JOURNAL OF MATERIALS SCIENCE 31 (1996) 6523–6527

An *In-situ* investigation on the critical phase transformation stress of tetragonal zirconia polycrystalline ceramics

L. S. PAN, S. HORIBE
Department of Materials Science and Engineering, Waseda University, 3-4-1, Ohkubo, Shinjuku-ku, Tokyo, 169, Japan

The popularly accepted concept of "stress induced phase transformation (SIPT)" for tetragonal zirconia polycrystalline (TZP) ceramics has been re-evaluated in this work using an *in-situ* X-ray diffraction technique that was facilitated by the use of a novel stressing fixture. At stress levels of 700 MPa, which is close to the sample's rupture strength very little of the tetragonal phase transformed to a monoclinic phase, regardless of whether a tensile or compressive stress was applied. However the intensity of the peak $(2\,0\,2)_t$, $(2\,2\,0)_t$, $(1\,1\,3)_t$, and $(1\,3\,1)_t$, compared with the peak, $(1\,1\,1)_t$ did display a significant change after the tetragonal zirconia was loaded. In the fractured surface, a large amount of monoclinic phase was discovered. Thus we infer that for a homogenous TZP ceramic, the critical phase transformation stress is close to the material's rupture strength. On the basis of the observation of a non-linear deformation before the phase transformation, we suggest that the TZP material may have a four step response to an increasing applied stress. This response consists of; (i) anelastic behaviour which may be explained by "ferroelastic domain switching" or another anelasticity theory; (ii) $t \rightarrow m$ phase transformation; (iii) microcracks emerging and then growing; (iv) final fracture of the material and a possible reverse transformation.

1. Introduction

Following the initial report of Garvie *et al.* [1] that a strong and comparatively tough alloy could be developed in metastable tetragonal zirconia-based ceramics, this area has been intensively investigated in recent years. It is generally believed that a t to m phase transformation is the probable toughening mechanism in tetragonal zirconia. This transformation can be induced by an applied stress. Marshall and James [2] have claimed that the transformation in Mg-PSZ occurs at a stress as low as 200 MPa at room temperature and that it is reversible.

Virkar and Matsumoto [3, 4] found no transformation in the ground surfaces of their strong tetragonal zirconia samples, and this result does not accord with the concept of transformation toughening. From X-ray diffraction (XRD) patterns, they showed that the intensity ratios of the peaks t(0 0 2)/(2 0 0) and t(1 1 3)/(1 3 1) showed significant differences between the as-fired and ground surfaces. This led to the proposal of the ferroelastic domain switching (FDS) toughening mechanism.

Kitano *et al.* [5, 6] have reported that for 2Y-TZP samples almost no monoclinic phase remained in polished surface but that it was present in significant quantities in ground surfaces and in samples that had experienced a high compressive load (80% of compressive strength).

Other reports in the literature [7–9] also clearly show that transformation occurs near crack tips and leads to dilatation in these areas. Heuer *et al.* [10] have suggested the presence of a shear-induced transformation.

We believe that there is a critical stress level for the phase transformation, and only those tetragonal grains in the area where the applied stress exceeds this critical level can transform into the monoclinic phase. Research on this topic is very important if we are to understand why tetragonal zirconia possesses such high strength and high toughness properties. Although this concept is often evoked in theories concerning transformation [11, 12], this critical stress value remains unknown.

In this paper we investigate the critical stress using an X-ray diffractometer equipped with a novel stressing fixture.

2. Experimental details

2.1. Materials

3Y-TZP, tetragonal zirconia polycrystals containing 3 mol% Y_2O_3 were provided by Nikkato. All the samples were hot isostatically pressed at 1400 °C for 1.5 h. The sample size was 4 × 8 × 40 mm. The bending strength σ_b and fracture toughness K_{Ic} are about 800 MPa and 5.6 MPa $m^{1/2}$ (IF method), respectively.

