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Effect of initial α-phase content of SiC on microstructure and mechanical properties of SiC–TiC composites

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Abstract

By using α- and β-SiC starting powders, the effects of initial α-phase content of SiC on microstructure and mechanical properties of the hot-pressed and subsequently annealed SiC–30 wt.% TiC composites were investigated. The microstructures developed were analyzed by image analysis. Their microstructures consist of uniformly distributed elongated α-SiC grains, equiaxed TiC grains and an amorphous grain boundary phase. During annealing, the β→α phase transformation of SiC leads to the in-situ growth of elongated α-SiC grains. The average diameter of SiC increases with increasing α-SiC content in the starting powder and the aspect ratio shows a maximum at 1% α-SiC and decreases with increasing α-SiC content in the starting powder. Such results suggest that microstructure of SiC–TiC composites can be controlled by changing α-SiC content in the starting powder. The strength increased with increasing α-SiC content when α-SiC content is higher than 10% while the fracture toughness decreased with increasing α-SiC content, i.e. the same trend with the variation of aspect ratio of SiC in the composites.

Keywords: Composites; Mechanical properties; Microstructure; SiC–TiC; TiC

1. Introduction

Composites of SiC–TiC, consisting of finely distributed TiC grains in a SiC matrix, can be fabricated by hot-pressing with Al or Al compound and C aid to a nearly full density at temperatures higher than 2000°C[1–3] or with metal oxide aid, such as Al_2O_3 and Y_2O_3 at 1850°C.[4] Several investigations have shown that the dispersion of TiC particles results in the improved fracture toughness of SiC ceramics by deflecting the cracks around the TiC particles.[1,3,5]

Several attempts to fabricate the in situ-toughened SiC–TiC composites have been reported, including the use of chemical vapor deposition route for fabricating SiC-TiC nanocomposites with needle-like microstructure,[6,7] the addition of Cr_3C_2 as sintering aid,[8] and the addition of metal oxides and the heat treatment at high temperatures (⩾1900°C) for taking advantage of the β→α phase transformation of SiC, which leads to the in-situ growth of elongated α-SiC grains.[9,10] It is claimed that the improvement of toughness is achieved by bridging and deflecting the cracks around the elongated α-SiC grains.[9]

It has been shown that the crystalline phase of the starting powder has a large influence on the microstructure and, as a consequence, mechanical properties of SiC ceramics which depends strongly on the morphology.[11,12] An equiaxed grain morphology is obtained with high α-SiC powders, whereas an elongated grain morphology resulted from β-SiC or β-SiC containing α-SiC seed powders due to the β→α phase transformation during sintering or annealing.[11,12] By deliberately adding a small (⩽10%) amount of α-SiC seeds into β-SiC, a more elongated structure of α-SiC can be obtained by liquid-phase sintering and subsequently annealing.[13] Thus, microstructure and mechanical properties of SiC–TiC composites are expected to be influenced by the crystalline phase (the volume contents of α-SiC and β-SiC) of the starting SiC powder.

In the present work, the effect of the crystalline phase of the starting SiC powder on the microstructure and the mechanical properties of the hot-pressed and subsequently annealed SiC–30 wt.% TiC composites has been investigated. A process in two-step, hot-pressing with Al_2O_3 and Y_2O_3 at 1820°C and subsequent annealing at

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1930°C for 6 h, has been used to develop in-situ-toughened microstructure. The microstructures developed after annealing were observed by scanning electron microscopy (SEM) and then characterized morphologically by image analysis, on the polished and etched surfaces. The strength and the fracture toughness of annealed materials were presented and correlated with microstructure.

2. Experimental procedure

The characteristics of SiC and TiC starting powders are listed in Table 1. Commercially available Al_2O_3 (AKP-30, Sumitomo Chemicals, Tokyo, Japan) and Y_2O_3 (99.9% pure, Shin-Etsu Chemical Co., Ltd, Tokyo, Japan) powders were used as sintering additives. Six batches of powder were mixed, each containing 60 wt.% SiC (α and/or β), 30 wt.% TiC, 7 wt.% Al_2O_3 and 3 wt.% Y_2O_3. The relative content of α-SiC powder in those batches was 0, 1, 3, 10, 50 and 100 vol.%. All individual batches were milled in ethanol for 24 h using polyethylene jar and SiC grinding balls. Contamination of polyethylene and SiC from grinding media during milling was minimal (~0.2% for polyethylene and ~0.5% for SiC). The milled slurry was dried, sieved and hot-pressed at 1820°C for 1 h under a pressure of 25 MPa in an argon atmosphere. The composites hot-pressed at 1820°C for 1 h were heated further at 1930°C for 6 h under an atmospheric pressure of argon to enhance grain growth and the β→α phase transformation of SiC. The batch compositions and the sample designations are given in Table 2.

