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A Raman microprobe study of a magnesia partially stabilized zirconia fracture surface

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Raman microprobe analysis has been used to determine the extent of phase transformation on the fracture surface of a magnesia partially stabilized zirconia test bar. This has been found to vary across the fracture face and is considered to be related to the amount of microcracking which occurs in the sample during fracture.

1. Introduction

Magnesia partially stabilized zirconia (Mg–PSZ) ceramics show good flexural strength ($\leqslant 800$ MPa), fracture toughnesses (≈ 9 MPa m^{-1}) and excellent wear resistance leading to their many potential engineering applications [1]. The ceramic microstructure is the result of a carefully controlled firing cycle and consists of large (50 to 80 μm) cubic grains containing optimally aged lenticular tetragonal precipitates which are about 300 nm in their longest dimension [2]. At the cubic grain boundaries there are smaller (1 μm) monoclinic zirconia grains and there is generally a wetting magnesium silicate phase present. The enhanced toughness values observed in this system are due in part to the transformation toughening mechanism in which the bulk expansion associated with a transforming wake of tetragonal zirconia precipitates adjacent to the crack tip to monoclinic symmetry inhibits crack growth [3]. Further toughening is encouraged by microcracking mechanisms [3]. These fracture processes combine to result in R curve behaviour for the ceramic in which the measured value of fracture toughness increases during the early stages of crack propagation [4]. The toughness increment due to transformation toughening is held to vary with the volume of material susceptible to transformation during crack propagation and hence it is important to prepare the sintered ceramic in such a way that this parameter is maximized.

In earlier studies of zirconia transformation, workers have estimated both the fraction of tetragonal phase transforming during fracture and the thickness of the transformation layer by a variety of techniques, including *in situ* straining experiments in the transmission electron microscope [5, 6] and X-ray diffraction studies [7]. Raman spectroscopy has also been used to estimate the zirconia phase contents of yttria stabilized zirconia and zirconia toughened alumina ceramics particularly around Vicker's indents, introduced to induce the tetragonal to monoclinic transformation locally in the sample surface [8, 9]. In the latter instance microspot Raman spectroscopy has enabled phase determinations to be made from areas as small as 1 μm diameter and hence it has been possible to produce maps of surface transformation on samples at this resolution [9].

In this contribution microspot Raman spectroscopy has been used to investigate the extent of phase transformation associated with the fracture of a standard Mg–PSZ test sample in three-point bending during a modulus of rupture determination.

2. Experimental considerations

The principles of Raman spectroscopy have been described extensively elsewhere and will not be considered further here [10]. In the microspot Raman configuration the laser beam (in this case from an argon laser tuned to 514.5 nm) is focused onto the sample, and the backscattered light collected from the sample using the objective lens of an optical microscope. The backscattered signal is processed in a double monochromator to produce a spectral plot of intensity against Raman shift. The use of a $\times 20$ objective lens and appropriate microscope conditions enabled a spot size of about 5 μm to be used for data collection. Due to broad fluorescence from the samples studied here in the Stokes region data were collected exclusively from the anti-Stokes side of the scattering spectrum. The Raman spectra from the Stokes and anti-Stokes regions are highly correlated with the peak shifts being symmetrically distributed about the zero line. Corresponding peak amplitudes are related by the expression

$$I_{as} = I_s \exp(-E_t/kT) \quad (1)$$

where I_s and I_{as} represent the intensities of corresponding peaks on the Stokes and the anti-Stokes sides of the spectra, respectively, E_t is the energy of the measured transition, k Boltzmann's constant and T the absolute temperature.

