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Residual stress effects and t → m transformation in ion-implanted yttria-stabilized zirconia

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Ion-beam treatment affects the near surface region of ceramic materials and is a potential technology in altering the surface microstructure and properties. In this study, a preliminary surface modification in yttria-stabilized zirconia was investigated through the employment of ion implantation. Fracture toughness and hardness were measured and evaluated by the indentation method for specimens implanted by direct As^+ bombardment. With the aid of residual stress measurement by X-ray diffraction, the properties of the implanted specimens can be related to the residual compressive stress induced by irradiation effects. Thermal stability of zirconia is improved due to the suppression of the tetragonal to monoclinic transformation in the presence of the residual compressive stress.

1. Introduction

Few materials show as much potential as zirconia-based ceramics for such a wide range of advanced and engineering ceramic applications, including extrusion dies, cutting tools, machinery wear parts, insulation and coating. The technological opportunities so available are attributed to the discovery that the stress-induced tetragonal to monoclinic t → m phase transformation in fine ZrO_2 grains occurs in the vicinity of a propagating crack [1–3]. To its full potential, the properties of zirconia have been modified by the addition of MgO, Y_2O_3 and Al_2O_3 [1, 4–9]. However, the advantages afforded by t → m phase transformation have to be offset against the disadvantages, particularly with regard to the effects of low-temperature ageing in air or in a humid atmosphere, in which degradation of properties is observed [10–14]. To solve this problem, approaches have been employed including the addition of cerium oxide [6, 15–18] or doping ceria on the surface through a solid state reaction [19]. Nevertheless, it is still a challenge to suppress the ageing degradation and at the same time to retain good mechanical properties in ZrO_2-based ceramics.

The properties of ceramics are sensitive to surface conditions such as flaws, compositions and residual stresses. Ion-beam treatments affect only the near-surface region, and possess the potential to change the surface composition, stress state and microstructure [20]. Direct ion implantation is available with its diverse advantages, including no loss of bulk properties, no effect on solid solubility limit, its low-temperature process and no adhesion problems. In the present study, yttria-stabilized zirconia (YSZ) was chosen as the starting material because of its high mechanical properties. Surface modification in YSZ was investigated through ion implantation with As^+ ions at different doses. Microstructure, phase, hardness, and fracture toughness of the implanted samples are measured and evaluated with the aid of electron microscopy, X-ray diffraction and mechanical testing. The effects of ion implantation on the tetragonal to monoclinic phase transformation will be probed.

2. Experimental procedure

The materials selected for this study were 2 mol % Y_2O_3–ZrO_2 (2YSZ) and 3 mol % Y_2O_3–ZrO_2 (3YSZ). Samples were prepared through a conventional ceramic fabrication process. Specimens were sintered at 1500 °C for 3 h prior to ion implantation. The morphology of the as-sintered specimens was investigated with a scanning electron microscope and the average grain size was estimated using the method proposed by Mendelsohn [21]. X-ray diffractometry (XRD) was used to investigate the structure.

Ion implantation was carried out in an ion implanter and specimens were bombarded by As^+ ions at applied voltages of 140 and 175 keV. Doses in the range 2×10^{15} to 3×10^{16} ions cm^{-2} were used. The hardness of implanted specimens was measured by the indentation method with a Vickers hardness indentor and the fracture toughness was calculated on the basis of equations proposed by Niihara *et al.* [22]. The surface residual stress on the implanted specimens was evaluated by XRD using CuK_α radiation. The ZrO_2 (2 2 2) diffraction peak was chosen for its high intensity and higher diffraction angle to maximize the measured peak shift. Each measurement was carried out with three tilt angles ranging from 0°–20°. The peak of the diffraction profile at each tilt angle was determined by the apex of a least-square parabola fitting to the top

