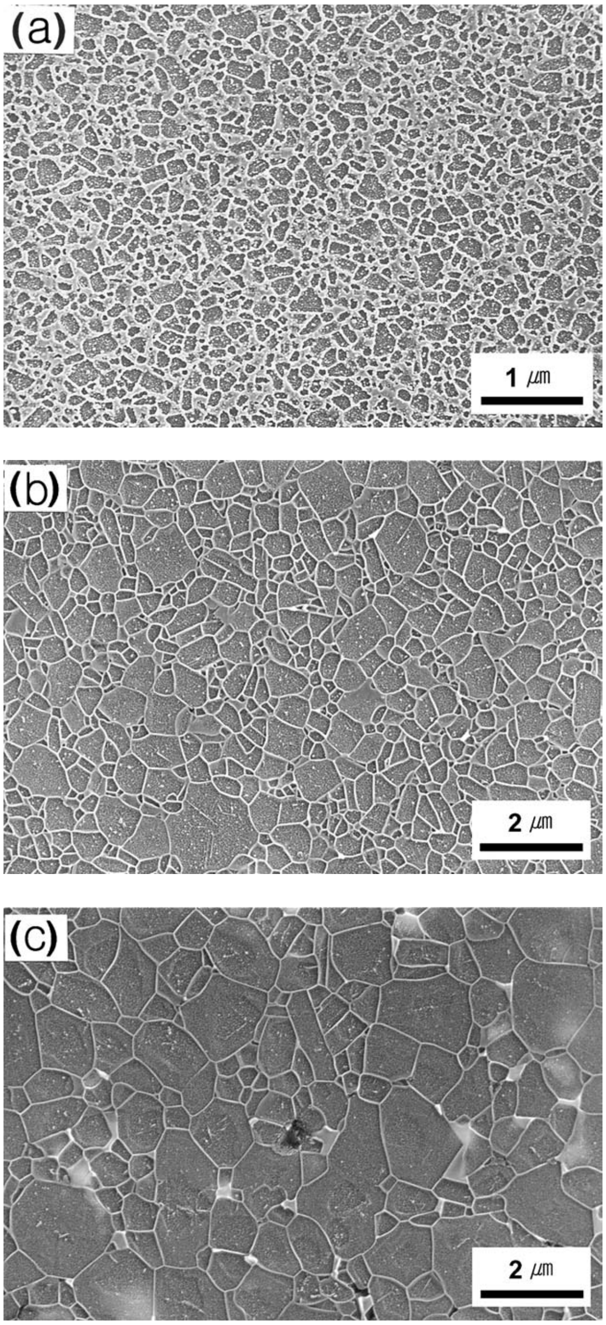

Figure 2 Microstructures of hot-pressed and annealed specimens: (a) hot-pressed ON-SiC, (b) 6 h annealed ON-SiC, and (c) 12 h annealed ON-SiC.

produced in AYC-SiC after annealing, whereas the unimodal microstructure was formed in ON-SiC. The difference in the microstructure of annealed specimens originated from the difference in the additive composition.

Phase analysis of the hot-pressed and annealed specimens by XRD showed the occurrence of the $\beta \rightarrow \alpha$ phase transformation of SiC in annealed AYC-SiC (Table I). The result clearly shows that the $\beta \rightarrow \alpha$ phase transformation accelerated the growth of large grains during annealing. This suggests that a homogeneous microstructure cannot be maintained if the occurrence of the phase transformation is favored during annealing. Nader *et al.* [6] also reported that the suppression of the $\beta \rightarrow \alpha$ phase transformation led to a homogeneous microstructure consisting of equiaxed grains, even for long sintering times, whereas a significant change in grain morphology was observed in the presence of the phase transformation.

The changes of grain size and aspect ratio with annealing time are shown in Fig. 4. The grain size of ON-SiC increased gradually with annealing time. In contrast, the grain size of AYC-SiC increased gradually up to 6 h and rapidly up to 12 h-annealing, owing to the morphological change of SiC grains from equiaxed to platelet grains, i.e., the occurrence of the $\beta \rightarrow \alpha$ phase transformation of SiC. The average grain size in AYC-SiC increased more than 19 times the original during annealing at 1850°C for 12 h. By contrast, the increase was only about 4 times the original size after annealing at 1850°C for 12 h in ON-SiC. This might be due to different mechanisms in grain growth of the two