The density of the specimens was determined by the Archimedes method. The theoretical density of the specimens, 3.682 g/cm^3, was calculated according to the rule of mixtures. The microstructures were observed by SEM. According to the procedure described in previous studies,[13,14] the SEM micrographs of the specimens were analysed by image analysis (Image-Pro Plus, Media Cybernetics, Silver Spring, MD, USA). The diameter of each grain (d) was determined directly from the shortest grain diagonal in its two-dimensional image. The apparent length of each grain (L) was obtained from the longest diagonal. The mean value of the 10% highest observed aspect ratio (L/d) was taken to be the mean of the actual values. A total of 800 to 1000 grains was used for statistical analysis of each specimen. X-ray diffraction (XRD) using CuK_α radiation was performed on ground powders.

The bar samples (2.5×3×25 mm^3) were cut and polished up to 1 μm finish for flexural testing. Bend tests were performed at room temperature on five specimens at each condition, using a four-point method with inner and outer spans of 10 and 20 mm, respectively, and a crosshead speed of 0.5 mm/min. The fracture toughness was estimated from indentation technique[15] on the surface of bars by measuring crack lengths generated by a Vickers indentor with a load of 98 N.

Table 1
Characteristics[a] of starting powders

Powder	Average particle size (μm)	Specific surface area (m^2/g)	Impurity (wt.%)			Supplier
			SiO_2	TiO_2	Free C	
α-SiC	0.45[b]	15.0	0.4	–	1.1	Showa Denko, Tokyo, Japan
β-SiC	0.27[b]	17.5	0.3	–	0.4	Ibiden Co., Ltd, Nagoya, Japan
TiC	1.40[c]	–	–	1.7	0.1	H.C. Starck, Berlin, Germany

[a] Manufacturer's data.
[b] Light scattering.
[c] Fisher sub-sieve sizer (FSSS).

Table 2
Relative density and polytype of the hot-pressed and annealed SiC–30 wt.% TiC composites

Sample designation	Batch composition (wt.%)					Relative density (%)	Crystalline phase	
	α-SiC	β-SiC	TiC	Al_2O_3	Y_2O_3		Major	Trace
ST1	0	60	30	7	3	97.6	α-SiC, TiC	β-SiC
ST2	0.6	59.4	30	7	3	97.6	α-SiC, TiC	β-SiC
ST3	1.8	58.2	30	7	3	97.5	α-SiC, TiC	β-SiC
ST4	6	54	30	7	3	97.6	α-SiC, TiC	β-SiC
ST5	30	30	30	7	3	97.8	α-SiC, TiC	β-SiC
ST6	60	0	30	7	3	97.5	α-SiC, TiC	

3. Result and discussion

3.1. Microstructure

The characteristics of the hot pressed and annealed SiC–30 wt.% TiC composites are summarized in Table 2. The relative densities of >99% were achieved by hot-pressing with a holding time of 1 h at 1820°C for any composition. However, 6 h-annealing at 1930°C resulted in a decrease of the relative density, probably due to the formation of volatile components such as AlO, Al_2O, and CO.[16] Relative densities (97.5~97.8%) of the hot pressed and subsequently annealed specimens were insensitive to changes in the crystalline phase of the starting SiC powder.

The hot-pressed composites were a two phase particulate composites that consisted of randomly distributed TiC grains in the relatively fine, equiaxed SiC matrix. The microstructure of the hot-pressed composites in this study was similar to that of a previous study.[9] The microstructures of the hot-pressed and annealed SiC–30 wt.% TiC composites with different α-SiC content in the starting powders are shown in Fig. 1. The bright phase is TiC and the gray phase is SiC. All specimens showed

