

Effect of stress-induced phase transformation on the properties of polycrystalline zirconia containing metastable tetragonal phase

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Polycrystalline zirconia containing a high content of metastable tetragonal phase shows high strength (~ 700 MPa), high fracture toughness ($K_{IC} = 6$ to $9 \text{ MN m}^{-3/2}$) and small grain size ($< 0.3 \mu\text{m}$). The strength and grain size remain nearly constant over a wide range of tetragonal phase content (100 to 30%). At a low concentration of tetragonal phase $< 30\%$, there is a rapid decrease in strength accompanied by a rapid increase in grain size. These results are explained by means of a stress-induced phase transformation in the metastable tetragonal phase.

1. Introduction

The existence of a relatively tough partially stabilized zirconia ceramic, consisting of a dispersion of metastable tetragonal ZrO_2 inclusions within large grains of stabilized cubic ZrO_2 , has recently been reported [1]. Analogous to the case of TRIP steels, it has been suggested that the toughness of this polyphase zirconia ceramic is derived from the observed stress-induced tetragonal/monolithic transformation that occurs during crack extension [1]. More recently, Gupta *et al.* [2] have reported the fabrication of a dense, fine-grained, polycrystalline zirconia ceramic containing up to 98% of the metastable tetragonal phase. Small additions of Y_2O_3 were used to retain the metastable phase. They have shown that (a) the retention of the metastable tetragonal phase is critically dependent on the sintering conditions, (b) when the monoclinic phase is present, it first appears on the surface of sintered bodies, (c) a stress-induced tetragonal/monoclinic transformation occurs during fracture, and (d) high strength appears when the tetragonal phase content is high, and low strength when the monoclinic phase content is high.

This paper is concerned with reporting the toughness and strength of sintered materials containing the metastable, tetragonal phase. Theoretical arguments are presented to indicate the relationship between fracture toughness, strength and the volume content of the metastable phase. Toughness and strength data are discussed in relation to predicted behaviour and in terms of the observed grain size effect, which appears to be a critical factor governing the retention of the metastable phase.

2. Relationship of stress-induced phase transformation to fracture toughness and strength

For the case of metastable austenitic materials that undergo a stress-induced martensitic transformation, it has been suggested that the phase transformation in front of a crack is equivalent to a non-elastic deformation, and as such, is capable of absorbing energy that would have otherwise been available for crack extension [3]. Another reason for energy absorption can also be given for the case of stress-induced phase transformation during crack extension in brittle materials. Due to the

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volume change that occurs during phase transformation, stress-induced transformation can be accompanied by the formation of a small crack within or in the vicinity of the transformed particle. The formation of many small cracks in front of a larger crack would greatly increase the amount of surface area formed per unit extension of the larger crack and thus, in effect, greatly increase the energy absorbed during crack extension. Whatever mechanism one chooses, it is sufficient to assume for the following analysis that a certain amount of energy, U_0 , is absorbed per unit volume of stress-induced, transformed material.

The condition of crack extension can be obtained by determining the energy changes that would occur during crack extension and then invoking Griffith's thermodynamic criterion that the free energy change during crack extension must be ≤ 0 . This condition can be easily determined for the case of a slit crack of length, c , located within a sheet of material of unit thickness, T .

The energy changes that must be determined for a unit crack extension dc are the net work dU_w done by the applied tensile stress σ , the energy absorbed dU_s during the creation of new surface area, and the energy absorbed dU_p by the volume of material at the crack front that undergoes the stress-induced phase transformation.

As first shown by Griffith [4] for the same crack configuration examined here, the net work U_w and the energy U_s absorbed to form new surfaces per unit crack extension dc are $dU_w = 2\pi\sigma^2 cTdc/E$ and $dU_s = 2\gamma Tdc$, respectively, where γ = the surface energy per unit area, and E = the elastic modulus. Following similar arguments first proposed by Antolovich [3] for determining the energy absorbed by phase transformation at the crack front in TRIP steels, it can be shown that;

$$dU_p = U_0 fDTdc, \quad (1)$$

where U_0 = the energy absorbed per unit volume of stress-induced transformed material, and f = the volume fraction of the metastable phase within the material; D is one dimension of the volume of material undergoing transformation at the crack front for the critical condition, and dc , the unit

crack extension, is the other dimension of this volume.

