Journal of the European Ceramic Society **12** (1993) 377–383

Microstructure and Mechanical Properties of Yttria-Stabilised Tetragonal Zirconia Polycrystals (Y-TZP) Containing Dispersed Silicon Carbide Particles

Zh. Ding, R. Oberacker & F. Thümmler

Institut für Keramik im Maschinenbau, Zentrallaboratorium, Universität Karlsruhe (TH), Haid-und-Neu-Str. 7,
Postfach 6980, D-76131 Karlsruhe, Germany

(Received 25 November 1992; accepted 4 May 1993)

Abstract

The microstructure and mechanical properties of pressureless sintered and subsequently hot isostatic pressed Y-TZP ceramics containing up to 20 vol% of SiC particles were studied. The grain growth of the ZrO_2 *matrix was not significantly affected by SiC additions. It was found that the hardness, Young's modulus and fracture toughness* K_{IC} *increased, and the bending strength,* σ_b, *decreased with increasing SiC content. The maximum* K_{IC} *and* σ_b *were* $7{\cdot}8\,MPa\sqrt{m}$ *and 849 MPa, respectively. Silicon carbide additions caused increased flaw sizes, and reduced thermal stability of tetragonal zirconia during low-temperature ageing. The dominant toughening mechanism was microcracking. Stress-induced phase transformation played only a secondary role.*

Das Gefüge und die mechanischen Eigenschaften von SiC-partikelverstärkten Y-TZP-Keramiken mit bis zu 20 vol% SiC wurden untersucht. Die Herstellung erfolgte durch drucklose Sinterung in kontrollierter Atmosphäre und anschließende heißisostatische Nachverdichtung. Es zeigte sich, daß das Kornwachstum der ZrO_2*-Matrix nicht deutlich durch SiC beeinflußt wurde. Die Härte, der E-Modul und die Rißzähigkeit (*K_{IC}*) wurden durch SiC-Partikel erhöht, während die Biegefestigkeit erniedrigt wurde. Der Maximalwert von* K_{IC} *lag bei* $7{\cdot}8\,MPa\sqrt{m}$ *mit einer Biegefestigkeit von 849 MPa. Fraktographische Untersuchungen zeigten erhöhte Fehlergrößen in SiC-haltigem Y-TZP. Der Widerstand gegen thermische Degradation von Y-TZP wurde durch SiC erniedrigt. Der dominante Mechanismus für die* K_{IC}*-Erhöhung ist Mikrorißverstärkung. Die spannungsinduzierte Phasenumwandlung spielt nur eine untergeordnete Rolle.*

On a étudié la microstructure et les propriétés mécaniques de céramiques Y-TZP frittées sous pression normale puis pressées à chaud, contenant jusqu'à 20 vol% de particules de SiC. La croissance des grains n'a pas été particulièrement affectée par l'addition de SiC. On trouvé que la dureté, le module de Young et la résistance à la fracture K_{IC} *augmentent avec une teneur en SiC croissante. Les valeurs maximales de* K_{IC} *et* σ_b *sont, respectivement,* $7{\cdot}8\,MPa\sqrt{m}$ *et 849 MPa. Les additions de SiC sont la cause de défauts de plus grande taille et d'une moins bonne stabilité thermique de la zircone tetragonale lors du vieillissement à basse température. Le mécanisme principale de renforcement est la formation de microfissures. La transformation de phase induite par tension ne joue qu'un rôle secondaire.*

1 Introduction

Yttria-stabilised tetragonal zirconia polycrystals (Y-TZP) have received more and more attention due to their excellent mechanical properties, especially their extreme high strength at ambient temperatures[1] and their transformation toughening potential. Two disadvantages still limit the practical use of these materials. The first one is the brittle fracture behaviour; the second one is the degradation of strength at high temperatures caused by the loss of the stress-induced transformation toughening.[2,3] One of various strategies to strengthen and toughen ZrO_2 ceramics at high temperatures is the incorporation of particles, platelets or whiskers with high modulus within the microstructure.[3] It is also expected that such second phase inclusions enhance fracture toughness at room temperature by crack deflecting and microcracking effects.[4] Huang *et al.*,[5]

Journal of the European Ceramic Society 0955-2219/93/$6.00 © 1993 Elsevier Science Publishers Ltd, England. Printed in Great Britain

however, reported that both fracture toughness and bending strength of 2·8 Y-TZP were reduced by SiC particles. They attributed this phenomenon to the reduced transformability of the tetragonal zirconia matrix. The high temperature strength of their TZP ceramics was improved by SiC additions. Compared to the hot-pressed materials studied by Huang *et al.*,[5] Y-TZP–SiC particulate composites were fabricated by a special process consisting of pressureless sintering in controlled sintering atmosphere and subsequent hot isostatic pressing (HIPing). This process exhibits two advantages: firstly, the reactions between ZrO_2 and SiC during sintering were avoided by controlling the sintering atmosphere; secondly, the densification could be carried out at relative low temperatures so that the typical fine grained microstructure of TZP materials could be conserved.

