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Microstructure and toughening mechanism of the 3Y-TZP/Al_2O_3 composite reinforced by SiC whiskers

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Microstructures of 10 vol% SiC whisker reinforced 3Y-TZP (3 vol% yttria stabilized tetragonal zirconia polycrystals) composite with addition of 5 wt% Al_2O_3 have been investigated using electron microscopy. The investigation focused not only on the morphology of the composite but also on the martensitic transformation of ZrO_2. The results from high resolution electron microscopy (HREM) observations show that the boundaries between whiskers and the matrix are, in general, clean; however, in some areas, little glassy phases exist. The habit plane of t/m ZrO_2 during the transformation was found at $c_t//a_m$ in the present observations. The processes of t → m transformation in various conditions have been discussed. The fact that no whisker pull-out was found during material breakage indicates that the toughening of this composite would come mainly from a t/m transformation toughening mechanism, as well as crack deflection and bridging. Finally, a fracture strength enhancing mechanism is discussed.

1. Introduction

There has recently been considerable interest in the development of SiC whisker reinforced ceramic composites. Extensive research [1–3, 6] has been carried out and significant progress achieved in both the material processing technology and the further improvement of mechanical behaviours for the composite. The fracture toughness of brittle ceramics can be effectively improved via the incorporation of strong SiC whiskers into the matrix due to crack deflection, bridging and fibre pull-out. Moreover, these toughening mechanisms do not diminish as temperature increases. Therefore, they obviously have an advantage over t/m transformation toughening only.

Y-TZP ceramics should play an even more important role in the application of materials due to its spontaneous transformation toughening. However, the disappearance of transformation toughening at high temperatures limits its application. Y-TZP ceramics incorporated with SiC whiskers were thought to overcome this shortcoming and, eventually, higher strength and toughness was achieved. In fact, a small amount of Al_2O_3 dissolved in the matrix is generally used to enhance the strength of the composite so as to compensate strength reduction due to the presence of cracks introduced by transformation.

The object of this study is to investigate the toughening mechanism and to analyse the role of the interface in toughening the above composite.

2. Experimental procedure

The raw materials used in this study include Y-TZP, Al_2O_3 and SiC whiskers. The composite was hot-pressed at a pressure of 25 MPa at 1650 °C.

Flexural strength was determined in a three-point bending test by use of an Instron-1950. The measurements of the specimen of size $35 \times 5.0 \times 2.5\ mm^3$ were conducted at a crosshead speed of $0.5\ mm\ min^{-1}$.

Chevron-notched specimens were employed for the determination of fracture energy. Specimens with the same dimensions as those used for the strength test were first notched with a 0.25 mm thick diamond blade, and then fracture tested in three-point bending on the Instron-1950 at a crosshead speed of $0.05\ mm\ min^{-1}$.

Fracture surfaces of the composites were examined using scanning electron microscopy (SEM; JCXA-733 model). Specimens for transmission electron microscopy (TEM) observation were prepared by firstly cutting thin sections from the hot-pressed bulk and then thin sections, 2.3 mm in diameter, were mechanically polished to thin discs with a thickness of $<35\ \mu m$. Finally, the discs were ion-milled by use of a Gatan ion beam thinner at a voltage of 6 kV with an incidence beam angle of 15° until the specimens were perforated. And they were further milled at a beam incidence angle of 12° for another 30 min to yield a larger area, being pretty transparent to the electron beam.

0022–2461

TEM and HREM examinations were performed on a JEM-200CX with an operating voltage of 200 keV using a top entry and double-tilt specimen holder.

3. Results and discussion

3.1. Interface of the composite

Fig. 1 shows a typical microstructure and the interface of 3Y-TZP/Al_2O_3 (5 wt %) composites containing 10 vol % SiC whiskers. Fig. 1a was viewed perpendicular to the hot-pressing axis and revealed that the whisker distribution was homogeneous with the preferred long axis orientation on planes normal to the hot-pressing direction. The cross-section of SiC whiskers appeared hexagonal, representing β or H phases (β/H-S), and triangular, representing an R phase (R-S). The majority of the whiskers were located at matrix grain boundaries. When viewed parallel to the hot-pressing axis (Fig. 1b), the serrated surfaces of the whiskers appeared to have a good bond with Al_2O_3 grains and the interface between whiskers and ZrO_2 grains seemed clear. Extensive contrast bands across the matrix suggested that there were residual thermal stresses in the composite due to the difference in the thermal expansion coefficients between the whiskers and the matrix.

