Microstructure and Polytype of *in situ*-Toughened Silicon Carbide

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Fine (~0.09 μm) β-SiC powders with 3.3 wt% of large (~0.44 μm) α-SiC or β-SiC particles (seeds) added were hot-pressed at 1750°C using Y_2O_3, Al_2O_3, and CaO as sintering aids and then annealed at 1850°C for 4 h to enhance grain growth. The resultant microstructure and polytypes were analyzed by high resolution electron microscopy (HREM). Growth of β-SiC with high density of microtwins and formation of α/β composite grains consisting of α-SiC domain sandwiched between β-SiC domains were found in both specimens. When large α-SiC (mostly 6H) seeds were added, the β-SiC transformed preferentially to the 6H polytype. In contrast, when large β-SiC (3C) seeds were added, the fine β-SiC transformed preferentially to the 4H polytype. Such results suggested that the polytype formation in SiC was influenced by crystalline form of seeds added as well as the chemistry of sintering aids. The α/β interface played an important role in the formation of elongated grains as evidenced by presence of α/β composite grains with high aspect ratio.

Key words : SiC, Microstructure, Polytype

I. Introduction

Since the first successful sintering of SiC with small additions of boron and carbon in the early 1970s,[1] SiC ceramics have been attracted much attention as one of the promising candidates for structural applications due to their excellent high-temperature strength and creep, wear, oxidation, and corrosion resistance.[2-4] However, application of SiC ceramics as a structural material has been limited by their low fracture toughness, even though, in comparison to other ceramics, their superior other properties. Recently several reports have been published on in situ-toughened SiC,[5-10] akin to Si_3N_4.[11-14] The improvement of fracture toughness has been achieved through development of elongated α-SiC grains; i.e., microstructural control for toughening was based on β→α phase transformation.[5,7,9] Large elongated grains have been shown to increase fracture toughness in SiC by crack bridging[8] or crack deflection.[9] A fracture toughness > 8 MPa $m^{1/2}$ has been reported in oxide-doped, liquid-phase-sintered SiC.[5,10]

Silicon carbide nanoceramics (grain size ~0.1 μm) were fabricated previously from very fine β-SiC powders by hot-pressing.[15,16] In situ-toughened SiC with duplex microstructure has been fabricated by annealing the nanoceramics at a temperature as low as 1850°C without appreciable β→α phase transformation.[15] Previous studies also have shown that SiC nanoceramics can be superplastically deformed[16] and they can be considered as

a matrix for controlling the bimodal microstructure. The effect on microstructural development of adding large (~0.44 μm) α-SiC or β-SiC particles (seeds) during annealing was previously investigated,[17] where two kinds of in situ-toughened microstructures were obtained; annealed materials with β-SiC seeds had microstructures consisting of small matrix grains and large elongated grains while annealed materials with α-SiC seeds had uniform microstructures consisting of elongated grains. Further microstructural control and optimization in SiC is crucially dependent on an increased knowledge of polytype distributions in SiC grains and how α/β interface affects grain growth behavior in SiC.

Silicon carbide can form various crystal structures having the same chemical composition but a differing number of stacking layers in the unit cell. There is only one crystal structure with cubic symmetry, which is identified as the β-phase or 3C (Ramsdell notation[18]). At high temperature (~2000°C), the β-phase transforms to α-phases with hexagonal or rhombohedral symmetry, with 4H, 6H, and 15R being the major polytypes observed in SiC ceramics. Preference of the polytype formation during β→α phase transformation is found to be dependent on the chemistry of the sintering aids.[19] Beta to 4H phase transformation has been observed in SiC materials with Al, B, and C additives with β-phase starting powders[20] and SiC materials with BeO.[21] Beta to 6H phase transformation has been observed in SiC materials with B and C additives with β-phase starting

powders.[22] However, polytype distributions in *in situ*-toughened SiC with oxide additives have not been investigated well.

In this study, high . resolution electron microscopy (HREM) was used to investigate the polytype distributions in the SiC grains with various morphologies, in order to understand further how seed grains and α/β interface affect grain growth behavior in SiC.