0022–2461 © *1996 Chapman & Hall*

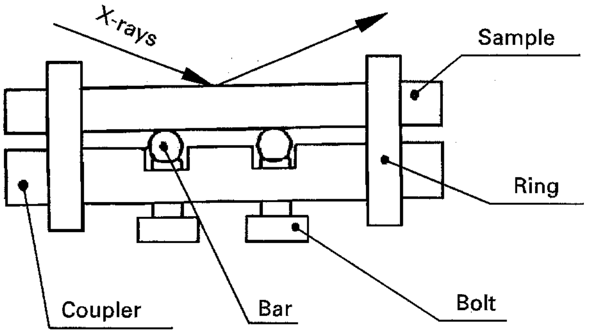

Figure 1 A stressing fixture for *in-situ* X-ray investigation.

2.2. The stressing fixture

X-ray diffraction is often used to analyse the phase composition of zirconia. Unfortunately the application of this technique to the problem of stress-induced phase transformation has been limited since the zirconia sample could only be examined after the applied stress is removed. Thus the relationship between phase transformation and applied stress cannot be directly investigated. In this work we have utilized a simple stressing fixture, as shown in Fig. 1, which allows *in-situ* investigation of the phenomenon.

The stressing fixture consists of two rings, two bolts and two bars produced in carbon steels. To create a tensile stress in the sample surface, the rings are set outside of the bolts. If a compressive stress is required, the bolts are set outside of the rings. However care is needed to ensure that the X-rays are not shielded by the rings. Driving the bolts can stress the sample until it is ruptured.

2.3. Experimental procedure

A strain gauge was attached to the sample surface near to one of its edges in order to monitor the stress level. The strain gauge and the rings were shielded by a lead sheet. The XRD difractometer used in this research is Rigaku RAD II C model with the CuK_α radiation being scanned at a speed of 0.01 deg s^{-1} across the sample. Data was collected for the 2θ range of 20–80° on the samples that had been stressed at 0, 200, 500 and 700 MPa. Finally, the ruptured surface of the sample was also investigated.

3. Results and discussion

The use of the XRD technique for phase analysis in zirconia systems has been reported in the literature by several groups [13–24]. Diffraction peaks corresponding to the monoclinic phase are observed at $2\theta = 28.3°$ for $(1\,1\,\bar{1})_\mathrm{m}$ and 31.7° for $(1\,1\,1)_\mathrm{m}$ [15]. The fraction of the monoclinic phase in the irradiated area, X_m, in a t–m two phase system, can be estimated by:

$$X_\mathrm{m} = [I(1\,1\,\bar{1})_\mathrm{m} + I(1\,1\,1)_\mathrm{m}] / [I(1\,1\,\bar{1})_\mathrm{m} + I(1\,1\,1)_\mathrm{m} + I(1\,1\,1)_\mathrm{t}] \quad (1)$$

where I is integrated intensity of the m or t peak [16]. The $(1\,1\,1)_\mathrm{t}$ reflection is the main reflection of the tetragonal phase and is located at $2\theta = 30°$.

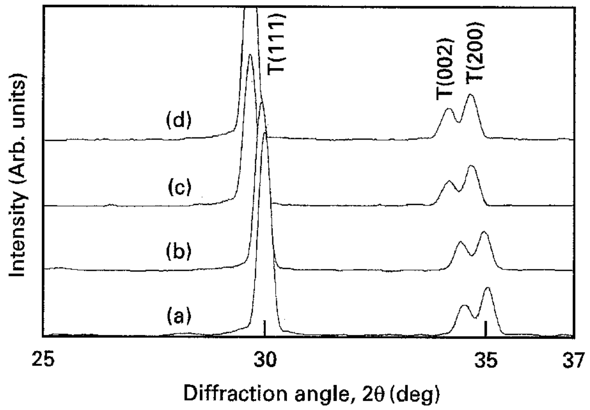

Figure 2 A series of diffraction patterns obtained at stress levels of (a) 0 MPa, (b) 200 MPa, (c) 500 MPa and (d) 700 MPa.

