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Silicon carbide-toughened zirconia ceramics

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Tetragonal zirconia polycrystalline (TZP) ceramics containing SiC reinforcement in the form of fine particles (nano-scale), particles (micro-scale), whiskers and platelets were synthesized by hot-pressing. The effects of morphology and grain size of SiC reinforcement on the strength and fracture toughness at room temperature were investigated. The addition of SiC (in whatever form) caused decreases in strength and toughness at room temperature with the exception of whisker-reinforced materials. Toughness fell off with increasing temperature, but nevertheless retained about one-half of the room-temperature value for that particular SiC reinforcement. However, the whisker- and particle-reinforced materials had higher K_{Ic} values at high temperature than fine particle- or platelet-reinforced materials, with values in excess of 7 MPa m$^{1/2}$ at 1000 °C. The microstructure was examined for SiC whisker-reinforced/TZP materials by TEM and HREM, to examine the nature of the whisker/zirconia interface.

1. Introduction

Whereas tetragonal zirconia polycrystalline (TZP) ceramics can be prepared with high strength and toughness at room temperature, these properties decrease rapidly with increasing temperature. This is attributed to a decrease in the transformation toughening effect exhibited by zirconia materials at high temperatures, as the tetragonal form becomes more stable relative to the monoclinic form. If the strength and toughness at high temperature were improved, zirconia materials would be attractive candidates for advanced structural applications, such as engine components. One potential method of improving the high-temperature properties would be to incorporate a dispersion of a crystalline second phase. Silicon carbide is a very attractive alternative reinforcing material for TZP ceramics because of its good refractoriness and high hardness. A few attempts have been made to achieve improved toughness and greater resistance to failure for TZP ceramics using combined transformation toughening with SiC-whisker or fibre reinforcement [1–6]. The whisker reinforcement counteracts the reduction in transformation toughening with increasing temperature, and a higher proportion of strength and fracture toughness can, in principle, be retained at high temperatures [1].

Previous work by the present authors [6–8] included adding SiC in the form of whiskers, platelets and particles to yttria-stabilized tetragonal zirconia ceramics (TZ3Y, 3 mol % yttria addition). The additions of SiC (in whatever form) always resulted in losses of strength and toughness at room temperature in varying degrees, and the decrease in strength at higher temperatures was consistent with what might have been predicted from a mixed ZrO_2–SiC composite system. Although decreased at higher temperature, the SiC–TZP composite strength values were improved, compared with those of monolithic TZP materials. The current work centred on studying the effects of adding SiC in the form of fine particles (nano-scale), particles (micro-scale), whiskers and platelets to a TZP matrix, and determining the fracture toughness at higher temperatures. Strength and fracture toughness at room temperature were also measured.

2. Experimental procedure

Yttria-stabilized tetragonal zirconia (TZ3Y, 3 mol % yttria) and SiC in the forms of fine particles (fp), particles (p), whiskers (w) and platelets (pl) were used as matrix and inclusions, respectively. Information about the additives used is listed in Table I. The amount of SiC was chosen to give an inclusion volume fraction of 20% based on the fully dense composite. Composite mixtures were prepared by co-precipitation, by co-dispersing $ZrOCl_2$, $Y(NO_3)_3$ and one of the four SiC inclusions in ammonia. All the composite mixtures were hot-pressed in an argon atmosphere at 1600 °C and 25 MPa for 60 min using a rectangular graphite die assembly. The fabrication procedure is illustrated schematically in Fig. 1.

Following hot-pressing, the resulting billets were cut and ground into $2.5 \times 5 \times 30$ mm^3 specimens for

TABLE I Morphological data for SiC reinforcements

	Fine particles	Particles	Whiskers	Platelets
Distributor	SICCAS[a]	SICCAS*	American Matrix Corp	C-Axis Tech. Canada
Phase	β	β	β	α
Diameter (μm)	0.04–0.05	1	1.0–3.0	11
Thickness (Length) (μm)	–	–	30–100	1
Ratio (L/D)	–	–	50–100	8–10

[a]SICCAS: Shanghai Institute of Ceramics, Chinese Academy of Sciences.

bend testing and $5 \times 2.5 \times 30$ mm^3 specimens with the notches of 0.25 mm width and 2.5 mm depth for measuring toughness. Flexural strength was determined by three-point bending with a span of 20 mm and a crosshead speed of 0.5 mm min^{-1}, while fracture toughness values were determined by the single-edge-notch beam technique with a span of 20 mm and a crosshead speed of 0.05 mm min^{-1}. All elevated temperature tests for fracture toughness were performed in an argon atmosphere. Test bars were allowed to come to an equilibrium state at the desired temperatures for a period of 15 min prior to testing. Fracture surfaces were examined by SEM. The microstructure of SiC_w/TZP composites was examined by TEM and high-resolution electron microscopy (HREM), to identify the nature of the whisker/matrix interface.

