Journal of the European Ceramic Society **5** (1989) 193–200

Yttria- and Ceria-stabilized Tetragonal Zirconia Polycrystals (Y-TZP, Ce-TZP) Reinforced with Al_2O_3 Platelets

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(Received 7 June 1989; revised version received 15 August 1989; accepted 18 August 1989)

Abstract

Composites of yttria- and ceria-stabilized tetragonal zirconia polycrystals (Y-TZP, Ce-TZP) with up to 20 vol% alumina platelets were fabricated by hot isostatic pressing. The microstructure and mechanical properties of these materials were investigated. The fracture toughness of Y-TZP increased by addition of platelets, e.g. K_{Ic} *of 2Y-TZP from* $8{\cdot}2\ MPa\sqrt{m}$ *to* $9{\cdot}5\ MPa\sqrt{m}$ *with 5 vol%* Al_2O_3*-platelets. The fracture strength of this composite, however, decreased from 1430 MPa to 735 MPa. Such decrease in strength was generally observed in Y-TZP platelet composites investigated in this work. Platelet-reinforced Ce-TZP exhibited a slight increase in strength and a decrease in fracture toughness in comparison to the non-reinforced matrix.*

Verbundwerkstoffe aus yttrium- und cerstabilisiertem, tetragonalen, polykristallinem Zirkonoxid (Y-TZP, Ce-TZP), die bis zu 20 vol% Aluminiumoxid enthielten, wurden durch heißisostatisches Pressen hergestellt und die Mikrostruktur sowie die mechanischen Eigenschaften untersucht. Die Bruchzähigkeit von Y-TZP stieg bei der Zugabe von Platelets an, z.B. der K_{Ic} *für 2Y-TZP mit 5 vol%* Al_2O_3*-Platelets von* $8{\cdot}2\ MPa\sqrt{m}$ *auf* $9{\cdot}5\ MPa\sqrt{m}$*. Die Biegebruchfestigkeit von diesem Komposit nahm von 1430 MPa auf 735 MPa ab. In dieser Untersuchung wurde ein solcher Festigkeitsabfall generell bei den Y-TZP-Plateletverbundwerkstoffen festgestellt. Dagegen zeigt plateletverstärktes Ce-TZP im Vergleich zur nicht verstärkten Matrix einen leichten Anstieg der Festigkeit und einen Abfall der Bruchzähigkeit.*

On a fabriqué par pressage isostatique à chaud des composites de polycristaux de zircone tétragonale stabilisée à l'oxyde d'yttrium et à l'oxyde de cérium (Y-TZP, Ce-TZP) contenant jusqu'à 20% volumiques de plaquettes d'alumine. On a étudié la microstructure et les propriétés mécaniques de ces matériaux. La ténacité du Y-TZP augmente lorsqu'on ajoute des plaquettes; par exemple, le K_{Ic} *du 2Y-TZP passe de* $8{\cdot}2\ MPa\sqrt{m}$ *à* $9{\cdot}5\ MPa\sqrt{m}$ *avec 5% volumiques de plaquettes d'*Al_2O_3*. Cependant, la résistance à la fracture de ce composite diminue, passant de 1430 MPa à 735 MPa. Une décroissance semblable de la résistance a été observée dans le cas de tous les composites à plaquettes de Y-TZP étudiés. Le renforcement du Ce-TZP par plaquettes entraîne une résistance légèrement supérieure et une ténacité inférieure.*

1 Introduction

Tetragonal zirconia polycrystals (TZP) are among the strongest and toughest engineering ceramics available today.[1–4] The strength–toughness relationship of TZP materials is shown schematically in Fig. 1.[5,6] In the linear low toughness regime the

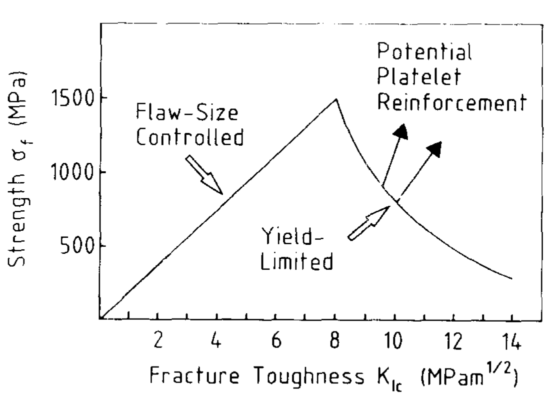

Fig. 1. Schematic diagram of strength–toughness relationship for tetragonal zirconia polycrystals.[6]

