TEM characterization of indented polycrystalline Y-PSZ

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The microstructural characterization of indented Y-PSZ polycrystals has been investigated by TEM. The observations show two different regions associated with the indent: a large core with a high density of monoclinic particles transformed from the initial tetragonal variant, and an inner core region with a high density of dislocations. The core region can be correlated with previous observations of a crack exclusion zone.

1. Introduction

Indentation techniques are widely used for mechanical characterization of ceramic materials [1]. In an idealized description, when the indentor advances, the impression is accommodated by a net radial flow of material, resulting in an approximately hemispherical plastic zone around the indent surrounded by the confining elastic matrix. In this description it is assumed that the plastic deformation process is volume conserving and, consequently, the indent volume is accommodated just by elastic deformation [2]. When the indentor is removed, the plastic zone inhibits elastic recovery from occurring completely so that a residual stress field is associated with elastic/plastic contact. These residual stresses are tensile in tangential directions outside the plastic zone, but hydrostatic compressive within the region. With this deformation configuration it is possible to assume that the cracks start in the elastic/plastic boundary and extend appreciably into the elastic zone.

Indentation fracture analysis is based on the observation that usually the driving forces responsible for the final crack configuration have their origin in the residual component of the elastic/plastic indentation field. On the other hand, this residual stress must be also taken into account in modelling the stable crack propagation observed during further bending tests.

It is well known that in zirconia-based ceramics the martensitic transformation from tetragonal (t) to monoclinic (m) phase can be induced by the high stresses ahead of the advancing crack tip, enhancing the material mechanical properties (transformation-toughening mechanism) [3]. In these materials the stress induced (t–m) transformation can be also activated in an indentation test (indentation transformation, IT); the shear stresses that induce the t–m transformation are high enough to overcome the compressive stress field around the indentor. This transformation serves, as does activation of dislocations, to displace the material when the indentor advances and constitutes a form of plasticity (transformation plasticity, TP) [4]. However, transformation plasticity is a volume increasing mechanism so that it gives a non-negligible contribution to the residual stress field and, consequently, must be considered in indentation fracture analysis.

In the present work we report the results of a transmission electron microscopy (TEM) microstructural characterization study of the indented region of 4Y-PSZ polycrystals. Owing to the small grain size, it was impractical to identify each individual grain by electron diffraction, consequently, more global, albeit more subjective, methods were employed. The possible role of indentation transformation as a plasticity mechanism, as well as its possible influence on the residual stress, has been analysed.

2. Experimental procedure

The study reported here was carried out on PSZ polycrystals containing 4 mol % Y_2O_3. The material was fabricated by isopressing powder at 200 MPa and air-sintering for 2 h at 1650 °C. From thermodynamic considerations, a multiphase structure is expected. In fact, X-ray diffraction quantitative analysis carried out in previous work [5] has shown that grains and/or particles of cubic (c) tetragonal (t and t′) and monoclinic (m) phases are all present. In this study, it is particularly important to distinguish between the two tetragonal phases, t and t′, because the former can

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undergo the classical t–m transformation leading to transformation toughening, whereas the latter cannot.

As-received samples were cut with a diamond saw and the surface to be indented was progressively polished with diamond paste from 9–1 μm. The specimens were indented with a Vickers hardness tester at 294 N load and a 40 $\mu m\, s^{-1}$ indentation rate; the indentor was kept at maximum load for 20 s.

The indentation crack profile can be directly observed from the fracture surface obtained during a subsequent bending test to failure [6]. To improve the optical appearance of the crack, a heat treatment was performed (annealing at 1000 °C for 30 min) prior to the bend test.

For TEM observations, we cut 3 mm diameter discs from the centre of the indented region using an ultrasonic cutting tool. The non-indented surface was mechanically polished with diamond paste, then dimpled to obtain a thickness of 40 μm. Finally, the sample was ion-thinned to electron transparency and coated with 5 nm carbon to avoid charging during the TEM studies. Observations of fracture surfaces were made by mechanical polishing and ion-thinning specimens from the reverse side to leave the surface of interest intact. A Philips CM10 electron microscope operating at 100 kV was used in the conventional observations.

