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Preferred Orientation of the Transformed Monoclinic Phase in Fracture Surfaces of Y–TZP Ceramics

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SUMMARY

X-ray diffraction (XRD) has been used in a study of yttria–tetragonal zirconia polycrystalline (Y–TZP) ceramics to assess the extent of transformation to the monoclinic phase of fracture surfaces. Comparison of powder diffraction patterns and those obtained from fracture surfaces indicated that there are changes in the relative intensities of the $(111)_m$ *and* $(11\bar{1})_m$ *reflections and also shifts in the angles at which the reflections appear.*

From the experimental data, lattice parameters for the monoclinic phase are recalculated, using four reflections, by an iterative technique. Using the new calculated lattice parameters the position of a fifth reflection is predicted accurately.

The integrated intensity of the $(11\bar{1})_m$ *reflection is increased compared with the* $(111)_m$ *reflection. The ratio of the integrated intensities is expected to be about 1·5, but is found to be as high as 7·5. This can give rise to an error in the predicted monoclinic phase content; a correction is proposed.*

The preferred orientation is considered to arise because of the importance of the shear component of the martensitic transformation. The importance of this finding for an understanding of the fracture process is discussed.

1. INTRODUCTION

X-ray diffraction (XRD) techniques form the basis of phase analysis of predominantly tetragonal zirconia polycrystalline ceramics (TZP). The

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transformation of the tetragonal phase to monoclinic symmetry on grinding or on fracture has received attention,[1,2] in particular in the determination of a 'depth of transformation'. A certain amount of doubt concerning the application of these techniques to TZP materials has arisen following the study of Rühle and his co-workers.[3] In an *in-situ* transmission electron microscopy (TEM) fracture study they showed that the monoclinic phase appears in irregular clusters in the crack-tip wake and that some tetragonal grains near the crack or on the crack plane do not transform. It is therefore difficult to assign a 'depth of transformation' in such a system. It should be remembered that such work takes place in a thin, electron transparent section and does not have the elastic constraint present in the bulk ceramic.

In this study it was noted that there is a substantial deviation of the relative intensities of the $(11\bar{1})_m$ and $(111)_m$ reflections from those anticipated in powder XRD and structure factor calculations.[4,5] It is suggested that this deviation arises from the monoclinic phase, formed during the fracture process, having a preferred orientation. In addition, a shift in the position of the $(11\bar{1})$ reflection was noted and this shift is analysed in terms of a distortion of the monoclinic cell from that expected, as a consequence of constraint in the development of the fracture surface.

2. EXPERIMENTAL

Powder XRD analysis was performed on commercially available yttria-doped zirconia powders (MEL, Manchester, UK and Toyo-Soda Co., Tokyo, Japan) that were thermally treated at 1600°C for sufficient time to ensure equilibrium distribution of the Y_2O_3, and to increase the crystallite size, thereby producing some monoclinic phase.

XRD was carried out on the fracture surfaces of single edge notched bar (SENB) specimens consequent to a study of the sintering behaviour, fracture toughness, and the extent of the tetragonal to monoclinic transformation possible.[6]

A Philips diffractometer using Cu–Kα radiation in continuous scan mode was used. The integrated intensities of the required *hkl* reflections were determined by planimetry.

3. RESULTS AND DISCUSSION

3.1. Recalculation of lattice parameters of the monoclinic phase in fracture surfaces

Initial results showed a significant shift in the $(11\bar{1})_m$ reflection obtained from the fracture surfaces when compared with those obtained using powder XRD samples (Fig. 1).

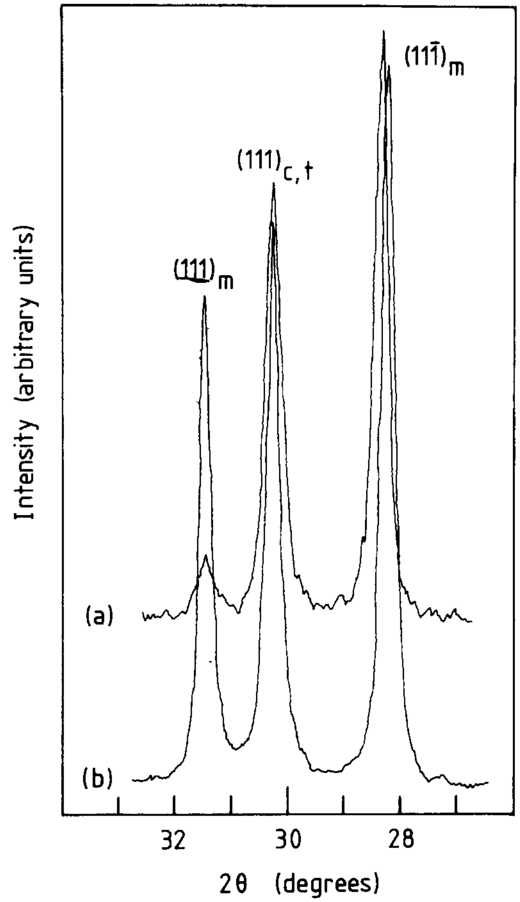

Fig. 1. XRD traces for (a) a TZP fracture surface and (b) Y_2O_3–ZrO_2 powder of the same composition, i.e. 2 mol% Y_2O_3. Note changes in the relative intensities of the $(111)_m$ and $(11\bar{1})_m$ and differences in the position of the $(11\bar{1})_m$ reflection.