3. Results

3.1. Mechanical properties of SiC/TZP composite ceramics at room temperature

Mechanical properties of five materials, namely, a monoclinic TZ3Y ceramic and four SiC/TZP composites with various SiC inclusions, are shown in Figs 2 and 3. Fig. 4 shows typical fracture surface characteristics of four types of composite. The results show that adding 20 vol % of either fine particles, particles or platelets to Y-TZP results in loss of fracture toughness and strength in varying degrees. While inclusions of SiC whiskers in a TZ3Y matrix resulted in a slight increase in both the fracture toughness and the strength, the results are different from those reported by others for SiC_w/TZP composites [1–3]. This is attributed to the significant elimination of agglomerates of whiskers through special dispersion-processing techniques, as shown by scanning electron

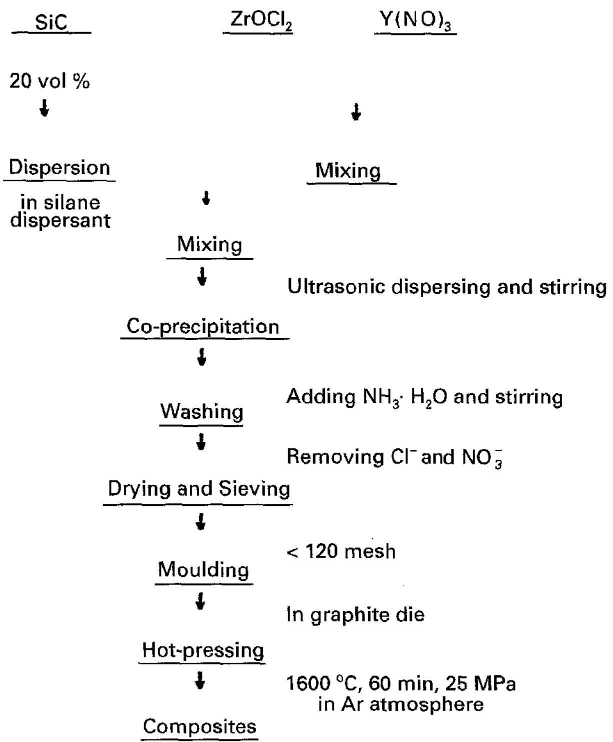

Figure 1 Fabrication procedure for producing SiC/ZrO_2 composite samples.

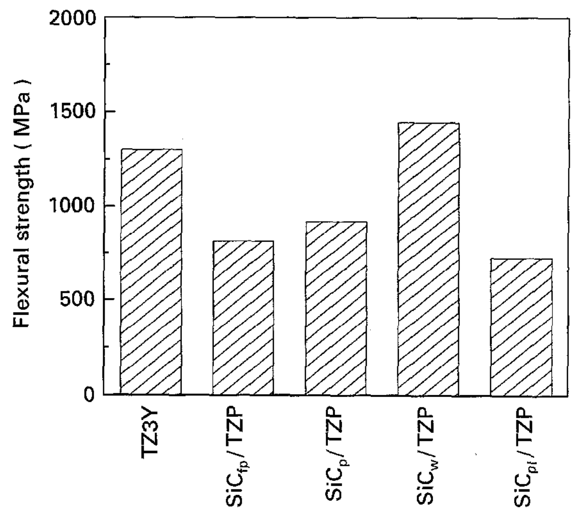

Figure 2 Flexural strength of SiC/TZP composites at room temperature.

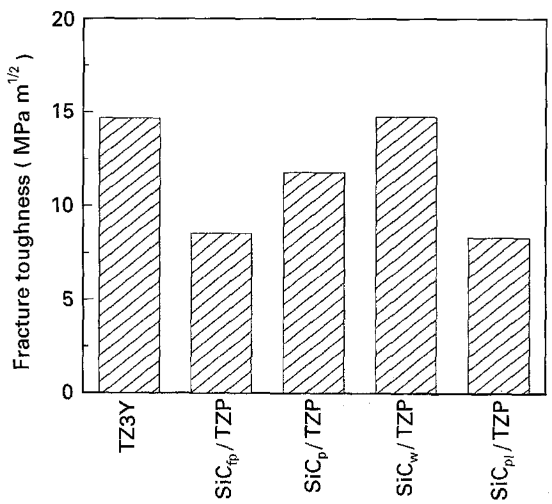

Figure 3 Fracture toughness of SiC/TZP composites at room temperature.

