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Fabrication and mechanical properties of silicon carbide–silicon nitride nanocomposites

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A powder mixture of ultrafine β –SiC–35 wt% α –Si_3N_4 containing 6 wt% Al_2O_3 and 4 wt% Y_2O_3 as sintering additives were liquid–phase sintered at 1800°C for 30 min by hot–pressing. The hot–pressed composites were subsequently annealed at 1920°C under nitrogen–gas–pressure to enhance grain growth. The average grain–size of the sintered bodies were ranged from 96 to 251 nm for SiC and from 202 to 407 nm for Si_3N_4, which were much finer than those of ordinary sintered SiC–Si_3N_4 composites. Both strength and fracture toughness of fine–grained SiC–Si_3N_4 composites increased with increasing grain size. Such results suggested that a small amount of grain growth in the fine–grained region ($\leq$250 nm for SiC and $\leq$400 nm for Si_3N_4) was beneficial for mechanical properties of the composites. The room–temperature flexural strength and fracture toughness of the 8–h annealed composites were 698 MPa and 4.7 $\text{MPa} \cdot \text{m}^{1/2}$, respectively. *© 2000 Kluwer Academic Publishers*

1. Introduction

One approach for strengthening ceramics is to incorporate a dispersion of ultrafine (100–300 nm) second–phase particles into a matrix of higher expansion coefficient [1, 2]. Niihara and his coworkers [3, 4] have reported that the strength of alumina and magnesia, both at room and elevated temperatures, can be dramatically improved by incorporating dispersions of ultrafine (100–300 nm) particles of SiC. They also suggested that the dispersion of ultrafine SiC particles inside the grains or at the grain boundaries of a Si_3N_4 matrix can lead to an improvement in the mechanical response of the material at both room and elevated temperatures [5, 6].

Another potential approach for strengthening ceramics is to decrease the size of flaws by fabricating ultrafine–grained ceramics [7]. The concept of using ultrafine particles as starting materials and sintering at as low a temperature and for as short time as possible, which would result in decreased grain sizes, has been considered to be one of the solutions to decrease flaw sizes in the ceramics [8]. Basic studies on the relationship between grain size and strength have been performed. For example, Rice *et al.* [9, 10], reviewed the grain–size dependence of tensile strength in many oxides and SiC ceramics. However, their experimental data were limited to the relatively large grain size region. For SiC, the investigated range was 2 to 100 μm, because of the difficulty of obtaining fine–grained SiC ceramics. Therefore, various properties in the fine grained region (below 1 μm) have not been well studied.

Previously, we have developed SiC nanoceramics with an average grain size of 110 nm by using ultrafine (~90 nm) starting particles and hot–pressing at as low as 1750°C [11]. Previous studies also have shown that SiC nanoceramics can be superplastically deformed [12] and can be used as a matrix for controlling the bimodal microstructure because of their fine microstructure [13]. Recently, we also suggested that grain growth of fine–grained SiC in some extent (up to ~300 nm) was beneficial in improving both room–temperature strength and toughness [14, 15].

Composites of SiC–Si_3N_4 can be fabricated by hot–isostatic pressing with the aid of La_2O_3 and Y_2O_3 [16] or hot–pressing with Al_2O_3 and Y_2O_3 [17] or an Y–Mg–Si–Al–O–N oxynitride [18] to a nearly full density at temperatures in excess of 1800°C. The best results in mechanical properties were obtained when the sintering additive was an Y–Mg–Si–Al–O–N oxynitride. The flexural strength and fracture toughness of the SiC–35 wt% Si_3N_4 composites were 1020 MPa and 5.1 $\text{MPa} \cdot \text{m}^{1/2}$, respectively. The reduced defect size and the enhanced bridging and deflection by the elongated β –Si_3N_4 grains have been identified as the principal elements of the improved mechanical properties [18].

Based on these research results and the above approaches, we have investigated the possibility for

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improving the mechanical properties of SiC ceramics by applying the following strategies simultaneously: (1) fabrication of ultrafine SiC matrix, (2) incorporation of a dispersion of ultrafine (100–400 nm) Si_3N_4 particles into a SiC matrix, and (3) post–annealing after sintering to enhance grain growth. In the present study, SiC–35 wt% Si_3N_4 nanocomposites were fabricated for the first time and the composites were subsequently annealed to enhance grain growth. The microstructure and mechanical properties of the resulting composites were investigated.

