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Cathodoluminescence observations of transformation induced toughening in Mg–PSZ

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In situ cathodoluminescence (CL) measurements have been carried out using a scanning electron microscope on 9 mol % MgO doped ZrO_2 (Mg–PSZ). Light intensity measurements across the fracture surface of a piece fractured in three point bending show a position dependence of the amount of transformation observed, with a maximum occurring in the volume of sample loaded in tension prior to failure. A consistent transformation zone approximately 8 μm wide was seen on either side of a scratch on a polished surface of Mg–PSZ.

1. Introduction

Magnesia partially stabilized zirconia (Mg–PSZ) ceramics show good flexural strength (< 1000 MPa) coupled with a high steady state fracture toughness (15–20 MPa $m^{1/2}$) following strong *R* curve behaviour [1]. They are of special interest in wear resistant applications [2]. The microstructure of Mg–PSZ is the result of a carefully controlled firing cycle and consists of large (50 μm) cubic zirconia grains containing optimally aged lenticular tetragonal precipitates that are about 300 nm in their longest dimension. At the cubic grain boundaries there are smaller (1 μm) monoclinic zirconia grains, together with a wetting magnesium silicate phase (Fig. 1). Enhanced toughness values are observed in this system, and 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, exerts a force on the crack tip opposing further growth. Further toughening is encouraged by microcracking mechanisms, resulting in a tuneable *R* curve behaviour dependent on the precise details of the microstructure [1]. The toughness increment attributed to transformation toughening is held to vary with the volume of material susceptible to transformation during crack propagation, and hence for maximum toughness applications it is important to prepare the ceramic in such a way that this parameter is maximized.

Direct spatially resolved observations of transformations in zirconia have been carried out at various levels of resolution using transmission electron microscopy [3], optical interference microscopy [4], microspot Raman spectroscopy [5] and cathodoluminescence microscopy (CL) [6, 7]. CL, used in this regard, offers a rapid means of examining phase distributions over SEM sized samples with a spatial resolution of better than 1 μm.

CL is a powerful tool for the characterization of ceramics and other wide band gap materials. Since electronic transitions are excited using high energy electrons, which have energies of (typically) tens of keV, transitions of several eV can easily be stimulated. The luminescence observed from such wide gap materials generally arises, however, from lower energy transitions involving defect or impurity induced states, rather than from band to band recombination. CL peaks from ceramics are notoriously broad [8], and so are extremely susceptible to modification by the spectral response of the particular CL system used to observe them. Care must therefore be taken when comparing spectra obtained using different apparatus without correction for the system response. It is, however, valid to use an uncorrected system to spatially map the occurrence of a particular phase or impurity, e.g. by monochromatic imaging. If one particular phase is much more strongly luminescent than its colleagues, then panchromatic imaging can be employed, often with the advantage of shorter acquisition times due to a higher signal to noise ratio. CL has several advantages over other spectroscopic techniques due to its very amenable probe: an electron beam is relatively easy to focus which, in conjunction with low accelerating voltages (to limit the volume in which the electron beam energy is dissipated), can give high spatial resolution. As an example, Warwick [9] demonstrated 60 nm CL resolution on a semiconductor heterostructure reflector stack in cross-section at 5 K using beam energies of 1–2 keV. The depth probed can be increased to several micrometres by increasing the accelerating voltage, but at the expense of reduced spatial resolution. An electron beam is also much easier to position accurately than (for example) a tightly focused light spot, because the beam itself can be used to form an image of the specimen and can then be directed to any point on that image.

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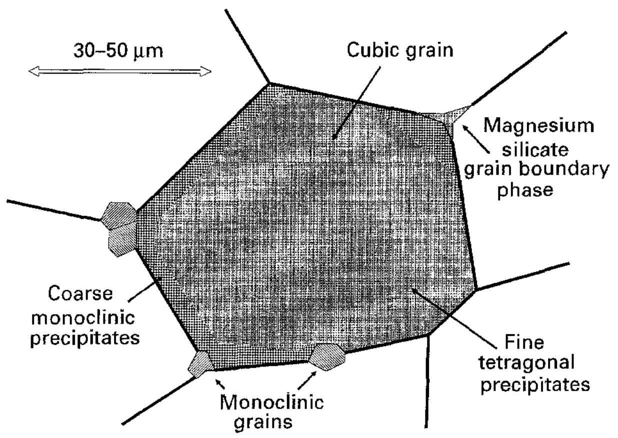

Figure 1 Microstructure of Mg–PSZ.

