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Microstructure and fracture toughness of liquid-phase-sintered β-SiC containing β-SiC whiskers as seeds

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The effect of seeding on microstructural development and fracture toughness of β-SiC with an oxynitride glass was investigated by the use of morphologically rodlike β-SiC whiskers. A self reinforced microstructure consisting of rodlike β-SiC grains and equiaxed β-SiC matrix grains was obtained by seeding 1–10 wt% SiC whiskers, owing to the epitaxial growth of β-SiC from the seed whiskers. Further addition of seeds (20 wt%) or further annealing at higher temperatures led to a unimodal microstructure, owing to the impingement of growing seed grains. By seeding β-SiC whiskers, fracture toughness of fine-grained materials was improved from 2.8 to 3.9–6.7 MPa $\cdot$ $m^{1/2}$, depending on the seed content.

1. Introduction

The general experimental experience with liquid-phase-sintered SiC shows that platelet α-SiC grains promote an increment of toughness in the presence of a relatively weak interface [1–5]. Platelet α-SiC grains can be introduced into the microstructure by the following two strategies: (i) taking advantage of the $\beta \rightarrow \alpha$ phase transformation of SiC at high temperatures, which usually accelerates the grain growth [1–4], and (ii) use of solution-reprecipitation process [5, 6]. These platelet grains can act as a reinforcing phase that promotes crack bridging and deflection, resulting in the improved toughness [1, 5, 6].

We have recently developed a new self-reinforced microstructure consisting of rodlike β-SiC grains and equiaxed β-SiC matrix grains by seeding rodlike β-SiC whiskers into fine matrix grains [7]. The requirements for microstructure control by seeding were suggested as follows: (1) appreciable solubility of the solid for solution-reprecipitation mechanism; (2) appreciable size difference between seeds and matrix grains; and (3) no phase transformation during sintering and annealing. Thus, it is interesting to observe the microstructural development in β-SiC ceramics with varying amount of rodlike β-SiC whisker seeds and to measure the fracture toughness of the resulting ceramics.

The objective of this research is to investigate the effect of β-SiC whisker (seeds) content on microstructure and fracture toughness of rodlike β-SiC reinforced β-SiC ceramics. In order to suppress the occurrence of the $\beta \rightarrow \alpha$ phase transformation completely, an oxynitride glass composition ($Y_{0.124}Mg_{0.160}Si_{0.414}Al_{0.302}O_{1.400}N_{0.151}$), which stabilizes β-SiC up to 2000°C, was used as a sintering additive [8, 9].

2. Experimental procedure

Ultrafine β-SiC powder (T-1 grade, Sumitomo-Osaka Cement Co., Tokyo, Japan) was oxidized at 600°C for 2 h in air to eliminate free carbon and then was treated with HF to remove SiO_2. The particle size was ~90 nm, as calculated from the specific surface area. 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 $Y_{0.124}Mg_{0.160}Si_{0.414}Al_{0.302}O_{1.400}N_{0.151}$ by ball milling in hexane for 3 h using SiC media and a SiC container. The oxynitride composition had an appreciable SiC solubility at high temperatures [10]. The SiC powder was eventually blended with 15 wt% powder mixture of the oxynitride composition and milled in hexane for 20 h using SiC media to avoid contamination during processing. Then, 0–20 wt% β-SiC whiskers (Tokamax, Tokai Carbon Co., Ltd., Tokyo, Japan) were added as seeds, and the composition was milled for 4 h. The batch compositions are given in Table 1. After

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TABLE I Batch composition and relative density of the sintered materials

Seed content (wt%)	Batch composition (wt%)	Relative density* (%)
0	85% β-SiC[a] + 15% oxynitride glass[b]	99.8
1	84% β-SiC + 1% β-SiC whisker[c] + 15% oxynitride glass	99.5
5	80% β-SiC + 5% β-SiC whisker + 15% oxynitride glass	99.8
10	75% β-SiC + 10% β-SiC whisker + 15% oxynitride glass	99.6
20	65% β-SiC + 20% β-SiC whisker + 15% oxynitride glass	99.5

