Ceramics International **21** (1995) 277–282

Low-temperature Aging of Zirconia Toughened Alumina Under Humid Conditions

D. Basu, A. Dasgupta, M. K. Sinha & B. K. Sarkar

Central Glass & Ceramic Research Institute, Calcutta - 700032, India

(Received 2 August 1994; accepted 21 November 1994)

Abstract: Changes in crystalline phases resulting from low-temperature annealing of different yttria (3 mol%) and ceria (14 mol%) doped PSZ and TTA compositions were investigated under controlled humidity conditions between 150 and 250°C up to 24 h. It was observed that 70% of the tetragonal phase in 3Y–PSZ had transformed to monoclinic phase while this effect decreased as alumina was added to the system. However, the composition with Al_2O_3 + 15 vol% 3Y–PSZ, which had the best mechanical properties, showed appreciable dependence on hydrothermal treatment. On the contrary, Ce-doped PSZ did not show any aging degradation.

1 INTRODUCTION

The discovery of the stress-induced martensitic tetragonal (t) to monoclinic (m) phase transformation of zirconia grains in the vicinity of the crack-tip has triggered a multifold research activity towards the development of a new class of strong, tough and relatively flaw-tolerant ceramics in which transformable ($m \rightleftharpoons t$) ZrO_2 phase is well dispersed in strong and stable cubic phase of the same material or in an Al_2O_3 matrix.[1-5] The stability of this metastable tetragonal phase of ZrO_2 increases with temperature,[5] making the stress-induced transformation to the monoclinic polymorph more difficult and resulting in rapid deterioration of toughness and strength with increasing temperature.

Further, the tetragonal phase in partially stabilised zirconia (PSZ) and tetragonal zirconia polycrystals (TZP) is transformed to the stable monoclinic phase by low temperature annealing at 150–300°C, particularly in humid atmospheres. This causes degradation of the mechanical properties[7-12] and therefore the utility of this material under such hostile hydrothermal conditions has been under question. Several workers have reported that the aging rate is high at 200–300°C in dry air,[10,13] while in humid atmospheres the highest rate is found between 125°C and 225°C.[8,9,14-16] Degradation of density, bending strength and fracture toughness due to aging was reported by Watanabe *et al.*[13] for 2–6 mol% Y_2O_3–PSZ and they concluded that the phase transformation from tetragonal to monoclinic played an important role in causing this degradation.[8,10]

Lange *et al.*[16] noticed the presence of small clusters of crystallites of α-yttrium hydroxide at the monoclinic/tetragonal grain boundary after annealing Y–PSZ, which indicated a reaction of water with yttria. On the other hand, Sato *et al.*[17] reported that this tetragonal to monoclinic phase transformation is accelerated even by non-aqueous solvents such as glycol, glycerol, ethanol amine, propylamine, etc.

Lu and Chen[18] studied the effect of grain size on the aging behaviour of Y–PSZ and claimed that below a critical grain size of 0·52 μm tetragonal symmetry could be retained, while Watanabe *et al.*[13] found that this critical grain size was dependent on the Y_2O_3 content. Several workers[12,14,19-21] have claimed that Ce-doped ZrO_2, either in TZP or PSZ, showed better retentivity of tetragonal phase even under the most hostile hydrothermal conditions.

Ceramics International 0272-8842/95/$9.50

However, the low-temperature degradation behaviour of transformation toughened alumina (TTA) has not been reported so far in the literature. The present investigation deals with the low-temperature aging behaviour of different TTA compositions in humid atmospheres and the results are compared with those of 14 Ce–PSZ and 3Y–PSZ.

2 EXPERIMENTAL PROCEDURE

Chemical analysis of the alumina, 3Y–PSZ and zirconia powders supplied by ALCOA (USA), Tyosoda Corporation (Japan) and Indian Rare Earth Ltd., respectively, for the present investigation are given in Table 1. Different compositions of zirconia toughened alumina (TTA) were prepared by wet milling alumina and various proportions of superfine 3Y–PSZ in a planetary ball mill in an isopropanol medium. Ce–PSZ powder was prepared by mixing the required quantity of cerium nitrate solution with ZrO_2 powder, which was subsequently calcined at 500°C and re-ground. These powders were uniaxially pressed into plates ($20 \times 20 \times 3$ mm^3) and bars ($55 \times 55 \times 5$ mm^3) at 100 MPa pressure with a single acting hydraulic press and were subsequently sintered in air at 1550°C with 1 h soaking.

