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Effects of Additive Amount on Microstructure and Fracture Toughness of SiC–TiB_2 Composites

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Abstract: Powder mixtures of β-SiC–30 wt% TiB_2 containing 5 wt% (ST1), 10 wt% (ST2), and 20 wt% (ST3) Al_2O_3–Y_2O_3 as sintering additives were liquid-phase sintered at 1850°C for 1 h by hot-pressing and subsequently annealed at 1950°C for 2, 6, and 12 h. These materials had a microstructure of 'in situ-toughened composites' as a result of the β→α phase transformation of SiC during annealing. The introduction of larger amount of additives accelerated the grain growth of elongated α-SiC grains with higher aspect ratio, resulting in the improved fracture toughness. The fracture toughnesses of 12-h annealed materials with 5, 10, and 20 wt% additives were 5.7, 5.9, and 7.1 $MPam^{1/2}$, respectively.

1 INTRODUCTION

Densification of SiC–TiB_2 composites without the aids of high pressure or sintering additives is very difficult owing to the covalent nature of their bonds. Therefore, sintering additives such as metals, oxides, and non-oxides are usually added to densify the composites. Composites of SiC–TiB_2 can be fabricated by hot-pressing with the aid of C and Al or B[1,2] or pressureless sintering with in-situ synthesis of TiB_2 through a reaction between TiB_2 and B[3] to a near full density at temperatures in excess of 2000°C. The role of additives for the sintering of covalent-bonded ceramics can be regarded as not only densification aids but also key elements for the microstructural development, since the related properties of materials are influenced by the kinds and amounts of additives.[4–6] Several investigations have shown that the dispersion of TiB_2 particles results in improved fracture toughness of SiC ceramics.[3,7,8] It is claimed that the residual stresses due to the thermal expansion mismatch between TiB_2 (8.6×10^{-6} C^{-1}) and SiC (4.2×10^{-6} C^{-1}) improve toughness by deflecting the cracks around the TiB_2 particles.[2,3]

Recently, liquid-phase sintering of SiC–TiB_2 composites at a temperature as low as 1850°C[9] and a new in-situ processing strategy based on liquid phase sintering and subsequent annealing for tailoring SiC–TiB_2 composites[10] have been reported. Using Y_2O_3 and Al_2O_3 as sintering additives, a unique microstructure consisting of uniformly distributed, elongated α-SiC grains, equiaxed TiB_2 grains, and yttrium aluminium garnet ($Y_3Al_5O_{12}$, YAG) as a grain boundary phase was obtained. The fracture toughness of the SiC–30 wt% TiB_2 composites after 6 h annealing at 1950°C was 6.7 $MPa\,m^{1/2}$, approximately 50% higher than that (4.4 $MPa\,m^{1/2}$) of as-hot-pressed composites. The presence of elongated α-SiC grains and weak interface boundaries have been identified as the principal elements of effective grain bridging and deflection, resulting in increased fracture toughness.[10,11]

In this study, we present the influence of additive amount on microstructure and fracture toughness of SiC–30 wt% TiB_2 composites with Al_2O_3–Y_2O_3

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Table 1. Characteristics of SiC–30 wt% TiB_2 composites

Materials	Composition (wt%)				Annealing time at	Relative density	XRD derived crystalline phase	
	SiC	TiB_2	Al_2O_3	Y_2O_3	1950°C (h)	(%)	Major	Trace
ST1	65	30	3.5	1.5	0	97.3	β-SiC, TiB_2	
					2	97.0	β-SiC, TiB_2	α-SiC
					6	96.9	α-SiC, TiB_2	
					12	95.6	α-SiC, TiB_2	
ST2	60	30	7	3	0	97.4	β-SiC, TiB_2	YAG,* α-Al_2O_3
					2	97.0	β-SiC, TiB_2	YAG, α-SiC
					6	96.8	α-SiC, TiB_2	YAG
					12	95.5	α-SiC, TiB_2	YAG
ST3	50	30	14	6	0	98.1	β-SiC, TiB_2	YAG, α-Al_2O_3
					2	97.2	β-SiC, TiB_2	YAG, α-SiC
					6	95.9	α-SiC, TiB_2	YAG
					12	94.7	α-SiC, TiB_2	YAG

*$Y_3Al_5O_{12}$ (yttrium aluminium garnet)

as sintering additives. The Al_2O_3–Y_2O_3 mixtures have been selected because of their effectiveness, compared to other additives, in decreasing the softening temperature and viscosity of secondary phase during liquid-phase-sintering of SiC ceramics.[12,13]