A perennial problem of using such a fine probe in a spatially very inhomogeneous polycrystalline material such as a ceramic is that many points must be measured to ensure that any single result is truly representative. If, for instance, the amount of a particular phase (which occurs both as fine precipitates within grains of another phase and as larger discrete grains as in the case of Mg–PSZ) is to be measured as a function of distance from a specific specimen feature (e.g. an edge or scratch) then simply moving the beam to successive points away from that feature and monitoring the CL intensity may result in very scattered data, as the beam encounters both forms of the phase investigated. Simply enlarging the probe size (either by defocusing or increasing the probe energy) or rastering the beam over a finite area in order to probe a larger, statistically more representative volume, would also lead to a loss of lateral resolution in the experiment. This may be acceptable if the effect under investigation varies on a much larger scale than the volume probed. A better solution for shorter range effects is to scan the tightly focused beam as a line, parallel to the feature in question, thereby exciting a larger volume of material (effectively a cylinder of diameter equal to that of the probe excitation volume and length equal to the length of the line scan) but all of which lies at the same distance from that feature. If the time for one line scan and fly back is much less than the specified counting period of the CL system, then the intensity read at the end of the counting period is effectively an average of all points excited along that line, assuming every point is irradiated for the same time. The validity of this assumption can be affected by one feature often found in SEM scanning electronics. The beam flies back and then pauses for a short time before beginning each line scan. The signal from the area irradiated while the beam pauses will tend to weight the average signal obtained.

In the case of zirconia ceramics, it is established that the luminescence properties of the monoclinic phase are much greater than that of the tetragonal phase or the stabilized (e.g. by magnesia) cubic phase [7]. These differences in luminescence efficiency have been used to produce panchromatic CL images mapping the distribution of the monoclinic phase, particularly in damaged zirconia ceramics.

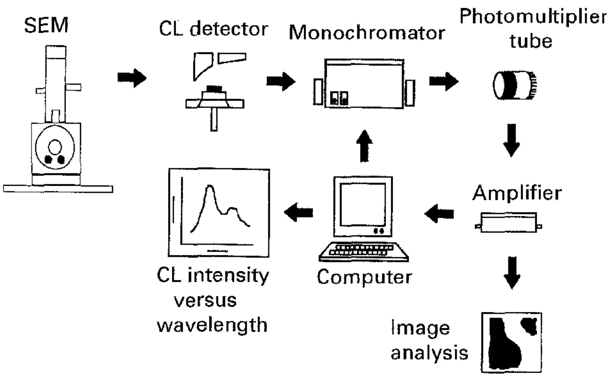

Figure 2 Schematic diagram of the SEM based CL detection system.

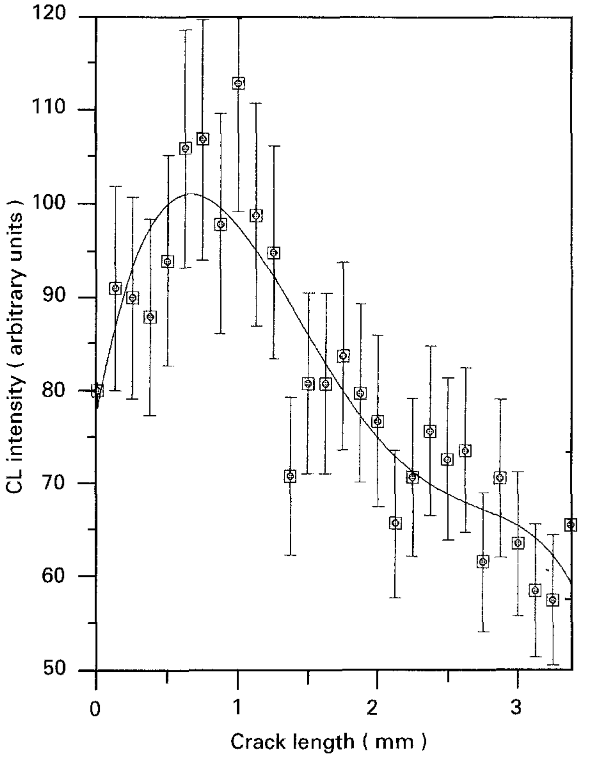

Figure 3 Variation of the CL intensity across the full width of the fracture surface. The crack propagation direction was from left to right.