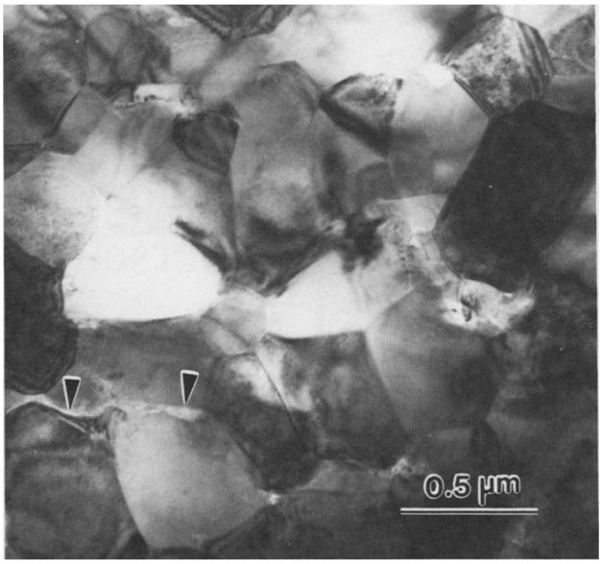


Fig. 1. TEM image showing the microstructure of a 3Y-TZP–20SiC composite after HIPing (bright: SiC).

2 Experimental Procedure

The starting ZrO_2 powders stabilised with 2 and 3 mol% Y_2O_3 (TZ2Y and TZ3Y, respectively) originated from Toyo Soda Co. Ltd (Shinnanyo, Yamaguchi 746, Japan). The β-SiC powders were supplied by Superior Graphite Co. (120 South Riverside Plaza, Chicago, IL 60606, USA). Two particle size grades of SiC (0·6 and 2 μm) were used, which are marked as SiC-1 and SiC-2, respectively, in order to study the grain size effect of second phase on the toughening. The powder property data as specified by the suppliers are shown in Table 1.

The starting powders were mixed in an attritor mill using ZrO_2 mill balls in a medium of isopropanol. After cold isostatic pressing the samples were sintered in a graphite furnace at temperatures of 1500–1550°C in controlled sintering atmosphere for 2 h. Subsequently, the samples were densified by post-HIPing at 1500°C under 150 MPa. Details about the fabrication of these composites were reported elsewhere.[6] The average grain size was determined by the linear intercept method[7] using transmission electron microscope (TEM) images. Young's modulus was measured by an ultrasonic technique. Vickers hardness was determined by indentation with a load of 98 N. Bending strength was measured in four-point bending (span 40/20 mm, loading speed 100 N/s) with a sample geometry of 45 × 4·5 × 3·5 mm^3. Fracture toughness was measured by three-point bending of specimens with a sharp and straight precrack, which was introduced by the bridge method.[8–10] Stress-induced tetragonal to monoclinic (*t–m*) phase transformation on the fracture surface was evaluated by using the method developed by Garvie and Nicholson.[11] The thermal stability was studied with samples, which were annealed at temperatures of 250, 300, and 400°C for 200 h in air.

3 Results and Discussion

3.1 Microstructure

All the samples have reached a relative density of 98·5–99·5%. The Y-TZP matrix was almost completely in the tetragonal phase after the densification process. Figure 1 shows the typical microstructure of ZrO_2–SiC particulate composites. No significant influence of SiC additions on the grain growth of the ZrO_2 matrix was observed. The average grain size of ZrO_2 in the TZ3Y and TZ2Y matrix varied between 0·3 and 0·4 μm. These fine grains are a consequence of the relative low consolidation temperatures. It seems that some spontaneous microcracking took place during cooling. Some microcracks could be seen in

Table 1. Properties of starting powders

Material	d_{50} (μm)	*BET* (m^2/g)	Al_2O_3 (%)	SiO_2 (%)	O_2 (%)	Fe_2O_3 (%)	*C(free)* (%)	*Si(free)* (%)
TZ3Y	0·26	15·1	0·005	0·002	—	0·004	—	—
TZ2Y	0·27	18·6	0·005	0·002	—	—	—	—
SiC-1	0·6	15	—	<0·6	—	—	0·85	0·03
SiC-2	2	4·9	—	—	0·2–0·9	—	0·6	0·03