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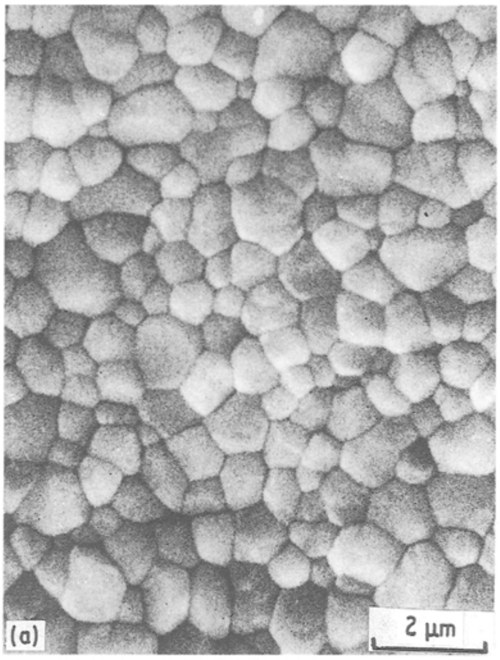
portion of the profile. The intensity of tilt peaks were kept higher than 10 000 counts for better accuracy in the evaluation.

3. Results and discussion

3.1. Properties prior to ion implantation

Fig. 1a and b, are scanning electron micrographs of the as-sintered surface for 2YSZ and 3YSZ specimens, respectively, before implantation, showing highly dense structure. The grain sizes estimated by the intercept method are 0.43 and 0.55 μm for 2YSZ and 3YSZ, respectively. The phase determined by XRD reveals that 3YSZ contains the major tetragonal phase with a slightly detectable cubic structure, while 2YSZ is fully tetragonal [23]. Table I lists the corresponding fracture toughness and hardness of 2YSZ and 3YSZ before implantation. The hardness of 3YSZ is larger than that of 2YSZ by about 10%. The fracture toughness of 3YSZ is, however, only half the value of 2YSZ. As reported by Tsukuma *et al.* [24], when the Y_2O_3 content is more than 2.5 mol %, a gradual decrease of K_{IC} in ZrO_2–Y_2O_3 is observed resulting from the occurrence of the cubic phase. It is argued that the variation in K_{IC} with Y_2O_3 content is also related to the degree of tetragonal to monoclinic transformation.



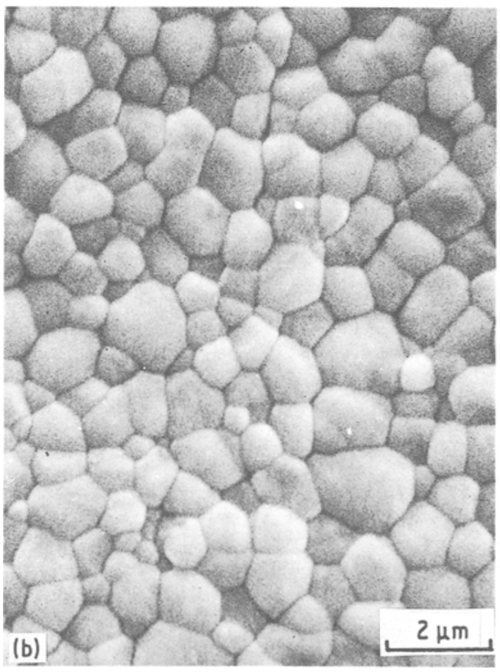


Figure 1 Scanning electron micrographs of specimens sintered at 1500 °C for 3 h: (a) 2YSZ, (b) 3YSZ.

TABLE I Fracture toughness and hardness of specimens 2YSZ and 3YSZ before ion implantation

Sample	H_V (MPa)	K_{IC} (MPa m$^{1/2}$)
2YSZ	11 870	9.83
3YSZ	12 830	4.28

3.2. Property changes after ion implantation

Table II represents the hardness and fracture toughness of 2YSZ and 3YSZ implanted under various doses with As^+ ion bombardment. For specimen 3YSZ, the hardness and K_{IC} values after 3×10^{16} $As^+ cm^{-2}$ implantation at 175 keV remain essentially identical to those prior to ion implantation. The hardness values for 2YSZ specimens under different implantation conditions vary between 11 610 and 12 010, only $\pm 2\%$ deviation from the initial value 11 870 prior to implantation. This is well within experimental error. The K_{IC} for 2YSZ specimens decreases by about 10% after 3×10^{16} $As^+ cm^{-2}$ implantation at 175 keV, as indicated in Tables I and II. However, for 2YSZ specimens implanted at 140 keV, K_{IC} increases from 8.17 with the dose rate of 2×10^{15} ions cm^{-2} to 10.78 with 3×10^{16} ions cm^{-2} dose.