2 EXPERIMENTAL PROCEDURE

Commercially available β-SiC (Ibiden Co. Ltd, Japan, Betarundum), TiB_2 (H. C. Starck, Germany, grade F), Al_2O_3 (Sumitomo Chemicals Co. Ltd, Japan, AKP-30), and Y_2O_3 powders (H.C. Starck, Germany, fine grade) were used as starting materials. The powder mixtures of SiC–30 wt% TiB_2 containing 5 wt% Al_2O_3–Y_2O_3 (designated as ST1), 10 wt% Al_2O_3–Y_2O_3 (ST2), 20 wt% Al_2O_3–Y_2O_3 (ST3) as sintering additives were ball-milled in ethanol with SiC grinding balls for 24 h. The ratio of Al_2O_3:Y_2O_3 was fixed as 7:3 by weight. Batch compositions are shown in Table 1. The milled slurry was dried, sieved through a 60-mesh screen, and then hot-pressed at 1850°C for 1 h with 20 MPa of applied pressure under Ar. The hot-pressed materials were subsequently annealed at 1950°C for 2, 6, and 12 h under argon to enhance the grain growth of TiB_2 and the β→α phase transformation of SiC.

Densities were measured using the Archimedes, method and the relative densities of the specimens were calculated based on the densities of SiC (3.215 g cm^{-3}), TiB_2 (4.495 g cm^{-3}), Al_2O_3 (3.987 g cm^{-3}), and Y_2O_3 (5.031 g cm^{-3}) assuming the rule of mixtures. Crystalline phases in the sintered specimens were determined by X-ray diffractometry (XRD) using Cu-K_α radiation. The microstructure was observed by scanning electron microscopy (SEM). Some specimens were polished and plasma etched for observing grain size of SiC. The length and width of SiC grains were determined from the longest and the shortest grain

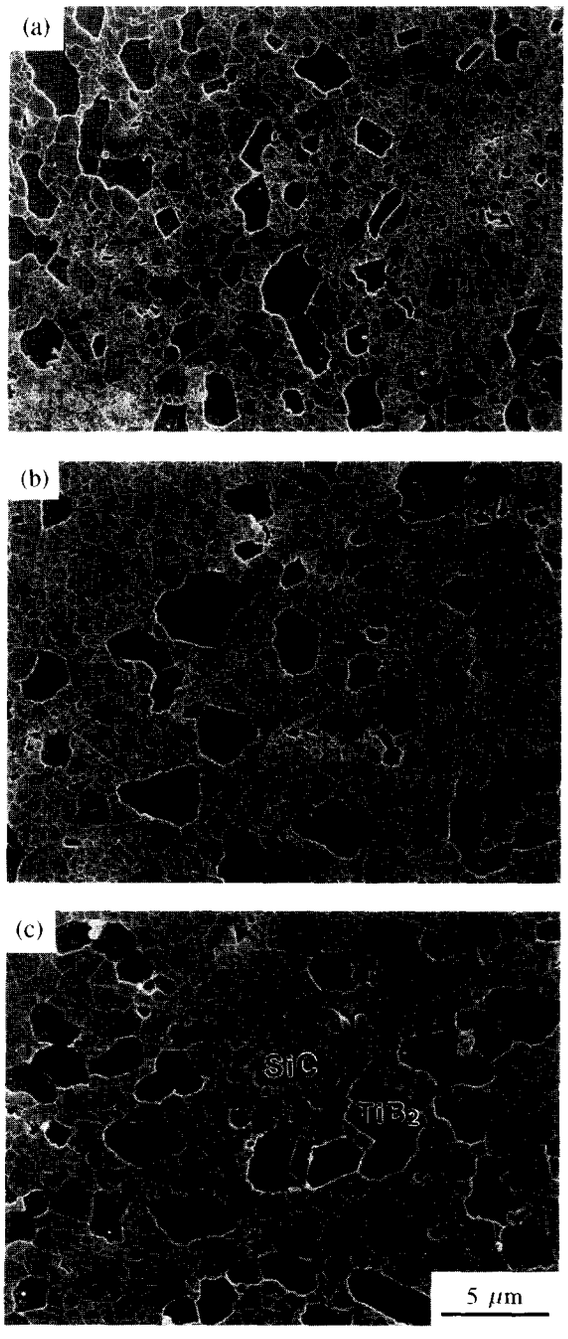

Fig. 1. SEM micrographs of hot-pressed SiC–30 wt% TiB_2 composites: (a) 5 wt% Al_2O_3–Y_2O_3; (b) 10 wt% Al_2O_3–Y_2O_3; (c) 20 wt% Al_2O_3–Y_2O_3.