When examined at high magnification, an amorphous film was observed at the periphery of the whisker with a pocket of glass at triple points (Fig. 2). The glassy phase may mainly contain SiO_2 due to contamination from two principal sources: the powder precursor ($ZrSiO_4$) and traditional milling media (SiO_2 and Al_2O_3) [2]. The investigations indicated that the existence of glass might generally be detrimental to mechanical properties of the composites, especially at high temperatures. For example, the amorphous phase largely locating at the whisker–matrix interface would embrittle the composite, allowing the crack to proceed across the whiskers avoiding deflection and thereby causing a catastrophic fracture [4, 5]. However, on the other hand, an intergranular glassy phase would accommodate any residual strains from the thermal expansion mismatch or phase transformation, and eventually strengthen the material if the glass were controlled at a reasonable level and proper distribution. Moreover, a thin layer of intergranular glassy phase would weaken the binding between the whiskers and the matrix, and would make fibre pull-out act as a contribution to the material toughening. But a thick layer of glassy phase would accommodate more residual strains and might hinder the progress of the transformation.

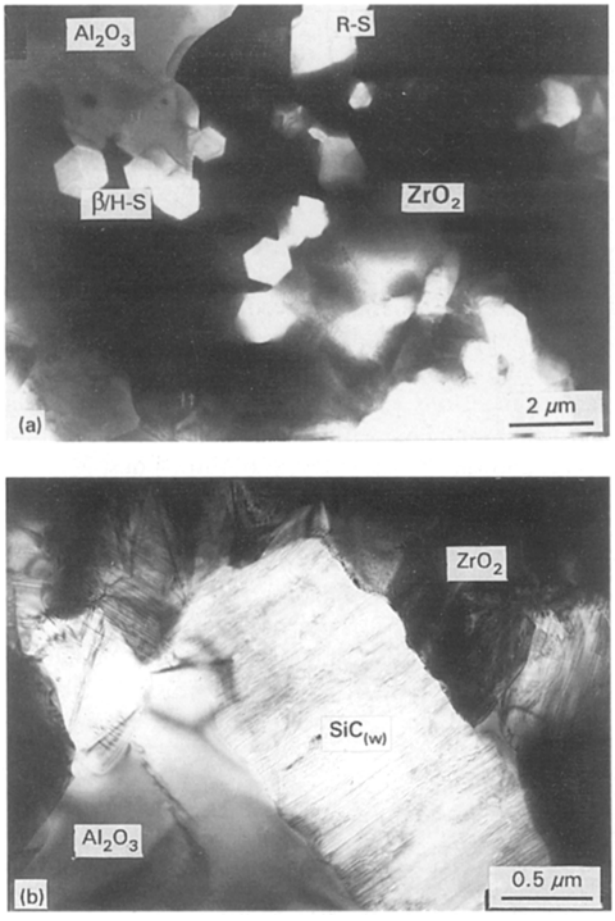

Figure 1 Typical morphology of the *in situ* composite viewed perpendicular (a) and parallel (b) to the hot-pressing axis.

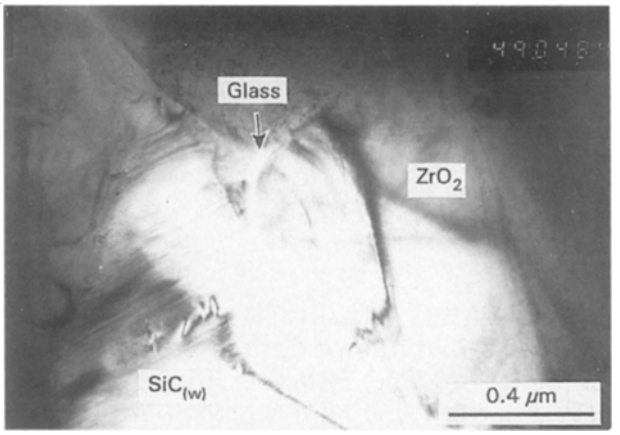

Figure 2 TEM micrograph of the Y-TZP–Al_2O_3– $SiC_{(w)}$ composite showing an amorphous phase at the whisker–matrix interface with a pocket of glass at the triple point.