2. Experimental procedure

Ultrafine β –SiC powder (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 aqueous solution to remove SiO_2. The particle size was ~90 nm, as calculated from the specific surface area. A mixture of 55 wt% SiC, 35 wt% α –Si_3N_4 (average particle size ~200 nm, grade E10, Ube Industries, Tokyo, Japan), 6 wt% Al_2O_3 (99.9% pure, Sumitomo Chemical Co., Tokyo, Japan) and 4 wt% Y_2O_3 (99.9% pure Shin–Etsu Chemical Co., Tokyo, Japan) was milled in ethanol for 3 h using SiC balls and a jar. After milling, the slurry was dried and hot–pressed at 1800°C for 30 min under a pressure of 20 MPa in a nitrogen atmosphere. The heating rate was 30°C/min, and the cooling rate was ~60°C/min from 1800°C to 1200°C. Some specimens were subsequently annealed at 1920°C for 4 h or 8 h under 2 MPa of nitrogen–gas–pressure.

The sintered density was determined by using the Archimedes method. The theoretical density of the specimens, 3.292 g/cm^3, was calculated according to the rule of mixtures. The hot–pressed and the annealed specimens were cut and polished; then, they were etched using a plasma of CF_4 that contained 7.8% oxygen. The microstructures were observed using scanning electron microscopy (SEM), and the average grain size was determined using image analyzer according to a procedure shown in previous studies [11, 13]. The grain size distribution of SiC was bimodal, i.e., the grains trapped in Si_3N_4 were relatively small (10–120 nm) while matrix grains were relatively large. Since the volume content of trapped SiC grains was small (less than 3%), an average grain size of SiC grains was presented in this paper. A total of 700–1000 grains was used for statistical analysis of each specimen.

X–ray diffractometry (XRD), using Cu K_α radiation, was performed on the ground powders. The bar samples (2.5 mm × 3 mm × 25 mm) were machined to a 1 μm finish for flexural testing. Bend tests were performed at room temperature on 4–5 specimens at each condition, using a four–point bending method with outer and inner spans of 10 and 20 mm, respectively, and a crosshead speed of 0.5 mm/min. The fracture toughness was estimated by measuring crack lengths that were generated by a Vickers indenter with a load of 98 N [19].

3. Results and discussion

The characteristics of both the hot–pressed and annealed SiC–Si_3N_4 composites are summarized in Table I. A sample with a relative density of >98.5% was obtained by hot–pressing at 1800°C with a holding time of 30 min. Gas–pressure annealing at 1920°C resulted in a little increase in the relative density ($\geq$99.0%), which is probably due to the additional densification during annealing at a higher temperature. Phase analysis of the hot–pressed and the annealed specimens, via XRD, showed that all specimens were composed of β –SiC and β –Si_3N_4. These results show that $\alpha \rightarrow \beta$ phase transformation of Si_3N_4, which usually accelerates the grain growth of elongated grains, has taken place during hot–pressing at 1800°C. The $\beta \rightarrow \alpha$ phase transformation of SiC was inhibited, because of a nitrogen–containing liquid (Si_3N_4 is soluble to the Al_2O_3–Y_2O_3 additive and forms an oxynitride glass) and nitrogen atmosphere during annealing [14, 20].

Fig. 1 shows microstructures of the hot–pressed and the gas–pressure annealed SiC–Si_3N_4 composites. As shown in Fig. 1, the microstructure of as–hot–pressed specimen consisted of very fine, equiaxed β –SiC grains (an average grain size of 96 nm) and relatively large β –Si_3N_4 grains (an average grain size of 202 nm). The Si_3N_4 grains can be identified in the micrographs that are shown in Fig. 1 based on their concave nature, because of the faster etching rate of Si_3N_4. The average grain sizes of both SiC and Si_3N_4 in the hot–pressed specimen were slightly larger than that of the starting powder, which indicates minimal grain growth during hot pressing. The average grain sizes of the specimen in the present work are very small compared to those of dense SiC–Si_3N_4 composites, which used the traditional powders, obtained in previous works [17, 18]. For example, the grain sizes of previous dense SiC–Si_3N_4 composites (made from commercial SiC powders of 0.27 μm average grain size and hot–pressed at 1800°C for 3 h with an Y–Mg–Si–Al–O–N oxynitride as a sintering additive) were ~800 nm for SiC and ~1 μm for Si_3N_4 [18]. On the other hand, the SiC and Si_3N_4 in the present work have the average grain sizes