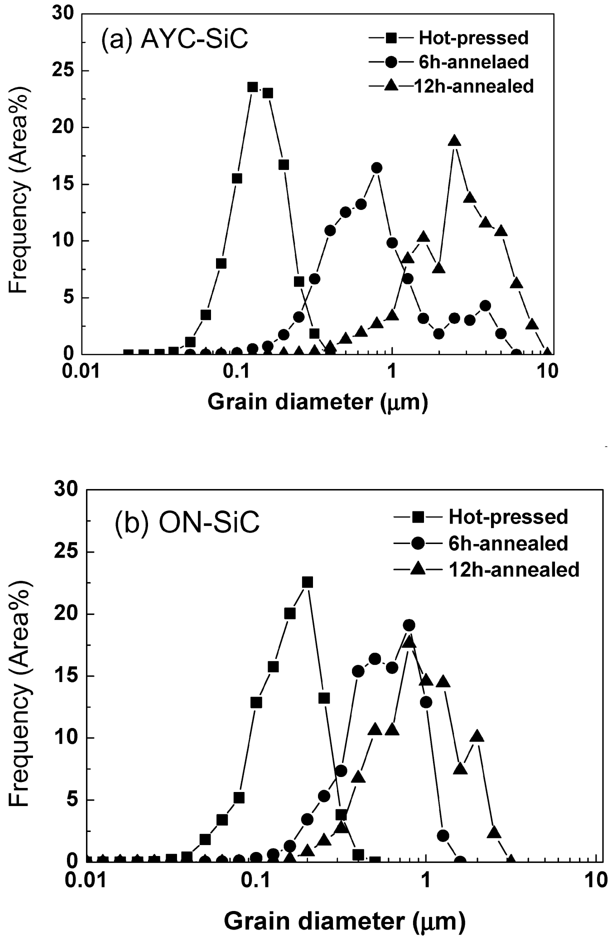

Figure 3 Grain size distribution revealed by the relation between grain size and areal frequency for hot-pressed, 6 h annealed and 12 h annealed: (a) AYC-SiC and (b) ON-SiC.

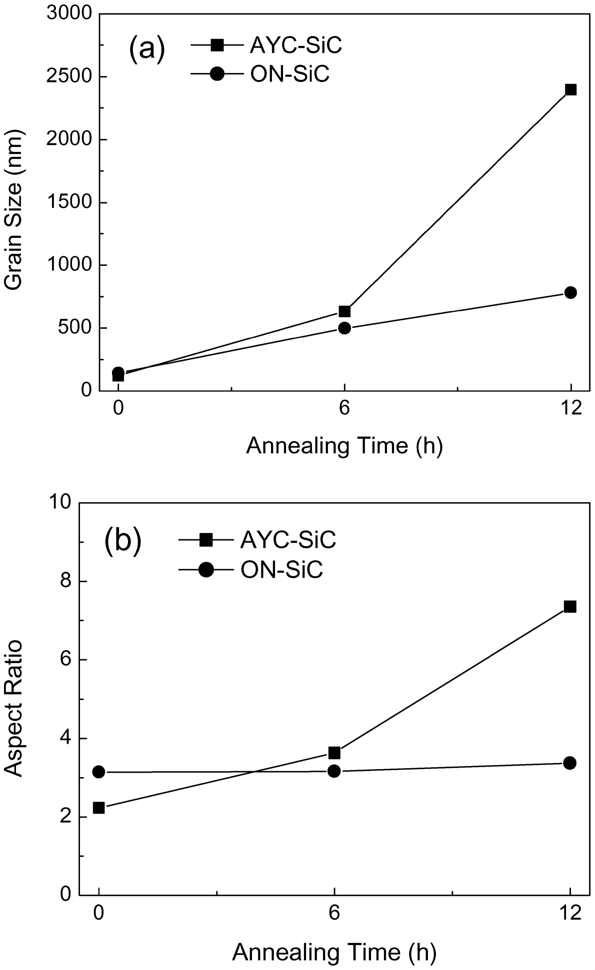

Figure 4 Change of (a) grain size and (b) aspect ratio of SiC grains in AYC-SiC and ON-SiC as a function of annealing time at 1850°C.

specimens. Most of the platelet grains in Fig. 2c show a core/rim structure, indicating grain growth through solution-reprecipitation [23]. The occurrence of phase transformation (see Table I) accelerated grain growth in AYC-SiC. Thus, both the solution-reprecipitation and the phase transformation are responsible for the rapid grain growth rate in AYC-SiC, whereas only solution-reprecipitation is observed in ON-SiC. Thus, the grain growth rate depends on both the chemistry of sintering additives and the occurrence of the phase transformation. Slow grain growth rate in ON-SiC is the basis for the superplasticity of fine-grained or nanostructured SiC ceramics.

The change of aspect ratio in AYC-SiC showed the same tendency as that characteristic of grain size. However, the aspect ratio of ON-SiC was kept constant during the annealing, owing to the normal grain growth during annealing. The result also shows that the grain growth of β-SiC is isotropic whereas that of α-SiC is anisotropic.

From the above results it can be concluded that the microstructure of ON-SiC is more stable than that of AYC-SiC. The stable microstructure of ON-SiC is confirmed by small grain growth and almost no change in aspect ratio even after 12 h-annealing at 1850°C (Fig. 4). Strain hardening has been observed during superplastic deformation of AYC-SiC [18]. The rate of deformation decreased under a constant applied stress due to dynamic grain growth during the deformation. Considering the previous work on superplastic deformation [10, 18], as well as our present work, microstructure stability is one of the necessary conditions for the development of superplastic ceramics.

4. Conclusions

The microstructure stability for superplastic deformation can be achieved by selecting both an additive composition that suppresses the phase transformation during superplastic deformation and a fine (<100 nm) starting powder with narrow particle size distribution.

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