Fig. 2 shows a high density of stacking faults in the whisker, and stress streaks both in the whisker and in the matrix, and also shows that some tetragonal ZrO_2 grains had partially transformed into the monoclinic phase. This is due to the difference of thermal expansion coefficients between the whisker and matrix ($\alpha_{SiC} = 30 \times 10^{-7}\,°C^{-1}$, $\alpha_{Y\text{-}TZP} = 100 \times 10^{-7}\,°C^{-1}$). Since the thermal expansion coefficient of the matrix is lower than that of whiskers, the matrix is under tangential tension and the whisker under compression [6]. As tensile stress could induce $t \rightarrow m$ phase transformation, the transformed particles expanded in volume would compress the neighbouring particles leading to the occurrence of stress streaks. Though high tensile matrix stresses due to the thermal mismatch should reduce the fracture strength of the composite, probable tensile stress-induced transformed ZrO_2 grains with expanded volume adjacent to the whisker would instead compress the whisker and hence may be somewhat beneficial for strength enhancement. Fig. 3 gives a lattice image of the interface of SiC whiskers and ZrO_2 grains, revealing a grain boundary with a very thin amorphous layer. In the

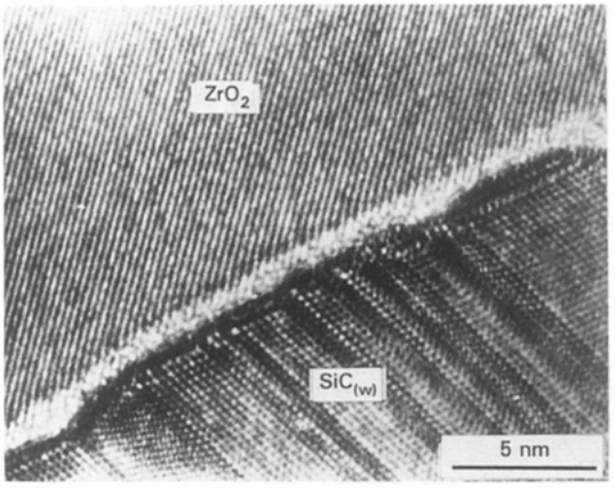

Figure 3 Lattice image of the whisker–matrix interface indicating a small amorphous phase between the whisker and the TZP matrix.

present investigations, the mechanical properties tests indicated that a little glassy phase existing between SiC whiskers and ZrO_2 grains, as shown in Fig. 3, combined with t → m phase transformation, could largely benefit an improvement of mechanical properties.

3.2. Martensitic transformation of t-ZrO_2

When ZrO_2 ceramics are nearly broken, t-ZrO_2 undergoes a stress-induced t → m martensitic transformation by which microcracks are introduced and propagated. All these might consume some fracture energy and together contribute to the toughening of the material [7, 8].

It is well known that ZrO_2 ultra-thin films autocatalystically transform when irradiated with the electron beam [9–12]. Fig. 4 presents two stages among a dynastic transformation process after t-ZrO_2 particles had been irradiated with a strong electron beam for ca. 45 min. (Photographs in Fig. 4 were taken with a weak electron beam so that the transformation might proceed better at low speed.)

From Fig. 4a, it was seen that after nucleation at the grain boundary, the transformation preferentially took place in a large grain (C), though the electron beam had been focused in the region of two small grains (A and B) on the left. The observation showed that a transforming band ca. 0.1 μm wide went forward in a fixed direction, indicated by 1 and 2. After it reached another grain boundary, for a while (ca. 5 s) the band returned into the original grain with a definite angle. As the band turned back again at the boundary, it proceeded parallel to the initial m-lath and the continuous bars exhibited a Z-shaped structure. This shows that the stress-induced transformation has a preferential orientation rather than it being diffuse.

Finally, as seen in Fig. 4b, the small grains nearby began to transform, in which some m-bars were transgranular (marked by an arrow). From the micrograph, it can be seen that the triple point of three neighbouring grains (circled area) was much more liable to be a nucleating site, which means that the highest stresses existed there.

The next step of the transformation was to develop the band. Fig. 5 is an HREM micrograph of the m/t transformation boundary showing that the t-ZrO_2 lattice in the middle of the micrograph was being transformed to the m-ZrO_2 lattice and, furthermore, lattice distortion had occurred (marked by an arrow). The two neighbouring m-ZrO_2 lattices exhibited symmetrical lattices with the same zone axes [0 1 1] which might be the precursor of the ultimate structures – "twins". According to the lattice image in Fig. 5a, the typical habit plane of t/m ZrO_2 should be at $c_t//a_m$, and a suggested structure model for this transformation is shown in Fig. 5b.

