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Subcritical crack growth in partially stabilized $ZrO_2(MgO)$

PAUL F. BECHER
Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA

The room temperature slow crack growth resistance in air (~50% relative humidity) and in water for large cracks in MgO-partially stabilized zirconia (PSZ) improves with increase in critical fracture toughness, K_{Ic}. Ageing the as-fired PSZ at 1400° C for 8 h results in decreasing K_{Ic} from 8.5 MPa $m^{1/2}$ to 6 MPa $m^{1/2}$. The ageing treatment also promotes the growth of eutectoid decomposition products on grain boundaries that is accompanied by a decrease in the dependence of the change in Region I crack velocity with a change in the applied stress intensity. Calculated times to failures are markedly decreased in the aged as compared to the as-fired PSZ ceramic.

1. Introduction

Transformation-toughened partially stabilized zirconia (PSZ) ceramics can exhibit both high critical fracture toughness and strength values. Considerable effort has been undertaken to develop PSZ ceramics which utilize the transformation of tetragonal precipitates in a cubic matrix to gain improvements in fracture toughness. For example, Hannink and Swain [1] have illustrated the effects of heat treatment on precipitate stability and size and hence mechanical properties.

However, for most applications of ceramics, their subcritical (or slow) crack growth behaviour will determine the applied stress levels which can be employed. In this regard the data are quite limited; for example, Li and Pabst [2] examined the crack growth behaviour of two PSZ ceramics but concentrated on the behaviour of a PSZ which contained only 5 to 10% tetragonal precipitates in a coarse grained cubic matrix which yielded a fracture toughness of only $\leqslant 4.6$ MPa $m^{1/2}$ and a fracture strength of 280 MPa. The lower toughness (and strength) of this PSZ compared to that obtained by Hannink and Swain [1] in ZrO_2 with approximately 9 mol % MgO is seen to be primarily as a result of the much lower tetragonal content in the material studied by Li and Pabst [2]. Lenz and Heuer [3] examined the material studied by Li and Pabst and found that it contained approximately 7 mol % MgO plus approximately 4 mol % CaO which would account for the lower tetragonal content.

Li and Pabst [2] also suggested that in water, the Region II-like crack growth behaviour (i.e. crack velocity remains nearly constant with increase in applied stress intensity) in this PSZ was a result of transformation toughening and not actually the diffusion-limited Region II behaviour observed in other ceramics. Lenz and Heuer confirmed that the tetragonal to monoclinic transformation had occurred along the crack path in this same PSZ ceramic during the Region II-like crack growth, but that this did not occur at lower velocities [3]. Similar Region II-like behaviour (but at lower velocities, 10^{-7} m sec^{-1}) was observed in water but not in 65% r.h. air by the present author in Al_2O_3 containing 20 vol % ZrO_2 particles alloyed with 3 mol % Y_2O_3 (K_{Ic} = 4.5 MPa $m^{1/2}$) [4]. Thus, the environment which influences crack growth appears to also alter the phase transformation behaviour in transformation-toughened ceramics.

While the effects of heat treatment and microstructure on critical fracture toughness have been examined [1], little is known about their influence on slow crack growth behaviour with the exception of the work of Li and Pabst [2]. More importantly there have been no reported studies of the crack growth behaviour of PSZ ceramics which exhibit high initial fracture toughness values. The current study was thus initiated to examine these effects in PSZ ceramics.

2. Experimental procedure

Samples* of partially stabilized zirconia containing approximately 7.2 mol % MgO in both as-fired (e.g. as-sintered) and after ageing at 1400° C in air for 8 h were examined to determine phase content by use of standard X-ray, laser Raman, and scanning electron microscopy (SEM) techniques to characterize the microstructure. Precipitation morphology was delineated by etching polished surfaces in 10% HF at 22° C. These results plus the mechanical properties and transformation temperatures (obtained by thermal expansion hysteresis techniques) of these materials are included in Table I.

Applied moment double cantilever beam (DCB) specimens [5] were prepared by sawing and surface grinding with metal-bonded diamond wheels. One

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*Samples were kindly provided by Dr M. Swain, CSIRO, Melbourne Australia.