II. Experimental Procedure

Fine β-SiC powder (Table 1) was prepared by grinding commercially available, β-SiC powder (T-1 grade, Sumitomo-Osaka Cement Co., Tokyo, Japan) in a SiC ball mill and then centrifuging to eliminate free carbon. The procedure also eliminated large agglomerates and extremely fine particles in the powder. The 87 wt% fine β-SiC powder mixed with 7 wt% Al_2O_3 (99.9% pure, Sumitomo Chemical Co., Tokyo, Japan), 2 wt% Y_2O_3 (99.9% pure, Shin-etsu Chemical Co., Tokyo, Japan), and 1 wt% CaO (high-purity grade, Wako Chemical Co., Osaka, Japan) was milled in ethanol for 2 h using SiC balls and a jar. Then 3 wt% α-SiC (A-1 grade, Showa Denko, Tokyo, Japan) or β-SiC (B-1 grade, Showa Denko) powder (seeds) was added and the mixture milled for 20 min. A 3 wt% addition of seeds corresponded to 3.3 wt% of the SiC. The powder mixture was dried and hot-pressed at 1750°C for 15 min under a pressure of 20 MPa in an Ar atmosphere. The hot-pressed materials were heated further at 1850°C for 4 h under an atmospheric pressure of Ar to enhance grain growth. The SiC material with α-SiC seeds and SiC material with β-SiC seeds are designated as materials A and B, respectively. The relative densities of materials A and B were 97.2% and 97.0%, respectively. The grain size distributions of each specimen were reported in previous paper.[17]

Several transmission electron microscopy specimens were prepared by slicing a specimen with a low-speed diamond saw at a thickness of ~300 μm and polishing it to a thickness of ~100 μm, using various grades of diamond pastes. Disks of 3 mm diameter were ultrasonically cut and thinned by mechanical microthinning and ion-beam milling to give electron transparency. Because of the complexity in the polytypic nature of SiC, crystal structure identification of each grain was accomplished by a select-

ed area diffraction pattern analysis and by direct resolution of the lattice images, using a transmission electron microscopy (H-9000UHR, Hitachi Co., Ltd., Japan).

III. Results and Discussion

Figure 1 shows typical microstructures of materials A and B Material B had a bimodal microstructure of small matrix grains and large elongated grains, which was relatively high aspect ratio grains but the volume fraction of those grains was small. In contrast, material A had a relatively uniform microstructure consisting of elongated grains, which was relatively small aspect ratio grains but the volume fraction of those grains was high. The differences in microstructure between material A and material B might have arisen from differences in the grain-growth behavior.[17] Shapes of the elongated grains are normally narrow and platelike, with short c-axis that appear to be prismatic.

The polytype analysis of material A by X-ray diffraction (XRD) indicated the presence of 3C and 6H as major phases.[17] The microstructure of material A consisted of two kinds of grains; one was a β-SiC grain with high density of microtwins (Fig. 2) and the other was a
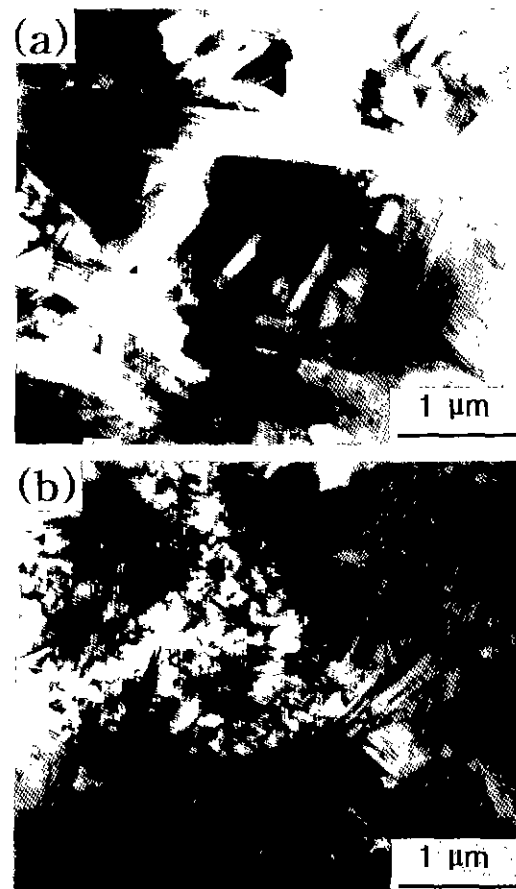

Fig. 1. Typical bright-field micrographs of (a) SiC material with α-SiC seeds (designated as material A) and (b) SiC material with β-SiC seeds (designated as material B).

