

THE SIGNIFICANCE OF MICROSTRUCTURE TO THE FRACTURE
TOUGHNESS OF PARTIALLY-STABILIZED ZIRCONIA

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ABSTRACT

The mechanical properties of zirconia partially-stabilized with calcia-, magnesia- and yttria (Ca-, Mg and Y-PSZ) have been studied. It was found that the critical stress intensity factor may be varied from 2.5 to 8.5 MNm^{-3/2} by subtle changes in heat treatment and stabilizer content. The maximum toughness was observed in Mg-PSZ. Transmission electron microscopy (TEM) revealed that in all PSZ systems a fine tetragonal precipitate phase was developed, the morphology of which varied with the stabilizer. TEM of the interaction of a crack with these precipitates indicated two main mechanisms responsible for improving the fracture toughness. These were, the volumetric expansion associated with the transformation of the tetragonal phase to monoclinic in the vicinity of the crack tip, and the formation of a narrow microcracked zone ahead of the main crack front. Analysis of the results suggested that transformation of the precipitate phase was the primary mechanism, and this toughening process was maximised for Mg-PSZ.

KEYWORDS

Partially-stabilized zirconia; Fracture toughness; Transformation toughened; Microcracking.

INTRODUCTION

Partially stabilized zirconia materials are a new class of strong-tough ceramics (Garvie et al., 1975; Sturhahn et al., 1975; Porter and Heuer, 1977). The improved toughness of these materials results from a distribution of tetragonal and/or monoclinic precipitates in a cubic matrix. The tetragonal phase, whose morphology depends upon the stabilizing anion (Hannink, 1978) precipitates upon cooling from the high temperature cubic phase. This tetragonal phase, which may be coarsened by subsequent heat treatment (ageing), is responsible for the improved mechanical properties due to its controlled transformation about the crack tip to the room temperature stable monoclinic form. The transformation is accompanied by volumetric dilation and shear strains, the former is considered to be primarily responsible for the enhanced fracture toughness.

At the last International Fracture Conference, Evans et al. (1977) outlined a number of mechanisms by which the toughness of brittle ceramics may be improved.

These included the following processes at the crack tip; microcracking, pullout of elongated fibres or grains, crack bowing due to interaction with a dispersed phase, and the development of a compressive zone by controlled transformation of a metastable volumetric expanding phase in the tensile field at the crack tip. Under certain conditions of stabilizer and heat treatment different combinations of the toughening mechanisms are thought to be operative in PSZ materials. In the present work discussion of the strengthening/toughening mechanisms will be limited to PSZ materials developed following pressureless sintering, solution heat treatment, and subsequent ageing.

EXPERIMENTAL

All materials were fired in the single phase region of the phase diagram, Fig.1, and cooled in a controlled manner. A detailed description of fabrication, firing and cooling procedures has been given elsewhere (Garvie et al., 1978).

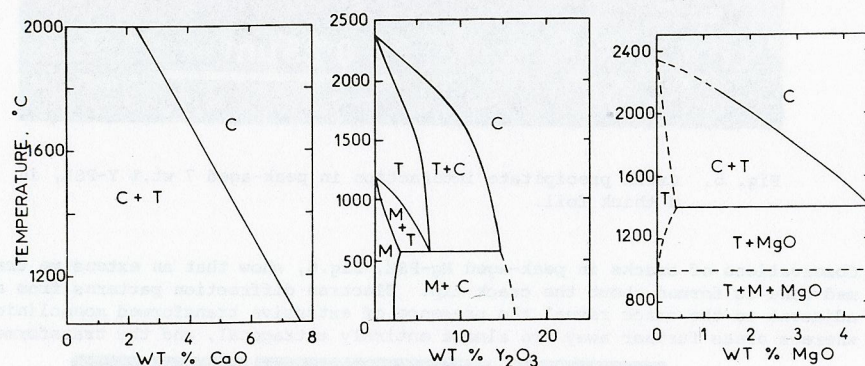


Fig. 1. Phase diagrams of the zirconia rich region of the a) Ca-PSZ, (Stringer, 1978) b) Y-PSZ (Scott, 1975), and c) Mg-PSZ (Grain, 1967).