An explanation of the effect of ion implantation on the mechanical property of YSZ specimens can be drawn on the basis of the tetragonal to monoclinic transformation and the radiation-induced stress due to ion implantation, as discussed below.

3.3. Evaluation of residual stress

As suggested by Lange [25], the examination of the thermodynamics in the constrained $ZrO_2(t) \rightarrow ZrO_2(m)$ reaction can be simplified by considering a stress-free, spherical inclusion of the tetragonal phase embedded within a matrix material. On transforming to the monoclinic phase, a state of stress arises within both the transformed inclusion and the surrounding matrix because of the constrained volume and shape changes. The differential free energy, $\Delta G^{t \rightarrow m}$, between these two states per unit volume of transformed material is

$$\Delta G^{t \rightarrow m} = (G_C^m - G_C^t) + (U_{SE}^m - U_{SE}^t) + (U_S^m - U_S^t) \quad (1)$$

or

$$\Delta G^{t \rightarrow m} = -\Delta G_C + \Delta U_{SE} + \Delta U_S \quad (2)$$

where G_C is the chemical free energy, U_{SE} is the strain

TABLE II Hardness and fracture toughness of specimens 2YSZ and 3YSZ after direct As^+ ion implantation

Sample	H_V (MPa)	K_{IC} (MPa $m^{1/2}$)	Voltage (keV)	Ion	Dose (ions cm^{-2})
3YSZ	12880	4.28	175	As^+	3×10^{16}
2YSZ	12010	8.25	175	As^+	3×10^{16}
2YSZ	11720	10.78	140	As^+	3×10^{16}
2YSZ	11730	9.21	140	As^+	1×10^{16}
2YSZ	11610	8.17	140	As^+	2×10^{15}

energy associated with the particle, U_S is the energy associated with the surface of the inclusion and superscripts t, m represent the tetragonal and monoclinic phase, respectively. For the case considered here, $U^t_{SE} = 0$. The condition for the transformation to proceed requires that $\Delta G^{t \to m} < 0$.

The magnitude of the strain energy will depend on the elastic properties of the transformed inclusion and the surrounding matrix, the inclusion shape and the transformation strain. Consider a spherical tetragonal inclusion in a state of residual stress and in its transformed monoclinic state. The residual stress, σ^r, arises from a stress-free strain, ε^r. Through the principle of superposition it can be shown that the free-energy change associated with the $t \to m$ transformation is [25, 26]

$$\Delta G^{t \to m} = -\Delta G_C + U^0_{SE} \pm \sigma^I_{ij}\varepsilon^r_{ij} \pm \sigma^r_{ij}\varepsilon^t_{ij} + \Delta U_S \quad (3)$$

where U^0_{SE} is the strain energy for the case where the tetragonal particle is initially stress-free, σ^I represents the uniform stress state within the transformed inclusion, and ε^t is the stress-free transformation strain.

Equation 3 shows that the residual stress will retard phase transformation of zirconia while tensile stress tends to promote it. The above equation can then be employed to explain the variation in mechanical properties for 2YSZ and 3YSZ specimens under different implantation conditions.

X-ray diffraction profiles of the implanted and unimplanted specimens is shown in Fig. 2. A clear peak shift implies the presence of a surface residual stress.

Stress measurement by X-ray diffraction has certain very definite advantages, as it is the only nondestructive method for determining initial or residual stresses in a specimen without cutting it up to relieve the stresses. With the angular geometry of a tested specimen as shown in Fig. 3 it can be shown that the stress component in the ϕ-direction is represented by

$$\sigma_\phi = \frac{d_\phi - d_z}{d_z} \frac{E}{(1 + \nu)\sin^2\psi} \quad (4)$$

where d is the lattice spacing, E and ν are the Young's modulus and Poisson's ratio of the specimen. By stressing the specimen in known increments and measuring the difference in d values at the two selected ψ angles, the stress component, σ, can be evaluated.