Owing to a significant difference in the yttria concentration that dissolves in the t and t′ phases, it is possible to differentiate these phases using X-ray microanalysis. A Jeol 200CX equipped with a Kevex high-angle detector and X-ray mapping capabilities was used for this purpose.

3. Results

3.1. Phase identification

Fig. 1 shows X-ray maps and the corresponding micrograph from a typical region remote from an indented region. Fig. 1a and e show the scanning transmission (ST) and TEM images, respectively, while Fig. 1b and c show images formed using emissions from ZrK_α and YK_α lines, respectively. A superposition of the yttrium-map and the ST image is given in Fig. 1d. The region marked A is seen to be of low contrast when imaged with the yttrium signal (Fig. 1c) and subsequent quantitative analysis showed its yttrium content to be 5.0 ± 0.2 wt %. On the other hand, the surrounding grains (B) that exhibited a characteristic mottled or "tweed-like" contrast but no bend contours are seen to contain a higher yttrium content. An analysis of such a grain revealed the yttrium content to be 12.9 ± 0.3 wt %. After repeated analysis from both types of grains yielded similar results, the following conclusion was reached: the B grains rich in yttrium are t′ phase and invariably exhibit the "tweed" contrast when tilted into strong diffracting conditions, whereas the A grains, lean in yttrium, are t phase and are identifiable by the characteristic bend contours they exhibit (e.g. see areas marked C in Fig. 1e).

To identify the monoclinic (m) phase the multiple twin characteristics of this phase illustrated in Fig. 2 were used. These distinguishing features of t, t′ and m enabled subsequent classification of the fine-grained microstructure to be carried out.

Cubic grains were not specifically identified but, because their crystallography remains unchanged by subsequent treatments, their presence in the material is benign.

3.2. Indentation tests

Polycrystalline yttria-partially stabilized zirconia (Y-PSZ), subjected to room temperature Vickers indentation tests, exhibits interesting behaviour. It is found that at small indentation loads the crack profile is radial (using the nomenclature of Cook and Pharr [7]). At higher indentation loads, the crack profile tends to become half-penny shaped as is found in single crystals [8], but rather than propagate through the whole sample the crack is found to be excluded from a nearly spherical zone below the indent [9].

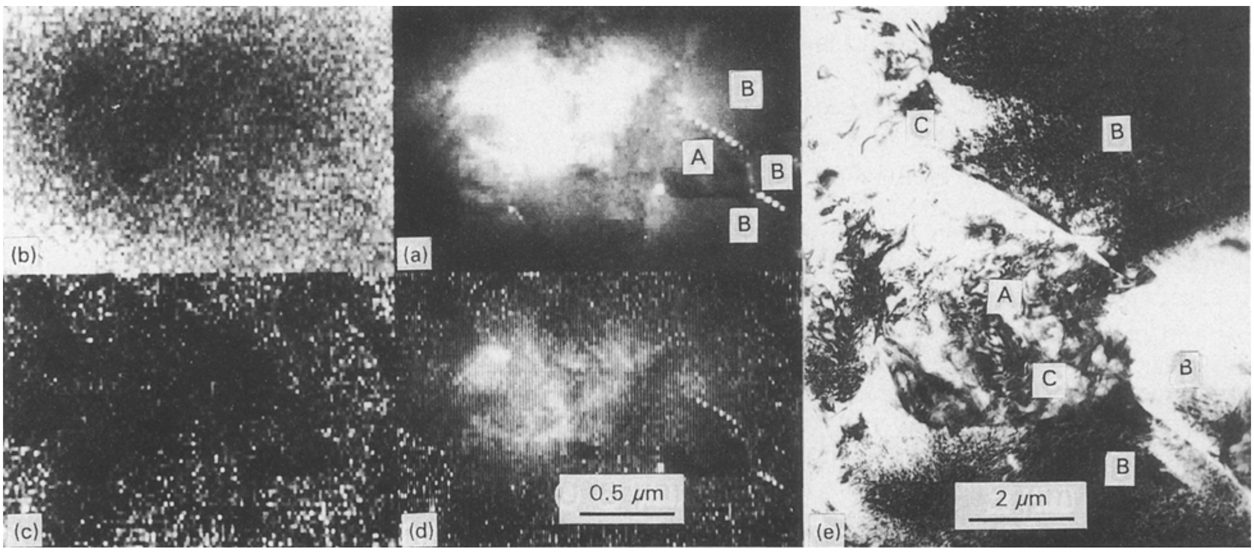

Figure 1 X-ray maps and micrographs illustrating the different properties of the t and t′ phases. See text for detailed discussion; (a–d) have the same magnification).