The sintered density of these specimens was measured by the water displacement method. The flexural (transverse rupture) strength (T.R.S) was measured on a 3 point bending fixture with a stressing rate of 10 MPa sec^{-1} using an Instron model No. 1185 instrument, while hardness measurements were carried out using a Vickers hardness tester. The fracture toughness, K_{IC}, was determined from the crack length emerging from the corners of the Vickers indentation at different loads using the following relationship:

$$K = 0{\cdot}016 \sqrt{\frac{E}{H}}\ \frac{P}{C^{3/2}} \qquad (1)$$

where E is the Youngs modulus, H is the Vickers hardness, P is the indentation load and C is the crack length. Photomicrographs of the polished surfaces of different PSZ and TTA specimens were taken by SEM and the grain size was measured by a line intercept method. The samples were prepared by lapping down to 0·5 μm followed by thermal etching at 1400°C for 30 min to delineate grain boundaries. The sintered plate samples were ground and polished and then aged in an air–steam mixture of controlled humidity with a flow rate of 10 ml/min at 150, 200 and 250°C for 6–24 h. Thereafter the specimens were analysed for crystal phase content by XRD using Cu targets. The transformed monoclinic fraction of ZrO_2 in the alumina matrix of the samples was determined by XRD from the ratio of the combined intensity of the (111) and (11$\bar{1}$) monoclinic peaks to the combined intensity of the (111) and (11$\bar{1}$) monoclinic peaks plus the (111) tetragonal peak.

3 RESULT AND DISCUSSION

The different physical properties of PSZ and TTA ceramics are shown in Table 2. It may be noted that for each composition about 98% of the theoretical density could be achieved, while the transverse rupture strength and fracture toughness were the highest in the TTA composition with 15 vol% 3Y–PSZ.

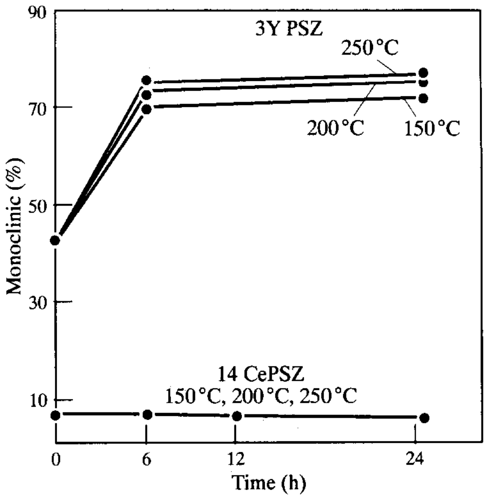


Fig. 1. Variation in transformed monoclinic phase with aging time at three different temperatures for 14 Ce–PSZ and 3Y–PSZ.

Table 1. Chemical analysis of alumina, zirconia and 3Y–PSZ powders

Constituents (wt%)	Alumina (Grade-XA-16, supplied by ALCOA, USA)	Zirconia (supplied by Indian Rare Earths Ltd., India)	3Y–PSZ (supplied by Tayosoda Corporation, Japan)
Y_2O_3	—	—	5·07
Al_2O_3	—	—	0·005
ZrO_2	—	98·00	—
SiO_2	00·02	00·25	0·002
Fe_2O_3	00·006	00·07	0·002
Na_2O	00·07	—	0·015
Loss on ignition	—	01·50	0·71
Crystallite size	7000Å	—	278 Å
Specific surface area	—	—	15·4 m^2/g