Fig. 6 shows that the transformed m-ZrO_2 particle before TEM observation gives a quite different appearance from those transformed by electron beam radiation. It is apparent that for originally transformed ZrO_2 grains, twins (which were much thinner compared with twins mentioned in the above paragraph) had formed and the particle was round, indicating no residual stress left in the particle. Whether it

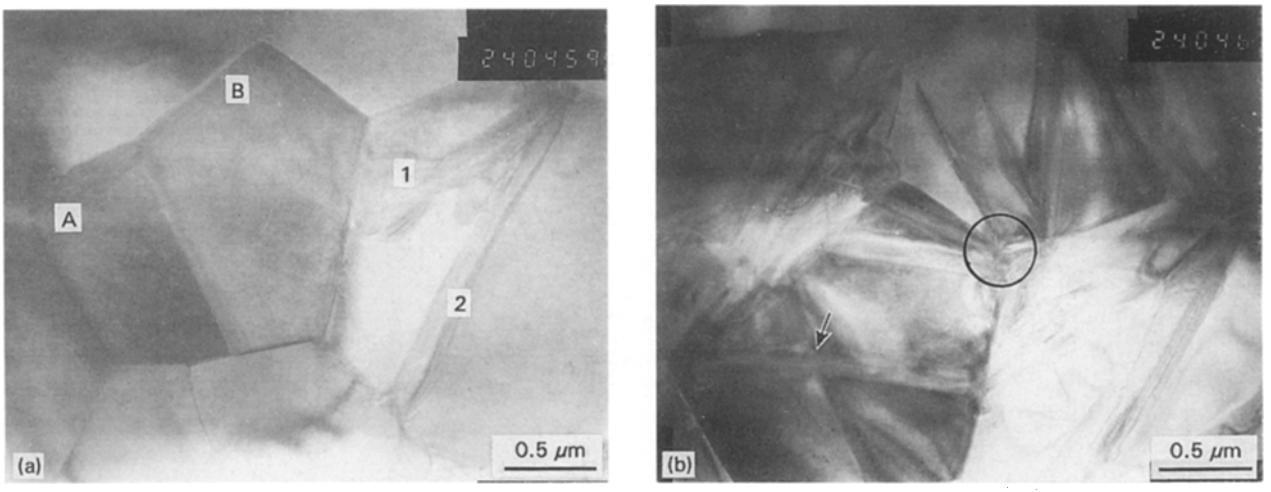

Figure 4 TEM micrograph of the dynamic transformation process after t-ZrO_2 particles had been irradiated with a strong electron beam for ca. 45 min. Diffraction patterns correspond to A and B grain particles, respectively.