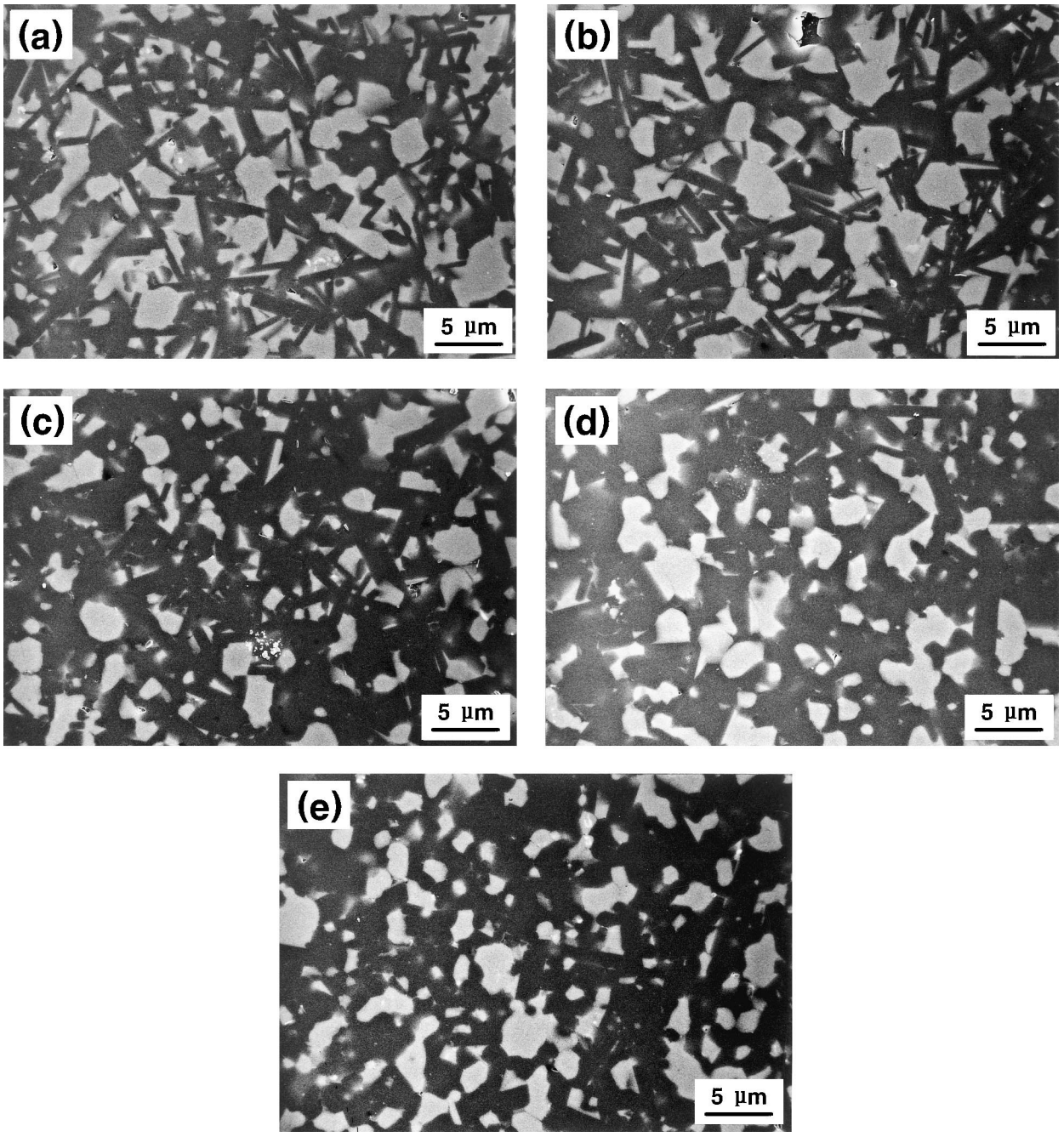

Fig. 1. Microstructures of the hot-pressed and annealed SiC–30 wt.% TiC composites: (a) ST1, (b) ST2, (c) ST4, (d) ST5 and (e) ST6 (refer to Table 2).

an in-situ-toughened microstructure consisted of elongated α-SiC grains, referring to the phase analysis in Table 2, and relatively equiaxed TiC grains. It is well documented that the β→α phase transformation of SiC led to the in-situ growth of elongated α-SiC grains.[11] However, the morphology of SiC grains was different depending on the initial α-phase content of SiC.[12] ST1 prepared from β-SiC [Fig. 1(a)] shows more elongated grains and ST6 prepared from α-SiC [Fig. 1(e)] less elongated grains, and ST2 from α/β mixture containing 1% α-SiC [Fig. l(b)] shows a little more elongation than that of the specimen from β powder. As shown in Fig. 2, the average diameter of SiC grains increased from 0.7 μm for ST1 to 1.3 μm for ST6 with increasing α-SiC content in the starting powder. In contrast, the aspect ratio showed a maximum at 1% α-SiC and decreased with increasing α-SiC content in the starting powder. SiC grains in ST2, therefore, were longer and thinner than those in ST6.

