PII: S0955-2219(96)00205-1

Influence of Aging Environment on Low-Temperature Degradation of Tetragonal Zirconia Alloys

Dae-Joon Kim

Ceramics Division, Korea Institute of Science and Technology, Seoul 130-650, Korea

Abstract

Y_2O_3-stabilized tetragonal zirconias, alloyed with Ta_2O_5 and Nb_2O_5, were annealed at 100–265°C in air, dry air, and vacuum to elucidate the role of moisture in the low-temperature degradation (LTD). Although the existence of moisture enhanced the extent of LTD in accordance with observations in the literature, the influence of H_2O on the extent of the degradation became less significant as the residual stress in 3Y-TZP was enhanced by the Nb_2O_5 alloying and with increase in the grain size. This suggested that a residual stress is accumulated on the specimen surface during low-temperature aging, which probably originates from diffusion of oxygen vacancies from the specimen surface into the interior. This rationalization was based on the observation that LTD is an isothermal process and the activation enthalpy for LTD is similar to that for the diffusion of oxygen vacancies in the Y_2O_3-stabilized tetragonal zirconia at low temperatures. © 1997 Elsevier Science Limited.

1 Introduction

Y_2O_3-stabilized tetragonal zirconia polycrystals (Y-TZP) exhibit high strength and toughness at room temperature. Thus these materials have been considered as potential structural ceramics for use at low to moderate temperatures. Despite their excellent mechanical properties, one of the drawbacks of TZPs is their instability due to the tetragonal (t) to monoclinic (m) phase transformation when aged at relatively low temperatures of 100 to 400°C, especially in moist air or hot water.[1,2] This transformation is accompanied by severe cracking on the surface of the ceramics and degradation of the material strength.[3,4]

The most salient features of the low-temperature degradation (LTD) are characterized by the following: a more extensive degradation with a lower stabilizer content and a larger TZP grain size, an accelerated degradation in the presence of water, and a progressive degradation from the specimen surface to its interior. Besides the water or humidity effect and the progressive degradation, the dependence of the degradation on the stabilizer content and the grain size is identical to that of the stress-induced phase transformation at ambient temperature on these parameters. LTD can be avoided by increasing stabilizer content or decreasing grain size. However, the solutions cause the TZP fracture toughness to decrease by lowering the t → m phase transformation temperature.

Although LTD has been well documented, the exact mechanism is not fully understood.[5–10] Nevertheless, there are several proposed models which attempt to explain only the fact that the presence of water promotes the degradation.[5,7,10] Sato and Shimada[10] proposed that the chemisorbed H_2O forms Zr-OH at the surface, which results in the release of strain energy that would ensue if the t → m transformation would occur. Yoshimura[7] suggested that the accumulated strain area resulting from the migration of OH⁻ at the surface and in the lattice serves as a nucleus of the m-ZrO_2 phase in the t-ZrO_2 matrix. Lange *et al.*[5] hypothesized that when water and Y_2O_3 react in Y_2O_3-stabilized TZP (Y-TZP), the formation of $Y(OH)_3$ depletes the stabilizer content at the surface and leads to the simple t → m phase transformation. Recently, however, it has been demonstrated that the depletion of Y_2O_3 is not involved in LTD and suggested that LTD is a relaxation process of internally strained lattice by a thermally activated oxygen vacancy diffusion.[11] Thus, it is necessary to explore systematically the role of moisture in LTD.

In the present study, 3Y-TZP co-doped with Ta_2O_5 or Nb_2O_5 was annealed in air, dry air, and

vacuum to determine the influence of moisture on the extent of LTD. Unlike stabilizers for t-ZrO$_2$ such as Y$_2$O$_3$ and CeO$_2$, the alloying of Ta$_2$O$_5$ and Nb$_2$O$_5$ raises t $\rightarrow$ m and m $\rightarrow$ t transformation temperatures, which then contributes to the increase in the fracture toughness of Y-TZP.[12] Because of the adverse alloying behaviours of Y$_2$O$_3$ and Ta$_2$O$_5$ or Nb$_2$O$_5$, it is expected that the investigation of the stability of Y-TZP and Y-TZP containing Ta$_2$O$_5$ or Nb$_2$O$_5$ during low-temperature annealing in the various environments would give insight into the role of moisture in the degradation.