diagonals, respectively, in the two-dimensional image. The grain sizes of SiC in as-hot-pressed composites and TiB_2 were determined from the diameter of circle approximation with equivalent area in the two-dimensional image. A total of 300 to 500 grains per specimens was used for the statistical analysis. The fracture toughness was estimated by measuring crack lengths generated by a Vickers' indenter with a load of 196 N.[14]

3 RESULTS AND DISCUSSION

The characteristics of SiC–30 wt% TiB_2 composites are summarised in Table 1. The relative densities of >97% were achieved by hot-pressing with a holding time of 1 h at 1850°C. However, prolonged annealing at 1950°C resulted in a decrease of the relative density, probably due to the formation of volatile components such as AlO, Al_2O and

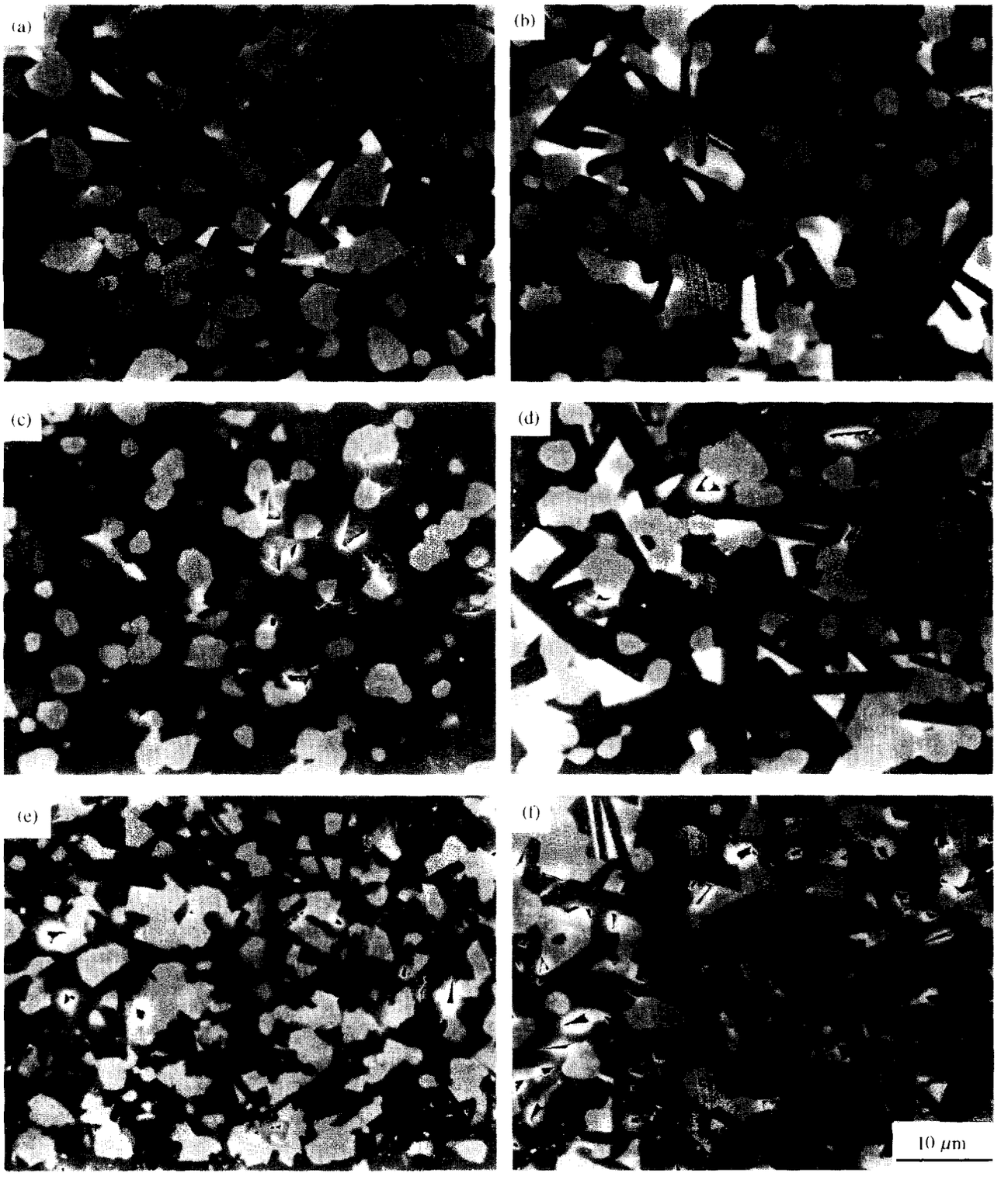

Fig. 2. SEM micrographs of polished cross-sections of annealed SiC–TiB_2 composites: (a) 6-h annealed ST1; (b)12-h annealed ST1; (c) 6-h annealed ST2; (d)12-h annealed ST2; (e) 6-h annealed ST3; and (f) 12-h annealed ST3 (refer to Table 1).

Table 2. Microstructural characteristics of hot-pressed and annealed SiC–TiB_2 composites

Materials	Annealing time at 1950°C(h)	SiC grain		TiB_2 grain size (μm)
		Aspect ratio	Length×width (μm)	
ST1	0	—	0.47*	1.40
	2	2.6	2.75×1.04	2.09
	6	3.0	6.37×2.10	2.32
	12	3.1	6.60×2.16	2.38
ST2	0	—	0.58*	1.71
	2	2.7	2.89×1.07	2.16
	6	3.9	7.73×2.00	2.44
	12	4.1	8.49×2.07	2.59
ST3	0	—	0.72*	1.74