[a]The average particle size is ~90 nm.
[b]The composition of oxynitride glass is $Y_{0.124}Mg_{0.160}Si_{0.414}Al_{0.302}O_{1.400}N_{0.151}$.
[c]The diameter and length are 0.1–0.5 μm and 1–10 μm, respectively.
*Hot-pressing conditions are 1900°C for 1 h under an applied pressure of 20 MPa in a N_2 atmosphere.

milling, the slurry was dried and hot-pressed at 1900°C for 1 h under a pressure of 20 MPa in a nitrogen atmosphere. The heating rate was 20°C/min, and the cooling rate was ~40°C/min from 1900°C to 1200°C. Some samples were further annealed at 2000°C for 4 h in a nitrogen atmosphere to observe microstructural development.

The sintered density was determined using the Archimedes method. The theoretical density of the materials, 3.21 g/cm^3, was calculated according to the rule of mixtures (theoretical density of the oxynitride glass was 3.18 g/cm^3) [10]. The hot-pressed and the 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). Grain diameters (d) and apparent lengths (L) of two-dimensionally exposed grains were evaluated using an image analyzer [11]. The diameter and length of each grain were determined from the shortest and the longest diagonal. The mean value of the observed aspect ratio (L/d) was considered to be an average aspect ratio. Grains deviating from the normal grain-diameter distribution are defined as large grains (abnormally grown grains) in the present work; the other grains belong to the normal grain-diameter distribution are defined as matrix grains. A total of 900–1200 grains was used for statistical analysis of each material. The grain diameter distribution was evaluated by plotting fractional area against grain diameter.

X-ray diffraction (XRD) using Cu Kα radiation was performed on the ground powders. Microstructure-crack interactions were investigated for cracks introduced by a Vickers indenter at a load of 196 N on the polished and etched surfaces. The fracture toughness was estimated by measuring crack lengths generated by a Vickers indenter [12].

3. Results and discussion

The relative densities of the hot-pressed materials are shown in Table I. As shown, all of the materials could be sintered to nearly full density (≥99.5% of theoretical density) after sintering at 1900°C for 1 h. XRD analysis of the hot-pressed materials indicated the presence of β-SiC as the unique crystalline phase, whereas the existence of a glassy phase was identified from the transmission electron microscopy observation of the materials [13].

Typical microstructures of the hot-pressed materials are shown in Fig. 1. The microstructure of β-SiC