Details of the measurements of the modulus of rupture (M.O.R.) have been described by Garvie et al. (1978). The stress intensity factor, K_{1C} , was measured using the single edged notched beam (SENB) technique, loaded in three point bending on specimens usually 5x5mm in section on a 40mm span. In all cases the cross head speed of the testing machine was $0.05\text{mm}\cdot\text{min}^{-1}$ and the notch depths were approximately equal to or greater than half the section. This procedure together with either annealing or severely etching the notched beam to relieve any compressive strains about the notch tip due to machining, resulted in stable crack propagation during loading. Under these conditions the measured values may be considered to underestimate K_{1C} .

Ageing temperatures were in the cubic-tetragonal region of the phase diagram, see Fig.1. Cracks were introduced into materials by indenting polished strain-relieved surfaces with a Vickers pyramid (3N load) prior to production of thin foils by Ar-ion.

OBSERVATIONS AND DISCUSSION

The size of the as-fired precipitates for the different materials was found to be

critically dependent upon the cooling rates of the furnace after solution heat treatment. Typical observations of the precipitate microstructure of the three PSZ materials, isothermally aged for optimum mechanical properties (peak-aged) are shown in Fig.2.

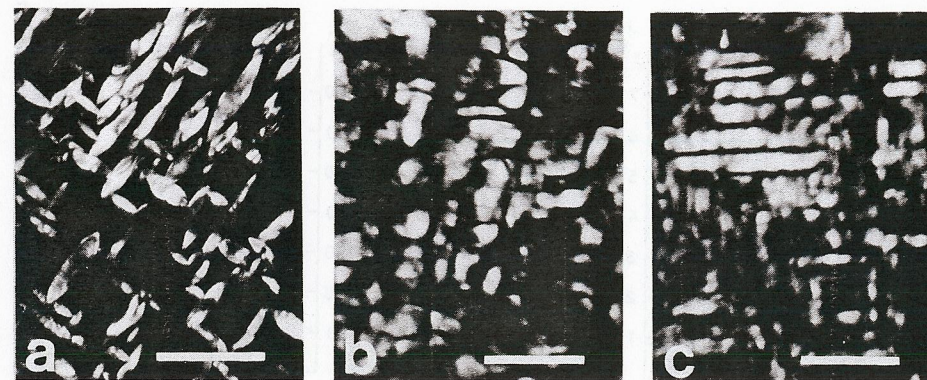


Fig. 2. Transmission electron micrographs of peak-aged a) 3.3 wt.% Mg-PSZ b) 3.8 wt.% Ca-PSZ, and c) 7 wt.% Y-PSZ. Dark field images. Bar length = $0.25\mu\text{m}$.

The morphology of the tetragonal precipitates in both the Ca-, and Y-PSZ materials were generally cubes or as irregular equi-axed forms. The Y-PSZ precipitates were generally observed to agglomerate into large rectangular plates. The tetragonal precipitates in Mg-PSZ were highly ellipsoidal (Porter and Heuer, 1977; Hannink, 1978) with an aspect ratio at peak strength of $\sim 1:2.5:10$. When the tetragonal precipitates exceed a critical size, which can be related to a misfit parameter determined from lattice parameter values, coherency is lost and they transform to monoclinic. The critical size of the precipitates was found to be (Hannink, 1978) $\sim 90\text{nm}$ for Ca-PSZ, $>100\text{nm}$ for Y-PSZ, and $\sim 50\text{nm}$ for the tetragonal c-axis direction of the precipitates in Mg-PSZ. Optimum mechanical properties were obtained for materials with precipitates just less than the critical size. A characteristic feature of the precipitates in Ca- and Y-PSZ was the regular alignment of the precipitate array. Precipitates are thought to grow by an Ostwald ripening process.

Strength and K_{1C} values of as-fired materials were usually found to improve upon subsequent heat treatment. It has been found (Garvie et al. 1978) that improvement in the mechanical properties only takes place if the ageing treatment temperature is sufficiently below the single phase boundary. The time taken to reach peak strength for the various materials was found to be a sensitive function of stabilizer composition and ageing temperature. The ageing kinetics of Y-PSZ materials were generally the most sluggish.

The influence of composition on the M.O.R. and K_{1C} of peak-aged Ca-, Y-, and Mg-PSZ is shown in Fig.3. The curve through the Mg-PSZ results is from Dworak et al. (1977). More extensive results at lower yttria content were difficult to obtain because of the high temperatures necessary for solution heat treatment in the cubic phase field (Pascoe and Urbani, unpublished results), see Fig.1.