Table 2. Physical properties of different types of PSZ and TTA ceramics

Composition	Theoretical density (g/cm^3)	Sintered density (g/cm^3)	Hardness (GPa)	Transverse rupture strength (MPa)	Fracture toughness (MPa·m$^{1/2}$)	Average grain size (μm)
3Y–PSZ	6·08	6·02	15·00	420·0	6·1	—
14 Ce–PSZ	6·20	6·05	9·0	375·0	—	—
Composition A (Al_2O_3 + 5 vol% 3Y–PSZ)	4·09	4·04	18·52	355·0	4·6	5·5 μm (Al_2O_3) + 0·5 μm (ZrO_2)
Composition B (Al_2O_3 + 10 vol% 3Y–PSZ)	4·18	4·13	17·4	465·0	4·6	4·5 μm (Al_2O_3) + 0·4 μm (ZrO_2)
Composition C (Al_2O_3 + 12 vol% 3Y–PSZ)	4·21	4·16	17·3	525·0	4·7	4·2 μm (Al_2O_3) + 0·4 μm (ZrO_2)
Composition D (Al_2O_3 + 15 vol% 3Y–PSZ)	4·26	4·22	17·0	775·0	5·7	3·5 μm (Al_2O_3) + 0·35 μm (ZrO_2)
Composition E (Al_2O_3 + 20 vol% 3Y–PSZ)	4·34	4·28	16·1	575·0	5·0	2·7 μm (Al_2O_3) + 0·3 μm (ZrO_2)

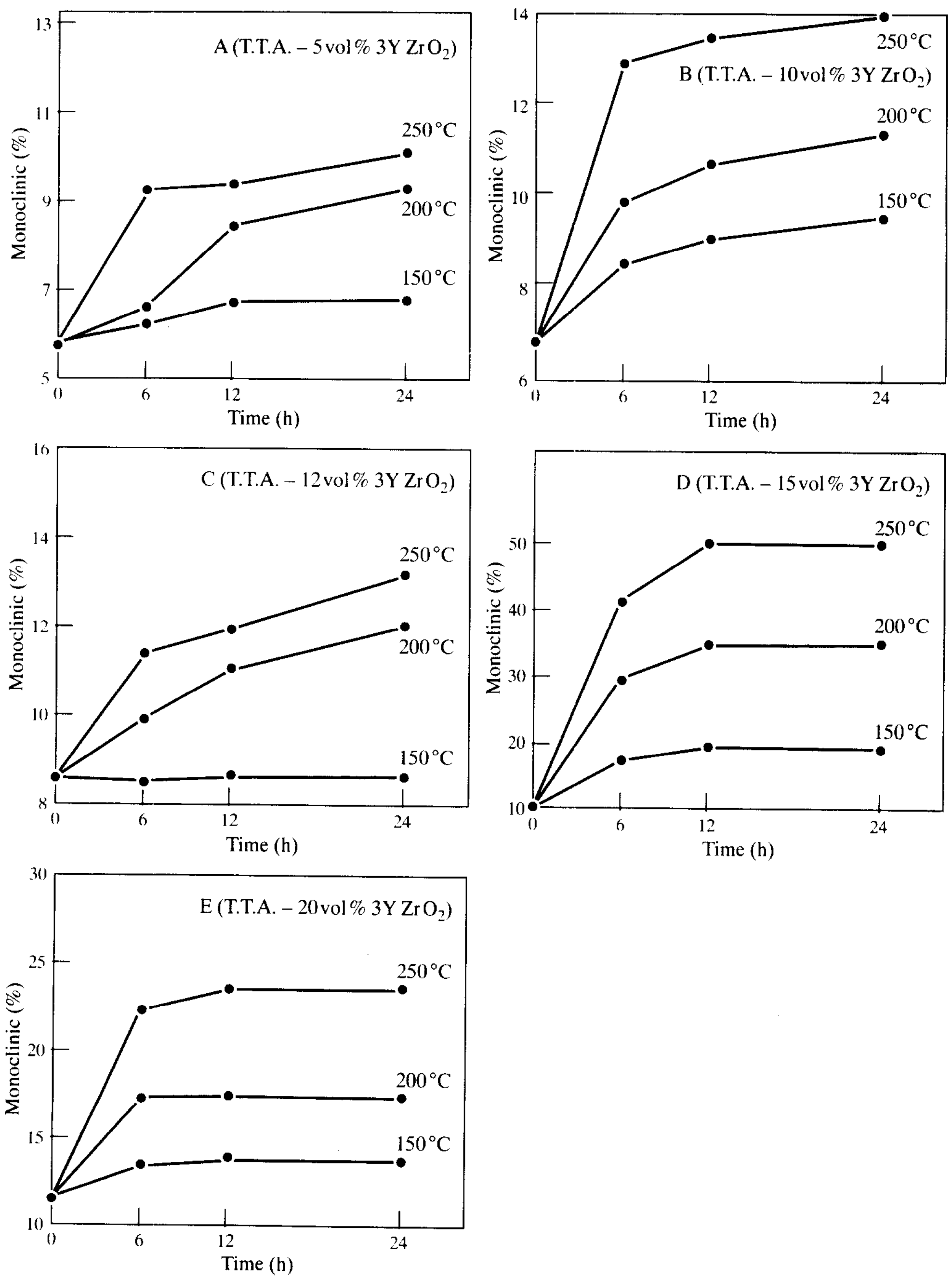


Fig. 2. Variation in transformed monoclinic phase with aging time when aged at three different temperatures for T.T.A. compositions A, B, C, D and E.