	2	3.0	3.25×1.08	2.22
	6	4.6	8.84×1.94	2.51
	12	5.4	11.02×2.03	2.60

*Average grain size.

CO.[15,16] Higher amounts of additive addition resulted in increase of the sintered density because of the increased amount of liquid phase during hot-pressing and resulted in lower relative density after annealing probably because of the increased volatilization of additives during annealing. Phase analysis of hot pressed ST2 and ST3 materials by XRD showed β-SiC, TiB_2, YAG and α-Al_2O_3. In contrast, phase anlysis of hot-pressed ST1 showed β-SiC and TiB_2 only. The 6-h annealed ST2 and ST3 materials were found to be composed of α-SiC, TiB_2 and YAG, indicating the volatilization of α-Al_2O_3 during annealing. Polytype of α-SiC was 4H, indicating the occurence of β→α phase tranformation of SiC during annealing.

Figure 1 shows the microstructures of hot-pressed SiC–TiB_2 composites with different amount of additives. As shown, the hot-pressed composites were a two-phase particulate composite consist of randomly distributed TiB_2 grains, whose diameters ranging from 0.5 to 5 μm, and relatively fine, equiaxed SiC matrix grains. The grain size of SiC grains in hot-pressed materials increased from 0.47 μm (ST1) to 0.72 μm (ST3) with increasing the amount of additives, probably due to the increased densification.[15,17]

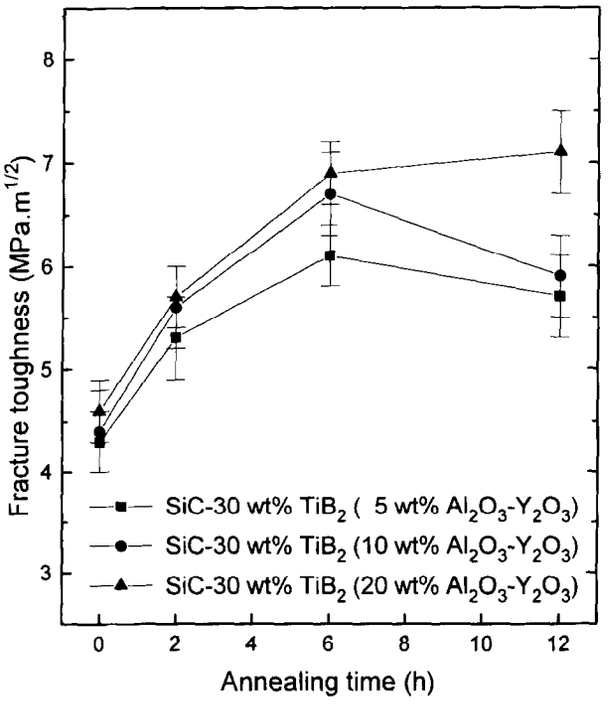

Fig. 3. Relation between fracture toughness and annealing time at 1950°C for ST1, ST2, and ST3 (refer to Table 1).