TABLE I Characteristics of SiC–Si_3N_4 nanocomposites

Sample designation*	Fabrication conditions	Relative density (%)	Average diameter (nm) SiC	Average diameter (nm) Si_3N_4
As–hot–pressed	Hot–pressed (1800°C, 30 min, 20 MPa, nitrogen)	98.8	96	202
4–h annealed	Gas–pressure–annealed (1920°C, 4 h, 2 MPa–nitrogen)	99.0	184	314
8–h annealed	Gas–pressure–annealed (1920°C, 8 h, 2 MPa–nitrogen)	99.1	251	407

*The composition of the sample is 55 wt% β –SiC + 35 wt% α –Si_3N_4 + 6 wt% Al_2O_3 + 4 wt% Y_2O_3.

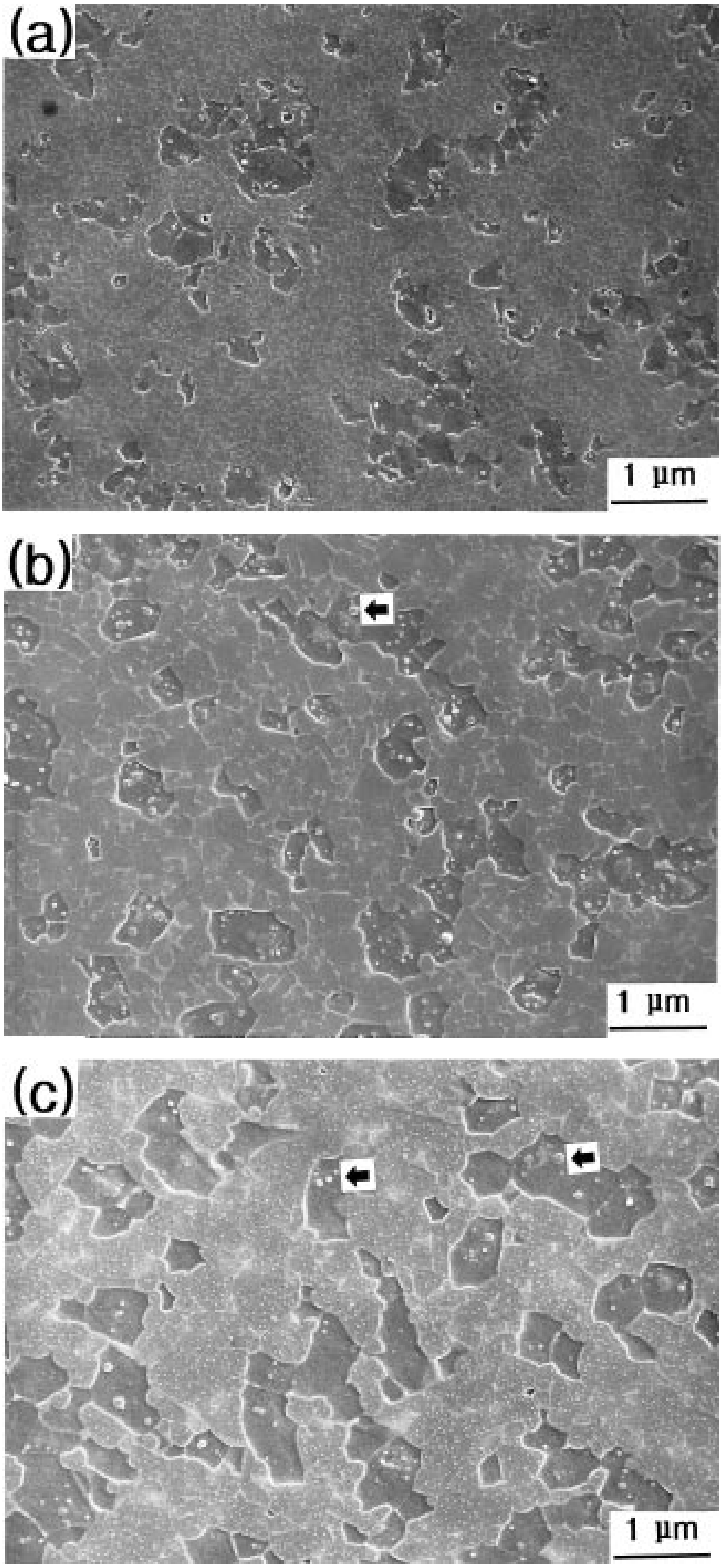

Figure 1 Microstructures of (a) as–hot–pressed, (b) 4–h annealed, and (c) 8–h annealed specimens (refer to Table I). Concave grains in the microstructure are Si_3N_4. Note the relatively small (10–120 nm) SiC particles are trapped in Si_3N_4 grains (marked by arrows).

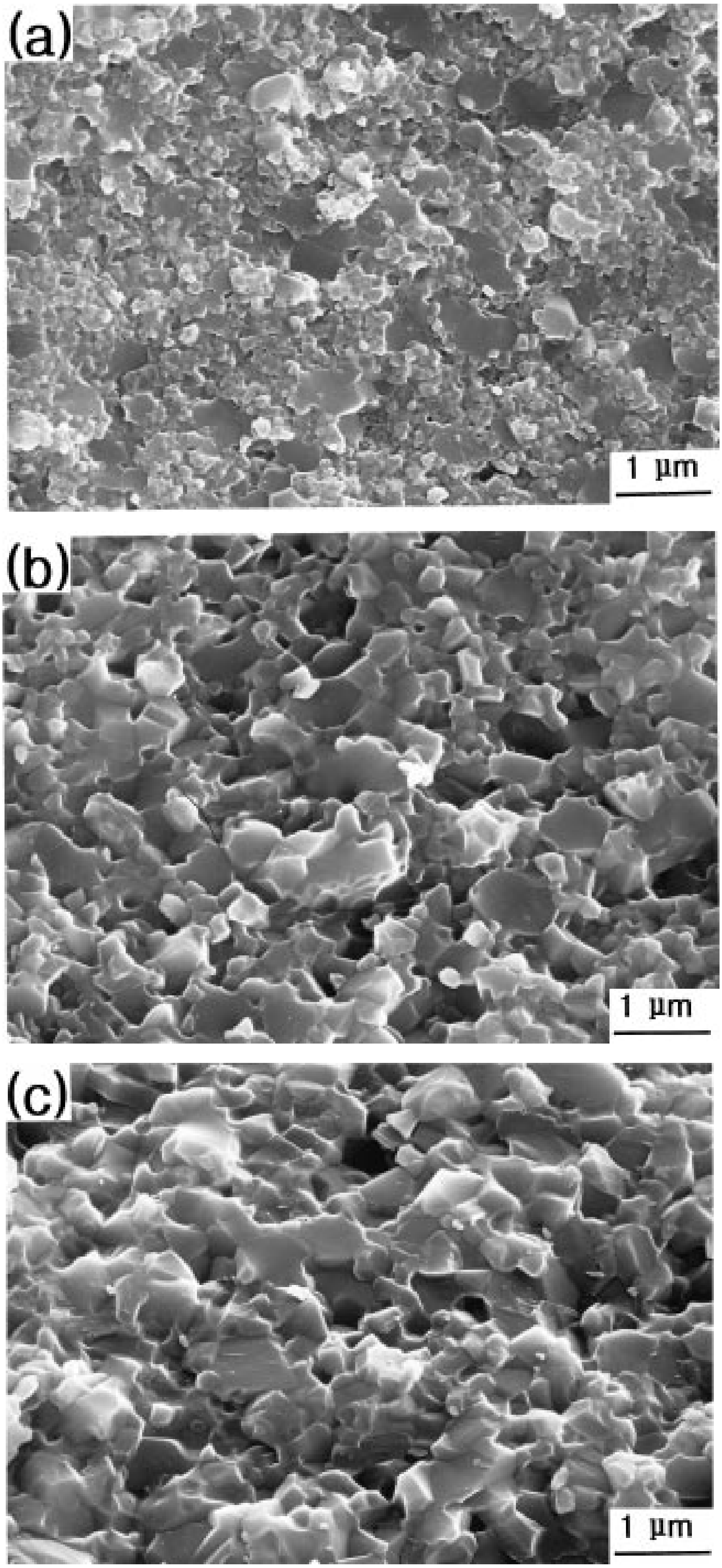

Figure 2 SEM micrographs of the fracture surfaces of (a) as–hot–pressed, (b) 4–h annealed, and (c) 8–h annealed specimens (refer to Table I).