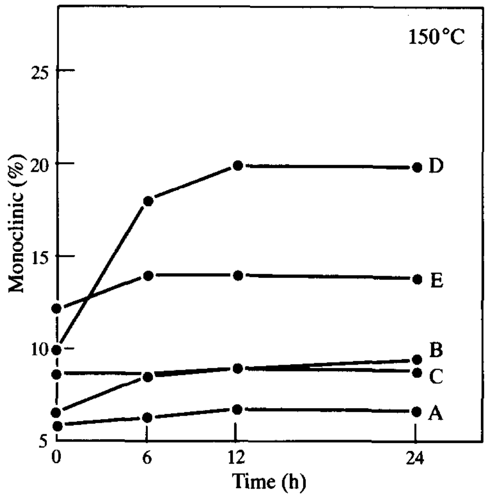


Fig. 3. Variation in transformed monoclinic phase with aging time for T.T.A. compositions A, B, C, D and E when aged at 150°C.

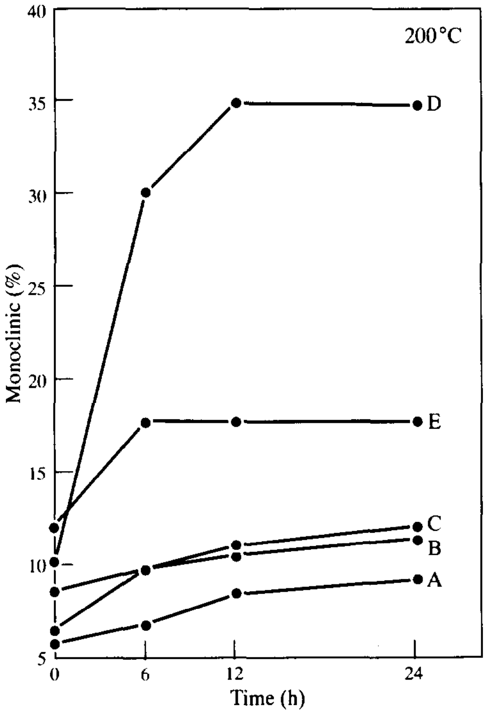


Fig. 4. Variation in transformed monoclinic phase with aging time for T.T.A. compositions A, B, C, D and E when aged at 200°C.