Journal of the European Ceramic Society 0955-2219/90/$3.50 © 1990 Elsevier Science Publishers Ltd, England. Printed in Great Britain

strength is limited by the critical flaw size (e.g. fine-grained Y-TZP). Beyond the maximum strength, the critical stress required to initiate the tetragonal (t) to monoclinic (m) transformation is assumed to control the strength in a 'yield'-like manner (e.g. Ce-TZP).[5]

Whisker reinforcement has been shown to improve the mechanical properties of ceramics.[7-14] Other reinforcing components, such as short fibers or platelets, could exhibit similar results. ZrO_2-toughened ceramics (ZTC) and, in particular, TZP ceramics are suitable matrix materials for this reinforcement strategy.[8] The potential toughening improvement of TZP by platelet addition is also indicated in Fig. 1.[6] In the flaw size controlled regime the fracture toughness would be increased by crack deflection,[15,16] pull-out,[17] crack bridging[18] and interaction with transformation toughening, resulting in an enhanced process zone size.[19] The strength, however, is expected to decrease due to particle clusters or large single particles acting as flaws. Reinforced high-toughness TZP, however, would exhibit an increase in strength since the effective stress at the crack tip would be lowered by modulus load transfer and thus a higher stress could be applied until the t–m transformation occurs.

Another advantage of particle reinforcement of TZP would be potentially improved high-temperature properties, because transformation toughening no longer operates above a critical temperature depending on stabilizer content and grain size ($\approx$700°C for Y-TZP and $\approx$200°C for 12 mol% CeO_2 (12Ce-TZP)). Hence, above these temperatures, toughening by whisker/fiber/platelet reinforcement would still be effective. Furthermore, the rather poor creep resistance of TZP is expected to be enhanced by addition of such reinforcing components, as already shown in SiC-whisker reinforced Al_2O_3.[20]

Mechanical property measurements of hot-pressed Y-TZP containing 3 mol% Y_2O_3 (3Y-TZP) reinforced with SiC whiskers have demonstrated a distinct increase in fracture toughness for the whisker-reinforced material, generally accompanied by a decrease in strength.[12,21] The system SiC–ZrO_2 is stable under reducing conditions during hot-pressing. After annealing in air, however, whisker oxidation and glass formation at the whisker/matrix interface was observed.[12] Furthermore, development of microcracks and cavities was found in the air-annealed composites, which was associated to stabilizer depletion followed by spontaneous t–m transformation[12,21] and oxidation of carbon which was taken up by grain boundary diffusion during hot-pressing.[12]

These results show that SiC/TZP composites are not suitable for high-temperature applications in an oxidizing environment. Thus, a better choice would be to use oxides, e.g. Al_2O_3, as the reinforcement material in TZP. The advantages of Al_2O_3 are its thermal stability and a lower thermal mismatch with the TZP matrix. Al_2O_3 whiskers are not readily available at present, and moreover, a health hazard is associated with inhaling whiskers due to their small diameter (<1 μm) needle-like geometry, which also renders their handling difficult. Thus, particles of uncritical geometries such as fibers or platelets are preferred reinforcing components. In the present work, Al_2O_3 platelets were chosen as reinforcing components in different TZP matrices.

2 Experimental Procedure

Various TZP powders (Tosoh, Tokyo, Japan) containing 2 (2Y-TZP) or 3 mol% (3Y-TZP) Y_2O_3 or 12Ce-TZP were attrition milled in isopropanol for 30 min, together with Al_2O_3 platelets (Showa Aluminum, Tokyo, Japan) using TZP milling balls (3 mm dia.). The platelets have 99·9% alumina content and their diameters are between 2 and 40 μm; their thickness is 1–2 μm (cf. Fig. 2). Powder mixtures with Al_2O_3-platelet volume fractions of 5, 10 and 20% were dried in a rotational vacuum drier and then cold isostatically pressed at 800 MPa to bars of 6 mm × 6 mm × 50 mm. Platelet-free ZrO_2 powders were pressed as-received without attrition milling. Platelet containing samples were presintered at 1500°C, and samples without platelets at 1350°C, for 30 min to obtain comparable relative densities. The final densification was carried out by hot isostatic pressing under various conditions. Y-TZP samples were HIPed conventionally with a