The total energy change during a unit of crack extension is;

$$dU = -dU_w + dU_s + dU_p \quad (2)$$

or

$$dU = \frac{-2\pi\sigma^2 cTdc}{E} + 2\gamma Tdc + U_0 fDTdc. \quad (3)$$

Using Griffith's criterion for crack extension;

$$\frac{dU}{dc} \leq 0 = \frac{-2\pi\sigma^2 cT}{E} + 2\gamma T + U_0 fDT, \quad (4)$$

one obtains the critical applied stress, σ_c , required to cause crack extension;

$$\sigma_c = \left[\frac{(2\gamma + U_0 fD)E}{2\pi c} \right]^{1/2}. \quad (5)$$

The factor in this equation representing the critical strain energy release rate G_c or the fracture energy is

$$G_c = 2\gamma + U_0 fD.$$

Relating the critical strain energy release rate to the critical stress intensity factor K_{Ic} ;

$$K_{Ic} = (G_c E)^{1/2} = [(2\gamma + U_0 fD)E]^{1/2}. \quad (6)$$

Both G_c and K_{Ic} are measures of the material's fracture toughness.

As shown above, the term $U_0 fD$, which is the energy dissipated at the crack front by the phase transformation, strongly suggests that a stress-induced phase transformation could increase the fracture toughness and strength of a ceramic material. The significance of this term on toughness and strength depends on the energy dissipated (U_0) by the transformation per unit volume of the metastable phase, the volume fraction (f) of the metastable phase, and the dimensions (expressed by D) of the material that is affected by the highly localized stress field at the crack front.

3. Experimental procedures

Discs and small rectangular billets were fabricated to contain different ratios of tetragonal to monoclinic phases by a technique previously described [2]. Phase determinations were made on as-sintered surfaces by X-ray diffraction.* Strength

*Powder samples could not be examined since pulverizing caused the tetragonal phase to transform to the monoclinic phase.

TABLE I Estimate of fracture toughness by indentation*

Specimen no.	\bar{a} (m)	(\bar{c}/a)	H (GN m ⁻²)	$\phi(H/\phi E)^{0.4}$	$K_c \phi(H/\phi E)^{0.4}$	K_c (MN m ^{-3/2})	% Tetragonal	
				$H\sqrt{a}$ (GN ⁻¹ m ^{3/2})	$H\sqrt{a}$ (dimensionless)		As-sintered	Polished
68	1.38×10^{-4}	1.31	12.1	5.04	0.0457	9.07	17	88
66	1.41×10^{-4}	1.99	11.6	5.11	0.0363	7.11	14	> 79
52	1.40×10^{-4}	1.66	11.7	5.10	0.0400	7.84	88	> 88
59	1.43×10^{-4}	2.39	11.2	5.18	0.0314	6.07	97	> 92
11	1.37×10^{-4}	1.74	12.3	5.00	0.0386	7.71	46	> 85
21	1.42×10^{-4}	1.29	11.4	5.18	0.0457	8.82	14	> 86
60	1.40×10^{-4}	1.31	11.7	5.10	0.0457	8.96	82	> 87

*Note: Load = 50 kg, $E \approx 145 \text{ GN m}^{-2}$

data were obtained using disc specimens (1.9 cm diameter and ~ 0.15 cm thick) which were placed in symmetrical biaxial flexure [5]. Fracture toughness was determined on polished specimens by an indentation technique with the Vickers indenter. From a measurement of hardness H , indentation crack length C and the indentation impression radius a , the value of K_c was determined by using the calibration curve developed by Evans and Charles [11].