Fig. 2 is a series of diffraction patterns measured at different stresses. When the surface stress is zero, the diffraction pattern consists only of reflections that can be assigned to the tetragonal phase. To our surprise, after the sample was stressed between 200–700 MPa, no reflections corresponding to the monoclinic phase were observed. However, two points should be considered. Firstly, with increasing stress, the 2θ values of all of the peaks proportionally shift to lower angles. For example, in the case of $\sigma = 700$ MPa (comparing with $\sigma = 0$ MPa), the most significant shifts were observed in the low angle peaks $(0\,0\,2)_\mathrm{t}$ ($\Delta 2\theta = -0.38°$), (where $\Delta 2\theta$ is designated as "the 2θ value under loading minus the 2θ value under zero-load"), $(1\,1\,1)_\mathrm{t}$ and $(2\,0\,0)_\mathrm{t}$ (both, $2\theta = -0.34°$). In this case, the smallest shift was observed in the large angle peak $(2\,2\,2)_\mathrm{t}$ ($2\theta = -0.24°$). These shifts were nearly fully recovered after the sample stress was removed.

This behaviour is thought to be associated with elastic deformation. In fact, Virkar and Matsumoto [4] also detected a $\Delta(2\theta) = -0.05°$ for $(2\,0\,0)_\mathrm{t}$ in the ground surface of TZP ceramics. However, for most other materials, an increase and not a decrease, in the 2θ value of a peak is expected if the surface is tensioned. Also the changes in the high angle reflections, will be larger than the lower angle reflections. Thus, this diffraction result is quite different from other materials, and it will be explored in detail in the future. Perhaps it is a unique property of TZP ceramics.

Secondly, the intensities of peaks $(2\,0\,2)_\mathrm{t}$, $(2\,2\,0)_\mathrm{t}$, $(1\,1\,3)_\mathrm{t}$ and $(1\,3\,1)_\mathrm{t}$ become weaker with increasing stress, whereas the $(1\,1\,1)_\mathrm{t}$ reflection did not undergo any great changes, as is shown in Fig. 3(a and b). The changes in relative intensity of these four peaks to the $(1\,1\,1)_\mathrm{t}$ reflection, that is I/I_0, is listed in Table I (a comparison of $\sigma = 700$ MPa and $\sigma = 0$ MPa).

This behaviour is believed to be associated with ferroelastic domain switching (FDS) which was proposed by Virkar and Matsumoto [3, 4], or to grain reorientation guided by applied stress. This can be considered as the switching of crystallites from [1 0 0] and [0 1 0] orientations into the [0 0 1] orientation.

Furthermore, this FDS or reorientation seems to occur more easily in compressed surfaces. For example,

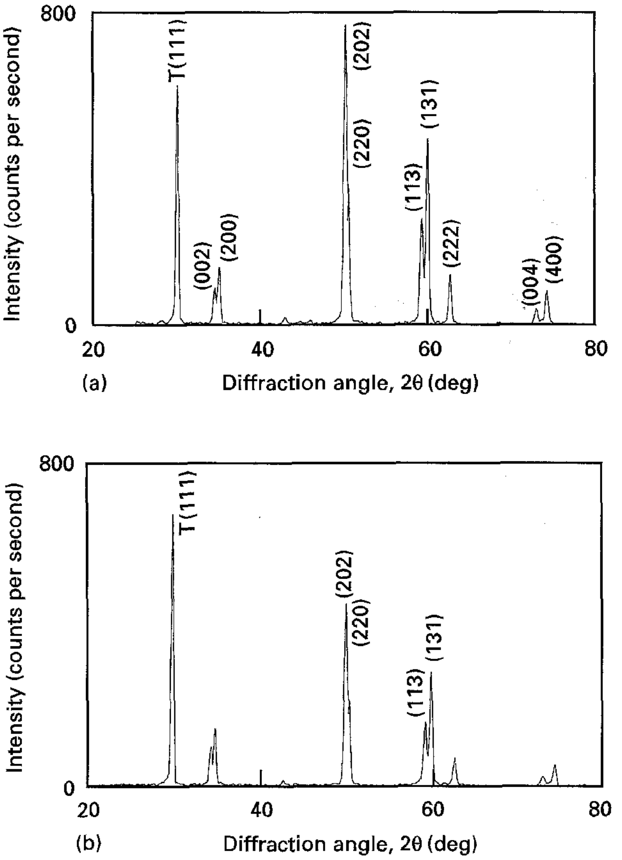

Figure 3 Comparison of two patterns: (a) $\sigma = 0$, (b) $\sigma = 700$ MPa.