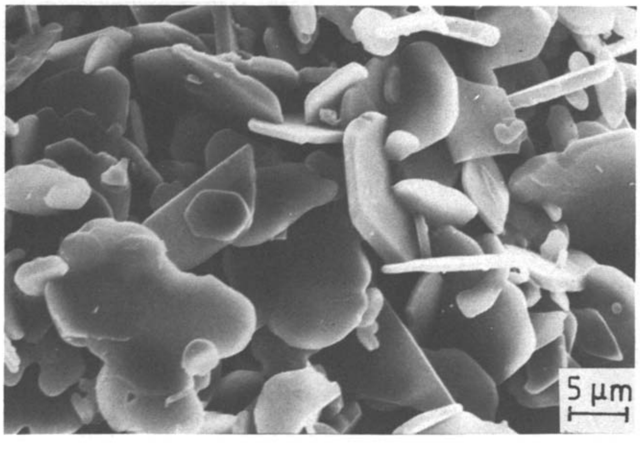

Fig. 2. SEM micrograph of as-received Al_2O_3 platelets. Platelet agglomerates were easily broken during mixing.

graphite heating element at 1400°C and 1600°C for 1 h at 200 MPa in Ar. To avoid C diffusion into the bulk, a Pt/Rh-heating element was also used. Recent investigations have shown that TZP materials exhibit higher strengths when HIPed in carbon-free pure Ar than in O_2-containing atmospheres.[22] Therefore, some samples were HIPed at 1400°C at 200 MPa in pure Ar with a Pt/Rh-heating element. Ce-TZP could not be HIPed under reducing conditions since CeO_2 was easily reduced to Ce_2O_3, destabilizing the t phase; hence extended spontaneous transformation lead to complete destruction of the samples.[23] Therefore, Ce-TZP materials were HIPed exclusively with the Pt/Rh-heater. In order to vary the grain size, dwelling times of 1, 2 and 4 h at 1400°C and 200 MPa were used.

Densities of pre-sintered and of HIPed samples were determined by the Archimedes method in water. Five rectangular bars (dimensions $4 \times 4 \times 40$ mm) of each sample were used to measure the chevron-notch fracture toughness in four-point bending (span 30/10 mm).[24] The specimen halves were then broken in four-point bending (span 18/6 mm) to determine the strength.

The phase composition of the bulk and fracture surfaces was determined by XRD.[25] Fracture surfaces and microstructures were analyzed by SEM.

Previous creep investigations were carried out in four-point bending at 1250°C and 35 MPa.[26]

3 Results

3.1 Densification

The relative densities after pre-sintering of pure 2Y- and 3Y-TZP were $\approx$97% TD. Y-TZP samples containing 5, 10 and 20 vol% of Al_2O_3 platelets had 98, 97 and 94% TD, respectively. The distribution of platelets was homogeneous in the 5 and 10 vol% composites (Fig. 3(a)). These composites and the matrices alone could be densified to >99% TD by HIPing (Figs 4 and 5). In the 20 vol% composites, platelet clusters were formed (Fig. 3(b)), preventing full densification. Therefore, relative densities after HIPing were generally <98% (Figs 4 and 5).

The density of the 12Ce-TZP matrix alone was 98% TD after pre-sintering, and those of the 5, 10 and 20 vol% composites were 97, 95 and 91% TD, respectively (Fig. 6). Again, samples with 20 vol% platelets could not be densified by HIPing. HIPed composites with 5 and 10 vol% Al_2O_3 platelets and the platelet-free material had relative densities >99% TD (Fig. 6).

3.2 Mechanical properties

The mechanical properties of 3Y-, 2Y- and 12Ce-TZP composites are shown in Figs 4, 5 and 6, respectively. In Y-TZP the addition of platelets results in a considerable decrease in strength to less than half of that of the matrix. The fracture