2 Experimental Procedure

The starting powders for the ZrO$_2$–Y$_2$O$_3$–Ta$_2$O$_5$ system were obtained by coprecipitation from aqueous solution mixtures using ammonia. Details of the procedure of powder preparation are described elsewhere.[12] The prepared powder compositions were 3 mol% Y$_2$O$_3$–ZrO$_2$ (3Y-TZP) with the addition of 0, 0·5, 1·0, and 1·5 mol% Ta$_2$O$_5$, respectively. The same set of powders containing Nb$_2$O$_5$ instead of Ta$_2$O$_5$ were prepared with the addition of Nb$_2$O$_5$ into 3Y-TZP (Tosoh Inc.). The mixing was performed by attrition milling with zirconia balls for 1 h. After drying, the mixed powders were calcined for 4 h at 1100°C followed by attrition milling for 2 h. Pellets of each composition were isostatically pressed at 135 MPa and then sintered for 1 h at 1500°C. The sintered specimens were removed from the furnace at 400°C during the furnace cooling period to avoid a possible t $\rightarrow$ m phase transformation due to a typically slow cooling rate below this temperature. The average grain size of sintered specimens was measured from scanning electron micrographs by the linear intercept procedure with the use of a correction factor of 1·56.

Four-point bend specimens of 2·5 mm $\times$ 3·0 mm $\times$ 30 mm were prepared for TZPs in the ZrO$_2$–Y$_2$O$_3$–Ta$_2$O$_5$ system by sintering for 1 h at 1500°C. The specimens were fractured at a crosshead speed of 0·5 mm/min. The aging treatments were carried out in the temperature range of 100 to 265°C in air, dry air, and vacuum. The dry air consisted of 79% N$_2$ and 21% O$_2$ and the H$_2$O content was less than 1 ppm. The dry air was passed through a column packed with the anhydrous CaSO$_4$ and 5-Å molecular sieve before flowing into a tube furnace where aging specimens were located. The dryness of the air, which passed the column, was 0·005 mg of H$_2$O/litre. The aging experiment under vacuum was performed in a vacuum furnace where the pressure was 2–3 $\times$

10^{-5} torr. The m-ZrO$_2$ phase contents on the aged and fractured surfaces were determined by the peak intensity ratio of [(11$\bar{1}$)m + (111)m]/ [(11$\bar{1}$)m + (111)m + (111)t] obtained from X-ray diffraction (XRD) analysis.

3 Results and Discussion

All specimens exhibited only the t-ZrO$_2$ phase after sintering for 1 h at 1500°C. Figure 1 compares the extent of t $\rightarrow$ m phase transformation after aging and fracture of TZPs in the ZrO$_2$–Y$_2$O$_3$–Ta$_2$O$_5$ system. The extents were determined by measuring the m-ZrO$_2$ phase contents on the specimens aged for 420 h at 265°C in air and on the fracture surface of bend test specimens. As Ta$_2$O$_5$ was added into 3Y-TZP, the extents of both the degradation and the stress-induced phase transformation were increased and the increasing trend of the m-ZrO$_2$ fraction was proved to be identical in both cases. For 3Y-TZP alloyed with Nb$_2$O$_5$, the m-ZrO$_2$ concentration in 3Y-TZP rose from 6 to 81, 89, and 96% as the Nb$_2$O$_5$ alloying content was increased to 0·5, 1·0, and 1·5 mol%, respectively, after aging for 100 h at 220°C in air.[11] There was no noticeable influence of the density and the grain size on the extent of degradation and the transformability of the resulting TZPs since the alloying effects on the parameters were not significant for the specimens sintered for 1 h at 1500°C.[11,12] Apparently the alloying of the pentavalent oxides into Y-TZP accelerates the degradation while the alloying improves the transformability of Y-TZP. Thus it appears that the mechanism responsible for LTD is related to the stress-induced martensitic t $\rightarrow$ m phase
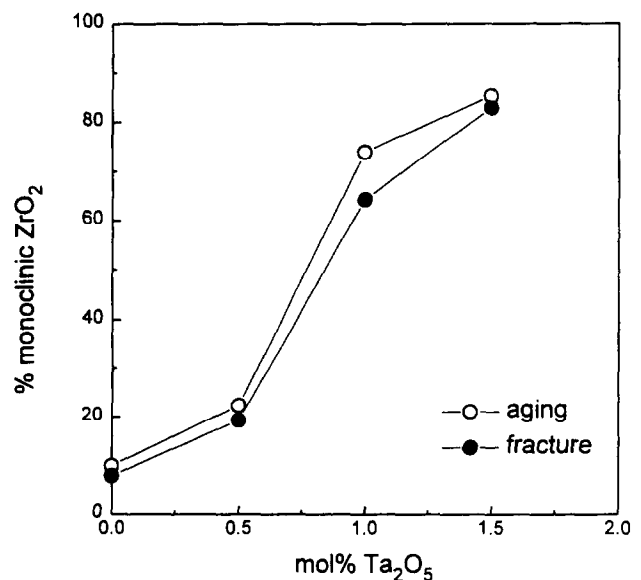