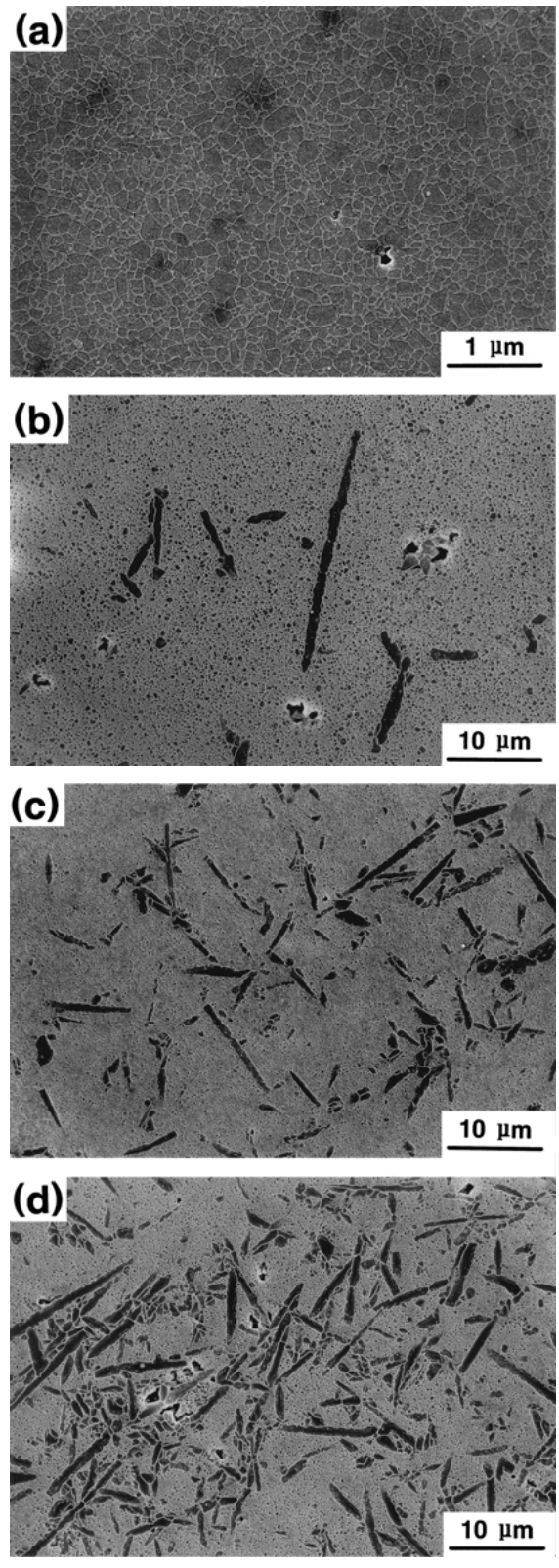

Figure 1 Typical microstructures of hot-pressed β-SiC ceramics containing (a) 0%, (b) 1 wt%, (c) 5 wt%, (d) 10 wt%, and (e) 20 wt% β-SiC whiskers as seeds.

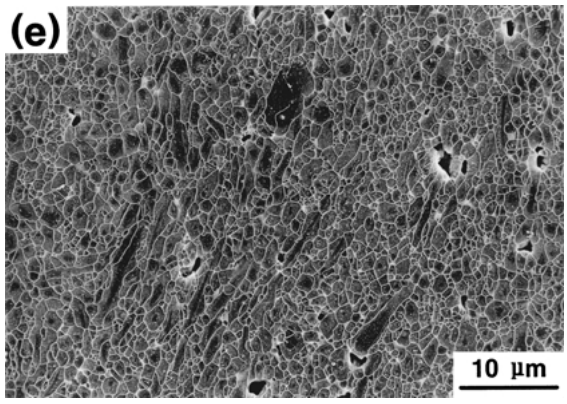

Figure 1 (*Continued*).

material without seeds consists of very fine equiaxed grains (average size ∼130 nm, Fig. 1a). In contrast, a self-reinforced microstructure having abnormally grown grains (large grains) in fine matrix grains has been developed in materials with 1–10 wt% seeds (Fig. 1b–d) after hot-pressing at 1900°C for 1 h. Materials with 1–10 wt% seeds exhibited a bimodal microstructure, as expected, composed of small matrix β-SiC grains similar to those of the material without seeds (Fig. 1a) [8] and large rodlike β-SiC grains with 0.5–1.8 μm in diameter and 4–18 μm long. Previously reported self-reinforced microstructures were composed of platelet α-SiC grains or platelet α/β composite grains [1–3, 5, 6]. Fig. 1e that contained 20 wt% seeds was composed of large grains only because of the impingement of growing grains.

The results of image analysis for the matrix grains and large grains are summarized in Figs 2 and 3. The materials with 1–10 wt% seeds exhibited a bimodal grain-diameter distribution whereas the β-SiC with 20 wt% seeds exhibited a unimodal distribution. We evaluated the bimodal microstructure by measuring the average diameter and aspect ratio of matrix grains and large grains (abnormally grown grains) using image analysis. The critical diameter for the definition of matrix and large grains was about 0.4 μm (Fig. 2). Although the β-SiC with 20 wt% seeds exhibited a unimodal grain-diameter distribution, the grains were analyzed as large grains. Interestingly, the grain diameter and aspect ratio of matrix grains is almost same for the materials with 1–10 wt% seeds (Fig. 3). Seeds seem to have no influence on the grain growth behavior of matrix grains as seen from grain-diameter measurements (Figs 2 and 3). The unimodal microstructure developed with 20 wt% seeds addition is similar to the material fabricated from submicrometer powder by hot-pressing, presumably due to the impingement between seeds [14].