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TABLE I Characteristics of $ZrO_2 \cdot 7.2$ mol % MgO ceramics

	As-fired	Aged at 1400° C for 8 h
Density (g cm^{-3})	5.73	5.67
Average grain size (μm)	60	60
% monoclinic*	5–7	33–35
%monoclinic†	3–4	88–92
Transformation temperatures		
M_s (° C)‡	-165	$+250$
M_f (° C)‡	-195	$\leqslant +22$
Fracture strength (MPa) four point flexure	630–700	350
Critical fracture toughness (MPa m$^{1/2}$)	8.5 ± 0.5	6.0 ± 0.3

*X-ray data using copper target; based on monoclinic and cubic plus tetragonal peak intensities.

†Laser Raman data; based only on monoclinic and tetragonal peak intensities.

‡Transformation of tetragonal to monoclinic phase during cooling where M_s represents the temperature transformation initiation and M_f is the temperature of completion.

surface of each DCB sample was then mechanically polished; the final polishing step used a 0.5 μm diamond paste. This approach facilitated viewing the crack tip motion with a travelling optical telescope. Samples were prepacked prior to testing. Crack growth studies involved the use of laboratory air and distilled water environments at 22° C. Crack velocities were determined by several measurements of changes in crack length as a function of time for each applied stress intensity (K_{Ia}) level on at least two different specimens in each environment. Average crack velocities were then obtained for multiple runs at each K_{Ia} level. After completing these measurements, the fracture surfaces were characterized using scanning electron microscopy.

3. Results and discussion

Scanning electron microscopy observations of the polished surface of the DCB specimen after etching reveal the change in both intragranular and intergranular precipitates sizes as a result of ageing. The as-fired PSZ contains $\leqslant 0.2\,\mu$m $\times$ $0.05\,\mu$m intergranular precipitates (tetragonal phase) with some clusters of larger precipitates at some grain boundaries (Fig. 1). Some of the grain boundaries in the as-fired PSZ exhibit a discontinuous layer of second phase approximately 0.2 μm wide which is a result of the eutectoid decomposition which yields monoclinic ZrO_2 (at room temperature) and MgO. Note that the etchant dissolves the cubic matrix faster than the monoclinic and tetragonal precipitates (presumably due to the difference in composition) thus the boundary phases are either monoclinic or tetragonal. Based on X-ray studies at ORNL and TEM studies by Farmer and Heuer [6], these grain boundary regions are considered to consist primarily of the monoclinic ZrO_2 phase.

The aged PSZ exhibits considerably larger intergranular precipitates (~ 0.4 to $0.6\,\mu$m long $\times$ $\sim 0.1\,\mu$m thick) and extensive grain boundary phase (Fig. 1). The grain boundary phase is nearly continuous and has grown much thicker and consumed the adjacent intergranular precipitates. This observation is consistent with the much higher monoclinic content determined for the aged material, Table I.

The slow crack growth behaviour of the PSZ in the as-fired condition is sensitive to the environment (i.e. air, 55% r.h. compared to distilled water) as seen in Fig. 2a. Analysis of the Region I data in water ($A = 10^{-96.4}\,\mathrm{m\,sec^{-1}}\,(\mathrm{MPa\,m^{1/2}})^{-120}$) reveals a considerable decrease in the K_{Ia} required to achieve comparable crack velocities to those in air ($A = 10^{-107.6}\,\mathrm{m\,sec^{-1}}\,(\mathrm{MPa\,m^{1/2}})^{-121}$). However, in both cases, the slopes (n) of the V–K_{Ia} plots in Region I are approximately 120. These high n values indicate that the PSZ in the as-fired condition may not be susceptible to slow crack growth until K_{Ia} is raised to levels quite close to the critical fracture toughness of the material.

Note, however, that the slow crack growth parameters, n and A, in Region I (Fig. 2b) are substantially altered as a result of ageing the PSZ. The as-fired PSZ exhibits much higher n values (~ 120) and lower A values ($< 10^{-96}$) as compared to the aged PSZ (~ 45 and $> 10^{-37.5}$ respectively). The lower n value and