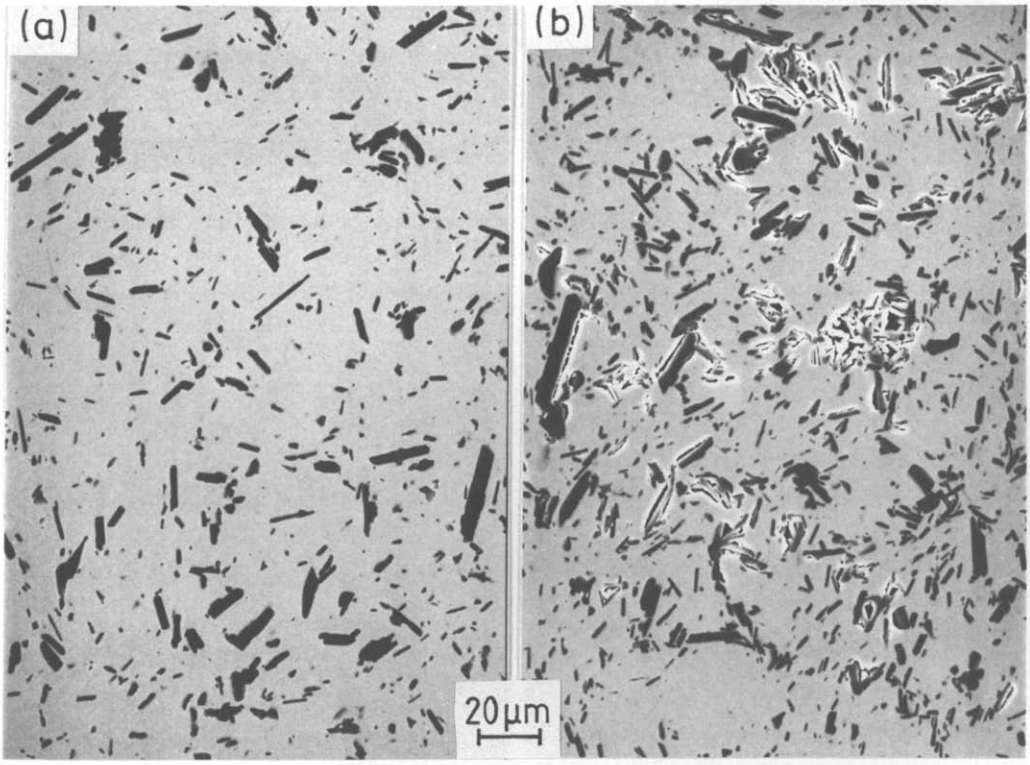

Fig. 3. 3Y-TZP/Al_2O_3 platelet composites pre-sintered at 1500°C for 30 min, and HIPed for 1 h at 1400°C and 200 MPa in Ar: (a) 10 vol% and (b) 20 vol% platelets.

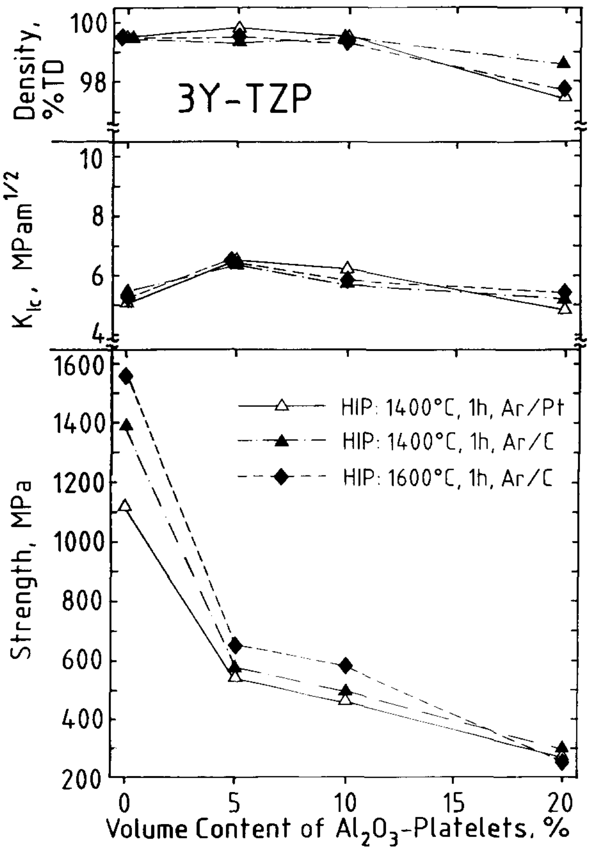

Fig. 4. Relative density, fracture toughness and fracture strength of 3Y-TZP/Al_2O_3 platelet composites HIPed under various conditions. Average standard deviations were about ±10% for both, toughness and strength measurements.