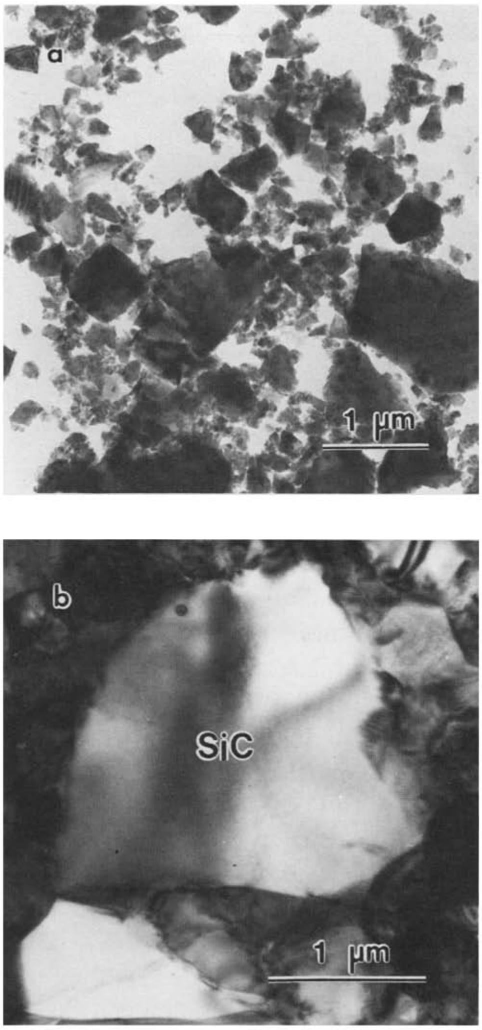


Fig. 2. Oversize SiC particles: (a) in the SiC powder, and (b) in a HIPed 3Y-TZP–20SiC specimen.

the microstructure of unloaded specimens, as arrowed in Fig. 1. This spontaneous microcracking was probably caused by thermal residual stresses, because almost no phase transformation of ZrO_2 associated with this microcracking was observed. Some oversize SiC grains were observed, which should have existed already in the starting powders (Fig. 2), as SiC agglomerates can not be sintered at the temperatures used. At the phase boundaries between ZrO_2 and SiC an amorphous layer with a thickness of about 3 nm was detected by TEM studies,[6] as shown in Fig. 3. The possible sources of this glassy layer are SiO_2 impurities in the SiC powder and/or the reaction of SiO_2 with ZrO_2 and Y_2O_3 dissolved from the matrix.[12,13] The influence of glassy phases can be very different. They can improve the densification process, but also enhance grain growth.[6] Claussen *et al.*[12] reported that the high temperature strength can be improved by the softening of glassy grain boundary layers by activating some modulus load transfer.[12] The creep resistance, however, will be reduced. Furthermore, the formation of liquid phases during sintering leads to benefication of agglomerate formation, i.e. the flaw size will be increased.[14]

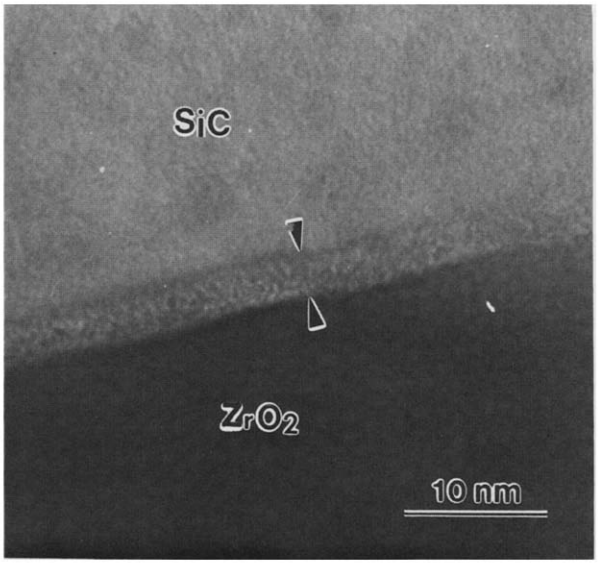


Fig. 3. Continuous amorphous grain boundary phase in Y-TZP–SiC ceramics (TEM image).

The microstructure of the composites was studied again after bending. The TEM foils were taken from the fractured bending specimens at a location between the inner span, where the bending moment is constant. TEM images revealed microcracking, associated with the *t–m* transformation of zirconia, as illustrated in Fig. 4. There are two reasons for the occurrence of microcracking. The first is the stress-induced *t–m* transformation with a dilatational volume change. The second are the residual stresses due to thermal mismatch between ZrO_2 and SiC. Following Taya *et al.*[15] the thermal residual stresses can be estimated to

$$\sigma_m = \frac{2 \times V \times \beta}{A} \times E_m \times (\alpha_p - \alpha_m) \times \Delta T \tag{1}$$

$$\beta = \frac{1 + \nu_m}{1 + \nu_p} \times \frac{E_p}{E_m} \tag{2}$$

$$A = (1 - V) \times (\beta + 2) \times (1 + \nu_p) + 3\beta V(1 - \nu_p) \tag{3}$$

where the subscripts m and p represent matrix and second phase particles, respectively; α and E are the thermal expansion coefficient and Young's modulus; ΔT is the temperature difference between processing and room temperature; V the volume fraction of second phase; and ν the Poisson's ratio.