Fig. 4a and b show the plot of d_ψ versus $\sin^2\psi$ for specimens 2YSZ and 3YSZ, respectively, on the basis of the standard X-ray diffraction method for stress measurement, in which a step scan of X-ray diffraction from CuK_α radiation was conducted to the ZrO_2 (222) plane with the angle $\psi = 0°$, 10° and 20°, respectively. The slope of the d_ψ versus $\sin^2\psi$ diagram

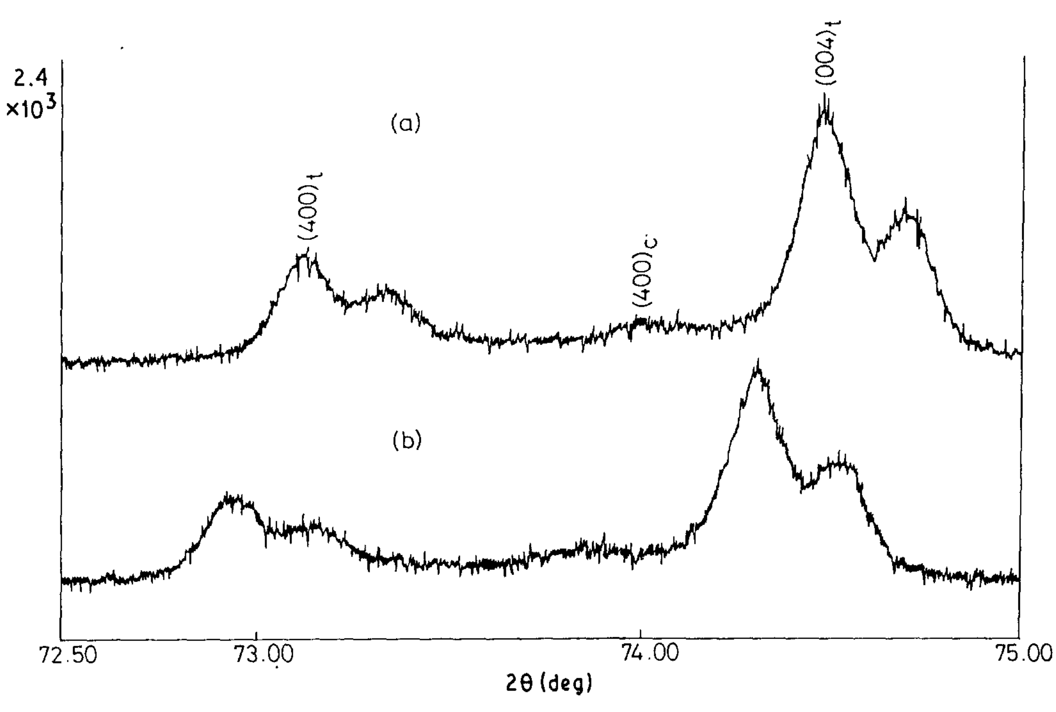


Figure 2 X-ray diffraction patterns obtained from the surface of as-sintered 3YSZ: (a) unimplanted, (b) As^+ implanted.

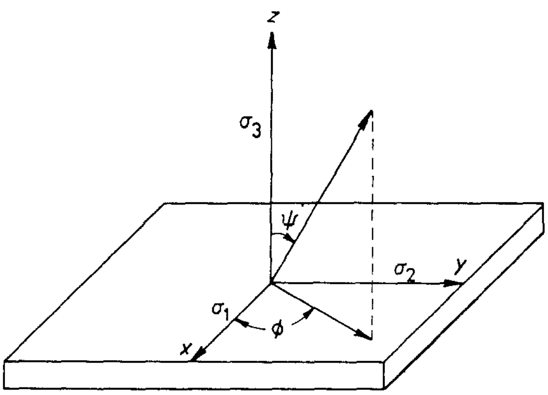


Figure 3 Angular relations for determination of the stress component in the ϕ direction.

will give the value for the stress component inside the specimen, provided that the Young's modulus and Poisson's ratio are known.