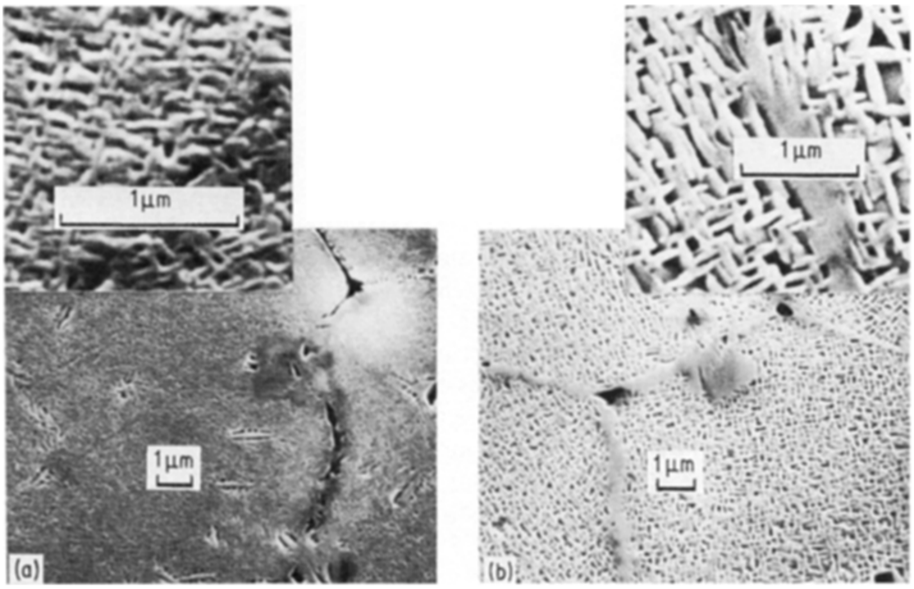

Figure 1 Precipitate growth and increase in grain boundary eutectiod decomposition products from ageing PSZ. (a) As-fired, (b) aged 1400° C, 8 h. ZrO_2 7.2 mol % MgO, grain size $G = 60\,\mu$m.

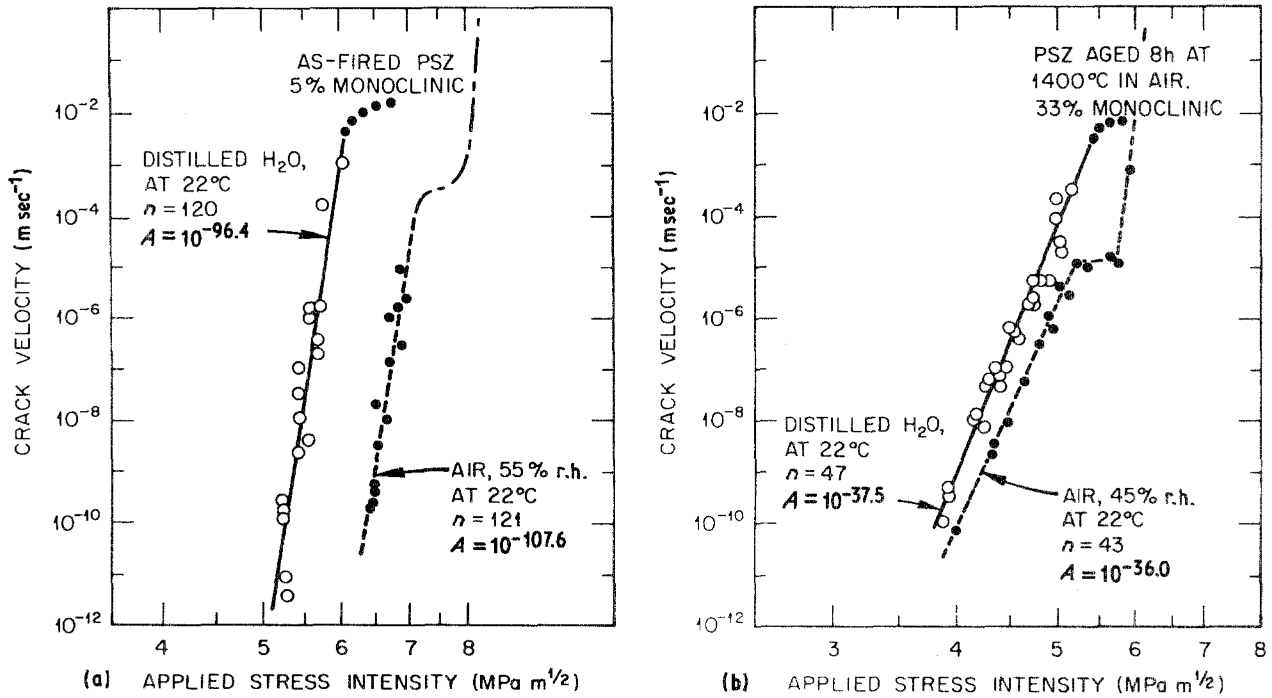

Figure 2 Slow crack growth behaviour is sensitive to environment: (a) as-fired PSZ; aged 8 h at 1400° C in air.

higher A value of the aged PSZ studied here also are comparable to the values obtained for a PSZ aged at 1500° C for 5 h by Li and Pabst [2].