A typical trace collected from a sample showing monoclinic and tetragonal zirconia peaks is shown in Fig. 1. Clarke and Adar [8] have correlated the peak intensities of selected monoclinic and tetragonal Raman peaks and have deduced the calibration

$$C_m = \frac{I_m^{181} + I_m^{192}}{F(I_t^{148} + I_t^{264} + I_m^{181} + I_m^{192})} \quad (2)$$

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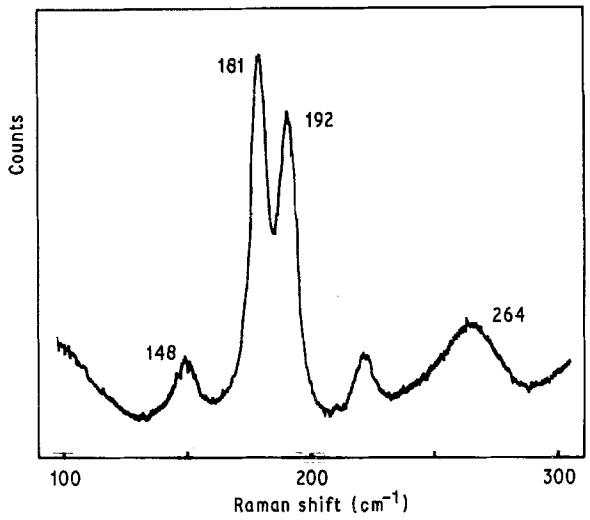

Figure 1 Part of the Raman spectrum taken from a zirconia sample showing the monoclinic 181 cm^{-1} and 192 cm^{-1} lines and the tetragonal 148 cm^{-1} and 264 cm^{-1} lines used in this study to determine the ratio of these phases.

where C_m represents the monoclinic concentration, F a constant (found to be 0.97), and I_p^x the intensity of the x line of the p phase. The peak intensities obtained in this work were converted to phase ratios using Equations 1 and 2.

2. Results and discussion

Carefully aged 9 mol % MgO Mg-PSZ bars* were fractured in three-point bending, yielding moduli of rupture of 620 ± 20 MPa and Raman traverses were carried out on the fracture planes parallel to the direction of crack propagation. Typical spectra obtained in this way are shown in Fig. 2. From these data the variation in the fraction of monoclinic phase across the fracture surface was calculated and plotted against distance along the traverse (Fig. 3). It can be seen that there is a steady decrease in monoclinic zirconia content measured from just below the tension face to within 200 μm of the compression face. Within 20 μm of the tension face there appears to be a small decrease in the monoclinic content on the fracture surface. Conversely, at the compression face there is a marked, significant increase in the transformed phase within 150 μm of the edge.

Scanning electron microscopy of polished cross-sections through fracture surfaces has shown that two types of microcracking are present. The first of these comprise cracks of the order of 1 μm and occur adjacent to the fracture plane up to a distance of 2 to 3 μm from the surface. Additionally there are large microcracks of dimensions greater than the average grain size. The density of large microcracks ($\geqslant 100\,\mu$m) occurring close to the fracture surface decreases in the direction of crack propagation (Fig. 4) and occur almost exclusively on the tension side of the fracture plane. Some coarse microcracking, on a $\geqslant 50\,\mu$m scale, particularly at grain boundaries is seen on the compression side but this is limited to small isolated areas, mainly occurring in a zone $< 5\,\mu$m from the fracture surface. On the tension face the coarse microcracking is seen to extend into the sample bulk for about 40 to 50 μm, which is significantly in excess of the calculated total depth resolution of the Raman analyses (about 8 to 10 μm [8]). This suggests that the information collected here is wholly from a coarsely microcracked zone, whereas in the compression side the majority of the observable microcracking occurs only to a depth of 2 to 3 μm. This indicates that some signal information may be coming from an uncracked volume although from an estimate of the absorption length of light in zirconia the contribution to the total signal is likely to be less than 25%.