The average diameters and aspect ratios of matrix grains are independent of the amount of seeds up to a 10 wt% seeds addition (Fig. 3). Similarly, the average diameters of large grains are nearly fixed up to 10 wt% seeds addition. The average aspect ratios of large grains are also nearly constant and larger than those of matrix grains up to 10 wt% addition. The aspect ratio decreases with 20 wt% addition of seeds. In the material with 20 wt% seeds, the driving force for grain growth in length direction decreases markedly because distances among large grains are very short and that for diameter direction increases due to contact among growing seeds grains, reflecting the equiaxed shape of those grains, i.e., grains with low aspect ratio (∼1.7).

To confirm the effect of seeds on grain growth, the number of large grains per unit area (1 mm^2), was noted versus the amount of seeds (Fig. 4) using the image analysis data. All grains in material with 20 wt% seeds are regarded as large grains due to the unimodal microstructure. The number of large grains is proportional to the amount of seeds added. These results suggest that larger elongated grains are grown from seed particles

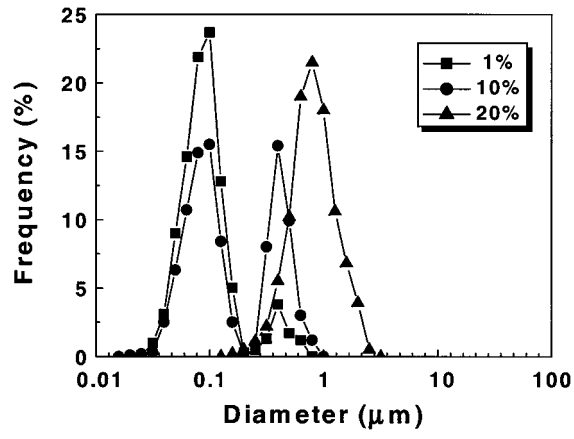

Figure 2 Grain diameter distribution revealed by the relation between grain diameter and areal frequency for 1 wt%, 10 wt%, and 20 wt% SiC whisker-seeded SiC ceramics.

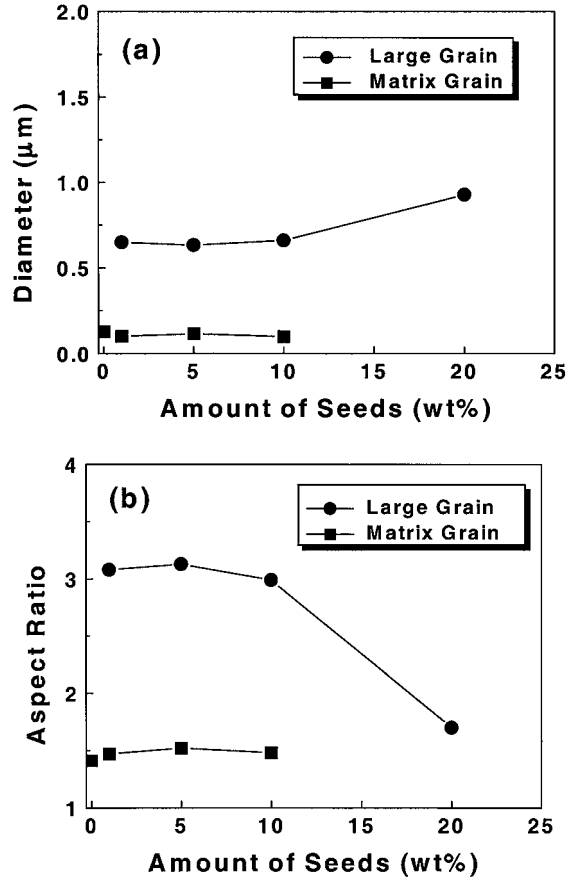

Figure 3 Change of (a) grain diameter and (b) aspect ratio of large grains and matrix grains for liquid-phase sintered β-SiC ceramics as a function of seeds content.