After being aged at 1400° C for 8 h, the slow crack growth behaviour of the PSZ is substantially altered with Region I shifted to lower K_{Ia} values. The K_{Ia} required for a velocity of 1×10^{-8} m sec^{-1} in air decreases from 6.6 MPa m$^{1/2}$ for the as-fired PSZ to 4.4 MPa m$^{1/2}$ for the aged PSZ. On the other hand, at a K_{Ia} of 5.1 MPa m$^{1/2}$, the crack velocity in air increases from approximately 4×10^{-12} m sec^{-1} for the as-fired to approximately 6×10^{-6} m sec^{-1} for the aged PSZ.

Crack growth in either the as-fired or the aged PSZ in both air and water occurs predominately by transgranular fracture. However, the aged material exhibits somewhat greater amounts of intragranular fracture as compared to the as-fired PSZ (Fig. 3). In either material, high crack velocity ($\geqslant 5 \times 10^{-4}$ m sec^{-1}) at or near Region II is accompanied by only slightly less intergranular fracture as compared to cracks moving at lower velocities (10^{-10} to 10^{-5} m sec^{-1}) in Region I.

The decreases in n values with thermal ageing correspond with the increase in both monoclinic phase content and intergranular fracture. Previous crack growth studies of zirconia-toughened alumina indicte that the presence of significant monoclinic phase ZrO_2 also promotes the susceptibility to slow crack growth as reflected by decreased n values [7]. The autotransformation during and/or after ageing of the PSZ diminishes the volume content of tetragonal precipitates. This diminishes the toughness, because fewer tetragonal precipitates are available to transform along the zone of the propagating crack. In addition, the autotransformation to monoclinic ZrO_2 is accompanied by approximately 1% linear strain due to the volume expansion. This autotransformation also introduces tensile strains (tangential) and compressive strains (radial) in the matrix adjacent to the precipitate and the grain boundary monoclinic phase which would promote crack growth. In non-cubic ceramics, internal tensile stress can result in decreases in n and increases in A parameter values similar to those observed after ageing the PSZ.

The decreased resistance to slow crack growth of the aged PSZ compared to the as-fired PSZ, of course, results in a significant decrease in the time to failure under stress ageing. The decrease in time failure (t_f) with ageing was determined by

$$t_f = [2/AY^2\sigma_a(2-n)(K_{IC})^{n-2}]\,[1-(\sigma_{IC}/\sigma_a)^{n-2}] \quad (1)$$

where Y is a geometric factor, σ_a is the applied stress level, and σ_{IC} is the critical fracture strength. The decrease in the calculated failure times as a result of ageing are shown in Table II.

4. Conclusions

Slow crack growth at 22° C in partially stabilized zirconia is enhanced in water as compared to air ($\sim 50\%$ r.h.). Based on Region I data, at a K_{Ia} level of 6 Mm$^{1/2}$ the as-fired PSZ exhibits a crack velocity of approximately 4×10^{-14} m sec^{-1} in air compared with approximately 1×10^{-3} m sec^{-1} in water. The

TABLE II Time to failure of PSZ ceramics based on their slow crack growth parameters

	n	A m sec^{-1} (MPa m$^{1/2}$)$^{-n}$	K_{IC} (MPa m$^{1/2}$)	σ_{IC} (MPa)	σ_a (MPa)	t_f (sec)	
						As-fired	Aged
As-fired	121	$10^{-107.6}$	8.5	600	200	4×10^{47}	2×10^{8}
Aged	43	$10^{-36.0}$	6.0	350	300	2×10^{26}	6