The difference in grain size and shape of SiC grains in composites, prepared from different phase assembly of starting SiC powder, reflects different growth behavior of SiC grains. It appears that new α nuclei may form and grow inside the β grain in ST1 during annealing, resulting in α/β composite grains, which we observed using high-resolution electron microscopy previously.[17] Strain at the α/β interface accelerates the growth of elongated grains as it was already shown by the team of Ogbuji.[18,19] In contrast, the grain growth of SiC grains in ST2 containing 1% α-SiC may have resulted from an overgrowth of β-SiC on α-SiC seeds during hot-pressing, resulting in the formation of an α/β interface at earlier stage than ST1. Strain at the α/β interface accelerated the elongation of the grains,[18,19] resulting in a higher aspect ratio than the other specimens. The difference in the microstructures of ST2 and the other specimens (ST3–ST5) may be due to the difference in the number of α-SiC nuclei in the starting powder. With an increasing content of additional α-SiC particles, grain growth of SiC grains is hindered by an increasing impingment, resulting in decreased aspect ratio and increased diameter. The observation of a smaller steric hinderance of small amounts of α-particles has also been reported by Padture[11] in SiC ceramics. In ST6, α-grains from α-powder may grow on larger relatively equiaxed α- particles through the Ostwald ripening mechanism[20] without having any need for nucleation of new grains, resulting in relatively equiaxed α-SiC grains. Present results suggest that microstructural development in SiC–TiC composites is largely influenced by the initial phase assembly of SiC. This finding is consistent with the previous experimental results on SiC sintered with oxide additives.[12]

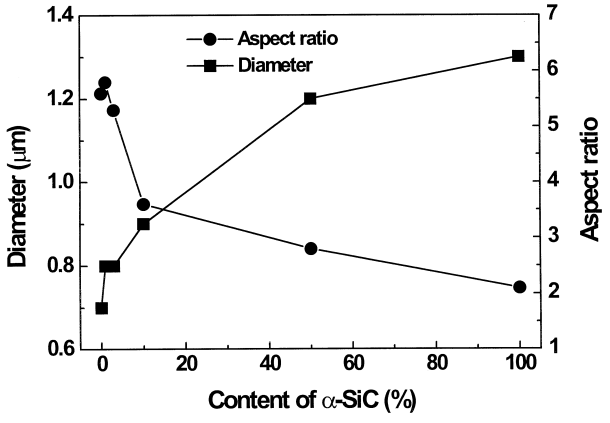

Fig. 2. Change of grain diameter and aspect ratio of SiC grains for the hot-pressed and annealed SiC–30 wt.% TiC composites as a function of α-SiC content in starting powder.

3.2. Mechanical properties

The fracture mode of SiC–30 wt.% TiC composites was a mixture of transgranular and intergranular, 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 TiC grains on cooling after annealing.[1] A large addition of α-SiC particles leads to an increased tendency of intergranular fracture because of relatively equiaxed grain morphology and small grain size (Fig. 3). As it is shown in Fig. 3, ST6 showed an increased tendency of intergranular fracture, compared to ST2. However, there was a substantial tendency for relatively large, platelet-shaped SiC grains in ST2 to transgranular fracture.

Fig. 4 shows the variation of fracture toughness and strength of annealed specimens as a function of α-SiC content in the starting powders. The fracture toughness of the hot-pressed specimens were not affected by α-SiC content in the starting powders. They have fracture toughnesses of 3.9–4.1 MPa $m^{1/2}$. However, 6-h annealing at 1930°C increased the fracture toughness and the increment in toughness was dependent on the initial α-SiC content. ST2, which was composed of elongated α-SiC grains with relatively higher aspect ratio, has a fracture toughness of 6.0–6.7 MPa $m^{1/2}$ and flexural strength of 380–410 MPa. In contrast, ST6, which was composed of relatively equiaxed α-SiC grains, has a fracture toughness of 5.0–5.7 MPa $m^{1/2}$ and flexural strength of 475–505 MPa. The marked growth of elongated α-SiC grains produced improved fracture toughness and decreased the strength values. Thus, microstructures with highly, elongated α-SiC grains (aspect ratio $\geqslant 5$), which can be obtained from mostly β-SiC starting powders, are beneficial for producing improvements in toughness. Conversely, when we consider strength, high α-SiC content may be better because of relatively equiaxed microstructure as the elimination of large defects might be easy.