The parameters α, ν and E of Y-TZP and SiC are given in Table 2.[12,16] As the thermal expansion of

Table 2. Properties of Y-TZP and SiC

Material	$\alpha \times 10^{-6}$	*E(GPa)*	ν
Y-TZP	11	200	0·23
SiC	4·9	490	0·19

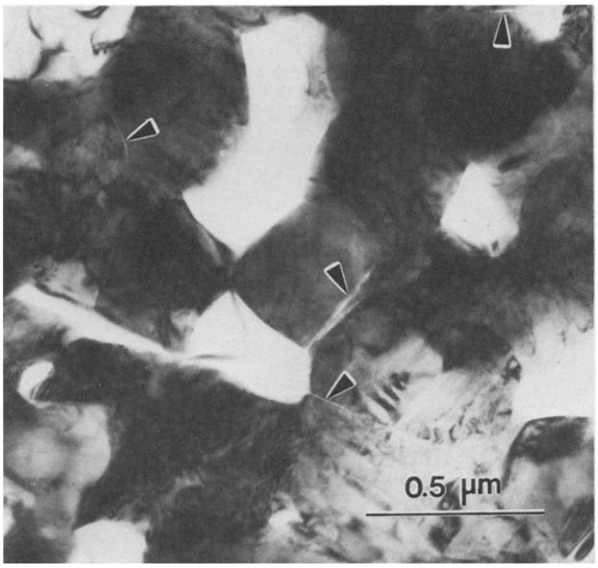


Fig. 4. TEM image showing microcracking in Y-TZP–SiC ceramics after bending test (bright: SiC).

SiC is lower than that of ZrO_2, tensile stresses are expected from eqn (1) to develop in the matrix during cooling. If the densification temperature is 1500°C, tensile stresses in the matrix as high as 400 MPa will be expected for $V = 0{\cdot}2$. It is well known that tensile stresses can benefit the nucleation of monoclinic zirconia, and hence, *t*–*m* transformation.[15] Additionally, the tensile stresses affect crack tip stress intensity additively to the external load.

3.2 Mechanical properties

Vickers hardness and Young's modulus of Y-TZP–SiC particulate composites are shown in Fig. 5 which increase with the SiC content. It is well known that the strength degradation of TZP materials with increasing temperature towards the equilibrium transformation temperature is attributed to the drastical decrease of toughening mechanism, which results from the stress-induced phase transformation.[3] The higher Young's modulus of SiC decreases less rapidly with temperature than that of TZP. The increase of the strain free energy change will stabilise the tetragonal symmetry of ZrO_2 at elevated temperatures. Therefore, the enhanced Young's modulus should have a positive influence on high temperature strength.

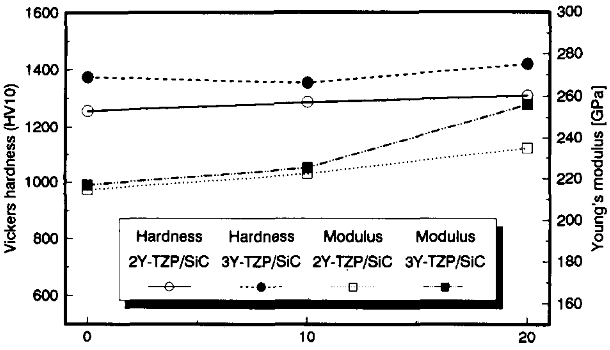


Fig. 5. Young's modulus and Vickers hardness (HV10) of Y-TZP–SiC composites.

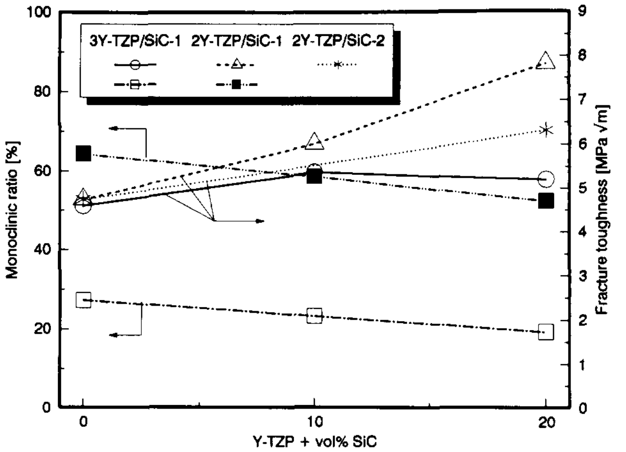


Fig. 6. Stress-induced phase transformation and fracture toughness of Y-TZP–SiC composites.

A physical stabilisation effect of the *t*-phase by SiC incorporation can be derived from the X-ray phase analysis on the fracture surfaces. Figure 6 shows the monoclinic ratio in the fracture surfaces of different Y-TZP–SiC composites. The *m*-ZrO_2 content is reduced to about 50% by 20 vol% SiC additions, compared with 65% in the fracture surface of pure 2Y-TZP. This is attributed to the enhanced Young's modulus of the composites, hence, the increase of the strain free energy change, by SiC additions. The stress-induced transformation of 3Y-TZP–SiC composites is changed in a similar manner by the SiC additions. However, it is much less pronounced as with the lower stabiliser content.