Table 1. Characteristics of Starting Powders

| Powder | Average particle size (μm) | Specific surface area (m²/g) | Impurities | | Phase |
| | | | Oxygen | Free C | |
			(wt%)		
Fine powder	0.09	21.4	1.00	1.88	β
α-SiC seeds*	0.45	15	0.38	1.08	α
β-SiC seeds*	0.43	15	0.55	1.67	β

*Manufacturer's data.

composite grain consisting of α-SiC (6H) domain sandwiched between β-SiC domains (Fig. 3). An example of lattice image in a β-SiC grain with microtwins is shown in Fig. 4, where the structural lattice image spacing of 2.5 Å indicates the 3C structure. The formation of microtwins can occur commonly during grain growth of β-SiC, owing to its low formaion energy,[23] as observed by other researchers.[24-26]

The formation of α/β composite grain is one of the unique features of this material. The presence of a coherent envelope of recrystallized β-SiC on the basal planes of every α-SiC plate, i.e., "sheath" arrangement of β- and α-structures, was reported in partially transformed boron- and carbon-doped SiC materials.[24,25] Material A, which was liquid-phase-sintered using Y_2O_3, Al_2O_3, and CaO as sintering aids and adding α-SiC (mostly 6H)[27] seeds, has also similar α/β composite grains, i.e., a composite grain consisting of α-SiC (6H) domain sandwiched between β-SiC domains (Fig. 3),

even though it has different chemistry of sintering aids. A grain with high aspect ratio was mostly 3C/6H composite grain and has parallel grain boundaries (or domain boundaries) along the basal plane of 6H. These results suggest that α/β interface plays an important role in abnormal grain growth of SiC. An example of the lattice image in a 3C-6H interface boundary is shown in Fig. 5, where the structural lattice image spacing of 15 Å indicates the 6H structure.

The polytype analysis of material B by XRD indicated the presence of 3C and 4H as major phases.[17] The microstructure of material B consisted of two kinds of grains; one was a β-SiC grain with microtwins and the other was a composite grain consisting of α-SiC (4H) domain bordered by β-SiC domains (Fig. 6). Small matrix grains were β-SiC grains while elongated grains were mostly α/β composite grains, which was consisted of α-SiC (4H) domain bordered by β-SiC domains. An example of the lattice image in a 3C-4H interface boundary is shown in Fig. 7, where the structural lattice image spacing of 10 Å indicates the 4H structure. Several long period polytypes containing some combinations of 4H and 3C have also been observed in material B (Fig. 7), which may be some intermediate structure in the tranformation from 3C to 4H.

It is recognized that preference of the polytype formation during β→α phase transformation is dependent on the chemistry of the sintering aids.[19] However, the
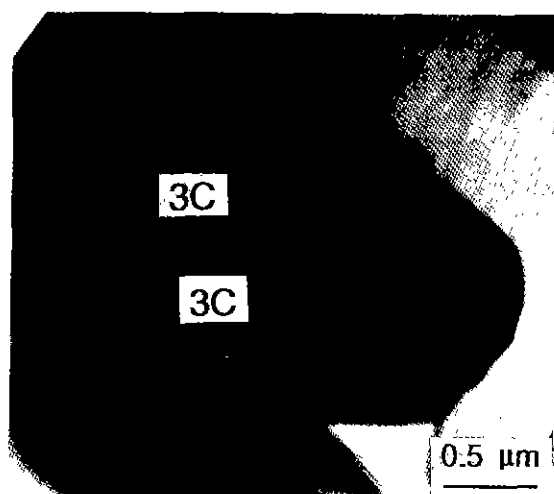

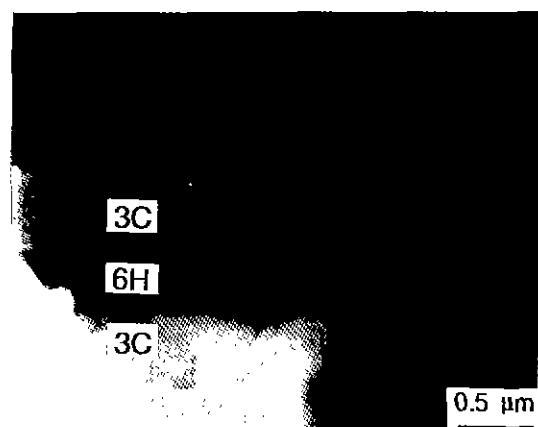Fig. 2. Bright field micrograph of a β-SiC grain with microtwins in material A.