TABLE I The change in intensity ratios of four peaks compared to the $(1\,1\,1)_t$ reflection after the sample was stressed

I/I_0	$(2\,0\,2)_t$	$(2\,2\,0)_t$	$(1\,1\,3)_t$	$(1\,3\,1)_t$
$\sigma = 0$ MPa	1.124	0.449	0.360	0.685
$\sigma = 700$ MPa	0.578	0.253	0.193	0.325

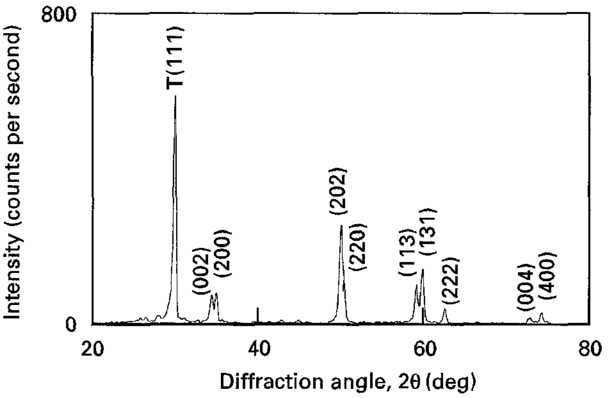

Figure 4 A diffraction pattern when the TZP was loaded with a compressive stress.

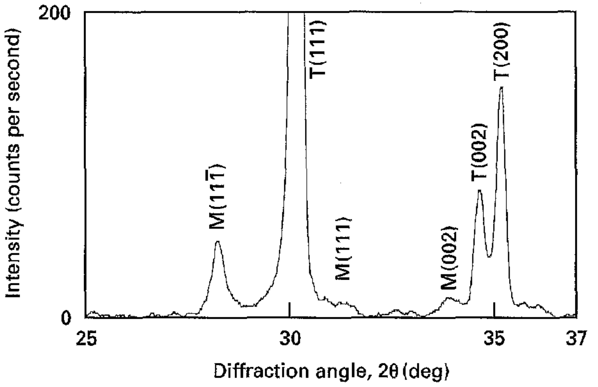

Figure 5 A diffraction pattern of a fractured surface indicating an evident monoclinic peak at $2\theta = 28.3°$.

a 300 MPa compressive stress has significantly altered the diffraction pattern, as is shown in Fig. 4.

Continuously increasing the stress, quickly leads to rupture of the sample. The XRD pattern of the ruptured sample contains satellite $(1\,1\,\bar{1})_m$ and $(1\,1\,1)_m$ peaks of the monoclinic phase (Fig. 5). This result agrees with the report of Kitano *et al.* [5], who also found the monoclinic phase in the fractured surface of TZP samples.

Based on the above investigation, we can tentatively conclude that the critical transformation stress is close to the rupture strength of the material. This is due to a fraction of the t particles transforming into relatively weaker m particles [25], and also the t → m transformation is very fast [12]. In addition, the sample contained no macro crack, and it is very difficult in this case to slow the stressing speed down when the first batch of t particles begin to transform. Therefore, it is thought that the bending sample suddenly ruptured.

We believe that in order to observe the phase transformation clearly, a non-uniform stress field is necessary. This is in agreement with several reports in the literature. For example, Liu *et al.* [7], Hannink *et al.* [26], Ruhle *et al.* [27], Marshall [28], Marshall and Swain [29], Grathwohl and Liu [30], showed that evident dilatation bands (these are verified to be a result of t → m transformation) exist around the macrocracks or the indented traces, but very few occur in relatively lower stress areas.

In the work of Kitano *et al.* on Y-TZP ceramics, monoclinic phases were only detected in very small quantities in as-fired or polished surfaces [5], but were found in fractured and ground surfaces [6] in a sample that had experienced a stress of 80% of the compression strength. We suppose that there is not enough stress to drive transformation during the polishing process.