4. Results

4.1. Fracture toughness

Fracture toughness data for several specimens as determined by an indentation technique are shown in Table I. The value of the stress intensity factor K_c ranges between 6 and 9 MN m^{-3/2}. These values were obtained by first estimating the quantity $\phi[H/\phi E]^{0.4}/H\sqrt{a}$ by using $E \approx 145 \text{ GN m}^{-2}$ and $\phi \approx 3$, E and ϕ being the Young's modulus and the constraint factor [11] respectively, and knowing the values of a and H from experimental measurements. The dimensionless parameter $K_c \phi[H/\phi E]^{0.4}/H\sqrt{a}$ was then obtained from the calibration curve [11] by using the experimentally obtained values of c/a . The ratio of the two quantities yielded the magnitude of K_c . All the experimentally obtained and calculated parameters are shown in Table I. The table also contains the amount of tetragonal phase present in the specimens which were subjected to fracture toughness measurement. As seen in the table, these specimens contained initially a varying amount of tetragonal phase as determined from the X-ray analysis of the "as-sintered" surface, but the "polished" surface on which the fracture toughness measurement was made showed the tetragonal phase as the major

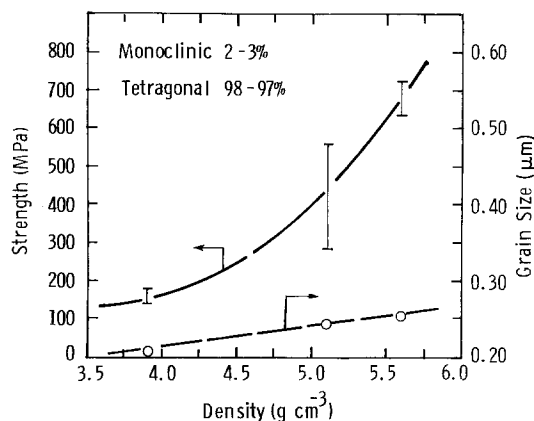


Figure 1 Strength and grain size as a function of density in ZrO₂ ceramics.

constituent irrespective of the original surface conditions. The difference in bulk and surface structure was also observed previously [2].

4.2. Strength versus density

The biaxial flexure strength of incompletely dense materials is illustrated in Fig. 1. The tetragonal content of these materials was $\geq 97\%$. As shown, the strength increases with increasing density as commonly observed for conventional ceramics.

4.3. Strength versus tetragonal phase content: dense materials

The biaxial tensile strength as a function of the metastable tetragonal phase content[†] is illustrated in Fig. 2. As previously reported [2], the phase content of each material was controlled by the sintering conditions. The density of all materials indicated in Fig. 2 was $5.6 \pm 0.1 \text{ g cm}^{-3}$. The scatter is the observed range of four strength determinations for each material.

[†]It should be emphasized that the phase content was determined by X-ray diffraction of the materials' surfaces. Other work shows that the ratio of the tetragonal to monoclinic phases is much greater within the material than on its surface [2].

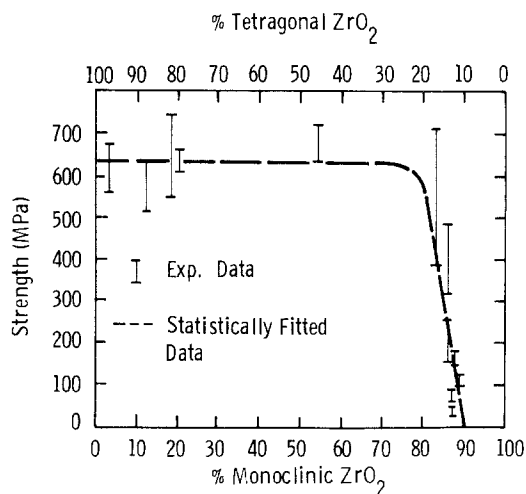


Figure 2 Strength versus tetragonal phase content in ZrO_2 ceramics.