Fig. 3. Bright field micrograph of a composite grain consisting of α-SiC (6H) domain sandwiched between β-SiC domains in material A.
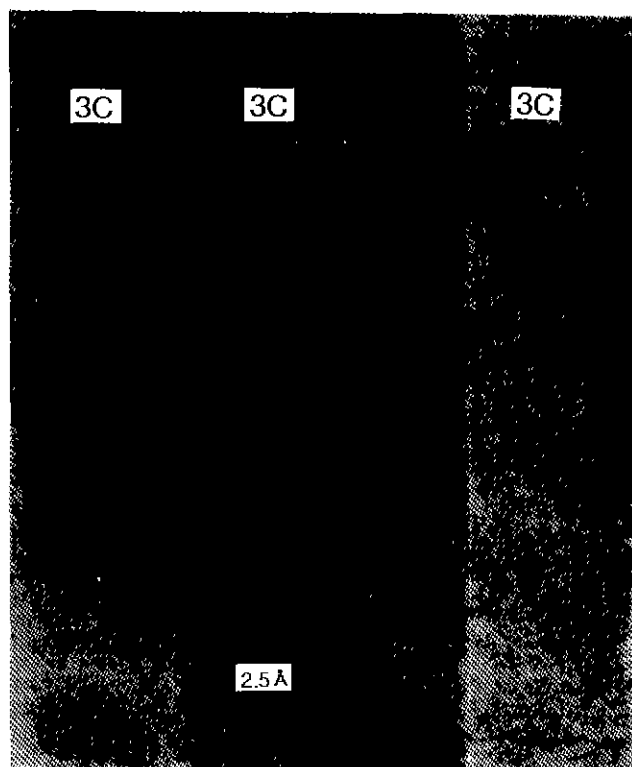

Fig. 4. High resolution structural lattice image shows a typical microtwins of a β-SiC grain in material A. The structural lattice image spacing of 2.5 Å indicates the 3C structure.
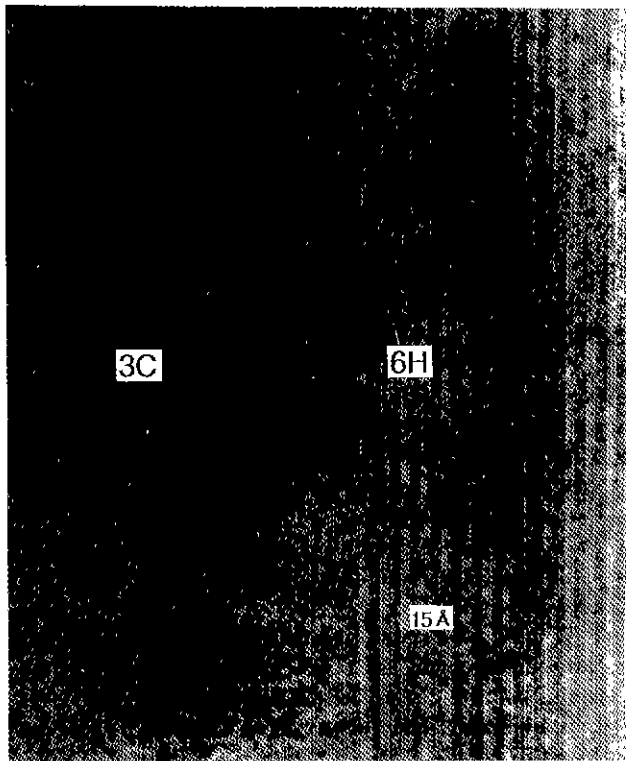
Fig. 5. High resolution structural lattice image shows a typical 3C-6H boundary in material A. The structural lattice image spacing of 15 Å indicates the 6H structure.
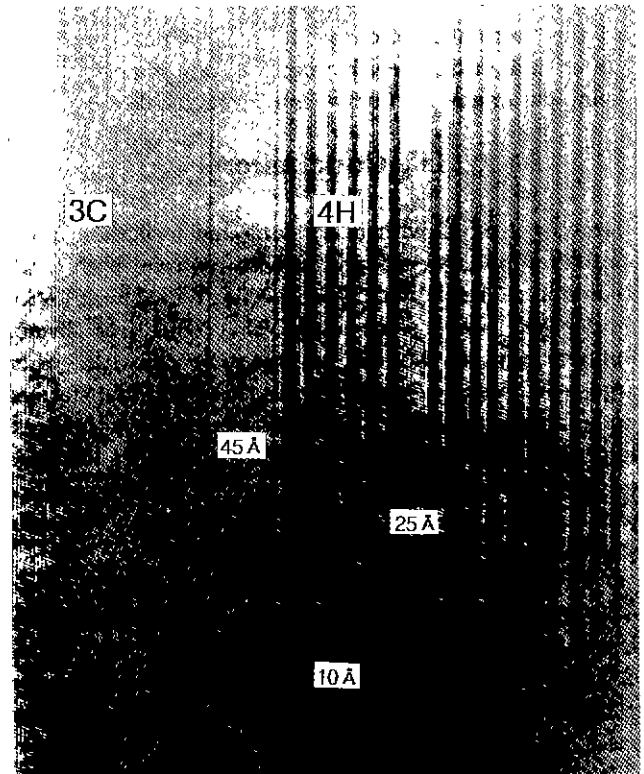