An interactive program was developed which permitted the calculation of the systematic variation of the lattice parameters, starting with the values given by JCPDS card 13-307 (baddeleyite). After modification of a lattice parameter value, the *d*-spacings anticipated from the current values were then calculated and compared with the experimental values. This was done for four reflections: (002), (200), (020) and $(11\bar{1})$. Finally, when a good correspondence between the calculated and experimental values (better than 0·001 Å) was obtained, the *d*-spacing for the $(111)_m$ reflection was calculated and compared with the measured value. This provides an independent check of the iterative method described, using all four lattice parameters. The initial lattice parameters, the final lattice parameters and the calculated and measured *d*-spacings for the (111) reflection are given in Table 1.

TABLE 1

Lattice parameters	*JCPDS 13-307*	*Recalculated*
a	5·1477 Å	5·1275 Å
b	5·203 Å	5·200 Å
c	5·3156 Å	5·3018 Å
β	99·383°	98·505°
Unit cell volume	140·47 Å^3	139·81 Å^3

Calculated $(111)_{\mathrm{m}}$ d-spacing = 2·847 Å
Measured $(111)_{\mathrm{m}}$ d-spacing = 2·844 Å

It is apparent from Table 1 that the prediction of the d-spacing of the (111) reflection using the modified lattice parameters is satisfactory.

From these results it can be seen that compared with standard monoclinic zirconia the monoclinic cell in TZP fracture surfaces is slightly distorted, having a shorter c axis tilted slightly towards the normal. The a lattice parameter is also shorter, the overall effect resulting in a 'strained' structure.

The unit cell volume of the monoclinic phase in the fracture surface is smaller than that calculated for baddeleyite powder. This suggests that the distortion of the monoclinic cell arises in order to minimise the matrix strain energy increase resulting from the transformation in the fracture surface. This also suggests a lower barrier to transformation than would be anticipated from consideration of the volume change in pure phases.[7]

3.2. Preferred orientation of the monoclinic phase in fracture surfaces

The TZP materials investigated in this study had no monoclinic phase present prior to fracture. Figure 1(a) shows the XRD trace of a fracture surface. The three reflections, in order of increasing 2θ, are $(11\bar{1})_{\mathrm{m}}$, $(111)_{\mathrm{c,t}}$ and $(111)_{\mathrm{m}}$. It is apparent from a comparison of the relative intensities of the monoclinic reflections with those in the powder sample (Fig. 1(b)) that the $(11\bar{1})_{\mathrm{m}}$ plane is found parallel to the fracture surface more often than would be anticipated from random transformation of tetragonal grains.

Table 2 shows the ratio of the relative intensities of $(11\bar{1})_{\mathrm{m}}$ to $(111)_{\mathrm{m}}$ for a number of TZP ceramics sintered using a variety of temperatures and times. The results indicate that for both small or extensive amounts of transformation, preferred orientation of the monoclinic phase can be detected in the fracture surface.

This raises certain difficulties in the accurate computation of the monoclinic phase content, since the validity of the expressions used[8-10] relies on the assumption that transformation in the fracture surface is

TABLE 2

Composition	*Treatment*		$\frac{I(11\bar{1})_m}{I(111)_m}$	X_m	X_m *corrected*	V_m	V_m *corrected*
	Temperature/ °C	*Time/ h*					
2·5Y	1 675	2	7·125	28·5	26·0	34·8	32·1
2·5Y	1 400	2[a]	4·51	8·4	7·7	10·9	10·0
2·5Y	1 400	2[b]	4·88	6·6	6·1	8·7	7·9
2Y	1 400	2	6·5	20·6	18·7	25·8	23·6
2Y	1 575	2	6·61	55·3	52·4	62·4	59·6
2Y	1 575	1	7·33	39·6	36·6	46·7	43·7

[a] Notch width 500 μm.
[b] Notch width 100 μm.

crystallographically random. The net effect of this is to give an overestimate of the monoclinic phase content by a few percent. A correction may be applied:

$$I_T = 1{\cdot}255I(111) + 0{\cdot}833I(11\bar{1})$$

where I_T is the corrected intensity of $I(111)_m + I(111)_m$, based on the assumption that the expected relative intensity ratio is 1·5 for randomly oriented grains (see Appendix). The results are calculated for the uncorrected and corrected integrated intensities using the equation of Toraya *et al.*:[8,9]

$$V_m = \frac{PX_m}{1 + (P-1)X_m}$$

where X_m = the monoclinic intensity relative to the total intensity of the $(111)_m$, $(11\bar{1})_m$, $(111)_{c,t}$ reflections; P = the experimental constant for these systems (about 1·31); and V_m = the volume fraction of monoclinic phase. The experimental results and relevant corrections are listed in Table 2.