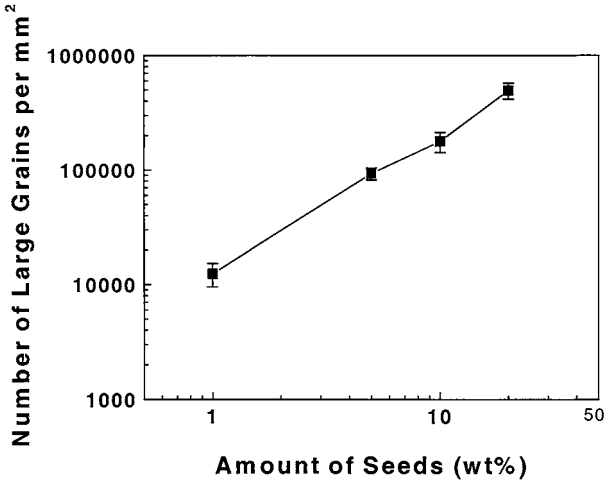

Figure 4 Number of large grains as a function of seeds content.

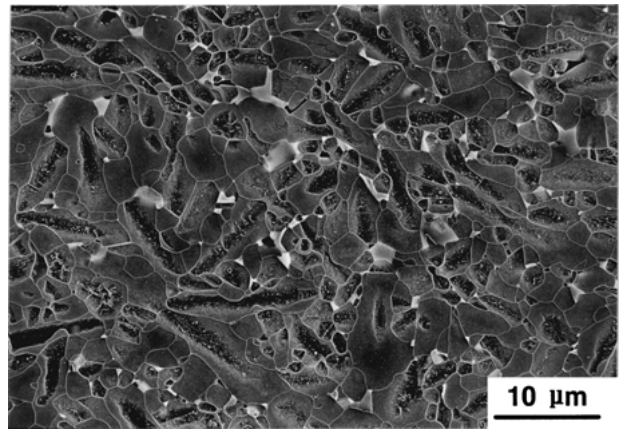

Figure 5 Typical microstructure of the hot-pressed and annealed β-SiC ceramics with 10 wt% seeds.

(whiskers) and smaller matrix grains are grown from fine β-SiC starting powder, i.e., only coarse grains (whiskers in this experiment) operate as seeds for abnormal grain growth. Since the grain-size difference between seeds and matrix grains is quite large, the driving force for grain growth of seeds is high, causing seeds to grow selectively [15, 16]. The results are similar to those of a previous study on Si_3N_4 [17]. The fraction of large grains increases with an increase in the amount of seeds (Fig. 2), as would be expected [15].

Each seed has an effective space around the seed grain, in which smaller grains transport to seed by solution-reprecipitation mechanism through the liquid phase [17, 18]. The microstructure may depend on the situation of effective space. In a small amount of seeds (less than 10 wt% in this system), each seed has an independent effective space due to the enough distance from each other. Therefore, both diameter and aspect ratio of large grains are almost same for materials with 1–10 wt% seeds, as can be seen in Fig. 3. When the amount of seeds increases further (20 wt%), the interaction of each seed increases, i.e., individual effective spaces begin to overlap and the diffusing materials in overlapped effective spaces are shared by each seed, resulting with the decrease in grain size of large grains (Fig. 3). The interaction also leads to the transition in grain-diameter distribution from bimodal to unimodal (Fig. 2).

Annealing of the hot-pressed material with 10 wt% seeds at 2000°C for 4 h changed the self-reinforced microstructure to the equiaxed microstructure (Fig. 5) with a unimodal grain-diameter distribution. X-ray diffraction for ground powders of the annealed material showed β-SiC as the unique crystalline phase, indicating no phase transformation during annealing. It is consistent with the previous results that the oxynitride glass enlarges the stability region of β-SiC [8, 9]. Annealing of the hot-pressed materials at higher temperature (2000°C) leads to further growth of the seed grains (large grains) and results in the impingement of the seed grains. The same effect is observed with the increase in the number of seeds. Thus, annealing of the hot-pressed materials leads to unimodal grain-diameter distribution. The average aspect ratio (1.9) of the annealed material with 10 wt% seeds was almost same as that (1.7) of hot-pressed material with 20 wt% seeds. Thus, self-reinforced microstructure with bimodal grain-diameter distribution can be obtained by adding 1–10 wt% seeds to a fine matrix. The present study shows that it is possible to control the bimodal microstructure consisted of large, rodlike β-SiC grains and fine, equiaxed β-SiC grains by seeding 1–10 wt% SiC whiskers to a fine β-SiC powders.