The principle of residual stress toughening of ceramic materials is the introduction of compressive residual stresses by thermal expansion mismatch.[15,17] This requires that the matrix exhibits a lower thermal expansion than the incorporated particles. In the SiC toughened Y-TZP composites just the opposite is realised. But despite of the wrong thermal mismatch and the reduced stress-induced phase transformation, the fracture toughness of Y-TZP is significantly increased by the incorporation of SiC particles (Fig. 6). Significant crack deflection was not observed. Therefore, microcracking must be the dominant toughening mechanism, not transformation toughening. The contributions to toughening and strengthening from transformation mechanisms in a transformable composite, however, is not negligible. Furthermore, the dilatational volume change caused by *t*–*m* transformation leads also to microcracking. Therefore, the higher fracture toughness of 2Y-TZP–SiC composites compared to that of 3Y-TZP–SiC can be interpreted by the larger *t*–*m* transformability of the 2Y-TZP matrix.

The bending strength of the matrix is partially drastically reduced by silicon carbide additions,

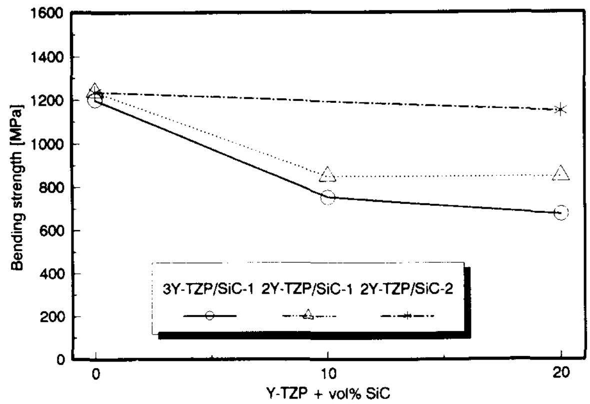
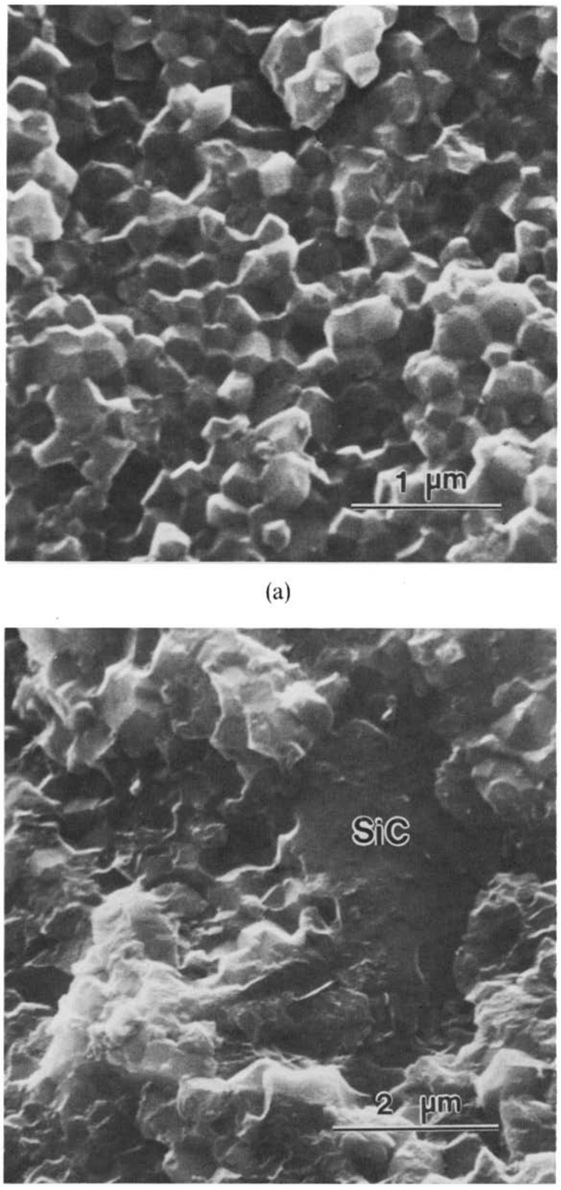


Fig. 7. Four-point bending strength of Y-TZP–SiC composites.

as illustrated in Fig. 7. In comparison with pure 2Y-TZP (1286 MPa) the strength of the composite of 2Y-TZP with 20 vol% SiC was only about 850 MPa (SiC-1) and 1150 MPa (SiC-2), respectively. 2Y-TZP–SiC composites showed a higher strength than 3Y-TZP–SiC. The fact that the strength of 2Y-TZP ceramics containing coarse silicon carbide particles was much higher than that of 2Y-TZP containing fine silicon carbide particles can probably be attributed to the density difference. The specimens containing fine SiC (SiC-1) had a relative density of 98·8%, while the specimens containing coarse SiC were densified to 99·3% of the theoretical density. Because of the sensitivity of the strength of ceramic materials to flaws, this improvement of density can lead to a large increase of strength.