These results indicate that the $(11\bar{1})_m$ plane is preferentially developed parallel to the crack plane 2·5–5 times more often than would be the case if grains transformed randomly. This suggests an important implication and gives evidence to the effect that the directional component of the shear transformation is very important in the toughening process. An indication of the nature of the directional component can be deduced from a comparison of the areas of $(111)_t$, $(111)_m$ and $(11\bar{1})_m$ planes in the unit cell. These results are shown in Table 3.

The deviatoric component of the transformation can be considered to give rise to toughening of TZP materials ahead of a stationary crack.[11] This model is preferred to the hydrostatic, crack wake model[12] in the light of the

TABLE 3

Plane	*Area*/Å^2	$\Delta A(111)_t$/%
$(111)_t$	22·70	—
$(111)_m$	24·55	+8·2
$(11\bar{1})_m$	22·2	−2·3

preferred orientation observed in the fracture surfaces. It appears that the transformation occurs in grains oriented in such a way that the maximum volumetric expansion occurs parallel to the tensile stress field, thus reducing the strain energy associated with the untransformed grains ahead of the crack. The relatively small number of grains that transform into other orientations may do so through autocatalytic mechanisms (suggested by Rühle *et al.*[3]) or as a result of crack deviation from the plane, microcracking and other phenomena. These represent some 20–25 % of all transformation events.

The distinctive difference between partially stabilised zirconia (PSZ) transformation toughening and TZP transformation toughening appears to reside in the difference in importance of the hydrostatic and deviatoric components of the shear transformation, the latter being of major importance in the TZP system and relatively less important in the PSZ materials.[12]

The results of the present study have been applied to the interpretation of the experimentally determined toughening increment, $\Delta K^{\mathrm{T}}_{\mathrm{1c}}$, in TZP materials using the equation proposed by Seyler *et al.*[11] in a modified form.[6]

4. CONCLUSIONS

(i) The lattice parameters of the monoclinic phase in TZP fracture surfaces are modified, compared with the powder XRD value, in a manner that reduces the unit cell volume.

(ii) There is a tendency for the $(11\bar{1})$ plane of monoclinic grains to be generated parallel to the crack surface more often than would be the case if transformation of tetragonal grains took place irrespective of their orientation.

(iii) This preferred orientation can be interpreted in terms of the directional nature of the transformation, which occurs so as to minimise the volume increase in the plane of the crack, and more importantly, to maximise it in the direction of the tensile stress field in order to reduce strain energy ahead of the crack tip.

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APPENDIX: ESTIMATION OF THE CORRECTION FACTOR FOR THE CALCULATION OF THE MONOCLINIC PHASE IN SURFACES WITH A PREFERRED ORIENTATION OF THE PHASE

In a random sample 40% of the integrated intensity of $(111)_m$ and $(11\bar{1})_m$ reflections is generated from $(111)_m$. Thus the ratio of the intensity of $(11\bar{1})_m$ to $(111)_m$ is approximately 1·5.

In a non-random sample, the total intensity can be considered to be made up of a random contribution and a non-random contribution due to preferred orientation; the 'random' contribution can be calculated from the intensity of the $(111)_m$ reflection if this intensity is considered to arise randomly.

Thus, $I(11\bar{1})_{mR}$, the random contribution from the $(11\bar{1})_m$ reflection is $I(111)_m \times 1{\cdot}5$. Hence, the non-random contribution, $I(11\bar{1})_{mNR}$, is $I(11\bar{1})_{m\,total} - I(11\bar{1})_{mR}$. If this contribution had arisen randomly its intensity, $I(11\bar{1})_{m\,corr}$, would be

$$\begin{aligned}0{\cdot}5 \times I(11\bar{1})_{mNR} &+ 0{\cdot}5 \times 0{\cdot}66 \times I(11\bar{1})_{mNR}\\ &= 0{\cdot}83 \times (I(11\bar{1})_{mNR})\\ &= 0{\cdot}83(I(11\bar{1})_{m\,total} - I(111)_m \times 1{\cdot}5)\end{aligned}$$

Thus the total corrected intensity I_{mT} can be written

$$\begin{aligned}I_{mT} &= I(111)_m + I(11\bar{1})_{mR} + I(11\bar{1})_{m\,corr}\\ &= I(111)_m + (I(111)_m \times 1{\cdot}5) + (0{\cdot}83 \times (I(11\bar{1})_{m\,total} - I(111)_m \times 1{\cdot}5))\\ &= 1{\cdot}255 I(111)_m + 0{\cdot}833 I(11\bar{1})_m\end{aligned}$$

This equation leads to a correction of ~1% at 10% transformation and ~5% at the 60% transformation level.

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