Fig. 7. High resolution structural lattice image shows a typical 3C-4H boundary in material B. The structural lattice image spacing of 10 Å indicates the 4H structure.
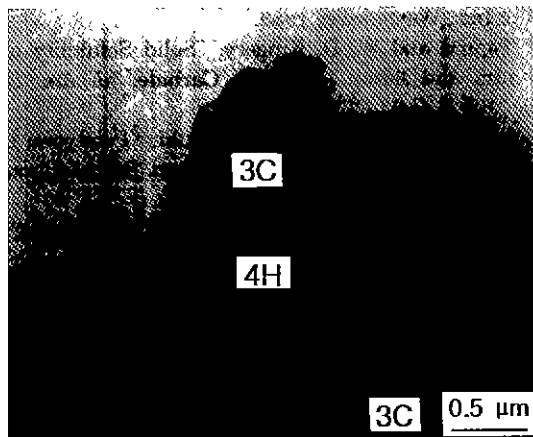

Fig. 6. Bright field micrograph of a composite grain consisting of α-SiC (4H) domain sandwiched between β-SiC domains in material B.

results of this investigation have shown that 6H polytype formation in SiC material with α-SiC (mostly 6H) seeds and 4H polytype formation in SiC material with β-SiC seeds may be strongly enhanced, even though they have the same chemistry of the sintering aids, i.e., 7 wt% Al_2O_3, 2 wt% Y_2O_3, and 1 wt% CaO. These results suggest that changes in the polytype distribution in SiC materials may thus be related preferentially to the polytype distribution in starting powders, rather than the chemistry of sintering aids.

For material B, only large β-SiC grains act as nuclei for the growth of large grains during hot-pressing at 1750°C, since the growth of SiC grains was controlled by Ostwald ripening.[28] Alpha-SiC nuclei might be formed inside the large grains due to β → α phase transformation during annealing at 1850°C, as observed in Fig. 7. Thus, small number of α-SiC acted as nuclei for abnormal grain growth in material B. In contrast, the grain growth of elongated grains in material A has resulted from the overgrowth of β-SiC on α-SiC cores because of hot-pressing and annealing temperatures as low as 1750 and 1850°C, respectively. Thus, even small α-SiC grains in material A acted as nuclei for abnormal grain growth. It is the reason why uniform microstructure consisting of elongated grains has been developed in material A (Fig. 1(a)). Hence, differences in the microstructure between material A and material B have arisen from the difference in the number of nuclei.

It is observed that the elongated grains were mostly α/β composite grains in the present study, indicating the important role of α/β interface in abnormal grain growth of SiC. Thus, the development of elongated grains might occur in two stages. The first stage involves the grain growth based on Ostwald ripening; the dissolution of small β-SiC grains and precipitation of β-phase on α-SiC or large β-SiC seeds. The second stage invovles the growth of composite grains consisting of α-SiC domain

sandwiched between β-SiC domains. Present results suggest that mutual relation between β→α phase transformation and grain growth might be an important processing parameter for further microstructural control.

IV. Conclusions

Growth of β-SiC with microtwins and formation of α/β composite grains were found in both material with α-SiC seeds and material with β-SiC seeds. When large α-SiC (mostly 6H) seeds were added, the β-SiC transformed preferentially to the 6H polytype. In contrast, when large β-SiC seeds were added, the fine β-SiC transformed preferentially to the 4H polytype. These results suggest that changes in the polytype distribution in SiC materials may thus be related preferentially to the polytype distribution in starting powders, rather than the chemistry of sintering aids.

Differences in microstructure between material with α-SiC seeds and material with β-SiC seeds have arisen from difference in the number of nuclei. The α/β interface played an important role for abnormal grain growth of SiC as evidenced by presence of α/β composite grains with high aspect ratio.

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