4. A fracture model for TZP ceramics

The stress to produce a rupture of the material could be rather complicated, with shear stress being thought to be important for transformation [10]. However the simplest stress is tensile stress which is usually used to analyse the mechanical properties of materials. Fig. 6 is typical stress–strain relation of a TZP sample measured in a monotonic tensile test with a stress speed of 2.5 MPa s^{-1}. It obviously shows that a pure-elastic relationship could not be maintained even at a low stress level and a non-linear deformation is evident.

Thus we suggest, that when a TZP sample is loaded in tension, its response may be divided into the following four stages with the increase of stress.

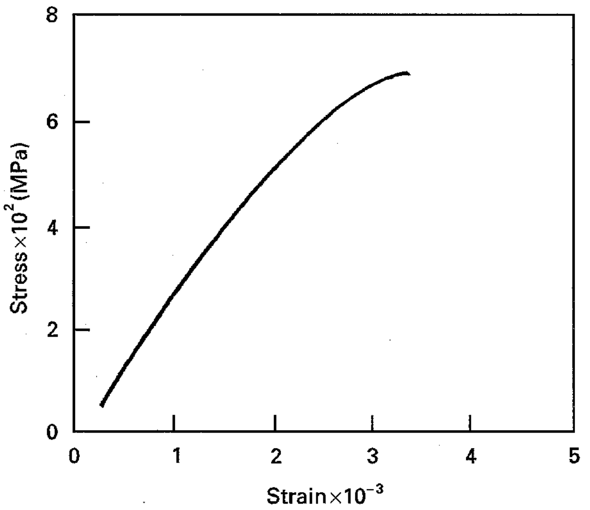

Figure 6 Stress versus strain curve of 3Y-TZP ceramic in monotonic tensile test. (2.5 MPa s^{-1}, at room temperature.)

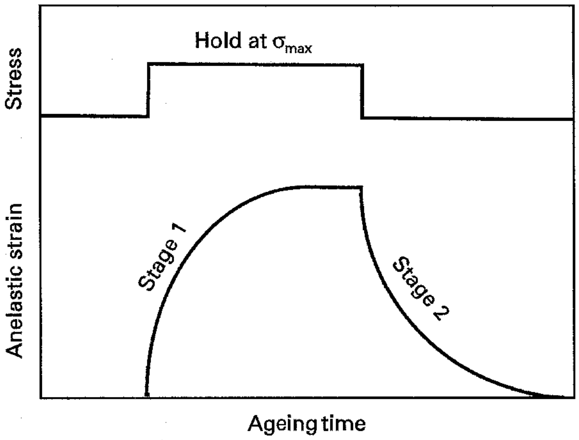

Figure 7 Schematic illustration of anelastic behaviour of TZP ceramics in prestage of phase transformation.

4.1. Anelasticity of TZP

In our research of hysteresis loops in TZP, we found that the TZP material exhibits an anelastic response (schematically represented in Fig. 7) to the applied stress, at any level lower than its rupture strength (that means the prestage of transformation.), as is shown in Fig. 8(a). This behaviour is thought to be concerned with grain reorientation by Virkar and Matsumoto [3, 4], or pseudo-elasticity and shape memory as discussed by Reyes-Morel *et al.* [31].

This stage is the longest one and depends on the stress (or crosshead) speed and rupture strength σ_b (or critical t → m transformation stress σ_{cT}). In a cyclic fatigue test, it is assumed that this anelasticity may affect the lifetime, and that it may depend on the load frequency. In the TZP sample containing a macrocrack it may absorb a part of the crack-driving energy and so results in a toughening effect which may even contribute more than transformation or microcracking, if the frequency (cyclic) or crosshead speed (monotonic) is not too high.

Detailed work on this subject will be reported in a future publication.