The change in fracture toughness (Fig. 4) is quite similar to that of the aspect ratio of SiC (Fig. 2). The

fracture toughness of the annealed SiC–TiC composites is plotted versus the aspect ratio of SiC grains in Fig. 5. As can be seen, a consistent increase can be found for all of the samples. According to a crack deflection model by Faber and Evans,[21] the fracture toughness is expected to increase linearly with the aspect ratio of grains. It indicates that the improvement in fracture toughness is produced mainly by crack deflection[21,22] by elongated SiC grains. SEM observation on crack paths induced by a Vickers indentor suggests the occurrence of both crack deflection[21,22] and bridging[23] by elongated SiC grains as operating toughening mechanisms in these composites (Fig. 6).

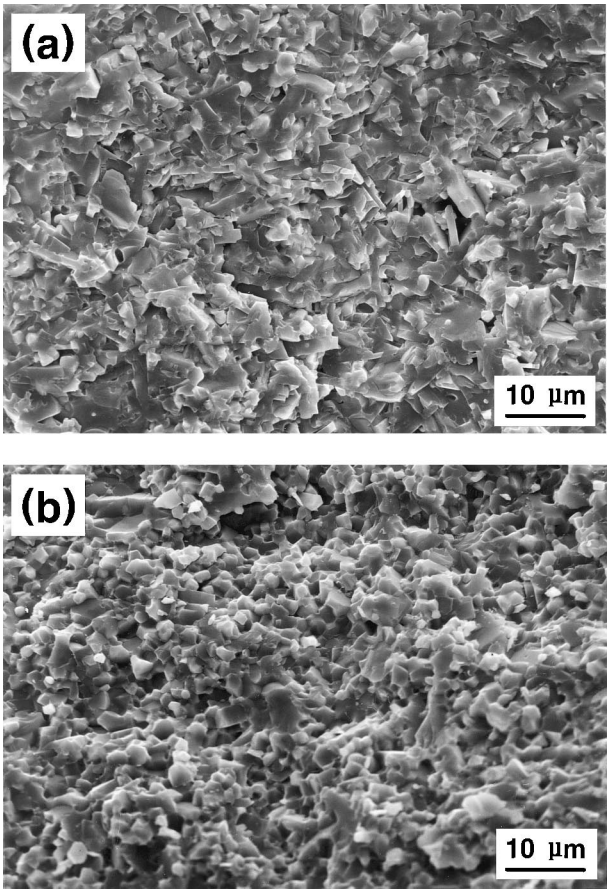

Fig. 3. SEM micrographs of the fracture surfaces of the hot-pressed and annealed SiC–30 wt.% TiC composites: (a) ST2 and (b) ST6 (refer to Table 2).

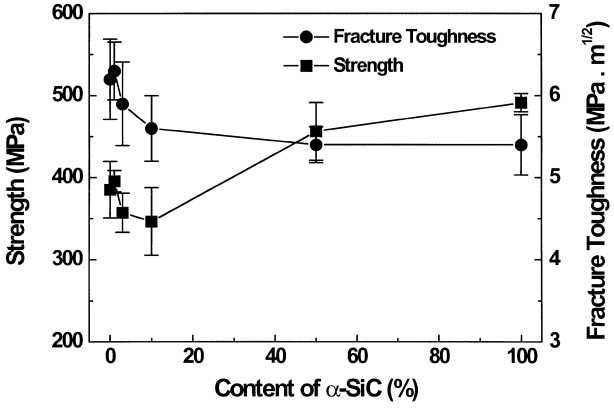

Fig. 4. Flexural strength and fracture toughness of the hot-pressed and annealed SiC–30 wt.% TiC composites as a function of α-SiC content in starting powder.