Several important observations can be made from the data presented in Fig. 2. First, when the ZrO_2 specimens contain a large amount of monoclinic phase ($\sim 90\%$), the strength is very poor (< 100 MPa). Second, as the metastable tetragonal content is increased to $\sim 30\%$, there is a rapid increase in strength. Finally, a constant high strength (600 to 700 MPa) is maintained when the apparent tetragonal content is between 30 and 100%.

A network of surface cracks was observed in materials containing $< 30\%$ of the tetragonal phase. The formation of cracks during the cooling of unstabilized ZrO_2 ceramics is usually attributed to the tetragonal to monoclinic phase transformation.

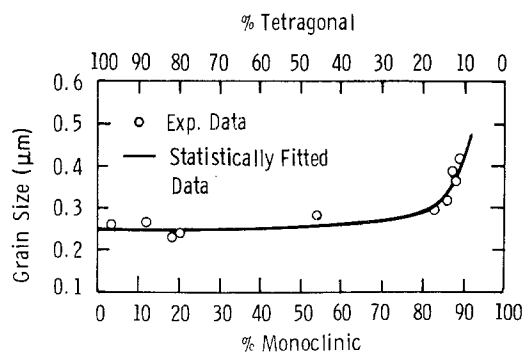


Figure 4 Grain size versus tetragonal phase content in ZrO_2 ceramics.

4.4. Microstructural observations

As illustrated by the two micrographs in Fig. 3, the fracture surface topography shows that the grains are equiaxed and that fracture is intergranular regardless of the tetragonal phase content.

The grain size of all the materials examined was $< 1 \mu m$. During densification, the average grain size increased from $\sim 0.2 \mu m$ for materials with a density of 4.0 g cm^{-3} to $\sim 0.25 \mu m$ for densities of 5.6 g cm^{-3} (see Fig. 1). Once a density of 5.6 g cm^{-3} was achieved, grain size remained nearly constant to a tetragonal content of $\approx 30\%$. Significant grain growth occurred only when the sintering conditions led to materials containing $\leq 30\%$ of the tetragonal phase, as illustrated in Fig. 4.

The strength of dense materials is plotted as a function of grain size in Fig. 5, illustrating that a critical grain size exists in order ($\sim 0.32 \mu m$) to obtain a high strength material. Materials with a grain size $> 0.32 \mu m$ contained substantial amounts

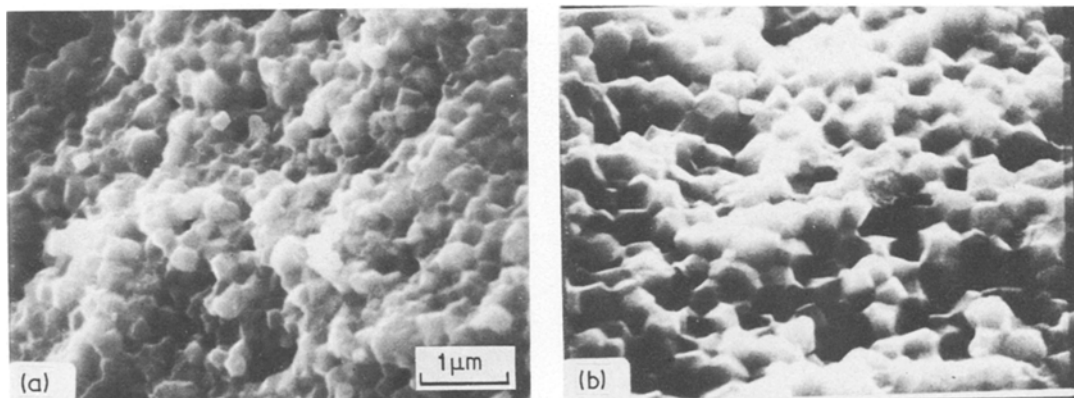


Figure 3 Scanning electron micrograph of PSZ ceramics containing (a) 97% tetragonal phase and (b) 13% tetragonal phase. The balance is the monoclinic phase in each case.