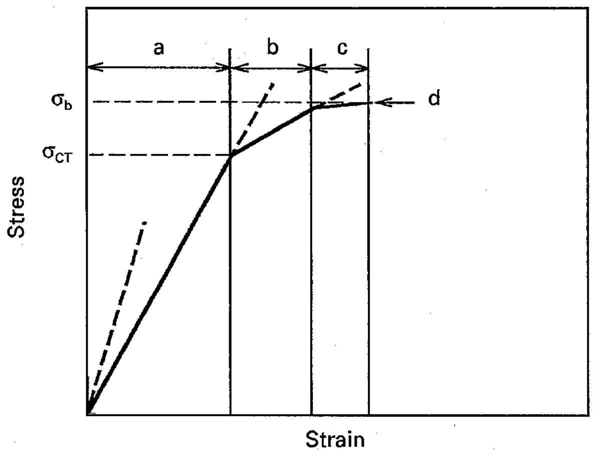

Figure 8 Schematic illustration of four stages response when a TZP ceramic was tensioned.

4.2. Transformation stage

From a microscopic viewpoint, stress distribution is actually inhomogeneous in a polycrystalline system. When the applied stress at some location increases up to critical level σ_{cT} (near the rupture strength, as discussed previously.), the first batch of t particles may begin to transform to m particles and thus the strength at this area becomes weaker, Fig. 8(b). Additional stressing may catalyse other t particles to transformation.

In the above analysis, the homogeneity of the stress field is very important for the process of phase transformation. If the grain size of the TZP sample is smaller, a relatively uniform stress may be formed, therefore the σ_{cT} value may be close to the σ_b value.

This t → m transformation is of the martensite type, and this stage may be very short.

4.3. Microcracking stage

This stage may occur simultaneously in the later period of the transformation stage. Microcracks most probably nucleate at high residual stress areas, e.g., the boundaries of t and m particles [32–34]. A larger grained material may possess much more stress inhomogeneity, which also favours the production of microcracks.

The microcracking may absorb energy, and thus can be regarded as contributing to the toughening mechanism. However a large number of microcracks may weaken the whole strength of the material (Fig. 8(c)).

4.4. Rupture stage

When the weakened TZP can no longer balance the applied load, an unsteady cracking and final fracture is unavoidable (Fig. 8(d)).

The fraction of the monoclinic in the fractured surface depends on; (1) the degree of anelasticity, which is related to the stress speed; (2) the tendency to microcracking which is related with grain size. This is because anelastic deformation and a large number of microcracks may reduce the driving energy for phase transformation.

A reversible transformation [2, 23] after rupture or load removal may also possibly reduce the amount of the monoclinic phase.

5. Conclusions

Based on the *in-situ* investigation of the critical transformation stress of Y-TZP ceramics, we conclude:

(1) The critical t → m phase transformation stress of toughened high-strength TZP ceramic, σ_{cT}, is close to its rupture strength, σ_b.

(2) An applied stress below this critical value can not induce t particles to transform to m grains, but it may cause strong anelastic behaviour related to grain reorientation, which is reflected in the weakening of the the diffraction intensities of the $(2\,0\,2)_t$, $(2\,2\,0)_t$, $(1\,1\,3)_t$ and $(1\,3\,1)_t$ peaks.

(3) Together with transformation and microcracking, anelasticity is also thought to contribute to the high toughness in TZP ceramics. A more evident toughening effect is expected in a lower load speed (monotonic) or frequency (cyclic) test.

(4) When a TZP ceramic is monotonously loaded, it is thought to experience four stages of deformation, namely, anelastic behaviour, t → m transformation, microcracking and catastrophic destruction.

Acknowledgement

We gratefully thank Mr. J. Yasui of Waseda University for his help during the experimental work and also for helpful discussion on this work.