Fig. 6 shows the fracture toughness as a function of seeds content. The material without seeds, which was composed of relatively equiaxed grains with an unimodal distribution, has a fracture toughness of $\sim$2.8 MPa $\cdot$ m$^{1/2}$. In contrast, the material with 10 wt% seeds, which was composed of large, rodlike grains and small matrix grains, has a fracture toughness of $\sim$6.7 MPa $\cdot$ m$^{1/2}$. The growth of rodlike β-SiC grains, i.e., development of self-reinforced microstructure, produced a remarkable improvement in toughness. However, further adding of seeds up to 20 wt% or further annealing at 2000°C led to the decrease in toughness, compared to the material with 10 wt% seeds because of the impingement of growing grains and resulting with an unimodal grain diameter distribution with low aspect ratio. The seeded materials showed a tortuous crack path and

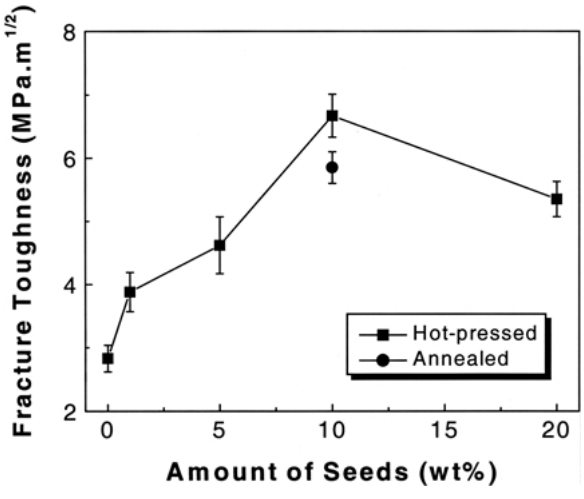

Figure 6 Fracture toughness of the liquid-phase sintered β-SiC ceramics as a function of seeds content.

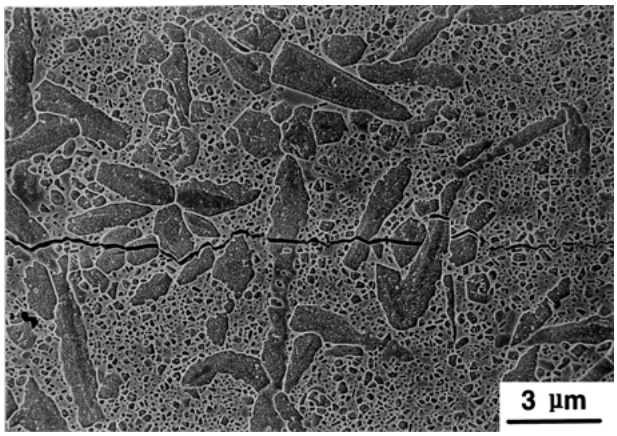

Figure 7 Scanning electron micrograph of a crack profile in the liquid-phase sintered β-SiC with 10 wt% seeds.

demonstrated significant crack deflection and bridging by the rodlike grains (Fig. 7), resulting in the improved toughness.

4. Conclusion

The microstructural development of fine-grained β-SiC ceramics with varying amounts of β-SiC whiskers (seeds) was investigated. Fine-grained β-SiC ceramics without seeds had a homogeneous microstructure with a unimodal grain diameter distribution. When 1–10 wt% whiskers were introduced in fine grained β-SiC ceramics, they grew abnormally, consuming neighboring fine grains which resulted in the development of a bimodal microstructure consisted of large, rodlike β-SiC grains and fine, equiaxed β-SiC grains. Further addition of whiskers (20 wt%) or further annealing at higher temperatures led to a unimodal microstructure, owing to the impingement of growing seed grains. The difference in microstructural development is explained in terms of effective space around seeds, as suggested in Si_3N_4 ceramics [17]. The fracture toughness of fine-grained β-SiC ceramics increased by adding β-SiC whiskers. Typical fracture toughness of fine-grained material without seeds and 10 wt% SiC whisker-seeded material were 2.8 and 6.7 MPa $\cdot$ $m^{1/2}$, respectively.

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