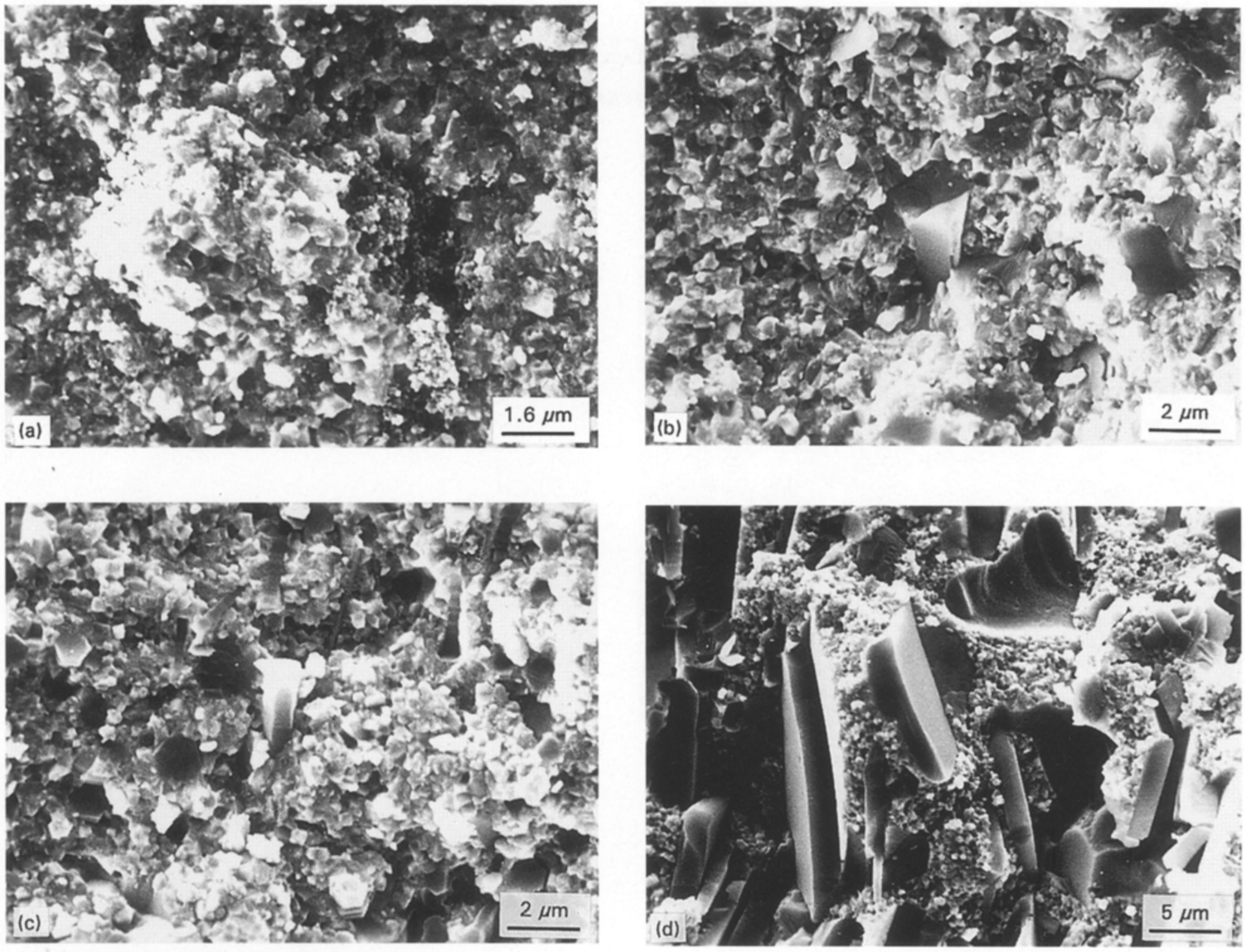

Figure 4 Scanning electron micrographs of four types of SiC-reinforced/TZP composites: (a) SiC_{fp}/TZP, (b) SiC_p/TZP, (c) SiC_w/ TZP, (d) SiC_{pl}/TZP composites.

micrographs of the fracture surface. The results with inclusion of SiC fine particles are inconsistent with what might have been expected from the nano-SiC fine particle clustering as seen in Fig. 5 (arrowed). The clustered regions were usually the origins of fracture.