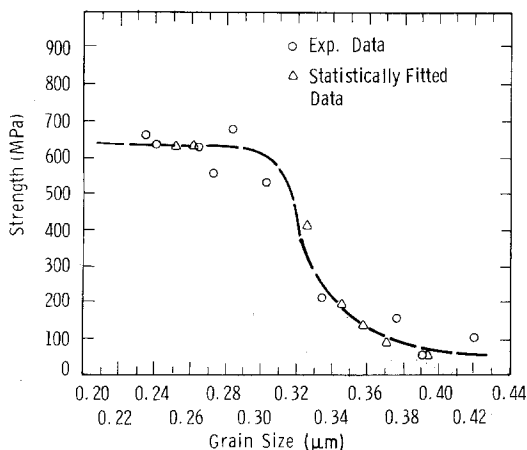


Figure 5 Strength versus grain size in ZrO_2 ceramics.

of the monoclinic phase, which resulted in large surface cracks and poor strengths.

5. Discussion

5.1. Fracture toughness

Evans and Charles [11] claim that the indentation technique enables fracture toughness data to be obtained within an accuracy of 10 to 30%. To resolve this uncertainty, fracture toughness was also obtained on two pre-cracked, double-beam cantilever [9] specimens ($0.1 \text{ cm} \times 1.5 \text{ cm} \times 3.0 \text{ cm}$) containing $>80\%$ tetragonal phase. The average K_{Ic} value obtained by this technique was $6.4 \text{ MN m}^{-3/2}$. Thus the two measurements agreed within experimental error.

These values of K_{Ic} are higher than those of most other structural ceramics and substantially higher than that of partially stabilized zirconia containing no metastable phase (Table II). This latter value was estimated roughly from the reported values of fracture surface energy γ_i and the Young's modulus E for a partially stabilized

TABLE II Fracture toughness of various materials

Materials	K_{Ic} ($\text{MN m}^{-3/2}$)	References
ZrO_2 (metastable phase)	6–9	Present study
ZrO_2 (PSZ-stable phase)	1.1	6
Si_3N_4	4.8–5.8	9
SiC	3.4	10
B_4C	6.0	11
Al_2O_3	4.5	Unpublished data
Sapphire (single crystal)	2.1	11
Spinel (single crystal)	1.3	11

zirconia containing a stable monoclinic phase [6]. The K_{Ic} value for the partially stabilized zirconia containing the monoclinic phase is estimated to be $\approx 1.1 \text{ MN m}^{-3/2}$ from the literature, whereas the observed K_{Ic} values for ZrO_2 containing the metastable tetragonal phase is between 6 and $9 \text{ MN m}^{-3/2}$. Since evidence has been obtained from these same materials that the tetragonal to monoclinic transformation occurs in the vicinity of the crack during fracture [2], it is reasonable to suggest that the stress-induced transformation is responsible for the material's high fracture toughness as outlined by the theoretical arguments in Section 2. However, an attempt to determine the fracture toughness of zirconia specimens containing a varying amount of tetragonal phase was not realized in the present study, since the bulk structure of the specimen on which the measurement was made contained high amounts of tetragonal phase, irrespective of surface conditions (Table I). In other words, specimens could not be prepared containing varying amounts of tetragonal phase which could verify the prediction of the theory. Further work is necessary in this area.

5.2. Strength

Unlike fracture toughness, strength values were found to be controlled by the outer surface conditions of the specimens, and a correlation was observed with the amount of tetragonal/monoclinic ratio on the outer surface. As shown in Fig. 2, as the amount of metastable tetragonal phase is increased from 0 to 30% there is a dramatic increase in strength, in agreement with the prediction in Equation 5. However, the most significant observation of the present study is that the strength remained constant to a high value of ~ 600 to 700 MPa when the tetragonal content was increased from 30 to 100%. This is not apparent from the theory. This inconsistency might be resolved by assuming that the stress-induced transformation zone (D) is changed with higher content of apparent tetragonal phase. Further work is necessary in this area. In spite of this difference between experimental observation and the theoretical argument it is clear from the data that the presence of metastable tetragonal phase has a significant influence on overall strength. However, this beneficial effect of tetragonal phase on strength is absent when the material is incompletely dense (Fig. 1). The strength values are then governed by porosities, as is observed in conventional ceramics.