Compared with pure Y-TZP, Y-TZP containing SiC showed an increased amount of transgranular fracture due to transgranular failure of the oversize SiC particles (Fig. 8). The transgranular fracture can be explained by the distribution of residual stresses in the composites. Due to the lower thermal expansion of SiC, tangential tensile stresses develop during cooling at boundaries between SiC particles and the matrix. In such materials, cracks tend to



(a)

(b)

Fig. 8. Fracture surface of (a) 3Y-TZP and (b) 3Y-TZP-20SiC ceramics (SEM).

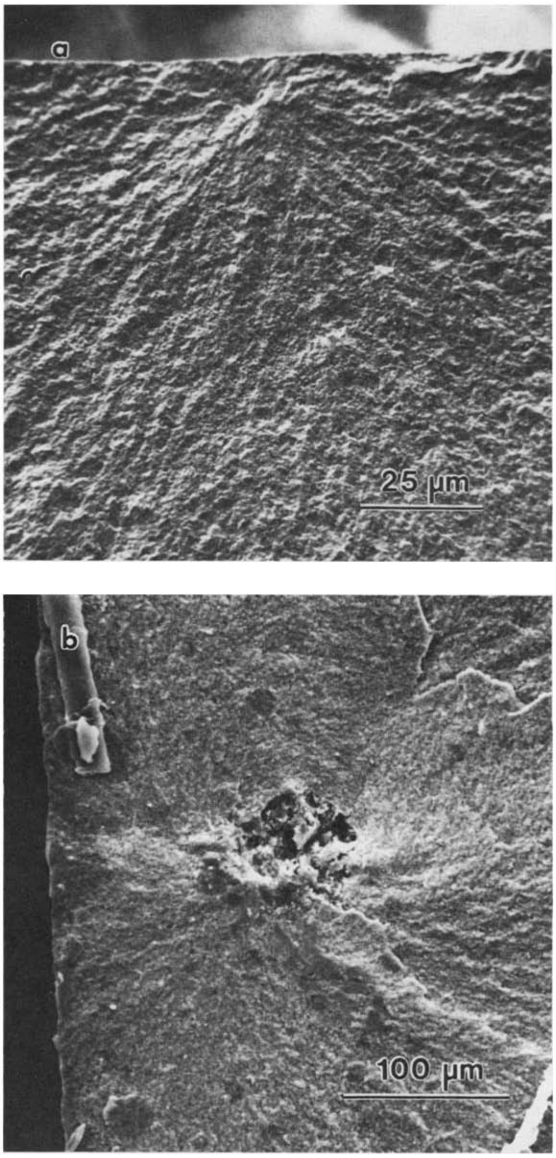


Fig. 9. Typical fracture origins of Y-TZP–SiC ceramics: (a) agglomerate and (b) SiC cluster (SEM).

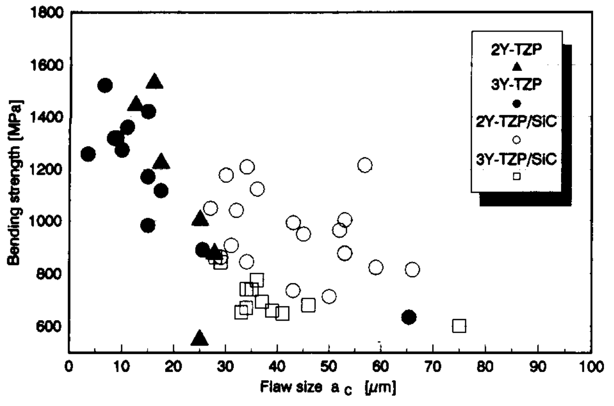


Fig. 10. Flaw size a_c of Y-TZP and Y-TZP–SiC composites.

propagate away from the inclusions through the matrix and, occasionally, through the inclusions. The latter is possible, if the fracture toughness $K_{IC,i}$ of the inclusions is lower than $K_{IC,m}$ of the matrix.[18] The stress concentration at the boundaries between SiC particles and the matrix increases with increasing grain size of SiC. Therefore, especially the larger silicon carbide particles tend to fracture transgranularly.

The fracture origins in the bending test specimens were mainly surface flaws which indicates a high flaw density. These flaws were mostly agglomerates, which consisted of ZrO_2 and SiC particles, and SiC clusters which consisted only of SiC particles. Two typical fracture origins are demonstrated in Fig. 9. The SiC cluster was almost not sintered and led to pore formation. In Fig. 10 the flaw size (a_c) of pure Y-TZP and Y-TZP containing SiC is shown. The a_c observed in the Y-TZP–SiC composites were much larger than in pure Y-TZP. These observations support the conclusion of Mecartney[14] that liquid boundary phases benefit the development of agglomerate induced defects during sintering. It is also possible that these agglomerates are substantially caused by the second phase due to the inhomogeneous distribution. Therefore, the reduction of strength caused by SiC additions can be attributed to the high residual stresses, which cause partially spontaneous microcracking, and the amorphous layers at the grain boundaries which lead to increase of flaw size.