2. Experimental procedure

A Jeol 840A SEM fitted with an Oxford Instruments CF301 CL collector and cryostat was used for all experiments. Light emitted from the sample under beam irradiation was detected using a type S20 photomultiplier. Panchromatic (Zero-order) imaging was used throughout, with the images and line scan intensity data being captured via a Kontron image analyser. A schematic diagram of the CL detection system is shown in Fig. 2 [10].

A reasonably planar fracture surface and a polished face from a sintered Mg–PSZ test piece were used in these experiments. The material used was as previously described [5]. CL intensity measurements were taken from 10 × 10 μm regions of the sample surface in order to smooth out emission variations due to sample roughness and the heterogeneity of the microstructure (grain size 50 μm). This area is much

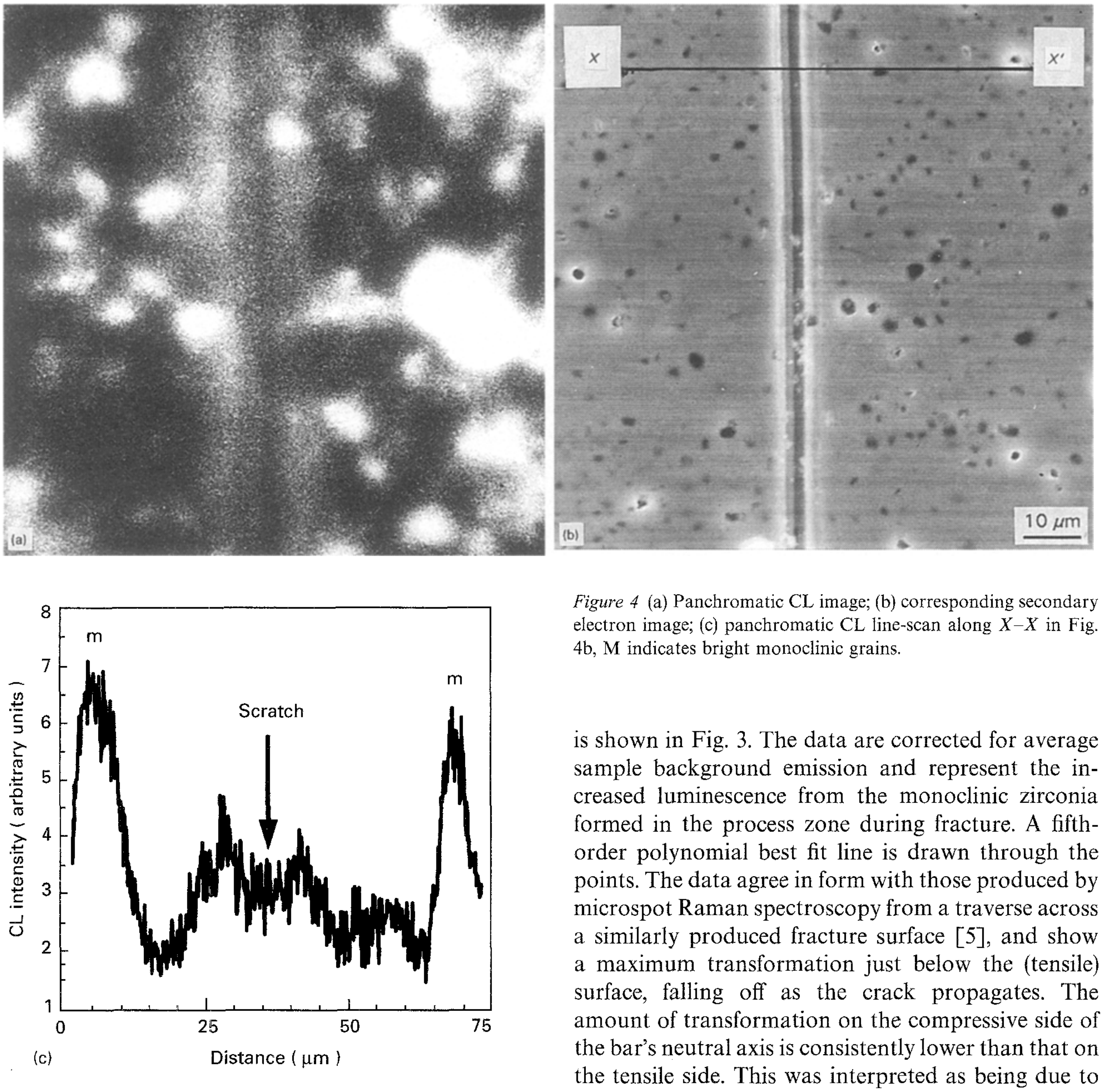

Figure 4 (a) Panchromatic CL image; (b) corresponding secondary electron image; (c) panchromatic CL line-scan along X–X in Fig. 4b, M indicates bright monoclinic grains.

smaller than the region of maximum collection efficiency for the mirror system being used, which is about 40 × 40 µm. Background CL emission levels, due to the bulk phase distribution, were determined as the mean of several readings from polished, undamaged, areas of the ceramic and were subtracted from the raw data.

On the fracture surface, a series of intensity measurements was taken in a line from the tensile side to the compressive side in order to observe luminescence variations associated with propagation of the crack through a three point bend test specimen.

A polished surface of the same material was scratched with a diamond tipped pen to a depth of 1–2 µm. Panchromatic CL images of the scratched surface and CL intensity line scans across a scratch were made in order to identify luminescence changes associated with sample damage.

3. Results and discussion

The variation of luminescence intensity across the fracture surface in the direction of crack propagation is shown in Fig. 3. The data are corrected for average sample background emission and represent the increased luminescence from the monoclinic zirconia formed in the process zone during fracture. A fifth-order polynomial best fit line is drawn through the points. The data agree in form with those produced by microspot Raman spectroscopy from a traverse across a similarly produced fracture surface [5], and show a maximum transformation just below the (tensile) surface, falling off as the crack propagates. The amount of transformation on the compressive side of the bar's neutral axis is consistently lower than that on the tensile side. This was interpreted as being due to increased transformation due to crack branching [5].