3.2. Fracture toughness of SiC/TZP composites at higher temperature

Fracture toughness of TZ3Y and SiC/TZP composites containing 20 vol % SiC in forms of fine particles, particles, whiskers and platelets at room and elevated temperatures is shown in Table II. With increasing temperature, the toughness falls off, with all samples retaining about one-half of the room-temperature value at 1000 °C. However, the SiC_p and SiC_w materials had higher toughness values at high temperatures than SiC_{fp} or SiC_{pl}, consistent with the room-temperature behaviour. Although strength at high temperature was not measured in this study, it is believed from previous results [6, 7] that the addition of SiC whiskers and particles to a TZP matrix enhances high-temperature strength.

3.3. Microstructure of 20 vol % SiC_w/TZP composite

The transmission electron micrograph in Fig. 6 shows a typical photograph of the 20 vol % SiC_w/TZP composite. Some amorphous phase was observed in triple junctions but rarely at whisker/matrix interfaces. However, a very thin layer of glassy material (thickness less than 1 nm) could still be observed in some whisker/ZrO_2 interfaces using HREM, as shown in Fig. 7. Fig. 8 shows evidence for a series of microcracks running along the SiC_w/m-ZrO_2 interfaces. It is believed that these cracks may be generated during cooling because of the thermal mismatch between ZrO_2 and SiC grains.

4. Discussion

The use of SiC as an additive for zirconia ceramics to achieve increased toughness at elevated temperatures relies on counteracting the normal fall-off of the transformation-toughening effect with increasing temperature by an increased amount of crack bridging (in the case of SiC platelets and whiskers) and crack branching/crack deflection (in the case of particles), assisted by the favourable thermal expansion mismatch between ZrO_2(Z) and SiC(S) ($\alpha_{Z(t)} = 11 \times 10^{-6}$ K^{-1}; $\alpha_s = 4.5 \times 10^{-6}$ K^{-1}), which puts the SiC grains under stress and hinders crack propagation.

Data in Figs 2 and 3 for pure TZ3Y materials show excellent values for room-temperature strength (1305 MPa) and fracture toughness (14.7 MPa $m^{1/2}$), higher than most other reported values in the literature. Previous work by the present authors [8] has

Figure 5 Fracture origin in a 20 vol % SiC_w/TZP composite showing the SiC fine-particle clustering (arrowed).

TABLE II Fracture toughness of SiC/TZP composite ceramics at higher temperatures containing 20 vol % SiC inclusions

Material and composition	K_{IC} (RT) (MPa $m^{1/2}$)	K_{IC} (500 °C) (MPa $m^{1/2}$)	K_{IC} (800 °C) (MPa $m^{1/2}$)	K_{IC} (1000 °C) (MPa $m^{1/2}$)
3Y-TZP	14.7			
SiC_{fp}/TZP	8.5	7.6	5.9	4.8
SiC_p/TZP	11.8	7.8	7.1	7.4
SiC_w/TZP	14.8	9.8	8.3	7.2
SiC_{pl}/TZP	8.3	5.7	4.8	4.1

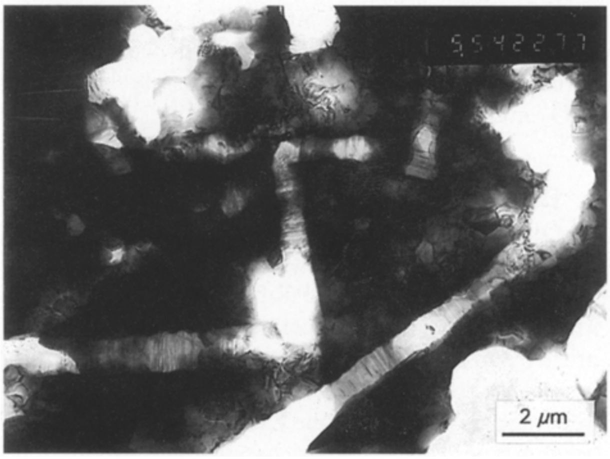

Figure 6 Typical transmission electron micrograph of a 20 vol % SiC_w/TZP composite.