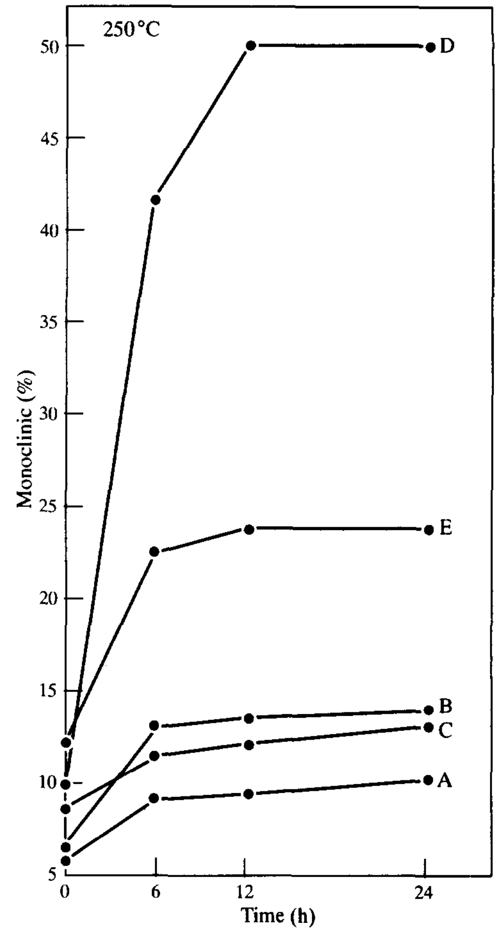


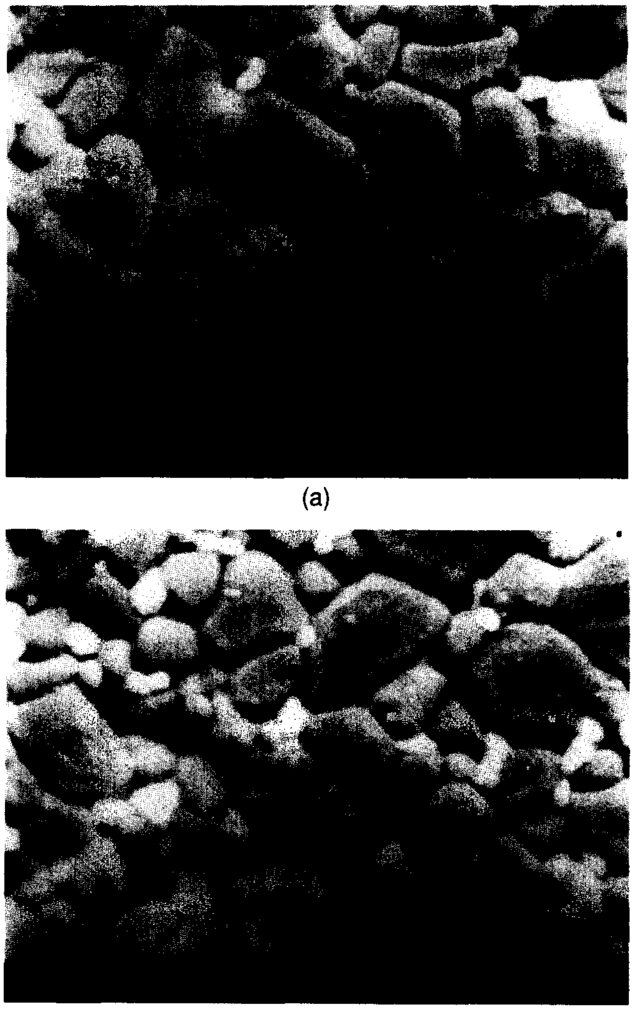
Fig. 5. Variation in transformed monoclinic phase with aging time for T.T.A. compositions A, B, C, D and E when aged at 250°C.

The percentage of monoclinic phase content of the aged 3Y–PSZ as analysed by XRD are represented in Fig. 1, which shows that in 3Y–PSZ samples the monoclinic content increases from 43% to more than 70% within 6 h of aging and thereafter no appreciable increment is noticed. Further, it may be noted that a temperature increase from 150 to 250°C does not have much effect on the phase transformation of the tetragonal form in 3Y–PSZ. This is probably because Y_2O_3 reacts rapidly with water vapour to form yttrium hydroxide, resulting in instability of the tetragonal phase and because the degree of phase transformation increases only slightly with temperature up to 250°C. This is in agreement with the findings of Tsukuma and Shimada.[22] Ce–PSZ however does not show any degradation tendency due to aging.

Figure 2 shows the effect of hydrothermal treatment on different TTA compositions and in all these cases the degree of destabilisation of tetragonal ZrO_2 depends to a great extent on the aging temperature. Further, Fig. 2 reveals that the rate of phase transformation is very high within the first 6 hours and thereafter the rate decreases. In compositions D and E, where 15 and 20 vol% of 3Y–PSZ are added to the system, the degree of transformation is much higher. Figures 3–5 reveal the comparative phase transformations of different TTA compositions at 150, 200 and 250°C, respectively, and it is clear from these figures that the composition with 15 vol% 3Y–PSZ is most sensitive to aging and at 250°C about 50% of the total tetragonal content transforms to monoclinic phase within 12 h. From the above figures and Table 3 it is clear that all TTA compositions show much lower dependence on aging compared with 3Y–PSZ, which is probably because the presence of alumina in the matrix produces a constraint which restricts the volume expansion involved in the t → m phase transformation of ZrO_2. This