References

1. R. C. GARVIE, R. H. HANNINK and R. T. PASCOE, *Nature* **258** (1975) 703.
2. D. B. MARSHALL and M. R. JAMES, *J. Amer. Ceram. Soc.* **69** (1986) 215.
3. A. V. VIRKAR and R. L. K. MATSUMOTO, *ibid* **69** (1986) C-224.
4. *Idem* "Advances in Ceramics Vol. 24: Science and Technology of Zirconia III". (American Ceramic Society, Westerville OH, 1988) 653–62.
5. Y. KITANO, Y. MORI, A. ISHITANI and T. MASAKI, *J. Amer. Cerm. Soc.* **71** (1988) C-382.
6. *Ibid, idem.* **72** (1989) 854.
7. T. LIU, Y. W. MAI, M. V. SWAIN and G. GRATHWOHL, *J. Mater. Sci.* **29** (1994) 835.
8. P. E. REYES-MOREL and I. W. CHEN, *J. Amer. Ceram. Soc.* **71** (1988) 343.
9. M. V. SWAIN, "Zirconia Ceramics 10" (1988) 47.
10. A. H. HEUER, F. F. LANGE, M. V. SWAIN and A. G. EVANS, *J. Amer. Ceram. Soc.* **69** (1986) i–iv.
11. S. HORI, "Toughened High Strength Zirconia Ceramics" (Uchida Rokakuho, Tokyo, 1990) (in Japanese).
12. D. J. GREEN, R. H. HANNINK and M. V. SWAIN, "Transformation Toughening of Zirconia" (CRC Press, 1989).
13. T. KOSMAC, R. WAGNER and N. CLAUSSEN, *J. Amer. Ceram. Soc.* **64** (1981) C-72.
14. P. DUWEZ and F. ODELL, *ibid.* **32** (1949) 180.
15. T. K. GUPTA, J. H. BECHTOLD, R. C. KUZNICKI, L. H. CADOFF and B. R. ROSSING, *J. Mater. Sci.* **12** (1977) 2421.
16. R. C. GARVIE, R. H. J. HANNINK and M. V. SWAIN, *J. Mater. Sci. Lett.* **1** (1982) 437.
17. H. TORAYA, M. YOSHIMURA and S. SOMIYA, *J. Amer. Ceram. Soc.* **67** (1984) C-119.
18. Y. KITANO, Y. MORI, A. ISHITANI and T. MASAKI, in "Zirconia Ceramics 11" (1991) 15, (in Japanese).
19. P. M. KELLY and C. J. BALL, *J. Amer. Ceram. Soc.* **69** (1986) 259.
20. T. MITSUHASHI, M. ICHIHARA and U. TATSUKE, *ibid* **57** (1974) 97.
21. R. C. GRAVIE and P. S. NICHOLSON, *ibid* **55** (1972) 303.
22. E. H. KISI, C. J. HOWARD and R. J. HILL, *ibid* **72** (1989) 1757.
23. D. B. MARSHALL and M. V. SWAIN. *ibid* **72** (1989) 1530.
24. A. H. HEUER and M. RUHLE, in "Advances in Ceramics Vol. 12, Science and Technology of Zirconia II". (American Cermaic Society, Westerville OH, 1983). pp 1–13.
25. T. K. GUPTA, F. F. LANGE and J. H. BECHTOLD, *J. Mater. Sci.* **13** (1978) 1464.
26. R. H. J. HANNINK, C. J. HOWARD, E. H. KISHI and M. V. SWAIN, *J. Amer. Ceram. Soc.* **77** (1994) 571.
27. M. RUHLE, A. STRECKER, D. WAIDELICH and B. KRAUS, in "Advances in Ceramics Vol. 12, Science and Technology of Zirconia II". (American Ceramic Society, Westerville OH, 1983), pp. 256–74.
28. D. B. MARSHALL, *J. Amer. Ceram. Soc.* **73** (1990) 3119.
29. D. B. MARSHALL and M. V. SWAIN, *ibid* **71** (1988) 399.
30. G. GRATHWOHL and T. S. LIU, *ibid* **74** (1991) 3028.
31. P. E. REYES-MOREL, J. S. CHERNG and I. W. CHEN, *ibid* **71** (1988) 648.
32. A. G. EVANS and R. M. CANNON, *Acta Metall.* **34** (1986) 761.
33. M. BOWDEN, G. D. DICKSON, D. J. GARDINER and D. J. WOOD, *J. Mater. Sci.* **28** (1993) 1031.
34. I. W. CHEN and P. E. REYES-MOREL, *J. Amer. Ceram. Soc.* **69** (1991) 181.

Received 8 August 1995
and accepted 13 June 1996