The contribution of stress-induced phase transformation to high strength can be inferred from the strength versus grain size data presented in Fig. 5. At low strength (<200 MPa) the primary phase is monoclinic [2], so there is little contribution to strength from phase transformation, and therefore the strength shows an increase with decreasing grain size from ~ 0.42 to $\sim 0.34 \mu\text{m}$, as is common with conventional ceramics. At high strength (>600 MPa) where the primary phase is tetragonal [2], there is again a slight increase in strength with decrease in grain size from ~ 0.30 to $\sim 0.24 \mu\text{m}$, in accordance with the behaviour in conventional ceramics. The most significant observation in the present study is the rapid increase in strength, from 200 to 600 MPa, for a modest decrease in grain size from ~ 0.34 to $\sim 0.30 \mu\text{m}$. In view of the strength versus grain size behaviour at high and low strengths, this three-fold increase in strength in a narrow grain size range cannot be attributed to the small grain size alone. It is concluded that the rapid discontinuous increase in strength from 200 to 600 MPa is due to the rapidly increasing contribution of stress-induced phase transformation to strength in the narrow grain size region between 0.34 and $0.30 \mu\text{m}$. This grain size region appears to be very critical for the stability of the tetragonal phase as discussed in the next section.

Finally, when the values of $K_c = 6.4 \text{ MN m}^{-3/2}$ and $\sigma = 650 \text{ MPa}$ are substituted into the stress intensity relation for surface flaws [7],

$$K_c = 1.1 \sigma \sqrt{\pi c}, \quad (7)$$

one estimates that the smallest flaw size responsible for the fracture of the materials examined above is $\sim 25 \mu\text{m}$, that is a value several orders of magnitude larger than the average grain size of these materials. Thus it can be concluded that the grains within the material are *not* the incipient flaws responsible for fracture, and that the usual fracture mechanics expressions do not predict the observed strength–grain size effect.

5.3. Critical grain size

The data in Fig. 5 illustrate that a significant strength degradation occurs when the average grain size exceeds $\sim 0.30 \mu\text{m}$. Since these same low strength materials show surface cracks and are largely monoclinic, it can be assumed that the

surface cracks were caused by the tetragonal/monoclinic transformation which occurred during cooling from the fabrication temperature. Thus it appears that the retention of the metastable tetragonal phase, or conversely, the formation of the surface cracks due to the tetragonal/monoclinic transformation, is strongly influenced by grain size.

The concept of a critical grain size* for the stability of the metastable phase in a solid matrix can be viewed from a mechanistic standpoint. Consider a single grain of tetragonal material embedded within a matrix of the same material. If the matrix constrains the particle from increasing its volume at and below the transformation temperature, then the tetragonal structure will persist. If, on the other hand, a crack were to form adjacent to the particle, much (or all) of the matrix constraint would be released and the tetragonal/monoclinic transformation would be observed. With this view, the conditions required to retain the metastable tetragonal phase are the same as the conditions to prevent crack extension.

The conditions required to extend a crack within the highly localized stress field associated with an embedded particle have been previously presented [8] for the case where the stresses arise from the differential thermal expansion of the particle and the matrix materials. For the present case, the stresses arise from the constraints exerted by the matrix to prevent the volume change of the particle by phase transformation. If it is assumed that all dilations are isotropic, (or the tensor describing the dilations are the same for both cases) it can be shown that the stress distributions are identical for both cases and thus the previous analysis will apply to the present case.