Table 3. Phase analysis of PSZ and TTA samples under different aging conditions

Sample	Before aging	Monoclinic content $[\% = \frac{M(111) + M(11\bar{1})}{M(111) + M(11\bar{1}) + T(111)} \times 100]$								
		Aging condition								
		Temperature in presence of steam without any pressure								
		150°C			200°C			250°C		
		6 h	12 h	24 h	6 h	12 h	24 h	6 h	12 h	24 h
14 Ce–PSZ	7·30	7·30	7·30	7·30	7·30	7·30	7·35	7·30	7·30	7·37
3Y–PSZ	43·45	71·5	73·0	74·5	75·4	76·8	78·0	77·0	77·5	79·0
Al_2O_3 + 5 vol% ZrO_2 (A)	5·8	6·4	6·8	6·8	6·6	8·5	9·33	9·2	9·35	10·10
Al_2O_3 + 10 vol% ZrO_2 (B)	6·6	8·5	8·94	9·5	9·75	10·7	11·45	13·0	13·5	14·0
Al_2O_3 + 12 vol% ZrO_2 (C)	8·6	8·6	8·72	8·72	10·0	11·10	12·10	11·5	12·0	13·2
Al_2O_3 + 15 vol% ZrO_2 (D)	10·0	18·0	20·0	20·0	30·0	35·0	35·0	41·5	50·0	50·0
Al_2O_3 + 20 vol% ZrO_2 (E)	12·0	14·0	14·0	14·0	17·7	17·7	17·9	22·5	23·65	23·65


(a)

(b)

Fig. 6. Scanning electron micrographs of sintered samples of T.T.A. compositions (a) composition B and (b) composition D.

constraint decreases with increasing additive content, resulting in an increasing aging effect. However, it is surprising to note that the aging effect decreases from 15 to 20 vol% of 3Y–PSZ addition. This may indicate that lowering the grain size (due to further addition of 3Y–PSZ to the system) has a more important effect than the dilation strain. Figure 6 represents the SEMs of different sintered samples of TTA compositions, which show that in all the compositions very fine zirconia grains are well dispersed in both inter- and intragranular mode in the alumina matrix and that the average grain size decreases with increasing additive content (Table 2).

4 CONCLUSIONS

The tetragonal phase of 3Y–PSZ undergoes a phase change during low temperature aging in a humid environment, while in 14 Ce–PSZ this phenomenon is totally absent. The increment in temperature between 150 and 250°C showed slight increment in the transformation behaviour in 3Y–PSZ.

The addition of alumina to 3Y–PSZ has definitely restricted this degradation behaviour and the extent of degradation was quite low up to the 12% 3Y–PSZ composition. The transformation capability to tetragonal ZrO_2 phase in the TTA composition passes through its maximum in Al_2O_3–15 vol% 3Y–PSZ, which showed the best mechanical properties.

In all the TTA compositions degradation of the material is maximum at the highest aging temperature studied, viz. 250°C.

ACKNOWLEDGEMENTS

The authors are grateful to Dr E. Syskakis of Institut fur Reaktorwerkstoffe, Forschungszentrum, Julich, Germany, for providing 3Y–PSZ powder and Shri M. K. Basu, (Head) Technical Ceramics Division of Central Glass & Ceramic Research Institute, Calcutta, for his kind permission to use the facilities of his department.