It is important to note, however, that the degree of transformation is not constant across the fracture surface, and thus that the balance of the toughening processes occurring during crack propagation must vary. In this situation the estimation of material strength or, more importantly, fracture toughness by the breaking of bar specimens is convoluted by the variable materials response with crack length under the conditions of three point flexural testing. It indicates that a change in overall fracture mechanism occurs as the crack propagates through a small bar specimen, which in turn may affect the application of Weibull statistics and the scaling of results to different sample sizes.

Fig. 4a is a panchromatic CL image of a polished surface of Mg–PSZ that has been scratched with a diamond tipped stylus, and Fig. 4b the corresponding secondary electron image. The bright areas in Fig. 4a represent the distribution of monoclinic zirconia, and delineate both the grain boundaries and the outline of the scratch. The grain boundary (and isolated islands of) monoclinic zirconia are microstructural features of the sintered material and occur as a result of equilibration with the phase diagram. Superimposed on this, the CL intensity directly associated with the scratch damage represents the development of a process zone around the damaged region. Fig. 4c is a line scan across the scratch (along the line labelled X–X' in Fig. 4b) showing the variation of panchromatic CL intensity with distance. The two large peaks at the start and finish of the scan (labelled M in Fig. 4c) arise from monoclinic grains. From these data the width of the process zone has been estimated to be 8 μm. Although the damage induced by the stylus in this case is not quantified, it can be seen that CL is generally applicable to the direct measurement of process zone widths in transformation toughened materials.

The homogeneous nature of the process zone along the length of the scratch demonstrates that a steady state toughening increment due to transformation toughening brought about by damage is readily set up in Mg–PSZ, typically after 50–250 μm crack extension [1]. The toughening increment profile through the three point bend specimen defined by the CL intensity shows markedly different behaviour, with a fall off in transformation toughening as the crack propagates through the compressive side of the bar.

4. Conclusions

The transformation toughening increment measured by CL microscopy on the compressive side of the bar's neutral axis is consistently lower than that on the tensile side.

There appear to be changes in the overall balance of the fracture mechanism as the crack propagates through a small bar specimen. This may affect the application of Weibull statistics and the scaling of results to different sample sizes.

CL microscopy is generally applicable to the direct measurement of process zone widths in transformation toughened materials.

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