3.3 Thermal stability

Sato and Shimada[19] attributed the thermal degradation of TZP ceramics to the stress corrosion cracking of glass phases, which induces surface *t–m* transformation during low-temperature ageing. In contrast, Mecartney[14] observed that amorphous grain boundary phases in the microstructure of Y-TZP improved the resistance to thermal degradation. Hence, the effect of amorphous grain boundary phases on the surface *t–m* transformation during ageing at low temperatures is not yet clear. The thermal stability of Y-TZP should be improved by SiC incorporations by increasing the strain free energy change due to the high Young's modulus.[2]

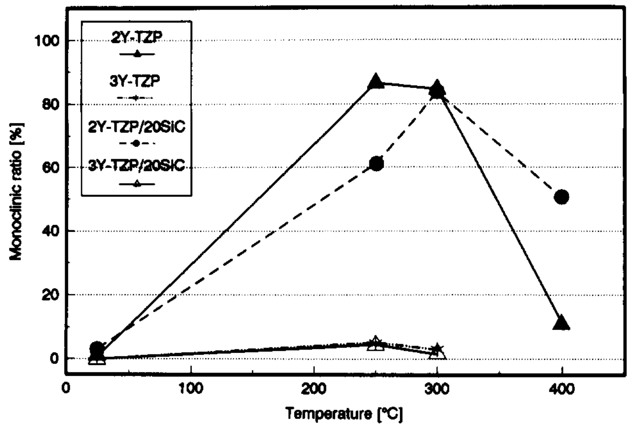


Fig. 11. Phase transformation on the polished surface of Y-TZP and Y-TZP–20SiC composite after ageing in air for 200 h.

The fraction of monoclinic ZrO_2 on the surface of Y-TZP and Y-TZP–SiC composites after a 200 h ageing in air is shown in Fig. 11, as a function of the ageing temperature. 3Y-TZP materials showed almost no transformation after ageing at temperatures of 250–400°C, i.e. SiC additions did not influence the stability of the ZrO_2 matrix containing 3 mol% Y_2O_3. Similar results were reported by Masaki.[20] In comparison to that, 2Y-TZP ceramics experienced an extensive phase transformation. Over 80% of *t* zirconia transformed into *m* after ageing at 300°C. The incorporation of SiC shifted the peak value somewhat towards higher ageing temperatures, but did not influence the absolute value.

The transformation profiles of 2Y-TZP and 2Y-TZP containing 20 vol% SiC after ageing at 300°C for 200 h are shown in Fig. 12. As visible from the figure, the addition of SiC resulted in a fast propagation rate of the transformation front. The transformed layer extended into the inward parts of the specimen containing SiC. It is believed that this result reflects the influence of residual stresses and microcracking on the transformation during ageing

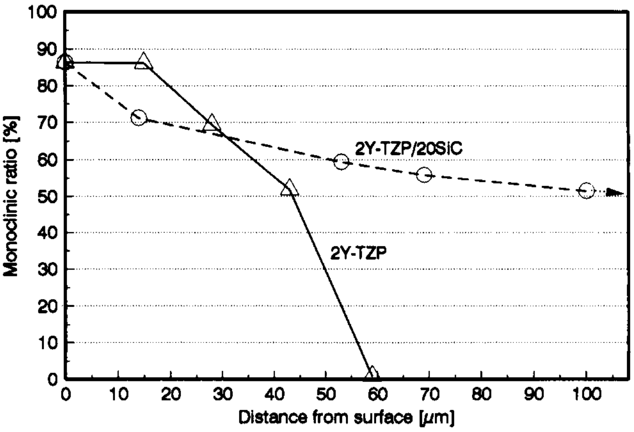


Fig. 12. Transformation profiles of 2Y-TZP and 2Y-TZP–20SiC composite after ageing at 300°C in air for 200 h.

treatment. The tensile stresses in the matrix favour phase transformation and microcracking. The transport of humid medium from the surface to the crack tip becomes easier. This enhances stress corrosion as a potential mechanism of the observed low-temperature degradation. According to the arguments of Mecartney,[14] the glassy grain boundary phases are believed not to be substantial for the surface *t*–*m* transformation of ZrO_2 during low-temperature ageing. This can be concluded from the high stability of the 3Y-TZP–SiC composites, which contain these grain boundary phases, but showed no transformation during low-temperature ageing. It can be concluded from literature results[20] that the extensive surface *t*–*m* transformation during ageing at low temperatures causes also substantial strength degradation.

4 Conclusions

Although 'wrong' thermal expansion mismatch in these materials hinders toughening by crack deflecting, and physical stabilisation effect of *t*-ZrO_2 due to the higher elastic modulus of SiC reduces transformation toughening, the fracture toughness of Y-TZP was significantly increased by SiC particles. The dominant toughening mechanism, therefore, is microcracking.