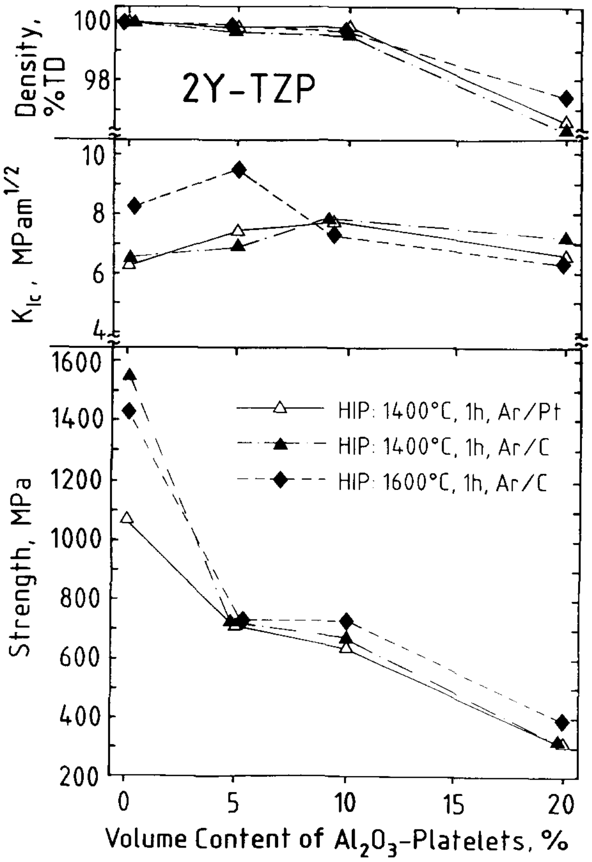

Fig. 5. Relative density, fracture toughness and fracture strength of 2Y-TZP/Al_2O_3 platelet composites HIPed under various conditions. Average standard deviations were about ±8% for toughness and ±10% for strength measurements, respectively.

toughness of 3Y-TZP increased with increasing platelet content, showing a maximum at 5 vol%. A similar behavior was observed in 2Y-TZP, except that the K_{Ic} maximum of the samples HIPed at 1400°C was slightly shifted to 10 vol% platelet content. Samples with 5 vol% Al_2O_3 platelets HIPed at 1600°C exhibited the highest K_{Ic} with 9·5 MPa$\sqrt{m}$.

The effect of platelet addition on the mechanical properties of 12Ce-TZP is quite different (Fig. 6). In this material, the strength increased slightly with increasing platelet content, while the fracture toughness decreased by the addition of 5 vol% of platelets and re-increased if the platelet content was 10 vol%.

Previous creep experiments with 12Ce-TZP showed a decrease in the steady state strain rate from $1{\cdot}5 \times 10^{-6}\,s^{-1}$ for the matrix alone to $2{\cdot}3 \times 10^{-7}\,s^{-1}$ for the composite with 10 vol% Al_2O_3 platelets.[26]

3.3 Microstructure

The average grain size of pure and platelet-reinforced TZP materials is shown in Fig. 7. Due to the lower pre-sintering temperature, the pure samples exhibit smaller grain sizes than the platelet-containing composites. An influence of the amount of platelet content on the grain size could not be observed. The size relationship between grains and platelets is demonstrated in Fig. 8.

The platelet size distribution in the composites seems to be comparable to the size distribution of the as-received platelets (Figs 2 and 3). Therefore attrition milling did not seriously reduce the platelet size.

In pure TZP and in Y-TZP/Al_2O_3 platelet composites no m phase was detected on polished surfaces. In platelets containing Ce-TZP, a 6–8% volume content of m phase was observed. The m-phase content of fracture surfaces is also shown in Fig. 7. The m-phase content on fracture surfaces of pure samples was higher than on that of platelet composites.

As demonstrated in Figs 9 and 10, crack deflection is a preferred toughening mechanism in platelet-reinforced TZP. Fracture was generally intercrystalline. Some large platelets broke after they had deflected the crack for some microns (Figs 9 and 11).

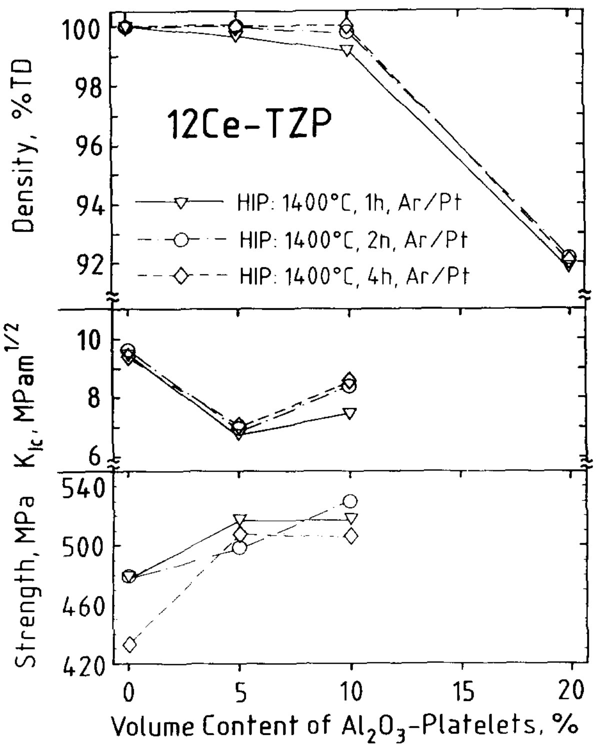

Fig. 6. Relative density, fracture toughness and fracture strength of 12Ce-TZP/Al_2O_3 platelet composites HIPed under various conditions. Average standard deviations were about ±4% for toughness and ±5% for strength measurements, respectively.