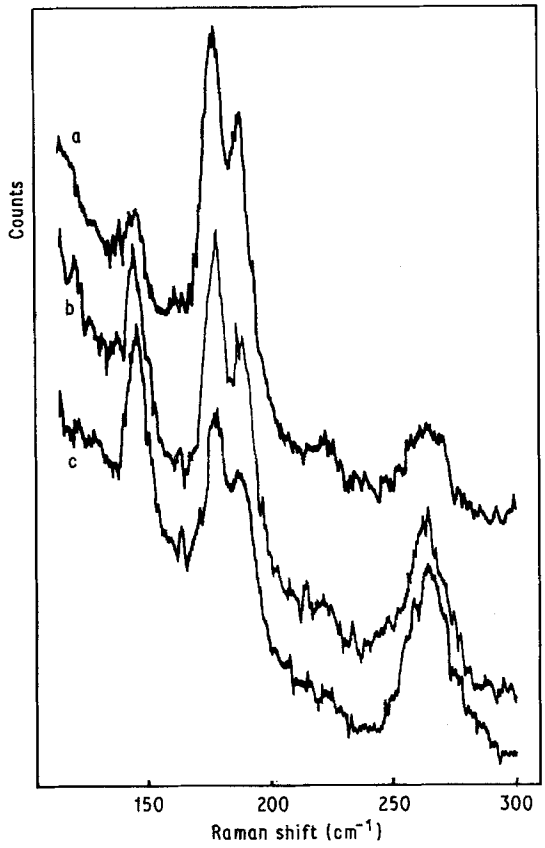

Figure 2 Typical mixed (monoclinic and tetragonal) Raman spectra obtained from the fracture surfaces of the test bars from (a) tensile, (b) central and (c) compressive regions respectively.

The amount of transformation of the tetragonal

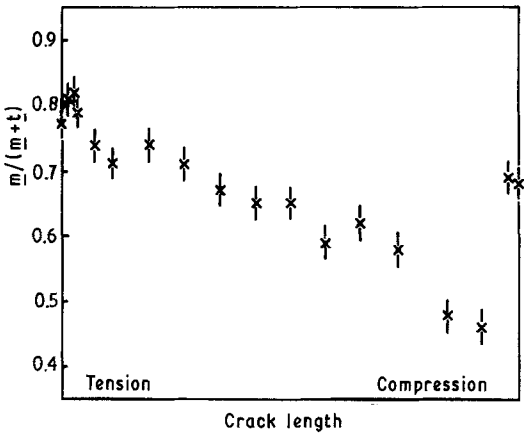

Figure 3 The variation in monoclinic zirconia (plotted as $m/(m + t)$) calculated on a traverse across a fracture surface in the direction of crack propagation. (crack length = bar depth = 2.82 mm.)

*Prepared from ZrO_2 powder supplied by Magnesium Elektron Ltd.

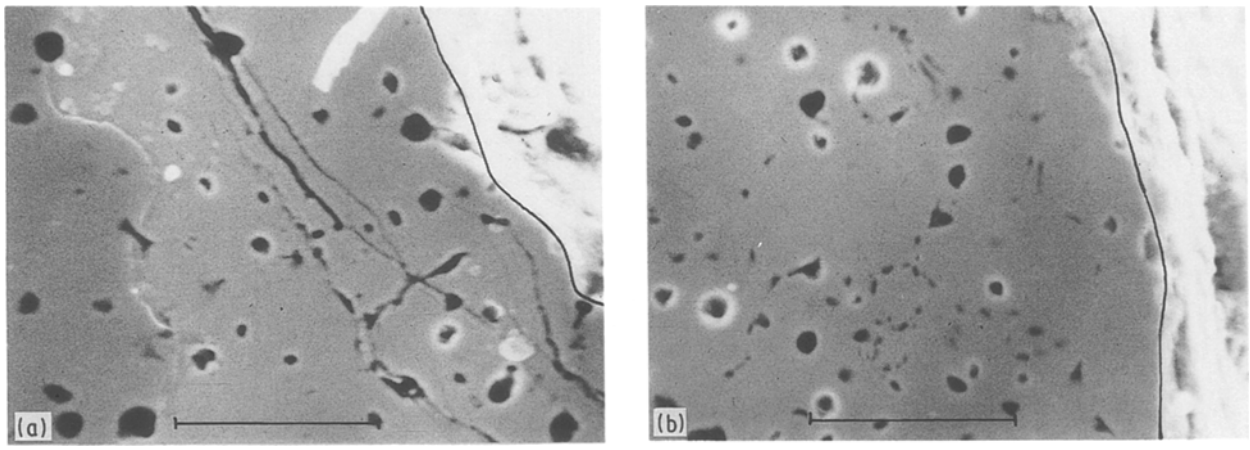

Figure 4 SEM micrographs of a polished section through the fracture plane of a Mg–PSZ test bar showing (a) extensive large microcracks in the tension side and (b) a compression side free from large microcracks. (Scale bar = 30 μm.)