The bending strength of Y-TZP was strongly reduced by SiC additions due to residual stresses and formation of amorphous phase boundary layers during sintering. It is expected, however, that the high temperature strength of Y-TZP will be enhanced by SiC due to activation of some modulus load transfer by softening the amorphous boundary phases and stabilising tetragonal symmetry of ZrO_2 at higher temperatures.

SiC additions decreased the stability of *t*-ZrO_2 during ageing at low temperatures. This means that the addition of secondary phases with high elastic modulus does not always depress the low-temperature degradation of Y-TZP. The stress corrosion cracking of glassy grain boundary phases is not decisive for the surface *t*–*m* transformation of TZP materials during low-temperature ageing. Many other factors, such as chemical stability and residual stresses, must be considered.

Acknowledgement

The authors thank Dr H. Frei for his contribution to TEM studies.

References

1. Tsukuma, K., Ueda, K. & Shimada, M., Strength and fracture toughness of isostatically hot-pressed composites of Al_2O_3 and Y_2O_3-partially-stabilized ZrO_2. *J. Am. Ceram. Soc.*, **68** (1985) C4–C5.
2. Sato, T., Fujishiro, H., Endo, T. & Shimada, M., Thermal stability and mechanical properties of yttria-doped tetragonal zirconia polycrystals with dispersed alumina and silicon carbide particles. *J. Mater. Sci.*, **22** (1987) 882–6.
3. Claussen, N., Strengthening strategies for ZrO_2-toughened ceramics at high temperatures.*Mater. Sci. Engng*, **71** (1985) 23–38.
4. Faber, K. T. & Evans, A. G., Crack deflection process - I. Theory. *Acta Metall.*, **31** (1983) 565–76.
5. Huang, X., Gau, J., Gui, L. & Li, B., SiC particulate reinforced Y-TZP composites. Paper presented at the 4th International Symposium on Ceramic Materials & Components for Engines, June 1991, Gothenberg, Sweden.
6. Ding, Zh., Oberacker, R., Frei, H. & Thümmler, F., Consolidation of SiC particulate reinforced Y-TZP by pressureless sintering and post HIPing. *J. Eur. Ceram. Soc.*, **10** (1992) 255–61.
7. Wurst, J. C. & Nelson, J. A., Lineal intercept technique for measuring grain size in twophase polycrystalline ceramics. *J. Am. Ceram. Soc.*, **55** (1972) 109.
8. Brugger, N., Zum Verhalten von Rissen in keramischen Werkstoffen unter statischer, langsam ansteigender und schwingender Belastung. PhD thesis, University of Karlsruhe, Germany, 1986.
9. Brown, W. F. & Strawley, J. E., *Plane Strain Crack Toughness Testing of High Strength Metallic Materials* (ASTM STP 410). ASTM, Philadelphia, PA, USA, 1966.
10. Wilson, W. K., Stress intensity factors for deep cracks in bending and compact tension specimens. *Engng Frac. Mech.*, **2** (1970) 168.
11. Garvie, R. C. & Nicholson, P. S., Phase analysis in zirconia systems. *J. Am. Ceram. Soc.*, **69** (1986) 638–40.
12. Claussen, N., Weisskopf, K.-L. & Rühle, M., Tetragonal zirconia polycrystals reinforced with SiC whiskers. *J. Am. Ceram. Soc.*, **69** (1986) 288–92.
13. Levin, E. M. & McMurdie, H. F., *Phase Diagrams for Ceramists*, Figs 2388 and 2586. American Ceramic Society Inc., Columbus, Ohio, 1975.
14. Mecartney, M. L., Influence of an amorphous second phase on the properties of yttria-stabilized tetragonal zirconia polycrystals (Y-TZP). *J. Am. Ceram. Soc.*, **70** (1987) 54–8.
15. Taya, M., Hayashi, S., Kobayashi, A. S. & Yoon, H. S., Toughening of a particulate reinforced ceramic–matrix composite by thermal residual stress. *J. Am. Ceram. Soc.*, **73** (1990) 1382–91.
16. *Ceramic Source '92* (Vol. 7, Annual Company Directory and Buyer's Guide). American Ceramic Society Inc., Westerville, Ohio, 1992.
17. McMurty, C. H., Boecker, W. D. G., Seshadri, S. G., Zangghi, J. S. & Garnier, J. E., Microstructure, and material properties of SiC particulate composites. *Am. Ceram. Soc. Bull.*, **66** (1987) 325–9.
18. Evans, A. G., The role of inclusions in the fracture of ceramic materials. *J. Mater. Sci.*, **9** (1974) 1145–52.
19. Sato, T. & Shimada, M., Transformation of yttria partially stabilized zirconia by low temperature annealing. *J. Am. Ceram. Soc.*, **68** (1985) 356–9.
20. Masaki, T., Mechanical properties of Y-PSZ after ageing at low temperature. *Int. J. High Technol. Ceram.*, **2** (1986) 86–98.