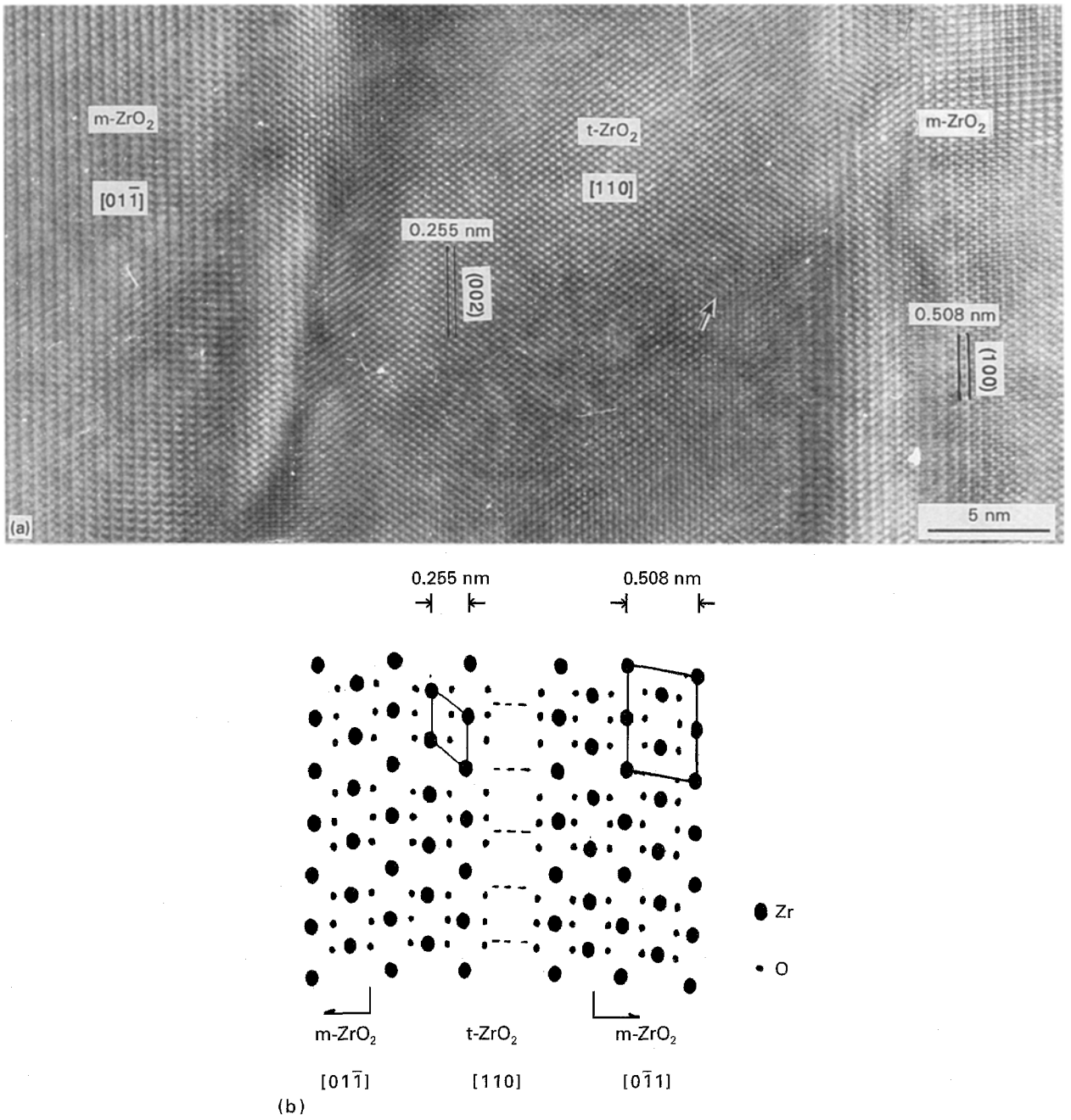

Figure 5 (a) Lattice image of the transforming region showing that t-ZrO_2 was being "swallowed" by the m-ZrO_2 lattice at each side; (b) corresponding illustration of the atomic structure model.

formed due to cooling from the hot-pressing temperature or ion-beam thinning, which is uncertain, the formation of twins was inconsistent with the above discussion. We suggest that for rapid t → m transformations in conditions such as cooling, except electron irradiation, microtwins and twins with much thinner widths have to form in order to accommodate some of the volume and shape changes associated with the transformation and reduce the constraint imposed by the surrounding material and, hence, benefit the retention of the tetragonal phase [7]. In the present investigation, the microtwins in the transformed m-ZrO_2 lattice, as shown in Fig. 7, also served a similar function. On the other hand, transformation with electron irradiation progresses comparatively more slowly and microtwins do not occur. The Z-shaped structure eventually forming the twins is due to the definite orientation relationship among the m-bands nucleated on different boundaries.

When the t → m transformation takes place, some microcracks, as shown in Fig. 8, formed which may be quite beneficial in enhancing the fracture toughness of the material. These microcracks can decrease the stress concentration at the tip of the main crack. In addition, microcracks increase the surface area and absorb more fracture energy and, hence, toughen the matrix [13–17]. Fig. 9 shows the lattice image at the tip of a crack. Transformation had taken place and the stress streak had spread inside the grain.

Fig. 10 presents the transformation condition of t-ZrO_2 particles adjacent to the whisker. The clear grain boundary indicated that there were few amorphous phases inside it. When the transformed m-lath propagated to the boundary, it could be re-nucleated

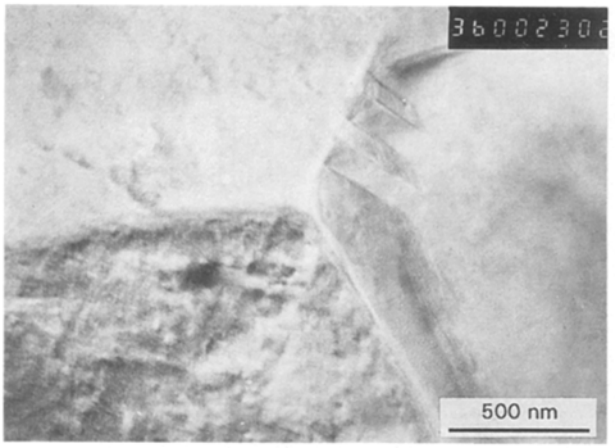

Figure 6 TEM micrograph showing that twins and rounded periphery occurred in transformed particles.