The present observations indicate that the maximum toughness occurs in Mg-PSZ showing a three fold increase in K_{1C} over that of completely stabilized material (5 wt.% Mg-PSZ). Consistent with the observations of Dworak et al. (1977) for

Mg-PSZ, the peak values in strength and toughness occur when the percentage of the metastable tetragonal phase is $\sim 50\%$.

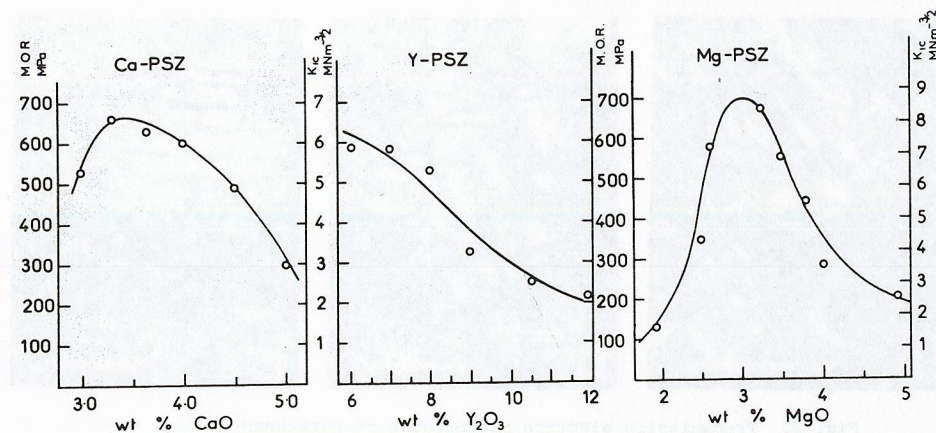


Fig. 3. Variation of M.O.R. and K_{1C} with stabilizer content of Ca-, Y-, and Mg-PSZ.

Observations of a crack interacting with precipitates in Ca-PSZ are shown in Fig.4. For as-fired material with very small precipitates few of which were transformed by the crack tip stress field, the crack path was only slightly perturbed by the precipitates and there was no evidence of microcracking. However in a peak-aged material, Fig.4, there is a substantial zone about the crack within which the tetragonal precipitates are transformed to monoclinic and usually twinned. In general the through going crack preferred cube planes and directions. The other significant feature is the presence of a narrow microcracked zone just ahead of the main crack. These microcracks appear to form in the matrix between the precipitates. Other observations of highly overaged material revealed the presence of microcracks between the very large transformed precipitates without requiring a through going crack to initiate them.



Fig. 4. Crack precipitate interaction in peak-aged 3.8 wt.% Ca-PSZ.

Somewhat similar observations of a transformed zone and extensive microcracking were made in Y-PSZ, Fig.5. In this material the width of the transformed zone is much less than for Ca-, and Mg-PSZ.

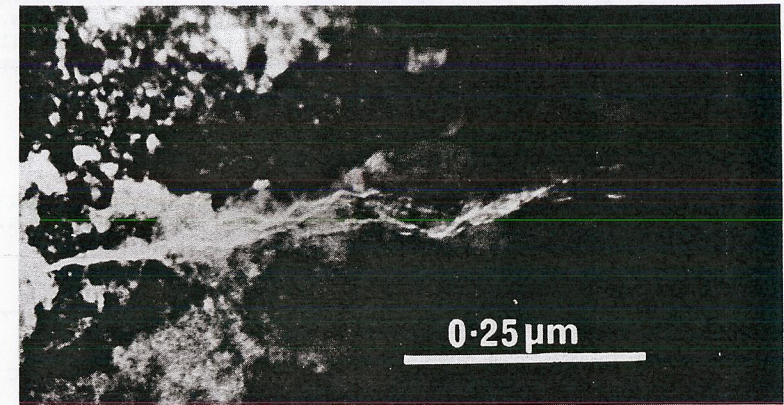


Fig. 5. Crack precipitate interaction in peak-aged 7 wt.% Y-PSZ, in a thick foil.