Figure 2 shows the microstructural change of the composites after annealing at 1950°C for 6 and 12 h, respectively. The bright phase is TiB_2, the dark grey phase is SiC, and white phase is oxide additives, presumably YAG. The effect of annealing became apparent after 6 h, as indicated by the phase analysis in Table 1, which shows the marked growth of α-SiC. It is well documented that grain growth through the solution–reprecipitation and the β→α phase transformation of SiC takes place at high temperatures (≥1950°C), especially at the presence of proper liquids.[11,18,19]

The results of image analysis are summarised in Table 2. The average aspect ratio and width of SiC grains increase gradully with annealing time. It indicates that grain growth and β→α phase transformation of SiC take place simultaneously during annealing and the anisotropy in the grain shape of SiC grains increases. As shown in Table 2, the amount of additives also influenced the morphologies of SiC and TiB_2. The average aspect ratio of SiC grains increased, i.e. from 3.1 for 12-h annealed ST1 to 5.4 for 12-h annealed ST3, with increasing the amount of additives. In contrast, the width of SiC grains decreased slightly, i.e. from 2.2 μm for 12-h annealed ST1 to 2.0 μm for 12-h annealed ST3, with increasing the amount of additives.

SiC grains in ST1 therefore were thicker and shorter than those of ST3 because of the impinge-

ment of grains. It indicates that the anisotropy in the grain shape of SiC grains increases with increasing the amount of additives. Coarsening of TiB_2 grains took place during annealing because of the grain growth of TiB_2 grains. Interestingly, shape of TiB_2 grains changed from equiaxed to matrixlike grains during annealing (Figs 1 and 2). This may be due to the ductile nature of TiB_2 grains yielding to the grain growth of elongated α-SiC grains and forming a matrixlike microstructure.

Variation of fracture toughness with annealing time is shown in Fig. 3. As shown, the fracture toughnesses of materials increase with annealing time at 1950°C. The fracture toughness of 12-h annealed ST3 (7.1 MPa $m^{1/2}$) was approximately 50% higher than that of as-hot-pressed composites (4.6 MPa $m^{1/2}$). The increased fracture toughness