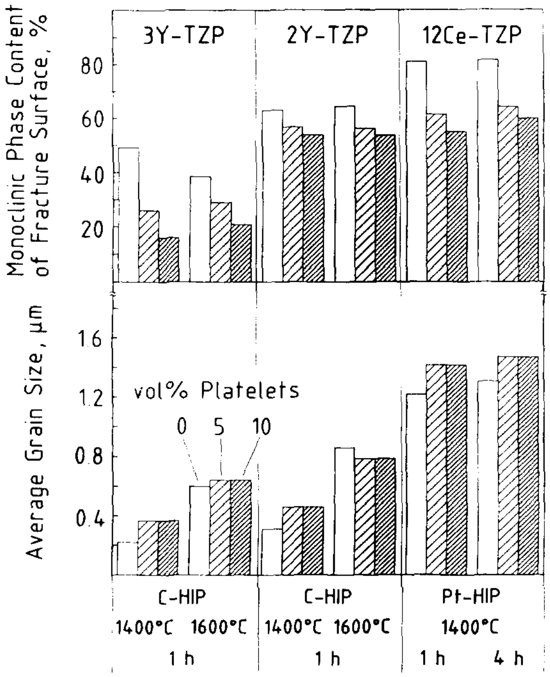

Fig. 7. Average grain sizes and monoclinic phase contents in fracture surfaces of TZP and platelet-reinforced TZP materials densified under various conditions.

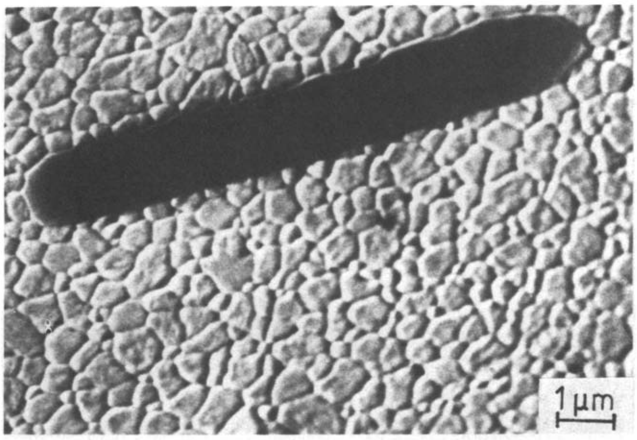

Fig. 8. Al_2O_3 platelet in 3Y-TZP matrix.

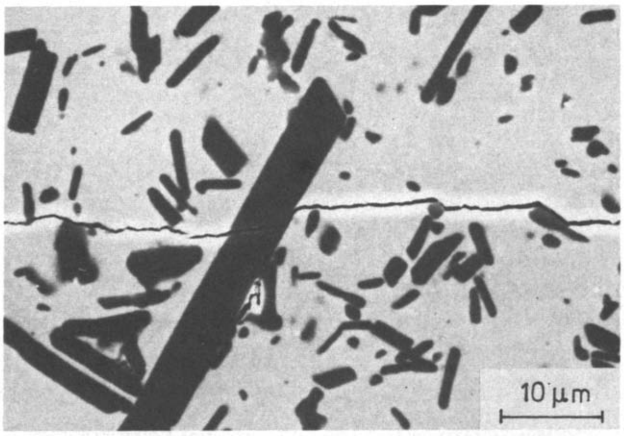

Fig. 9. Crack deflection and broken platelet in 3Y-TZP/Al_2O_3 platelet composite.

Fig. 10. Fracture surface of 2Y-TZP containing 10 vol% Al_2O_3 platelets.

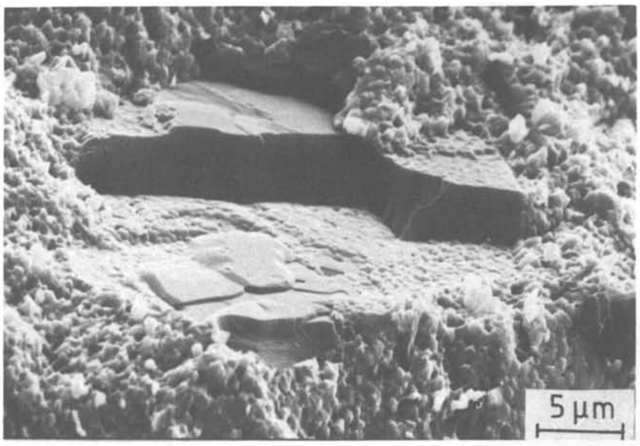

Fig. 11. Broken platelet in fracture surface of 2Y-TZP/Al_2O_3 platelet composite.