The principal result obtained by examining the energetics of crack extension adjacent to (or within) an embedded particle is that the condition for crack extension not only depends on the maximum stress (σ_m) associated with the particle, but also depends on the particle size (d) which determines the amount of stored strain energy. This result can be summarized by an equation that states that crack extension can only occur when

$$\sigma_m^2 d > \text{constant}. \quad (8)$$

*The concept of a critical particle size for the stability of the metastable phase in the powder form has been discussed by Garvie [12] from a thermodynamic standpoint.

The constant on the RHS of this equation contains the fracture energy and elastic properties of the material and a factor that includes the size of the pre-existing crack (or flaw) at the particle–matrix interface.

The importance of this result as it applies to the present case is that it predicts a critical particle size (d_c) (or grain size) below which crack extension cannot occur, namely

$$d_c = \frac{\text{constant}}{\sigma_m^2} \quad (9)$$

Thus, if the retention of the metastable tetragonal phase depends on the constraint of the surrounding matrix and crack extension is the mechanism which releases this constraint, it can be concluded that the retention of the metastable tetragonal structure within a polycrystalline ZrO_2 body will depend on the grain size. This conclusion is qualitatively consistent with observations.

6. Summary and conclusions

It is shown that the partially stabilized zirconia ceramics containing a metastable tetragonal phase in the range of ~ 100 to 30% show high strength and high fracture toughness. The strength values were observed in the neighbourhood of 700 MPa and the fracture toughness (K_{Ic}) was estimated to be ~ 6 to $9 \text{ MN m}^{-3/2}$. The grain size remained constant at a value of about $\sim 0.25 \mu\text{m}$ up to a tetragonal content of $\sim 70\%$, followed by a slow increase between the tetragonal content of ~ 70 to 30%. In the range of ~ 20 to 10% of the tetragonal phase, there was a major change in both strength and grain size. There was a steep decline in strength to ~ 100 MPa, accompanied by a steep increase in grain size to $> 0.3 \mu\text{m}$. The mode of fracture was, however, always intergranular, irrespective of the amount of phases present. From the data presented in this paper,

it is concluded that the metastable phase, due to its ability to undergo stress-induced phase transformation, contributes to high strength and high fracture toughness in partially stabilized zirconia. It is also concluded that there is a critical grain size of $\sim 0.32 \mu\text{m}$ below which the metastable phase is stable.

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References

1. R. C. GARVIE, R. H. J. HANNINK and R. T. PASCOE, *Nature* **258** (1975) 703.
2. T. K. GUPTA, J. H. BECHTOLD, R. C. KUZNICKI, L. H. CADOFF and B. R. ROSSING, *J. Mater. Sci.* **12** (1977) 2421.
3. S. D. ANTOLOVICH, *Trans. Met. Soc. AIME* **242** (1968) 2371.
4. A. A. GRIFFITH, *Phil. Trans. Roy. Soc.* **A221** (1920) 163.
5. T. R. WILSHAW, *J. Amer. Ceram. Soc.* **51** (1968) 111.
6. D. J. GREEN, P. S. NICHOLSON and J. D. EMBURY, *J. Amer. Ceram. Soc.* **56** (1973) 619.
7. G. R. MARRS and C. W. SMITH, "Stress Analysis and Growth of Cracks", ASTM STP 513 (1972) p.22.
8. F. F. LANGE, "Fracture Mechanics", Vol. 2, edited by R. C. Bradt, D. P. H. Hasselman and F. F. Lange (Plenum, 1974) P. 599.
9. F. F. LANGE, *J. Amer. Ceram. Soc.* **56** (1973) 518.
10. A. G. EVANS and F. F. LANGE, *J. Mater. Sci.* **10** (1975) 1959.
11. A. G. EVANS and E. A. CHARLES, *J. Amer. Ceram. Soc.* **59** (1976) 371.
12. R. C. GARVIE, *J. Phys. Chem.* **69** (1965) 1238.

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