REFERENCES

1. GARVIE, R. C., HANNINK, R. H. & PASCOE, R. T., Ceramic steel? *Nature* (London), **258** (5537) (1975) 703–4.
2. PORTER, D. L. & HEUER, A. H., Mechanisms of toughening partially stabilised zirconia (PSZ). *J. Amer. Ceram. Soc.*, **60** (1977) 183–4.
3. PORTER, D. L., EVANS, A. G. & HEUER, A. H., Transformation toughening in partially stabilized zirconia (PSZ). *Acta Metall.*, **27**(2) (1979) 1949–54.
4. HEUER, A. H., CLAUSSEN, N., KRIVEN, W. M. & RÜHLE, M., Stability of tetragonal ZrO_2 particles in ceramic matrices. *J. Amer. Ceram. Soc.*, **65**(12) (1982) 642–50.
5. LANGE, F. F., Transformation toughening: 1 — Size effects associated with the thermodynamics of constrained transformation. *J. Mater. Sci.*, **17** (1982) 225–34.
6. SWAIN, M. V., GARVIE, R. C., HANNINK R. H. J., HUGHAR, R. & MARMACH, M., Material development and evaluation of partially stabilised zirconia for extrusion die application. *Proc. Brit Ceram Soc.*, **32** (1982) 343.
7. KOBYASHI, K., KUWAJIMA, H. & MASAKI, T., Phase change and mechanical properties of ZrO_2–Y_2O_3. *Solid State Ionics*, **3–4** (1981) 489–93.
8. SATO, T. & SHIMADA, M., Crystalline phase change in yttria–partially stabilised zirconia by low-temperature annealing. *J. Amer. Ceram. Soc.*, **67**(10) (1984) C-212-213.
9. SATO, T. & SHIMADA, M., Transformation of yttria-doped–tetragonal zirconia polycrystals by annealing in water. *J. Amer. Ceram. Soc.*, **68**(6) (1985) 356–9.
10. SATO, T., OHTAKI, S. & SHIMADA, M., Transformation of yttria–partially stabilised zirconia by low temperature annealing in air. *J. Mater. Sci.*, **20** (1985) 1466–70.
11. SATO, T. & SHIMADA, M., Control of the tetragonal to monoclinic phase transformation of yttria–partially stabilised zirconia in hot water. *J. Mater. Sci.*, **20** (1985) 3988–92.
12. SATO, T. & SHIMADA, M., Transformation of ceria-doped tetragonal zirconia polycrystal by annealing in water. *Amer. Ceram. Soc. Bull.*, **64**(10) (1985) 1382–4.
13. WATANABE, M., JIO, S. & FUKUURA, J., Aging behaviour of Y–TZP. In *Advances in Ceramics, Vol. 12, Science & Technology of Zirconia, II*, ed. N. Claussen, M. Rühle & A. H. Heuer. The American Ceramic Society, Columbus, OH, 1984, pp. 391–8.
14. MATSUMOTO, R. L., Strength recovery in degraded yttria doped tetragonal polycrystals. *J. Amer. Ceram. Soc.*, **68**(8) (1985) C-213.
15. RÜHLE, M., CLAUSSEN, N. & HEUER, A. H., Microstructural studies of Y_2O_3-containing tetragonal zirconia polycrystals (Y–TZP). In *Advances in Ceramics, Vol. 12, Science & Technology of Zirconia II*, ed. N. Claussen, M. Rühle & A. H. Heuer. The American Ceramic Society, Columbus, OH, 1984, pp. 352–70.
16. LANGE, F. F., DUNLOP, G. L. & DAVIS, B. I., Degradation during aging of transformation toughened ZrO_2–Y_2O_3 materials at 250°C. *J. Amer. Ceram. Soc.*, **69**(3) (1986) 237–40.
17. SATO, T., OHTAKI, S., ENDO, T. & SHIMADA, M., Changes in crystallographic phase and microstructure on the surface of the yttria-doped tetragonal zirconia polycrystals (Y–TZP) by annealing in humid condition. In *Advances in Ceramics, Vol. 24, Science and Technology of Zirconia III*, ed. S. Sömiya N. Yamamoto & H. Yanagida. The American Ceramic Society, Colombus, OH, 1988. pp. 501–8.
18. LU, H. Y. & CHEN, S. Y., Low temperature aging of t-ZrO_2 polycrystals with 3 mol% Y_2O_3. *J. Amer. Ceram. Soc.*, **70**(8) (1987) 537–41.
19. MATSUMOTO, R. L., Aging behaviour of Ce-stabilised t-ZrO_2 polycrystals. *J. Amer. Ceram. Soc.*, **71**(3) (1988) C-128–9.
20. LEACH, C. & KHAN, N., Stability of ZrO_2–CeO_2–Y_2O_3 ceramics in hostile environments. *J. Mater. Sci.*, **26**(8) (1991) 2026–30.
21. HIRANO, M. & INADA, H., Hydrothermal stability of Y and Ce doped t-ZrO_2 + Al_2O_3 composites. *J. Mater. Sci.*, **26**(18) (1991) 5047–52.
22. TSUKUMA, K. & SHIMADA, M., Thermal stability of Y_2O_3–partially stabilised zirconia (Y–PSZ) and Y–PSZ/Al_2O_3 composites. *J. Mater. Sci. Lett.*, **4**(7) (1985) 857–61.