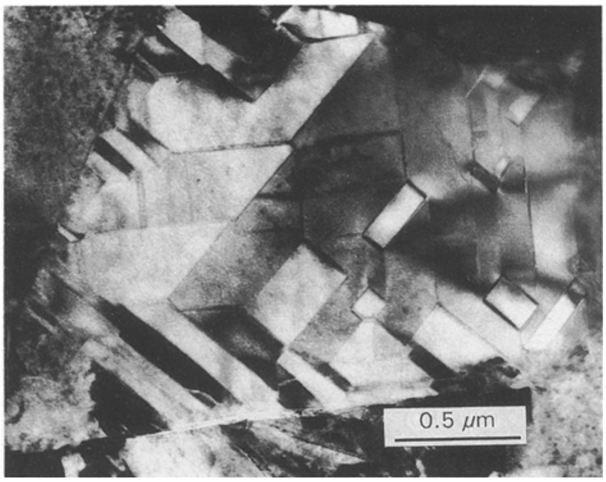

Figure 2 Monoclinic grain exhibiting characteristic multiply-twinned structure associated with this phase.

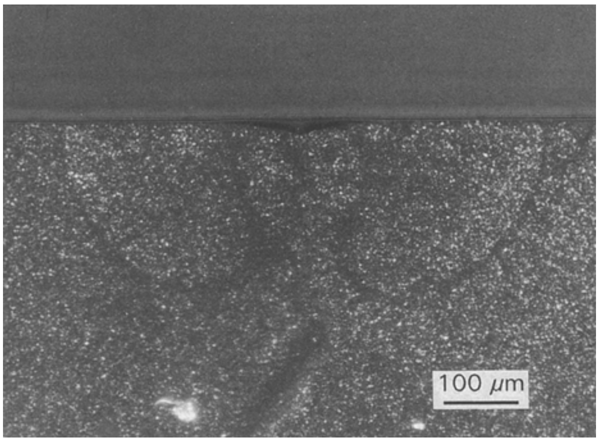

Figure 3 Optical microscopy of a fracture surface showing Vickers crack profile introduced with a 294 N load.

Fig. 3 shows the crack profile obtained with an intermediate indentation load. As can be observed, the cracks have a configuration intermediate between the radial and half-penny shapes, and are referred to as "kidney crack" elsewhere [10]. A crack exclusion region is seen beneath the indent crater (core region), which has a spherical shape of about 95 μm radius with a centre at a depth of 65 μm from the top surface; its volume is at least 15 times larger than the residual impression volume. When the indentation load was increased (up to 490 N), a half-penny crack was formed, but with a large core region [10]. These results suggest the existence of compressive residual stresses acting on the core region making it highly resistant to crack propagation. Effectively, in previous works [9–11], we have shown the inaccessibility of the crack to the core region during further stable propagation produced by a subsequent bending test; only when the crack propagates catastrophically is the core region fractured.

An explanation of the origin of the compressive residual stress in the core region would be to assume that this region corresponds to the plastically deformed zone introduced by the indentation test, which is surrounded by the elastically restraining matrix [2]. In the present work we employ TEM observations in order to detect the possible microstructural changes around the indent, that is, dislocation activity and t–m transformation.

3.3. Microstructural observations

A micrograph from a typical area of an as-received specimen is shown in Fig. 4 for comparison with subsequent micrographs. Different grains are marked according to their identity and the microstructure is seen to be composed principally of t′ and t grains and just occasionally m grains are found. Sometimes a small t particle is contained within a large t′ grain.