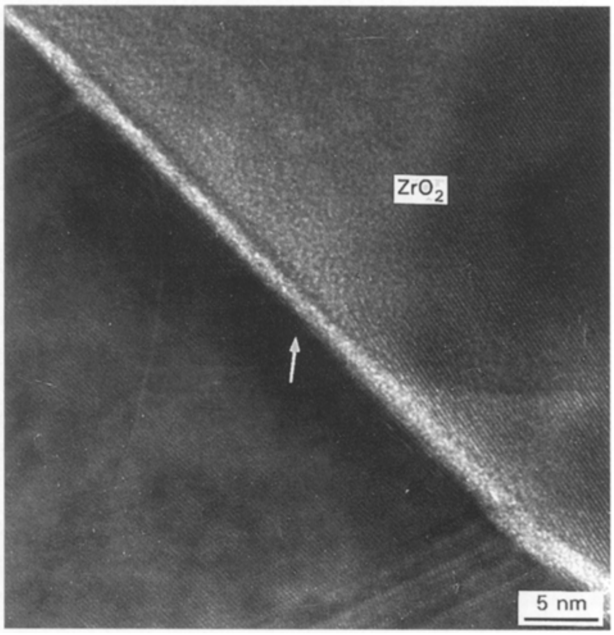

Figure 7 High-resolution electron micrograph of the SiC_w/TZP composite showing glass phase (indicated by arrow) in the SiC/ZrO_2 interface.

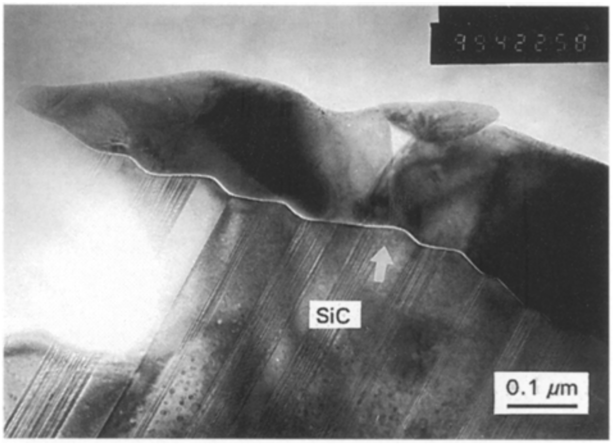

Figure 8 Transmission electron micrograph of the SiC_w/TZP composite showing microcrack (arrowed) in the SiC/m-ZrO_2 interface.

shown that in the range 0–1000 °C, the monolithic material reduces in strength by ≈100 MPa per 100 °C increase in temperature, and K_{Ic} decreases in similar proportion. Also, addition of SiC platelets to TZ3Y materials results in a reduction in room-temperature strength of approximately 50% compared with that of the monolithic TZ3Y material for a 30 vol % SiC_{pl} addition, without any clear evidence of any strength benefit at 1000 °C. This behaviour was attributed to the relatively large size of the platelets (diameter 11 μm, thickness 1 μm), compared with the sub-micrometre grain size of the final sintered TZP ceramic, as a result of which the plates behave as large flaws, which reduce the strength of the composite at all temperatures, more so at elevated temperatures when the benefits of the compressive stresses arising from the mismatch in thermal expansion coefficients are no longer operative. Similar behaviour was also observed in the case of the fracture toughness of the SiC_{pl}-containing composites, both at room and elevated temperatures.

The present results compare the previous strength and fracture toughness data obtained for SiC_{pl}-reinforced TZP with similar data for SiC_p, SiC_{fp} and

SiC_w-reinforced TZP ceramics. It is immediately clear that for all materials, the synergism between strength and fracture toughness, characteristic of dense transformation-toughened zirconia ceramics, is also preserved in the composite ceramics. Moreover, as shown in Figs 2 and 3, there is an enormous difference between the behaviour of the different morphologies, with the whiskers giving the best performance compared with the rest, which are all broadly similar, with the exception of the SiC_p materials, which show a better fracture toughness than SiC_{fp} or SiC_{pl}. With increasing temperature, strength and toughness fall-off, with all samples retaining about one-half of the room-temperature strength and toughness at 1000 °C. The result for particles appears unusual in showing an increase in K_{Ic} between 800 and 1000 °C, and further work is needed to confirm this result. The fall-off in properties is noticeably less than exhibited by pure TZP materials [6, 7], and retention of K_{Ic} values of ≈ 7 MPa $m^{1/2}$ at 1000 °C is certainly of merit. The fall off in K_{Ic} with temperature (Table II) is not only because the transformation-toughening contribution is decreasing, but also because the compressive stresses induced by thermal-expansion mismatch are also decreasing. Because the fall-off is less than shown by pure monolithic TZP ceramics, this shows that there must be an effect of crack deflection/crack branching, giving a positive contribution to K_{Ic}, which opposes the negative contributions arising from the first two effects.