The slopes of these two lines in Fig. 4 fitted by regression are negative and the residual stresses calculated are 0.61 and 1.56 GPa for 2YSZ and 3YSZ, respectively. The result confirms that ion implantation introduces the residual compressive stress into the surface of the specimens.

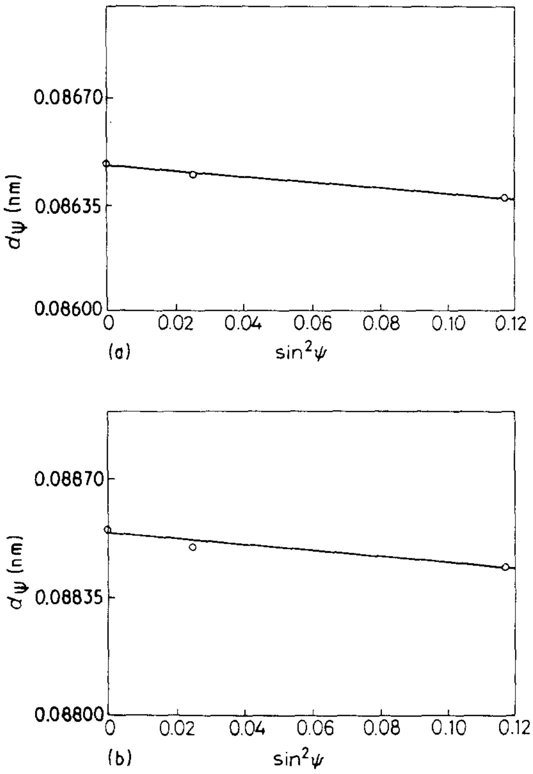


Figure 4 d_{ψ}–$\sin^2\psi$ diagram of specimens implanted with 3×10^{16} As^{+} cm^{-2}: (a) 2YSZ, (b) 3YSZ.

3.4. Ageing behaviour and t → m phase transformation

ZrO_2-based ceramics represent one class of new structural materials, which exhibit superior mechanical properties. However, there exist certain disadvantages for ZrO_2 ceramics with regard to the environmental conditions. The strength degradation associated with low-temperature ageing around several hundred degrees Celsius has been explained by the formation of microcracks induced by the tetragonal to monoclinic transformation on the surface [13–15]. For investigation of ageing behaviour in this study, the originally fully tetragonal 2YSZ specimen was aged at room temperature for 6 months. Fig. 5a shows the X-ray diffraction pattern, in which monoclinic peaks (1 1 1) and (0 0 2) are visible. The occurrence of the monoclinic phase may result in strength degradation, as reported in the literature [10–15]. However, fully tetragonal phase is retained in the implanted and then aged specimen, as shown in Fig. 5b. It appears that the tetragonal to monoclinic phase transformation of zirconia is suppressed by the presence of the residual