The series of micrographs in Fig. 5 illustrates the microstructures found in an indented specimen. For reference, the regions from which the transmission electron micrographs were taken relative to the positions of the ion-thinned hole and indent crater, are indicated in the optical micrograph of Fig. 5a. The microstructure in the region marked b, far from the indent, is indistinguishable from the as-received material, as comparison of Fig. 5b with Fig. 4 shows. Again, mainly t′ and t grains are present and m grains are found only rarely. By contrast the region marked c, which we designate the outer core region, shows the t′ grains present in the same proportion but the t grains have been replaced by an equal proportion of m grains (Fig. 5c). Evidently in this region the stress level is sufficient to induce the t–m martensitic transformation.

The most dramatic change in the microstructure, however, is evident in the region d, right under the indent, designated the inner core region. Here it is seen (Fig. 5d) that all grains have undergone heavy plastic deformation. A uniformly high dislocation density throughout the region has produced a microstructure reminiscent of a highly cold-worked metal. Because of the high density, only short segments of individual dislocation are seen and a clear impression of the structure is gained only during observation while tilting the foil. In general, phase identification was masked by the deformation but in some regions it was

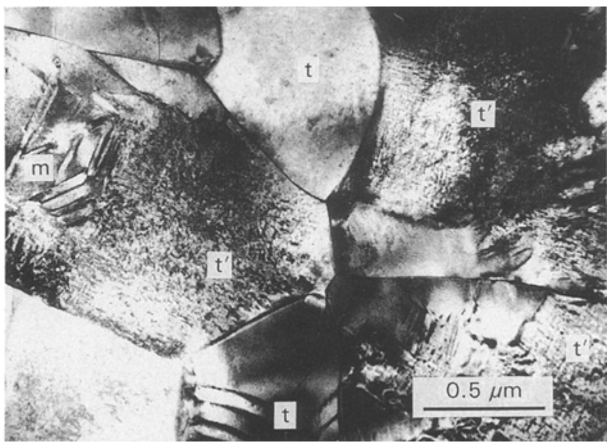

Figure 4 Typical micrograph from as-received Y-PSZ with grain identification.