Observations of cracks in peak-aged Mg-PSZ, Fig.6, show that an extensive transformed zone is formed about the crack tip. Electron diffraction patterns from areas adjacent to the crack reveal the presence of extensive transformed monoclinic, whereas areas further away are almost entirely tetragonal, and the transformed

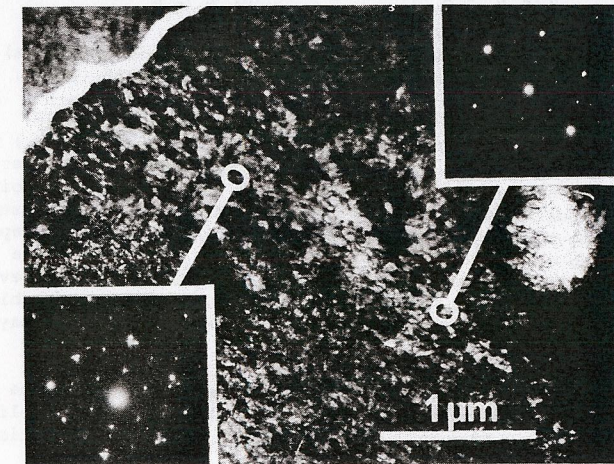


Fig. 6. Crack precipitate interaction in peak-aged 3.3 wt.% Mg-PSZ. The electron diffraction patterns indicate the presence of monoclinic adjacent to the crack plane. Electron diffraction patterns corrected for notation.

zone extends $\sim 2\mu\text{m}$ from the crack plane. More detailed observations, Fig. 7a,b, reveal the presence of twinned monoclinic precipitates, an extensive microcracked zone ahead of the crack, and the highly tortuous crack path with associated crack branching. The crack appears to favour propagation along the matrix-precipitate interface rather than cutting a precipitate. Observations of both a transformed zone and crack propagation at the precipitate-matrix interface have also been observed by Porter and Heuer (1977) in 3.1 wt.% Mg-PSZ.

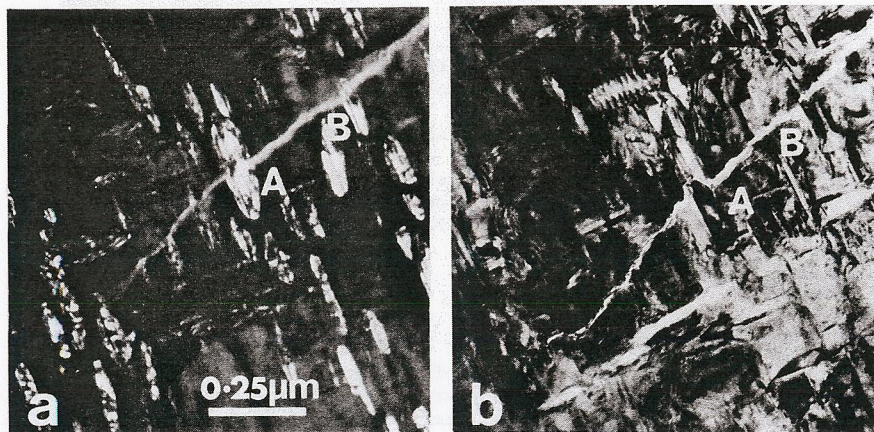


Fig. 7. Dark a) and bright b) field images of the same crack-tip region in peak-aged 3.3 wt.% Mg-PSZ.

Observations of the crack-tip precipitate interaction for peak-aged materials suggest there are at least three energy absorbing mechanisms present. The main mechanism appears to be the formation of a transformed zone about the crack tip. Additional mechanisms are the formation of the narrow microcracked zone directly ahead of the crack tip, and, particularly in the case of Mg-PSZ, the bridging of the crack by large ellipsoidal precipitates and the consequent crack path tortuosity induced by these precipitates. For underaged materials the crack-precipitate interaction will be reduced, it becoming a function of the metastability and strain associated with the precipitate.

Previous discussions and analysis of the mechanisms responsible for the improved toughness of PSZ materials have concentrated on the role of the phase transformation about the crack tip (Porter et al. 1979; Lange, 1979). Discussions of the toughening mechanisms of unstabilized mechanically dispersed zirconia in hot pressed alumina have advocated a microcracked process zone about the crack tip (Pabst et al., 1978, Pompe et al., 1978). The analysis of Pompe et al. (1978) considers the microcracked zone about the crack to consist of two regions, a dissipative zone of non-interacting microcracks with a narrow coalescence or process zone. They concluded the ratio of the size of the latter zone to the length of the microcracks and the density of microcracks that determines the increased toughness of the material.