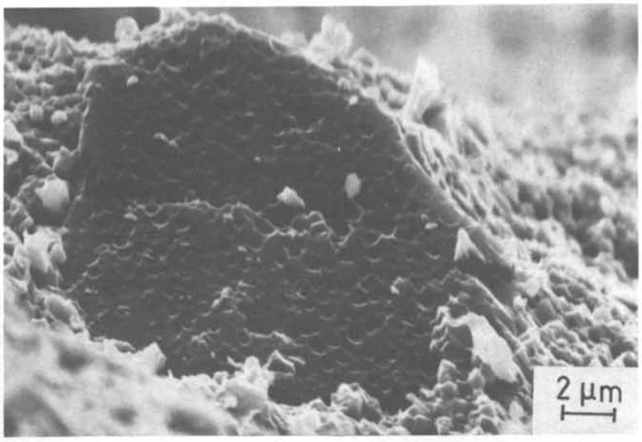

Fig. 12. Dimples on platelet surface in 2Y-TZP/Al_2O_3 platelet composite.

A relief structure was observed at platelet surfaces after cracking (Fig. 12) indicating that a liquid phase was formed at the platelet/matrix interfaces. No pull-out of platelets was observed.

4 Discussion

4.1 Y-TZP

In Y-TZP, addition of platelets acts to increase the flaw size and thus lower the strength. The thermal mismatch between Al_2O_3 ($\alpha = 8{\cdot}3 \times 10^{-6}\,K^{-1}$) and t-$ZrO_2$ ($\alpha = 10{\cdot}0 \times 10^{-6}\,K^{-1}$) causes tensile hoop stresses in the matrix and may further reduce the strength of the composites. No liquid phase is reported in the ZrO_2–Al_2O_3 phase diagram below 1710°C.[27] However, liquid phases may form due to Si and Mg impurities.[28] This is obviously the case at the platelet/matrix interfaces. The resulting dimples (cf. Fig. 11) may lead to a reduction of the inherent platelet strength.

The increase in fracture toughness of Y-TZP is due to two effects. One is crack deflection at platelets (Figs 10 and 11), while the other is modulus load transfer ($E_{Al_2O_3} \approx 410$ GPa, $E_{TZP} \approx 210$ GPa). Therefore the stress at the crack tip is transferred along the high-modulus platelets to regions further away from the crack plane. This yields a decrease in stress intensity at the crack tip and possibly an increase in process zone size, if additional grains transform to m symmetry.

Although the composites exhibit higher fracture toughnesses, the m-phase content is higher at fracture surfaces of the matrices alone (cf. Fig. 7), reflecting the higher fracture stresses of platelet-free materials. The 5 and 10 vol% composites show comparable strengths, but the decreasing fraction of transformed phase with increasing platelet addition indicated that the process zone size was reduced. It is assumed that the elastic load transfer by platelets lowers the effective shear stress at the crack tip, and thus less ZrO_2 transforms to m symmetry at the fracture surface. Hence, platelet reinforcement reduces the efficiency of transformation toughening. To compensate this toughness decreasing effect, the grain size of the composite should be increased such that t–m transformation is induced at reduced shear stress. The corresponding increase in process zone size would then improve the fracture toughness. The decrease in strength due to larger grains would be negligible due to the overriding effect of the platelets.

4.2 Ce-TZP

In Ce-TZP, platelet addition leads to a slight strength increase, but fracture toughness is decreased considerably in the 5 vol% platelet composites (Fig. 6). This is due to a reduction of the process zone size, as clearly demonstrated in Fig. 13. The typical zone height in 12Ce-TZP is 40 μm, and the length of the transformed zone ahead the crack tip can even be 200 μm.[29] Non-transformable particles have been reported to suppress the transformation by autocatalysis in 12Ce-TZP.[30] This is confirmed by the lower m-phase content at the fracture surfaces of Ce-TZP/platelet composites in comparison to the matrix alone (Fig. 7), although the fracture stresses are higher in the composites. The suppressed formation of enhanced shear bands increases the yield-stress σ_c^T and thus increases the fracture strength. A higher σ_c^T may also be caused by modulus load transfer. The re-increase in K_{Ic} in the 10 vol% composites may be due to crack deflection overruling reduced transformation toughening. Further investigations are needed in order to clarify this issue.