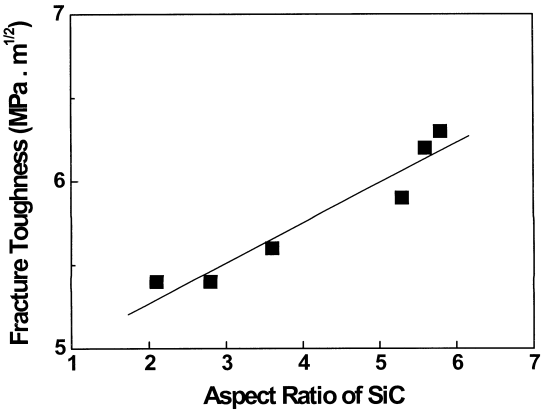

Fig. 5. Relationship between fracture toughness and the aspect ratio of SiC grains in the hot-pressed and annealed SiC–30 wt.% TiC composites.

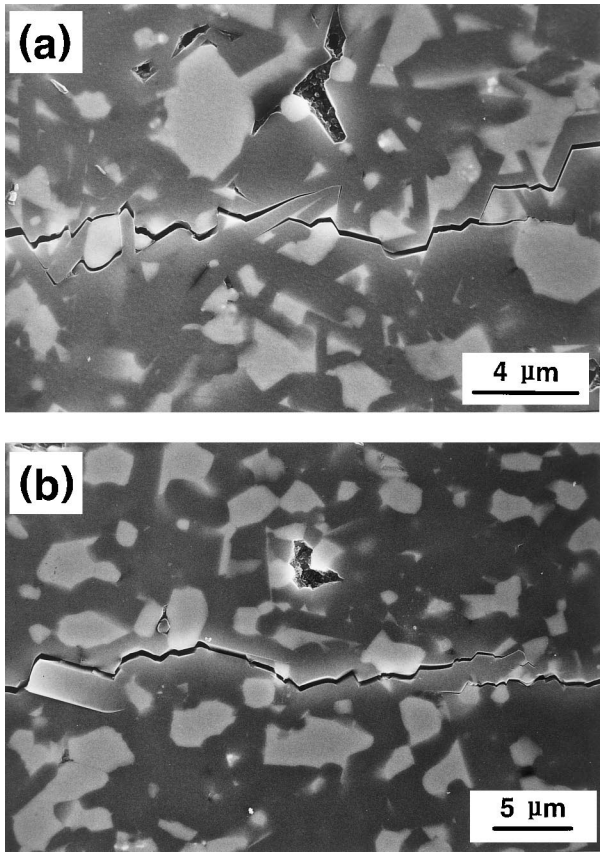

Fig. 6. SEM micrographs of crack paths induced by a Vickers indentor for (a) ST2 and (b) ST6 (refer to Table 2).

A few attempts have recently been made to improve the fracture toughness of SiC–TiC composites: Maupas et al.[6,7] fabricated SiC–TiC nanocomposites with needle-like microstructure via chemical vapor deposition and reported a maximum toughness value of 6.2 MPa $m^{1/2}$ in SiC–15 mol% TiC nanocomposites; Chae et al.[8] fabricated SiC–TiC composites by hot-pressing with the aid of 10 wt.% Cr_3C_2 and reported a maximum toughness of 6.2 MPa $m^{1/2}$ in SiC-30 wt.% TiC composites. Toughness values of 6.0–6.7 MPa $m^{1/2}$ measured in ST2 is slightly higher than the reported values.[7,8] The present results suggest that the mechanical properties of SiC–30 wt.% TiC composites with in-situ-toughened microstructure are mainly dependent on the morphology of SiC grains, which can be controlled by changing α-SiC content in the starting powders, as has already been demonstrated in SiC ceramics.[12]

4. Conclusion

The effect of initial α-SiC content in the starting powders on microstructure and mechanical properties in SiC–30 wt.% TiC composites has been investigated by using α-and β-SiC starting powders. A large addition of α-SiC leads to a decrease in aspect ratio of SiC grains, resulting in relatively equiaxed microstructure. Conversely, from β-powder or a mixture of α/β-powders containing small ($\leqslant 3\%$) amounts of α-SiC powder, a more elongated α-SiC grains can be obtained by liquid-phase sintering and subsequent annealing. The morphology of TiC grains was equiaxed, irrespective of the initial crystalline assembly of SiC particles.

The room-temperature strength increases with increasing α-SiC content when α-SiC content was higher than 10%, while the fracture toughness decreases with increasing α-SiC content. The present results suggest that microstructure of SiC–TiC composites, which influence the mechanical properties of resulting composites, can be controlled by changing α-SiC content in the starting powders.

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