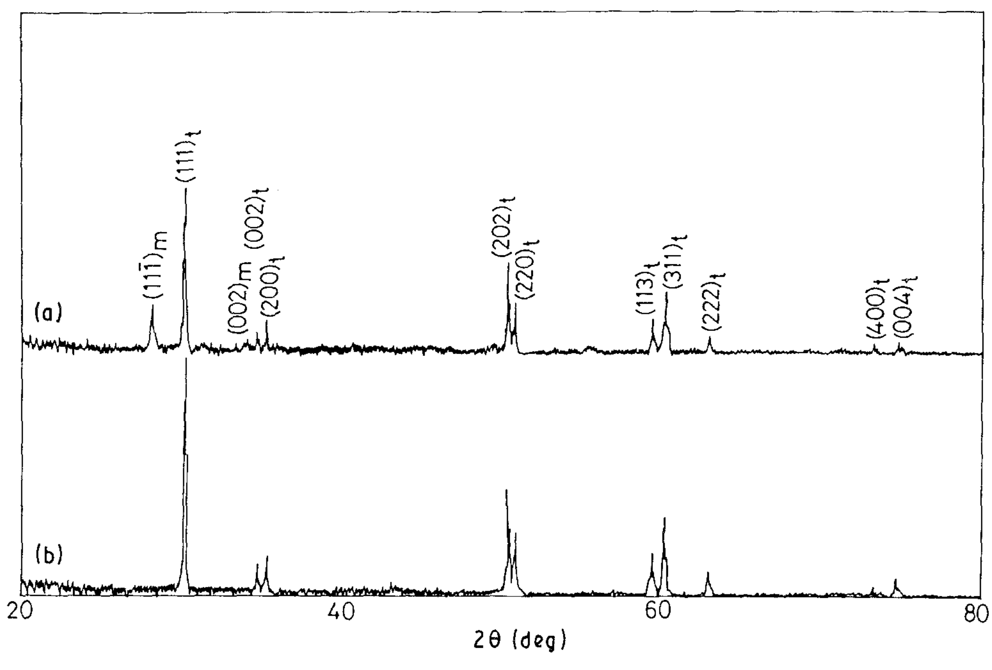


Figure 5 XRD patterns illustrating the phase difference between (a) unimplanted and (b) implanted surface of 2YSZ.

compressive stress due to the ion implantation process, as indicated in Equation 3.

It has been proposed that a decrease in the volume fraction of transformable tetragonal phase will decrease the fracture toughness [6, 25]. The presence of the residual compressive stress reduces the fraction of transformable tetragonal phase and thus decreases the effectiveness of transformation toughening in YSZ. Tsukuma *et al.* [24] reported that the fracture toughness in ZrO_2–Y_2O_3 would gradually decrease when Y_2O_3 exceeds 2.5 mol %. This implies that the transformation toughening mechanism is less dominating in 3YSZ as compared to 2YSZ. Consequently, the contribution of residual stress to the fracture toughness will be less significant than the reduction of $t \rightarrow m$ transformation toughening by alloying effect on ΔG_C in 3YSZ, compared to that in 2YSZ. The results summarized in Tables I and II clearly reveal this evidence.

Residual compressive stresses, if sufficiently high, are considered to prevent Type I crack opening of radial cracks near the surface [27], and to reduce the lateral crack opening forces [28] by superposition of the compressive stress pattern on the residual stress field from the indentation. The latter effect has been observed to result in the deflection of lateral crack trajectories away from the surface, thus preventing break-out spalling [20–28], shortening of the subsurface lateral cracks [20, 29] and even in complete suppression of the lateral cracking. Nevertheless, in the present study, it appears that the increase of fracture toughness for 2YSZ due to residual compressive stress is not appreciable, compared to the decrease in fracture toughness caused by the reduction of the tendency for phase transformation.

4. Conclusion

Direct As^+ ion implantation in 2 mol %–ZrO_2 (2YSZ) and 3 mol %–ZrO_2 (3YSZ) was employed in the modification of surface properties. Residual compressive stresses were developed near the surface of the ceramics due to ion implantation. Thermal stability in YSZ was improved in the presence of the residual compressive stress, which results in the suppression of the tetragonal to monoclinic transformation during the ageing process. The contribution of residual stress to the fracture toughness is less significant than the reduction of $t \rightarrow m$ transformation toughening by the alloy effect in 3YSZ, compared to 2YSZ. However, the increase in fracture toughness for 2YSZ due to residual compressive stress is not appreciable with respect to the decrease in fracture toughness due to the reduction in the degree of phase transformation. It is probable that appropriate implantation treatments can render ZrO_2 ceramics with better thermal stability and increased fracture toughness.