of 97 nm and 202 nm, respectively, which are almost one fourth those of ordinary dense SiC–Si_3N_4 composites. All the specimens, after annealing at 1920°C for 4 and 8 h, consisted of equiaxed β –SiC and β –Si_3N_4 grains. The gas–pressure annealing did not change the morphology of the grains but did increase the average grain sizes of the grains (Table I). Compared to the typical *in situ*–toughened microstructure of Si_3N_4 [21], the morphology of Si_3N_4 in the composites was less acicular, rather equiaxed, probably due to the hindered grain growth during gas pressure annealing [18]. It is well documented that the grain growth of Si_3N_4, which occurs via solution–reprecipitation process, is hindered by the presence of SiC particles [22]. Fig. 1 also shows that relatively small (10–120 nm) SiC particles were trapped in the Si_3N_4 grains (marked by arrows), which indicates the faster growth rate of Si_3N_4, compared to SiC. This result is similar to the Si_3N_4–SiC nanocomposites [23].

The fracture mode of hot–pressed SiC–Si_3N_4 composites with an Al_2O_3–Y_2O_3 was mostly intergranular (Fig. 2), which was a result of a weak interface created by the difference between the coefficients of thermal expansion of the liquid and the SiC and/or Si_3N_4 grains on cooling after hot–pressing. Gas–pressure annealing did not change the fracture mode. However, some large grains in an 8–h annealed specimen fractured transgranularly.

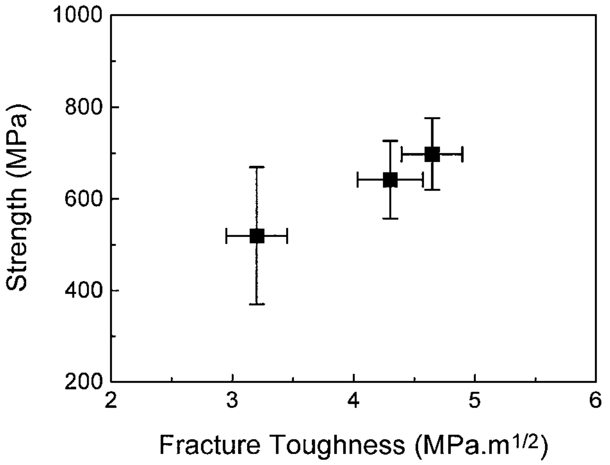

Figure 3 Relation between strength and fracture toughness of hot–pressed and annealed nanocomposites.

The mechanical properties of the hot–pressed and annealed SiC–Si_3N_4 composites were shown in Fig. 3. As–hot–pressed specimen had a relatively low fracture toughness of 3.2 $\text{MPa} \cdot \text{m}^{1/2}$, whereas 4–h annealed specimen had a higher value of 4.3 $\text{MPa} \cdot \text{m}^{1/2}$. A further increase to 4.7 $\text{MPa} \cdot \text{m}^{1/2}$ was observed when the annealing time was prolonged to 8 h. The increase in fracture toughness with annealing might be related to the microstructure of the composites; when the as–hot–pressed specimen was annealed at higher temperature, the average grain sizes of both SiC and Si_3N_4 grains increased with annealing time (Table I). SEM observation of the crack propagation profiles suggests that crack deflection was the main toughening mechanism in those annealed specimens. Thus, the increase in fracture toughness after annealing was due to the grain–coarsening effect, enhancing the crack–deflection mechanism [24].