The different behaviour of the various additives can be explained with reference to the morphologies and grain sizes. The whiskers would be expected to give the best performance because their diameter (1–3 μm) is not large enough to create strength-limiting flaws but the aspect ratio (>50) is more than adequate to give good pull-out from the matrix, aided by the favourable thermal expansion mismatch. The poor performance of the platelets has already been discussed [8, 9], and the poor strengths are attributed to the large grain size of the platelets (≈ 11 μm diameter). Moreover, platelets will not be as effective as whiskers or fibres (i.e. one-dimensional grains) in hindering crack movement, because of the two-dimensional nature of a crack, which, given some alignment of the platelets, could find an easy path through the microstructure, whereas in the case of a whisker/fibre-reinforced structure the crack is also having to break a high proportion of strong matrix bonds. A possible contribution to toughness arising from crack bridging in the case of platelets is, therefore, minimal compared with the advantages discussed above, whereas crack bridging is clearly operative in the whisker-reinforced materials.

The particulate additions give perhaps the most surprising results. The micrometre size powders give reasonable room-temperature results for strength and toughness, showing that the particle size is not big enough to produce strength-limiting flaws (even though some of the strength reduction compared to the pure monolithic TZP material can be explained in this way, because the SiC_p grains are larger than the grain size of the TZP grains). Nevertheless, the particles, assisted by the compressive stresses arising from the favourable thermal expansion mismatch are definitely giving a positive contribution towards toughness. The behaviour of the fine particle additions is certainly contrary to expectations. It was hoped that a reasonable proportion of these would be incorporated inside the growing TZP grains and provide additional gains in strength and K_{Ic} because of the smaller grain size and the resulting complex crack-deflection behaviour. However, careful TEM studies showed no evidence for this and, in fact, the particles remained totally in the boundaries between TZP grains. Moreover, evidence in other work using the same particles showed that agglomeration of the fine particles readily took place during processing, with the resulting aggregates ending up similar in size to the micrometre-size SiC_p grains; the lower density and weak bonds within these aggregates are detrimental to both strength and toughness. These regions therefore end up as flaws in the grain boundaries of the final ceramic.

The work shows that further efforts should be directed towards more detailed studies of the SiC_w and SiC_p-reinforced materials, and also towards preventing aggregation in SiC_{fp} materials. In particular, it is of advantage to explore the behaviour of coarser SiC_p additions to see whether higher toughnesses can be achieved at the expense of strength. Also larger proportions of whiskers and particles may offer advantages. In the present study it has been impossible to separate the various toughening mechanisms which operate for the different particle morphologies. It is clearly desirable to determine which mechanisms are important (and beneficial), and approximately how significant the contribution is towards the fracture toughness of the final composite. In previous work [9, 10], it was observed that alumina additions had a beneficial effect on the properties of SiC-reinforced/TZP ceramics. In fact, the results showed, in all cases, that it was better to have additions of silicon carbide *plus* alumina than merely the reinforcing SiC phase on its own. Because the alumina grains remained in the final microstructure with very similar size and morphologies as in the starting powder, it is believed that the only way they give a positive effect is by increasing the overall stiffness of the matrix, and also possibly by reducing the final grain size of the TZP grains. Clearly more work is needed to understand the behaviour of alumina additions in more detail and to design into the composite an optimum proportion for the most effective compensation of the fall-off of K_{Ic} with temperature in TZP materials. The present results show that values in excess of 7 MPa $m^{1/2}$ can be retained at ≈ 1000 °C, which is promising compared with competing ceramics.

5. Conclusion

Mechanical properties of TZP ceramics at high temperature can be improved by incorporating various types of SiC reinforcement, at the expense of strength and toughness in all cases except whisker reinforcement. For a 20 vol % SiC_w-reinforced TZP composite, the strength and toughness increase slightly compared with monolithic TZ3Y material. The different behaviour of various SiC additives is attributed to the morphologies and grain sizes. SiC_p- and SiC_w-reinforced materials have higher K_{Ic} values at high temperatures than SiC_{fp} and SiC_{pl}. The microstructure of SiC_w-reinforced TZP composites showed small amounts of liquid phase at the SiC/ZrO_2 interfaces and a series of microcracks running along the $SiC/m\text{-}ZrO_2$ interfaces because of the effects of thermal mismatch during cooling.

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