References

1. A. G. EVANS and A. H. HEUER, *J. Amer. Ceram. Soc.* **63** (1980) 241.
2. A. H. HEUER, *ibid.* **70** (1987) 689.
3. A. H. HEUER and M. RUHLE, in "Advances in Ceramics", Vol. 12, "Science and Technology of Zirconia II", edited by N. Claussen, M. Ruhle and A. H. Heuer (American Ceramic Society, Columbus, OH, 1984) pp. 1–13.
4. H. G. SCOTT, *J. Mater. Sci.* **10** (1975) 1527.
5. C. F. GRAIN, *J. Amer. Ceram. Soc.* **50** (1967) 288.
6. I. NETTLESHIP and R. STEVENS, *Int. J. Technol. Ceram.* **3** (1987) 1.
7. T. K. GUPTA and C. A. ANDERSSON, *Ceram. Engng Sci. Proc.* 7 (1986) 1150.
8. M. RUHLE, N. CLAUSSEN and A. H. HEUER, in "Advances in Ceramics", Vol. 12, "Science and Technology of Zirconia II", edited by N. Claussen, M. Ruhle and A. H. Heuer (American Ceramic Society, Columbus, OH, 1984) pp. 391–8.
9. F. F. LANGE, *J. Mater. Sci.* **17** (1982) 240.
10. K. KOBAYASHI, H. KUWAJIMA and T. MASAKI, *Solid State Ionics* **3–4** (1981) 489.
11. M. WATANABE, S. IIO and I. FUKUURA, in "Advances in Ceramics", Vol. 12, "Science and Technology of Zirconia II", edited by N. Claussen, M. Ruhle and A. H. Heuer (American Ceramic Society, Columbus, OH, 1984) p. 391.
12. T. MASAKI, *Int. J. High Tech. Ceram.* **2** (1986) 85.
13. F. F. LANGE, G. L. DUNLOP and B. I. DAVIS, *J. Amer. Ceram. Soc.* **69** (1986) 237.
14. M. YOSHIMURA, T. NOMA, K. KAWABATA and S. SOMIYA, *J. Mater. Sci. Lett.* **6** (1987) 465.
15. T. SATO and M. SHIMADA, *Amer. Ceram. Soc. Bull.* **64** (1985) 1382.
16. J. G. DUH, H. T. DAI and W. Y. HSU, *J. Mater. Sci.* **23** (1988) 2786.
17. J. G. DUH, H. T. DAI and B. S. CHIOU, *J. Amer. Ceram. Soc.* **71** (1988) 813.
18. J. G. DUH and M. Y. LEE, *J. Mater. Sci.* **24** (1989) 4467.
19. T. SATO, S. OHTAKI, T. FUKUSHIMA, T. ENDO and M. SHIMADA, *Mater. Res. Soc. Symp. Proc.* **78** (1987) 147.
20. C. J. McHARGUE, *Defect Diffusion Forum* **57–58** (1988) 359.
21. M. I. MENDELSOHN, *J. Amer. Ceram. Soc.* **52** (1969) 443.
22. K. NIIHARA, R. MORENA and D. P. H. HASSELMAN, *J. Mater. Sci. Lett.* **1** (1982) 13.
23. Y. S. WU, MS dissertation, National Tsing Hua University, Taiwan (1989).
24. K. TSUKUMA, Y. KUBOTA and T. TSUKIDATE, in "Advances in Ceramics", Vol. 12, "Science and Technology of Zirconia II", edited by N. Claussen, M. Ruhle and A. H. Heuer (American Ceramic Society, Columbus, OH, 1984) p. 382.
25. F. F. LANGE, *J. Mater. Sci.* **17** (1982) 225.
26. J. D. ESHELBY in "Progress in Solid Mechanics", Vol. 2, edited by I. N. Sneddon and R. Hill (North-Holland, Amsterdam, 1961) p. 89.
27. P. J. BURNETT and T. F. PAGE, *J. Mater. Sci.* **20** (1985) 4624.
28. C. ROSSINGTON, A. G. EVANS, D. B. MARSHALL and B. T. KHURI-YAKUB, *J. Appl. Phys.* **56** (1984) 2639.
29. P. J. BUMETT and T. F. PAGE, *J. Mater. Sci.* **19** (1984) 3524.

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