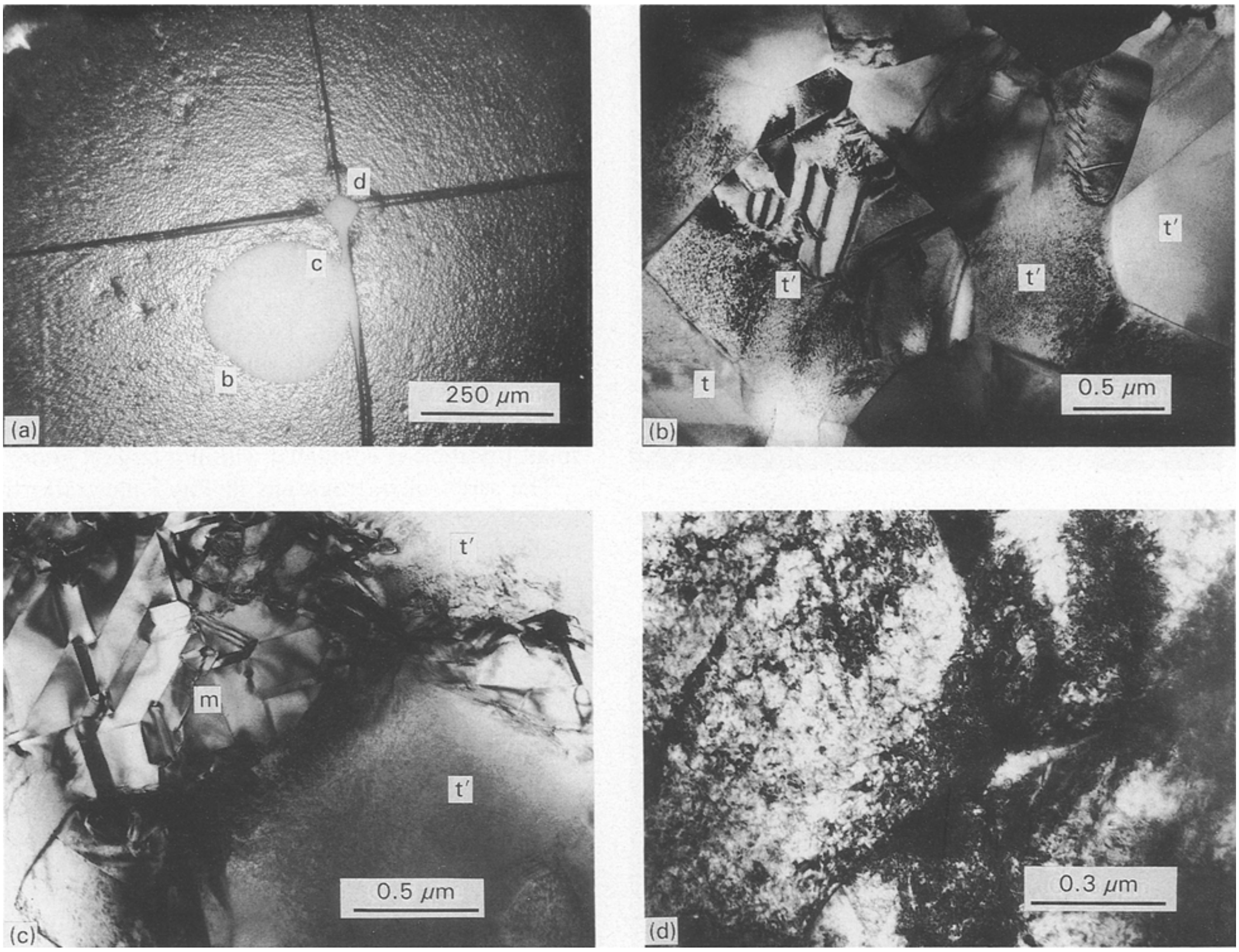

Figure 5 A series of micrographs illustrating the microstructures developed in various regions of a specimen indented under a 294 N load. (a) Low-magnification optical micrograph showing the regions from which transmission electron micrographs were taken: (b) a region remote from the indent; (c) outer core region; (d) inner core region.

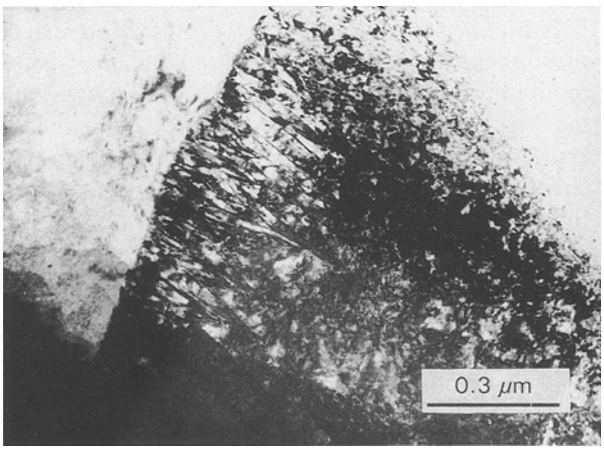

Figure 6 A region containing a highly deformed monoclinic grain.

possible to recognize the underlying monoclinic structure of the grain as illustrated in Fig. 6. The deformation has distorted, but not obliterated, the typical multiply-twinned microstructure.

An additional feature of the core region was a high density of microcracks in the grain boundaries. However, cracks were not confined to the core region only; the outer regions were also found to contain cracks when observed under optimal conditions.

An example of the microstructure in the fracture surface is given in Fig. 7. Only t′ and m grains are present, consistent with the expectation that the t grains will have transformed to m but the t′ grains will remain unchanged.

4. Discussion

As mentioned above, it is clear that the core zone is the plastically deformed region. The principle microstructural changes associated with the indentation are the t–m transformation in the entire core region and the high density of dislocations in the inner core region. Both features can be readily understood as follows.