phase appears qualitatively to decrease with the amount of large microcracking observed and it would seem reasonable that the two processes are related in that the microcracking acts as a stress release mechanism allowing the tetragonal phase to transform. Ruhle *et al.* [11] describe microcracking in zirconia toughened alumina (ZTA) as a mechanism for the release of stresses generated by the spontaneous transformation of tetragonal zirconia particles to monoclinic prior to their association with an external stress field and not as an accompaniment to the stress induced transformation. If this mechanism is valid here then the initial microcracking will be associated primarily with the cubic grain boundary regions where there are discrete monoclinic zirconia grains and also where the grain interior precipitates are most likely to have coarsened sufficiently to undergo spontaneous transformation on cooling. The work of Marshall and James [12] used optical microscopy observations of tension faces of Mg–PSZ bars loaded in flexure to demonstrate that "grain scale" microcracks are developed at the tension face at stresses $\geqslant 360$ MPa. These are generated in conjunction with a (reversible) transformation of the tetragonal phase at stresses in excess of 200 MPa, the transformation only being preserved upon unloading close to microcracks. In this study, the majority of the crack branching and extended microcracks are observed adjacent to the tensile side of the fracture plane and may have grown from nuclei introduced during fabrication or the early stages of loading prior to catastrophic failure. It appears from this that extensive microcracking on a grain scale, probably with much crack link-up, is the reason for the increase in monoclinic zirconia observed on the tension side of the fracture face, particularly when the effective depth of the Raman microprobe analysis is compared with the scale of the microcrack network observed in the SEM. In order to test this, acoustic emission studies of loaded test bars are currently being carried out to determine the extent and depth of microcracking occurring prior to failure in these samples.

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References

1. N. CLAUSSEN, M. RUHLE and A. H. HEUER, (eds) in "Advances in Ceramics, Vol. 12. Science and Technology of Zirconia", (The American Ceramic Society, 1984) Sections IV and V.
2. N. CLAUSSEN, in "Advances in Ceramics, Vol. 12, Science and Technology of Zirconia", edited by N. Claussen, M. Ruhle and A. H. Heuer (The American Ceramic Society, Columbus, Ohio, 1984) pp. 325–351.
3. A. G. EVANS, *ibid.*, pp. 193–212.
4. L. R. F. ROSE and M. V. SWAIN, *J. Amer. Ceram. Soc.* **69** (1986) 203–207.
5. M. RUHLE, B. KRAUS, A. STRECHER and D. WAIDELICH, in "Advances in Ceramics, Vol. 12. Science and Technology of Zirconia", edited by N. Claussen, M. Ruhle and A. H. Heuer (The American Ceramic Society, 1984), pp. 256–274.
6. L. H. SCHOENLEIN, M. RUHLE and A. H. HEUER, *ibid.* pp. 275–282.
7. T. KOSMAC, M. V. SWAIN and N. CLAUSSEN, *Mater. Sci. Eng.* **71** (1985) 57–64.
8. D. R. CLARKE and F. ADAR, *J. Amer. Ceram. Soc.* **65** (1982) 284–288.
9. S. KUDO, J. MIZUNO and H. HASEGAWA, Ext. Abs. 3rd International Conference on the Science and Technology of Zirconia, (Japan Ceramic Society, 1986) 20–21.
10. E. S. ETZ, in "Scanning Electron Microscopy", edited by Om. Johari (IIT Research Institute, 1979), 67–82.
11. M. RUHLE, N. CLAUSSEN and A. H. HEUER, *J. Amer. Ceram. Soc.* **69** (1986) 195–197.
12. D. B. MARSHALL and M. R. JAMES, *ibid.* **69** (1986) 215–217.

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