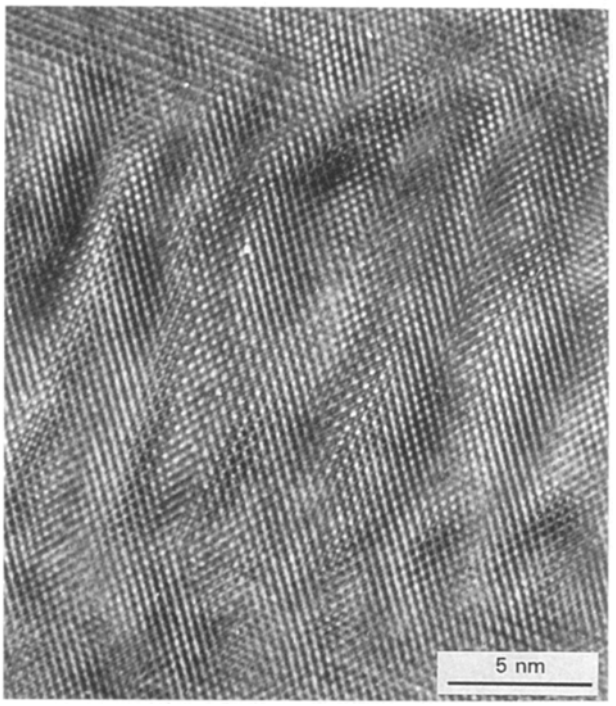

Figure 7 Lattice image showing microtwins in the transformed m-ZrO_2 lattice.

and transformation went on. So, a clear fibre–matrix boundary would be beneficial for the transformation toughening mechanism.

3.3. Enhancing mechanism of the composite

The flexural strength and fracture toughness of the *in situ* composite are 1329 MPa and 14.7 MPa $m^{1/2}$, respectively. High mechanical properties make it significant to analyse its enhancing mechanism. Fig. 11 shows the SEM micrograph of the fracture surface which reveals that, although fracture surface was quite uneven, few fibre pull-outs occurred. Most cracks were intergranular. Fig. 11 also shows that while a crack extended to the whisker–matrix boundary, it deflected and proceeded along the boundary. The TEM micrograph in Fig. 12 illustrates that the cracks were deflected and bridged by whiskers. So, the main toughening mechanism of the $SiC_{(w)}$/Y-TZP composite was transformation toughening, crack deflection and bridging.

As mentioned above, the thermal expansion coefficient of whiskers is lower than that of Y-TZP. When

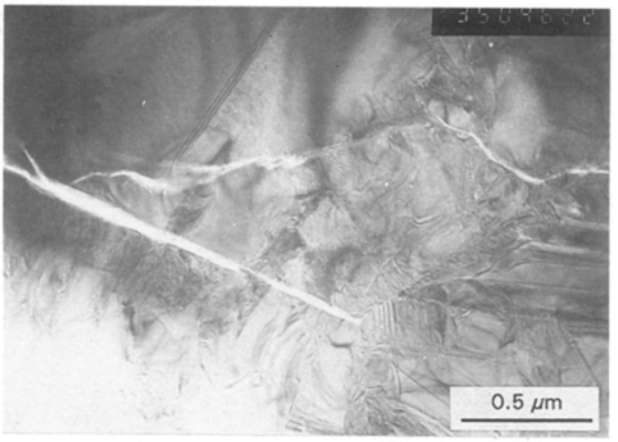

Figure 8 TEM micrograph showing the microcracks produced during transformation.

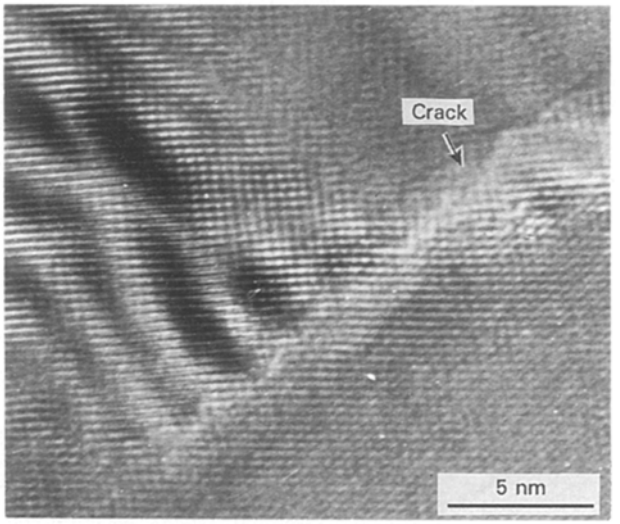

Figure 9 Lattice image of the tip of a crack showing stress streaks and transformation.

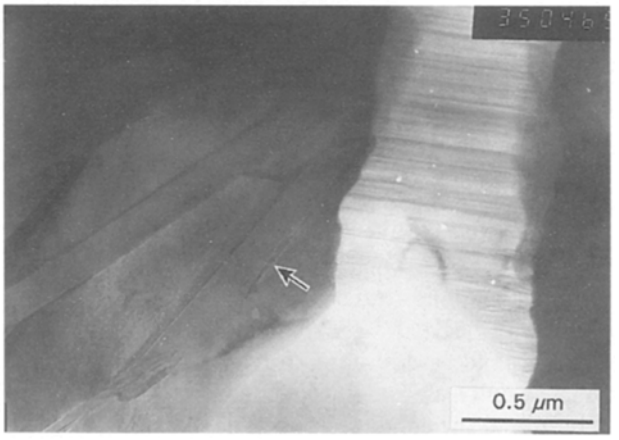

Figure 10 TEM micrograph showing the progression of transforming laths (arrow), indicating that a clean whisker–matrix interface is beneficial for a transformation toughening mechanism.