It is well known that brittle ceramic materials that fracture under a uniaxial stress can be made to exhibit plastic behaviour by dislocation activity if the specimen is confined in a superimposed hydrostatic stress field [12]. During the load half-cycle in an indentation test, the zone close to the indentor is placed under large hydrostatic pressure and, consequently, dislocation activities should be possible in this zone. However, the extent of the region where the dislocations are visible is appreciably smaller than the extent of the plastic zone (core region) and, consequently, another plasticity mechanism must be activated. The observation that all the core is a transformed t–m region

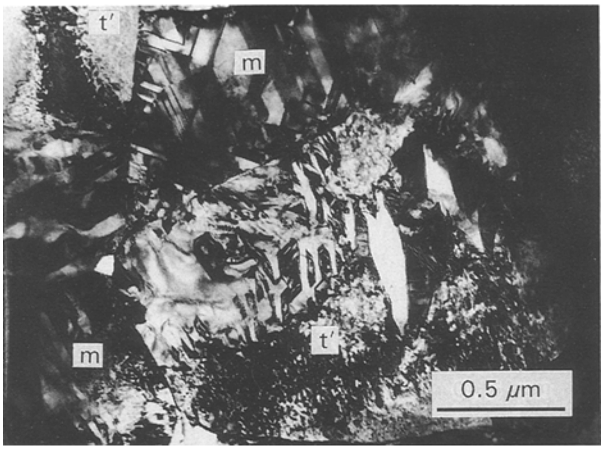

Figure 7 A typical area in the fracture surface obtained by the bending test.

suggest that in 4Y-PSZ the TP is an additional mechanism to displace the material as the indentor tip advances at room temperature, in agreement with results obtained by other authors in different transformation-toughened polycrystalline materials [4, 13].

The observation of extensive microcracking throughout the material is puzzling, until it is remembered that long-range stresses in the sample will be relaxed as the material is progressively thinned. In the thin electron-transparent regions of the foil, the relaxation will be essentially complete, allowing development of the incipient cracking associated with the t–m transformation.

In the following paragraphs we examine the possible indentation-transformation influence on the residual stress. As mentioned above, the TP is a volume increasing plasticity mechanism. Thus, an additional volume, associated with the IT, must be accommodated by elastic deformation, as well as the indent volume. Invoking the concept that the indentation residual field is derived from an elastic accommodation of volume, these results suggest that a contribution to the residual stresses should be expected if IT occurs. In order to gain insight into the importance of this contribution in our case, we have estimated the volume increase associated with IT, (ΔV_{IT}), which is given by

$$\Delta V_{IT} = f e^{T} V_{IT} \qquad (1)$$

where f is the fraction of volume that is transformed, e^T is the dilational transformation strain and V_{IT} the volume of the transformed region. In the calculation outlined below we have estimated the possible IT contribution taking into account the following experimental observations: (1) all the t particles within the core transform to monoclinic phase, and (2) the volume increase associated with IT is not accommodated by surface uplifting, as was confirmed by optical inspection of the top surface around the indent. With these considerations, V_{IT} is the core volume. Previous X-ray quantitative analysis data give $f = 0.25$ [5]. An increase in volume of 4% has been used for the t–m dilational effect. The obtained value for ΔV_{IT} is 3.17 $\times 10^4$ μm^3 which is nearly six times smaller than the residual indent volume. From this analysis it can be inferred that the effect of the IT on the residual stress must be taken into account; however, the main source of the residual stress arises from the indent volume accommodation effect.

At this stage it is of interest to invoke the possible partial or total accommodation of the volume increase associated with IT by elastic recovery of the indent during the unload half-cycle. Under complete accommodation, no effect on the residual stresses should be expected. In this case, the value of the ratio of hardness to elastic modulus (H/E) obtained from elastic recovery measurements of Knoop tests, using the equation proposed by Marshall *et al.* [14], would be overestimated. However, the H/E value obtained from this experiment is 0.050 ± 0.002, in contrast with the higher value obtained from the direct experimental estimation of the H and E values ($H/E = 0.061$) [11]. These results suggest that the increase in volume associated with IT is not accommodated by elastic recovery. On the contrary, it is possible that the presence of IT around the indent hinders elastic recovery during the unload half-cycle.

In light of the previous analysis, we think that it is quite possible that the IT has a non-negligible contribution to the residual stresses and, consequently, should be taken into account in indentation fracture analysis. However, the main source of the residual stresses is obviously the indent volume accommodation effect.

5. Conclusion

TEM observations of indented Y-PSZ have shown that the microstructure associated with a crack-exclusion region consists of a large hemispherical transformed zone, the inner regions of which contain a high density of dislocations.

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