Evans et al. (1977) considered the effect of the transformed zone in terms of a localised compressive zone at the crack tip. While Lange (1979) has considered the increase in toughness as a result of the energy absorbed from the crack tip stress field by transformation of tetragonal precipitates. The magnitude of the predicted toughness improvement due to both approaches is somewhat similar. Following Lange

(1979) we have

$$K_{1c} = \left[K_m^2 + \frac{2k \left(\frac{\Delta V}{V}\right)^2 E_c f_t R}{3(1-\nu^2)} \right]^{1/2} \quad (1)$$

where K_m is the matrix K_{1c} value, f_t the volume fraction of transformed precipitates, E_c is the modulus of the matrix, $k = \frac{2E_1E_2}{[(1-\nu_1)E_1+2E_2(1-\nu_2)]}$, R the radius of the transformed zone, and $\frac{\Delta V}{V}$ the volumetric expansion associated with the transformation. The value of $\frac{\Delta V}{V}$ for each PSZ material was derived from accurate lattice parameter measurements using a Guinier camera of the cubic matrix and the constrained monoclinic precipitates. It was found to differ for each material and to be least for Y-PSZ with $\frac{\Delta V}{V} = 0.026$; for Ca-PSZ $\frac{\Delta V}{V} = 0.038$ and for Mg-PSZ $\frac{\Delta V}{V} = 0.057$. Substituting these $\frac{\Delta V}{V}$ values in equation 1, together with $K_m = 2.5 \text{ MNm}^{-3/2}$, $f_t = 0.3$, $R = 2\mu\text{m}$, $E_1 = E_2 = E_c = 200 \text{ GPa}$ and $\nu_1 = \nu_2 = \nu = 0.25$, we get K_{1c} equal to $4.1 \text{ MNm}^{-3/2}$ for Y-PSZ, $5.3 \text{ MNm}^{-3/2}$ for Ca-PSZ and $7.4 \text{ MNm}^{-3/2}$ for Mg-PSZ.

These values are still slightly less than observed. In addition to K_{1c} , the influence of the transformed zone on the microcracked material will increase the fracture toughness through a surface area effect. An estimate of the energy absorbed in the microcracked zone may be had by assuming that associated with each precipitate is a microcrack of length equal to the mean free path between precipitates. The increase in toughness is then associated with the increased surface energy of the matrix, that is

$$G_m = 2\gamma_m \cdot g = \frac{K_m^2}{E} \cdot g \quad (2)$$

where γ_m is the matrix surface energy and g is the increase in surface area, and is given by

$$g = 1 + N \cdot a \cdot \lambda,$$

where N is the number of precipitates per unit area of mean dimension d , a is the width of the microcracked zone and λ is the mean free path, and equals $\frac{2d(1-f_t)}{3f_t}$, thus on simplification

$$g = \left[1 + \frac{2}{3} \frac{a}{d} (1 - f_t) \right].$$

Letting $a = 300\text{nm}$, $d = 75\text{nm}$ and $f_t = 0.3$ we have $g = 2.87$. Upon substituting for g in equation (2) and including in equation (1), the value of K_{1c} rises to $5.3 \text{ MNm}^{-3/2}$ for Y-PSZ, $6.4 \text{ MNm}^{-3/2}$ for Ca-PSZ and $8.1 \text{ MNm}^{-3/2}$ for Mg-PSZ. These

values are in reasonable agreement with measurements. However if the zone of microcracking were to become more extensive the localised modulus in the vicinity of the crack tip would be significantly decreased thereby reducing the energy absorbing capacity of the transformed zone. Finally, no attempt is made to quantify the increased K_{1c} of Mg-PSZ due to its highly ellipsoidal precipitates.

CONCLUSION

The interaction of a crack with precipitates in PSZ materials appears to be characterised by both a zone of transformed material and a narrower microcracked zone within this transformed zone. The microcracks appear to form between the precipitates with the through going crack propagating at the precipitate matrix interface. The predicted fracture toughness values were found to agree with the observed values provided the correct values of $\frac{\Delta V}{V}$ were used and some small allowance made for microcracking.

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