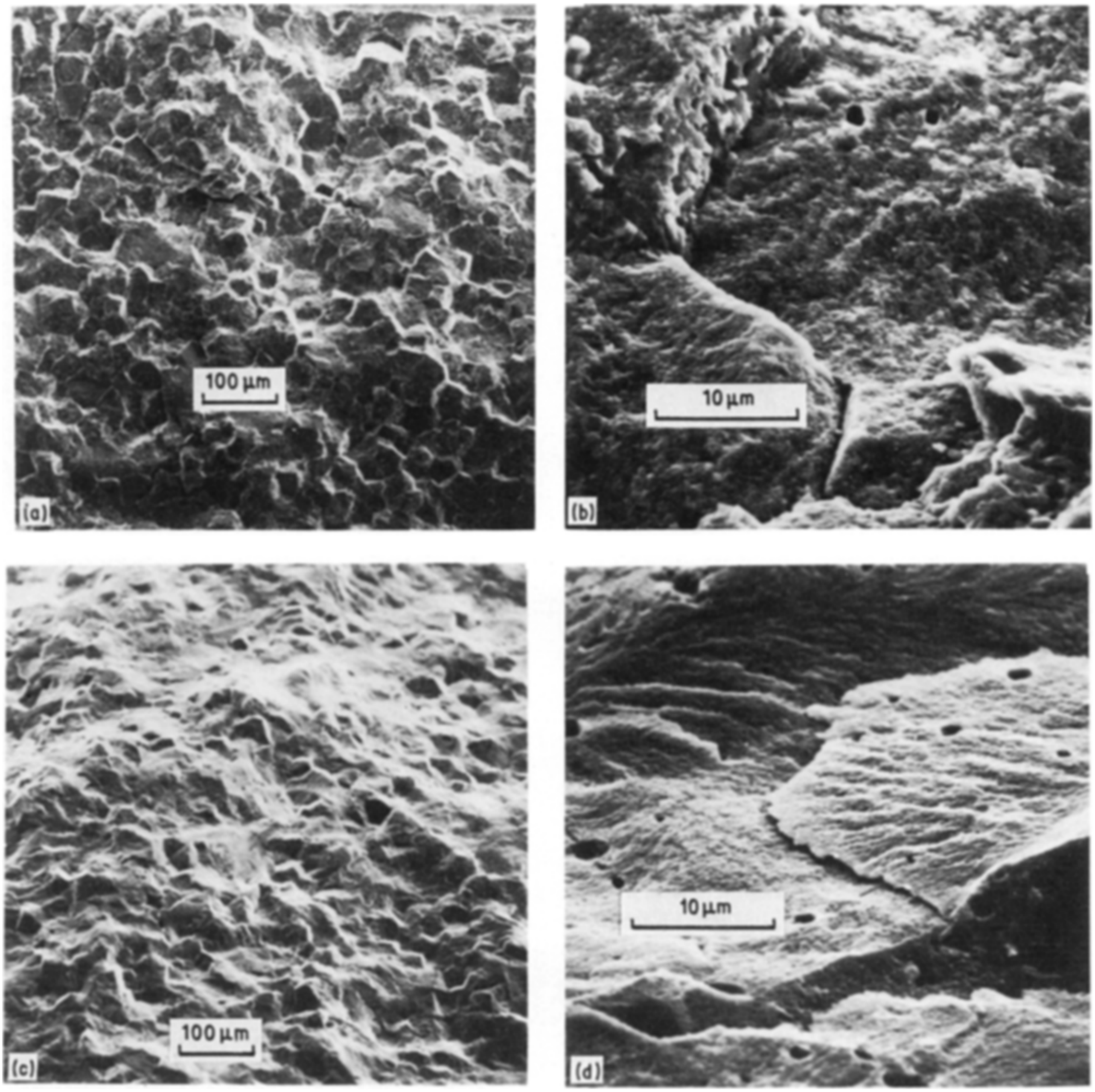

Figure 3 Greater proportion of transgranular fracture during crack growth in as-fired compared with aged PSZ. Proportion of transgranular to intergranular fracture remains constant for each material over velocity range (10^{-10} to $10^{-3}\,\mathrm{m\,sec^{-1}}$) tested and in both air and water environments. (a), (b) aged PSZ; (c), (d) as-fired PSZ.

aged PSZ exhibits a less pronounced effect of environment, with crack velocities in water only slightly enhanced as compared to those in air (e.g. at $K_{Ia} = 4.5\,\mathrm{MPa\,m^{1/2}}$ compared to approximately 2×10^{-7} and $1 \times 10^{-8}\,\mathrm{m\,sec^{-1}}$, respectively).

There is a significant decrease in slow crack growth resistance as a result of ageing the sintered PSZ at 1400° C for 8 h in air. Not only is the entire slow crack growth V–K_{Ia} curve shifted to lower K_{Ia} levels after ageing but the Region I slope, n, is decreased more than two-fold and the intercept, A is increased dramatically. These changes are associated with an increase in monoclinic phase content in the aged PSZ. Thus this ageing treatment not only diminishes the critical fracture toughness but will also decrease the time to failure under applied tensile stress ($\sigma_{Ia} < \sigma_{IC}$).

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