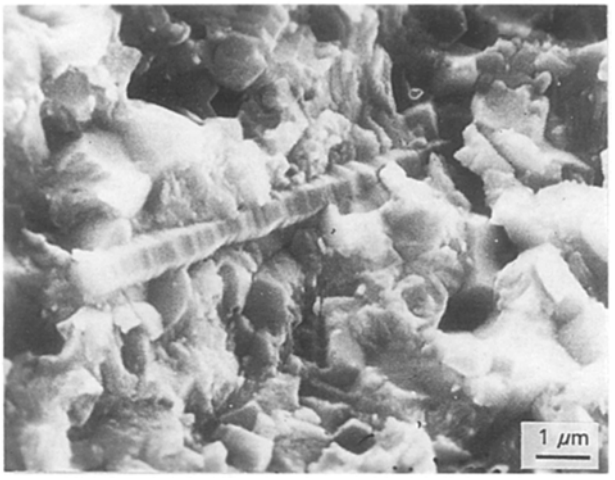

Figure 11 SEM micrograph showing that hardly any whisker pull-out occurred.

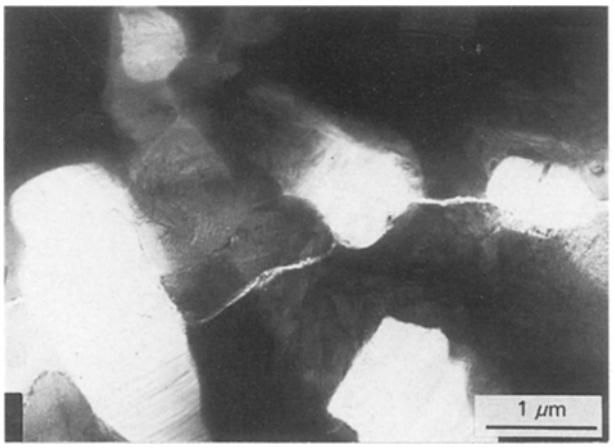

Figure 12 TEM micrograph illustrating cracks deflected and bridged by whiskers.

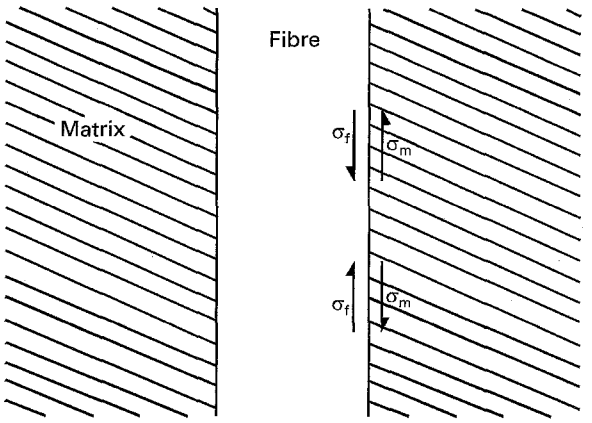

Figure 13 Stress–strain sketch at the whisker–matrix interface.

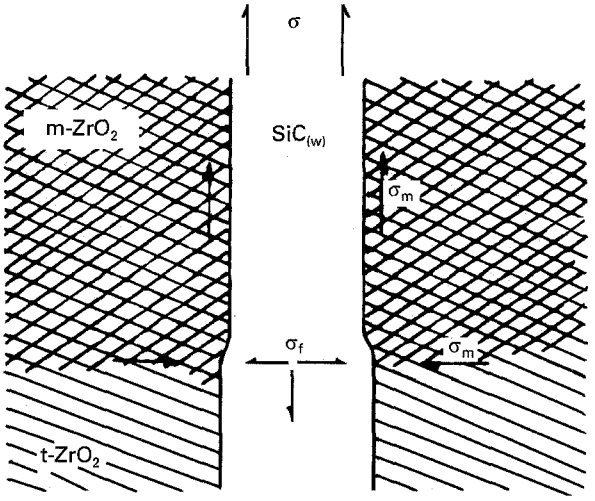

Figure 14 Toughening mechanism of the *in situ* composite.

cooled from the hot-pressing temperature, the matrix is under tangential tension and the whisker under compression, as shown in Fig. 13. When the material was being broken and cracks extended to the periphery of the whisker, as shown in Fig. 14, volume expansion introduced by phase transformation raised the shear strain between the whisker and matrix, and made it more difficult for whiskers to be pulled-out. Furthermore, when whiskers were being pulled, the matrix was under tangential tension and tensile stress induced the phase transformation with a volume expansion of nearly 4%. Expanded volume and rough interfaces increased friction force and hence hindered whisker pull-out. So, whisker pull-out had little contribution to the enhanced properties of the composite.