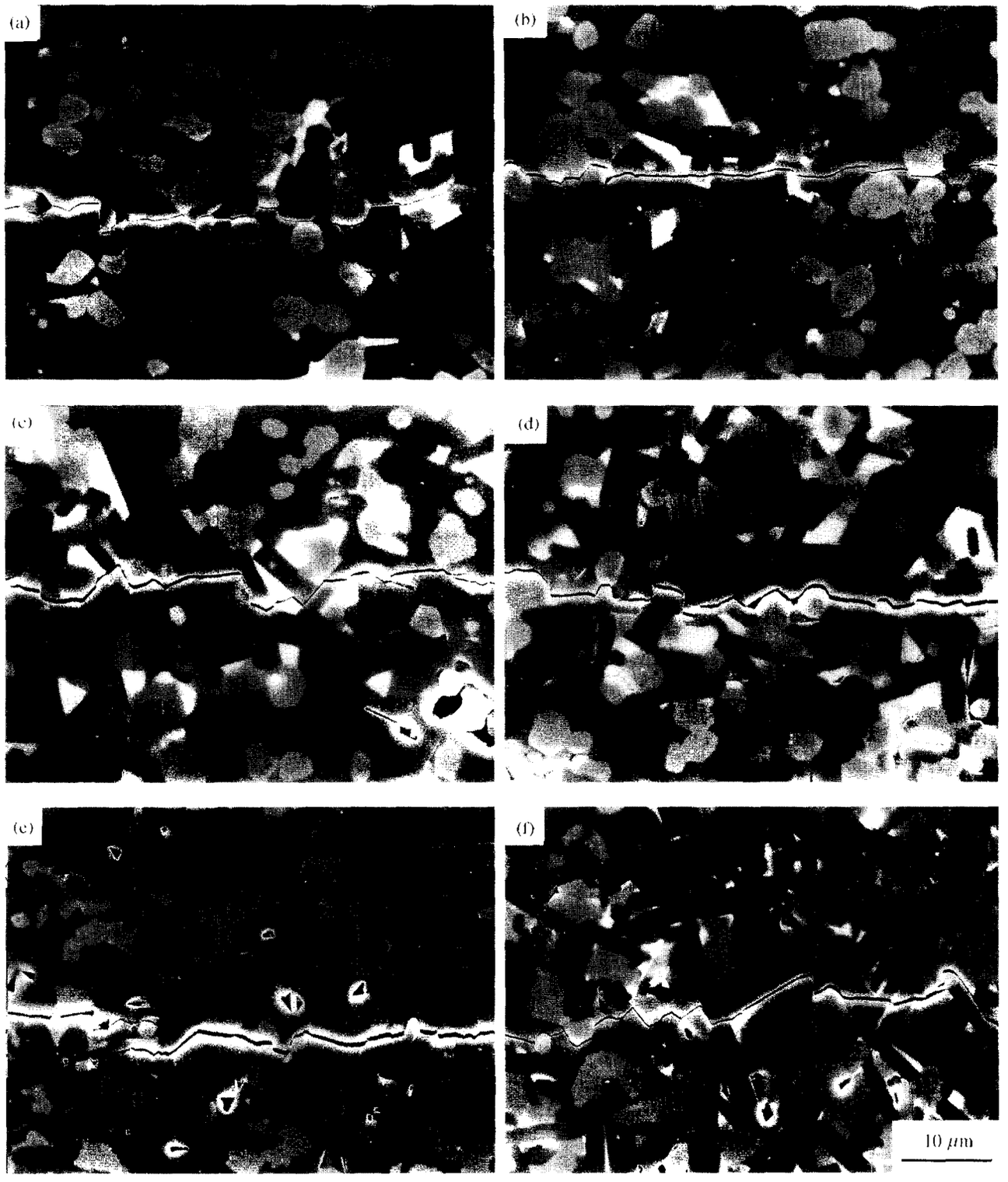

Fig. 4. SEM micrographs of crack paths induces by a Vickers indenter: (a) 6-h annealed ST1; (b) 12-h annealed ST1; (c) 6-h annealed ST2; (d) 12-h annealed ST2; (e) 6-h annealed ST3; and (f) 12-h annealed ST3 (refer to Table 1)

may be related to the microstructure. When the annealing time was increased, the shape of SiC grains changed from equiaxed (as-hot-pressed and 2-h annealed materials) to elongated grains (6-h and 12-h annealed materials) and the average aspect ratio and width of SiC grains and the average grain size of TiB_2 grains increased because of grain growth of both SiC and TiB_2 grains. The increase in fracture toughness with annealing time is due to the enhanced bridging and crack deflection by the elongated α-SiC grains and coarse TiB_2 grains, as observed in Fig. 4. The increase in fracture toughness of non-cubic ceramics with increasing grain size, owing to the enhanced crack definition and bridging, has been reported by several investigators.[20–23]

The effect of the amount of additives on the fracture toughness of the SiC–TiB_2 composites is also shown in Fig. 3. The fracture toughness increased with increasing the amount of additives. When relatively high amount of additives were added (ST3), weak interface boundaries due to thermal expansion mismatch between the second-phase YAG and SiC and/or TiB_2 was maintained after long-time annealing because of the sufficient amount of additives, leading to the enhanced crack bridging and deflection, as observed in Fig. 4(e) and (f). In contrast, when small amount of additives were added (ST1), the second phase-insufficient regions might be introduced due to the evaporation of additives during annealing,[19,24] leading to the increased tendency of transgranular fracture, as observed in Fig. 4(a) and (b). Therefore, the decrease in fracture toughness of 12-h annealed ST1 and ST2, although the length and width of α-SiC grains were increased compared with those of 6 h annealed ST1 and ST2, was attributed to the increasing tendency of transgranular fracture and pore formation with prolonged annealing, as shown in Fig. 4(b) and (d). This phenomenon is quite similar to the one observed in in-situ-toughened SiC–TiC_2 composites.[25] Present results suggest that further increase in fracture toughness of in-situ-toughened SiC–TiB_2 composites may be possible by controlling the length and width of the elongated α-SiC grains and adding the optimum amount of additives.

4 SUMMARY

In-situ-toughened SiC–30 wt% TiB_2 composites were fabricated from β-SiC and TiB_2 powders with Al_2O_3–Y_2O_3 additives by hot-pressing and subsequent annealing. The introduction of larger-amount of additives, within the amount range studied (5~20 wt%), accelerated the grain growth of elongated α-SiC grains with higher aspect ratio and maintained the weak interface boundaries after long-time annealing, resulting in the improved fracture toughness. The fracture toughness of 12-h annealed materials with 20 wt% additives was as high as 7.1 MPa $m^{1\backslash 2}$, owing to bridging and crack deflection by the elongated α-SiC grains and coarse TiB_2 grains, approximately 20% higher than that of 12-h annealed materials with 5 wt% additives (5.7 MPa $m^{1\backslash 2}$).

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