The improved creep resistance is assumed to be

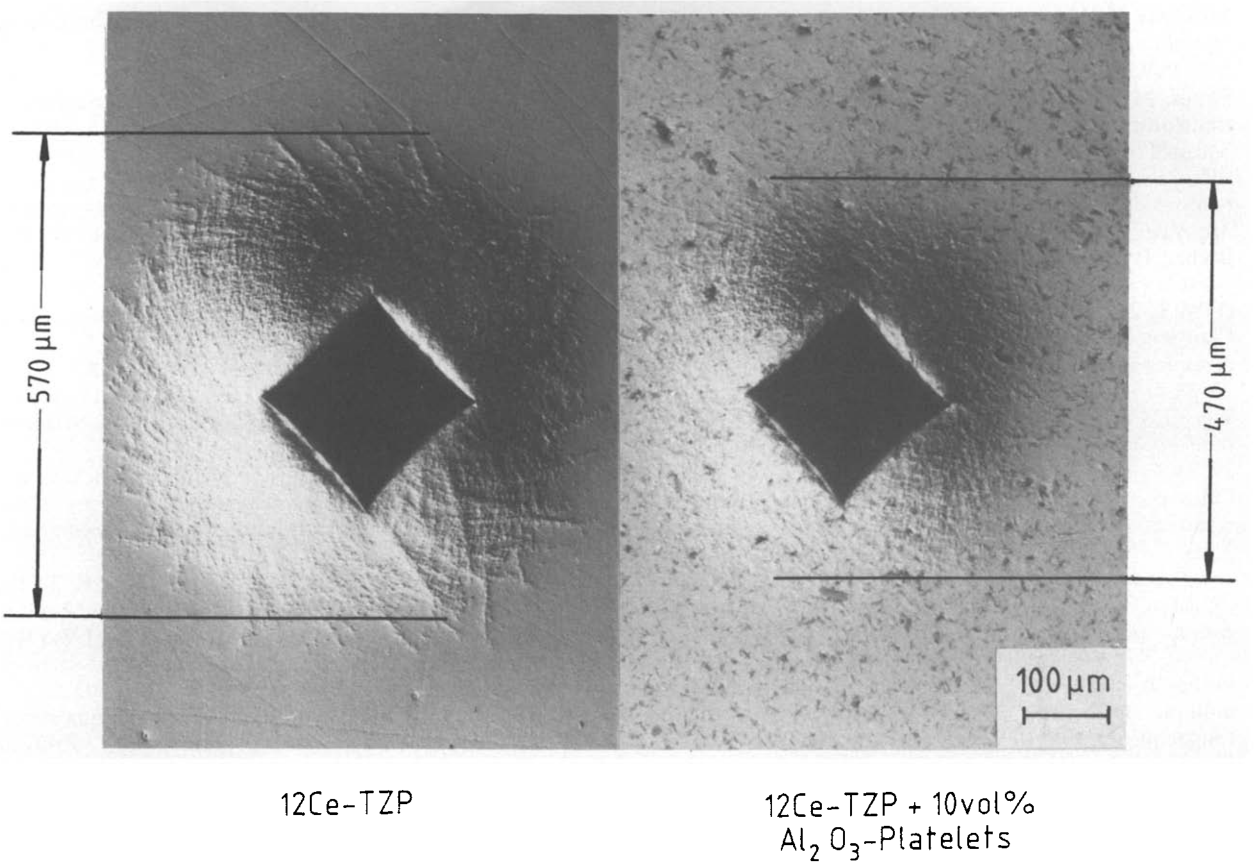

Fig. 13. Suppressed formation of shear bands around a Vickers indent (load = 294 N) in 12Ce-TZP/10 vol% Al_2O_3 platelet composite.

due to the large size of platelets when compared to the matrix grain size. The influence of the shape of coarse particles on the creep behavior has still to be investigated.

5 Conclusions

(1) High-strength Y-TZP and high-toughness Ce-TZP reinforced with up to 10 vol% Al_2O_3 platelets were fully densified (>99% TD) by pre-sintering and post-HIPing under various conditions. Composites with 20 vol% platelets would need encapsulation for full densification.

(2) The strength of Y-TZP is considerably reduced by platelet addition, e.g. from 1555 MPa to 645 MPa with 5 vol% platelets, which is due to the platelets acting in increasing the critical flaw size.

(3) The fracture toughness of Y-TZP is increased by Al_2O_3 platelet addition due to crack deflection and possibly to modulus load transfer. Reduction of stress intensity at the crack tip by elastic stress transfer along the platelets decreases the amount of t–m transformation at fracture surfaces and thus reduces the efficiency of transformation toughening.

(4) The strength of Ce-TZP is increased by Al_2O_3 platelets, which increase the yield stress of the matrix. The same effect, however, is responsible for a reduced fracture toughness.

(5) In both Y-TZP and Ce-TZP, grain sizes have to be increased to optimize the toughness.

(6) Platelet addition improves the creep resistance of TZP. The influence of platelet size and shape has to be investigated.

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