The flexural strength of 4–h annealed specimen increased significantly, and the scatter of the measured data decreased significantly, as compared to those of as–hot–pressed specimen. Further annealing up to 8 h increased the strength slightly. The critical defect sizes (c), calculated from the measured fracture–toughness (K_{IC}) and strength (σ) values (using the equation $K_{\text{IC}} = 1.35\sigma c^{1/2}$) [25], were almost similar, i.e., 21–25 μm for as–hot–pressed and annealed composites. Therefore, the higher strength of annealed specimens may be related to the increase in fracture toughness. Most coarse–grained, *in situ*–toughened SiC ceramics that has been sintered with oxide additives showed a trade–off in improving both the strength and the toughness: i.e., introducing large elongated grains in the microstructure has resulted in decreased strength and increased toughness [25, 26]. However, the present composites showed that both strength and toughness

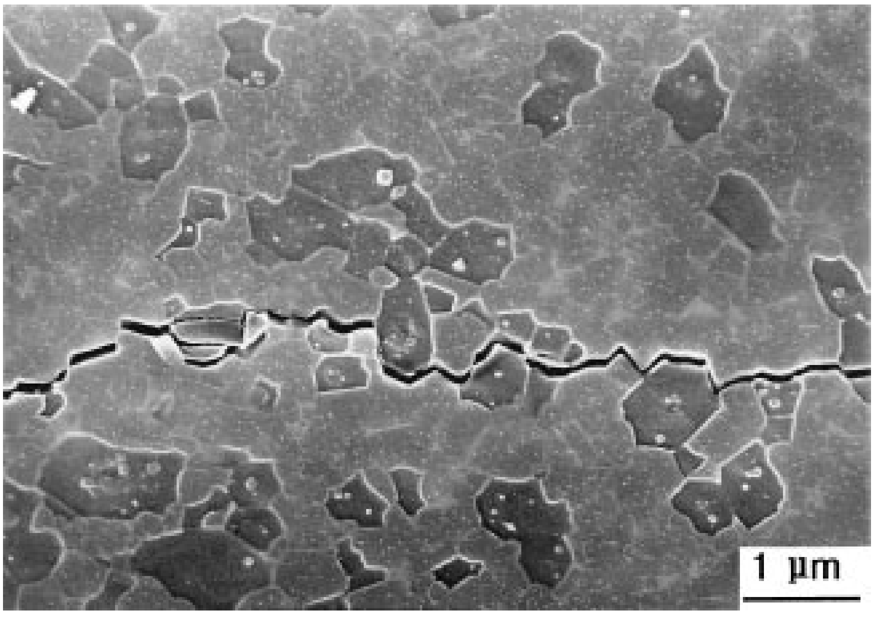

Figure 4 SEM micrographs of crack paths induced by a Vickers indentor for an 8–h annealed specimen (refer to Table I).

increased with increasing the grain size. The present results suggest that a small amount of grain growth in fine–grained SiC–Si_3N_4 composites is beneficial for improvement in both strength and toughness. The same trend has also been reported in fine–grained SiC ceramics [14, 15] and fine–grained Si_3N_4 ceramics [27]. Although SiC–Si_3N_4 composite specimens investigated herein have a smaller grain size, their flexural strengths do not significantly improve compared to previously hot–pressed SiC–Si_3N_4 composites [17]. From fracture surface examination, it was considered that the small number of pores or surface flaws introduced by grinding served as the fracture origin. Therefore, discussions relating the strength of these specimens directly to their grain sizes are not relevant. By eliminating these defects via hot isostatic pressing and careful polishing up to a size less than the average grain size, it seems possible to improve their strength.

4. Conclusions

Dense, fine–grained SiC–35 wt% Si_3N_4 nanocomposites with average grain sizes of 96–251 nm for SiC and 202–407 nm for Si_3N_4, which were much finer than those of ordinary sintered SiC–Si_3N_4 composites, were fabricated using ultrafine starting powders and low–temperature sintering by hot–pressing (1800°C for 30 min) and subsequent annealing (1920°C for 4 or 8 h).

Both strength and fracture toughness of fine–grained SiC–Si_3N_4 composites increased with increasing grain size. Such results suggested that a small amount of grain growth in the fine–grained region ($\leq$250 nm for SiC and $\leq$400 nm for Si_3N_4) was beneficial for mechanical properties of the SiC–Si_3N_4 composites. The room–temperature flexural strength and fracture toughness of the 8–h annealed composites were 698 MPa and 4.7 $\text{MPa} \cdot \text{m}^{1/2}$, respectively.

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