High strength is another advantage of the *in situ* composite. It has been widely reported that the addition of SiC whiskers may reduce the flexural strength of the composite due to the mismatch of thermal expansion coefficients between the whiskers and the matrix [3]. In order to make a comparison, Table I lists several mechanical data in which data of samples A are presented by Claussen *et al.* [3] and those of samples B are supplied for the present research. From Table I, it can be seen that although flexural strength values decreasing with addition of SiC whiskers was a common phenomenon, a lower percentage decrease was achieved in the present composites. This may be attributed in part to the incorporation of a small amount of Al_2O_3 grains (5 wt %). X-ray diffraction (XRD) analysis revealed that the monoclinic content of the present composite was ca. 20% according to the equation in Ref. [1]. A little high monoclinic content degraded the toughness of the composite at room temperature (see Table I), although the addition of SiC whiskers might otherwise increase it. But for flexural strength, it might be somewhat beneficial. From TEM investigation, fewer cracks at the junction of the matrix and whiskers due to thermal mismatch were observed. Instead, more ZrO_2 grains adjacent to whiskers had partially transformed to the monoclinic form (see Fig. 2), with a volume expansion which made the ZrO_2 grains and whiskers under compressive stresses and hindered degradation of the composite. Moreover, addition of a small amount of a high modulus second phase (Al_2O_3) might improve the mechanical properties of the composite. Al_2O_3 grains hindered the transformation progress during the hot-pressing procedure and cooling to room temperature, which might be helpful in retaining the high volume percentage of t-ZrO_2 grains and increase the residual compressive stresses

TABLE I Mechanical properties of different samples and their comparison

Sample		Flexural strength (MPa)	Decrease of σ_F values (%)	K_{Ic} (MPa $m^{1/2}$)
A	3Y-TZP	1150		6.7
	3Y-TZP/$SiC_{(w)}$	700	30.4	9.5
B	3Y-TZP	1570		15.3
	3Y-TZP/Al_2O_3/$SiC_{(w)}$	1329	15.3	14.7

as well. As a result, fracture strength of the present composite has been improved.

4. Conclusions

1. The microstructures of 3Y-TZP/(10 vol %) $SiC_{(w)}$ composite with addition of 5 wt % Al_2O_3 have been characterized. The whisker–matrix interfaces are generally clean and only a little glassy phase layer has been observed at the parallel grain boundary. This may benefit strengthening of the composite. However, at the triple point among grains there existed a glass pocket which may be detrimental to the mechanical properties of the composites. TEM observations found that a clear whisker–matrix interface might preferentially nucleate transformation and furthermore allow the transformation progress to proceed.
2. Due to the difference of thermal expansion coefficients between the whisker (with a lower value) and the matrix (with a higher value), some t-ZrO_2 grains would transform under tensile stresses. On the other hand, expanded m-ZrO_2 particles would compress the whisker leading to the occurrence stress streaks, which would be beneficial for strength improvement.
3. Stress-induced transformation by using an electron beam irradiation possessed its preferential orientation rather than a diffusive one. The typical habit plane of t/m ZrO_2 during transformation is found to be at $c_t//a_m$. The situation in transformation with the electron beam radiation is different from that of cooling from the hot-pressing temperature or thin film preparation. In the former situation, twins were formed but with a much thicker width. Anyhow, in the latter, twin laths were formed with much thinner widths and the transformed particles became round. We suggest that rapid transformation should allow the occurrence of microtwins and thin twins in order to swiftly accommodate some of the volume and shape changes associated with the transformation and reduce the constraint imposed by the surrounding material.
4. In *in situ* composites, a substantial contribution to toughness derives from transformation toughening, crack deflection and bridging, while the conventional mechanism of pull-out might only play a relatively minor role. This is due to the discrepancy of the thermal expansion coefficient between whiskers and the matrix.
5. Addition of a little high percentage monoclinic ZrO_2, introduced on cooling from the hot-pressing temperature, might reduce the fracture toughness; however, this was beneficial for fracture strength. A small amount of Al_2O_3 grains contributed to flexural strength enhancement.

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