Fig. 1. Comparison of the amount of m-ZrO$_2$ on the fractured and the aged surfaces of 3Y-TZP containing Ta$_2$O$_5$.

transformation, which is characterized by athermal and diffusionless process and involvement of a shape deformation.[13]

Figure 2 shows the amount of m-ZrO_2 in 3Y-TZP containing 1·5 mol% Nb_2O_5 as a function of aging time at various aging temperatures. The increase in the m-ZrO_2 concentration with time fits best into sigmoidal curves, indicating that the kinetics of LTD is characterized not by athermal but by isothermal phase transformation. This agrees with the earlier studies on LTD of Y-TZPs.[14-16] Thus m-ZrO_2 formed by low-temperature annealing can be termed isothermal martensite. The isothermal transformation was described by the first-order transformation kinetics when TZPs were annealed in water and water vapor[2,4,10] and in air.[11] In general, the time-dependent process is a close analogy to the kinetics of chemical reactions with the rates controlled primarily by defect diffusion.[17] The defect in the Y_2O_3-stabilized t-ZrO_2 solid solutions is the oxygen vacancy which is created to achieve electrical neutrality in the distorted cubic fluorite lattice as Y^{3+} substitutes for Zr^{4+}. In the system ZrO_2–CeO_2, t-ZrO_2 solid solution also possesses a limited number of oxygen vacancies due to a partial reduction of Ce^{4+} to Ce^{3+} at elevated sintering temperatures.[18] The involvement of oxygen vacancy diffusion in LTD was supported by the observation of a similarity of activation enthalpy for LTD and the bulk ionic conductivity of 3Y-TZP at temperatures below 500°C.[11] Recently, Sergo and Clarke[19] also have suggested that the aging is diffusion-limited from the study of deformation bands in CeO_2-stabilized t-ZrO_2/Al_2O_3 composites. Thus LTD is characterized by isothermal and diffusion-controlled process.

Figures 3(a)–3(c) show the influence of aging atmosphere on the extent of the degradation of
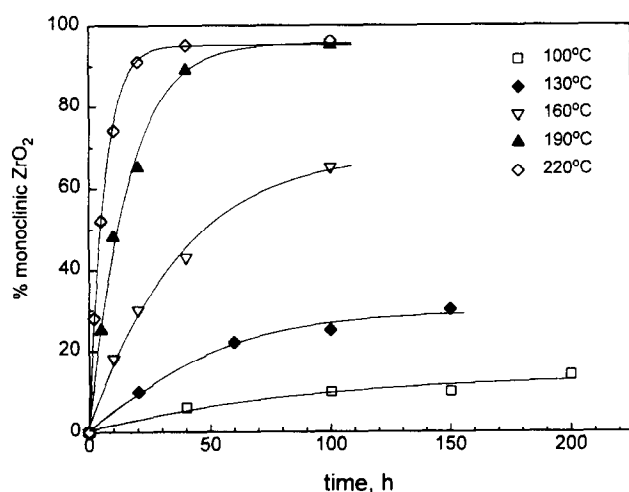

Fig. 2. m-ZrO_2 concentration on 3Y-TZP alloyed with 1·5 mol% Nb_2O_5 after aging at various temperatures in air as a function of aging time.

3Y-TZP alloyed with Nb_2O_5 after aging for 30 h at 220°C. The amounts of m-ZrO_2 in 3Y-TZP containing 0·5 mol% (Fig. 3(a)) and 1·0 mol% Nb_2O_5 (Fig. 3(b)) dropped from 11% and 76% to 0% and 64%, respectively, as the aging atmosphere changed from air to the dry air. Since no m-ZrO_2 was revealed after annealing under vacuum, it seems to support the contention that moisture content governs LTD. For 3Y-TZP containing 1·5 mol% Nb_2O_5, however, the amount of m-ZrO_2 did not vary significantly with the aging environments, ranging from 92 to 96% in Fig. 3(c). This suggests that LTD is accelerated not only by the existence of moisture, but by an enhanced transformability of 3Y-TZP which is achieved by alloying with Nb_2O_5 and Ta_2O_5.[12] The addition of the pentavalent oxides increases the tetragonality of t-ZrO_2, resulting in a rise in internal strain. That is, Y-TZP having a high residual stress is apt to be degraded even in a moisture-free environment. An involvement of the residual stress in LTD is supported in Figs 4(a) and 4(b), where the grain size of 3Y-TZPs, prepared by sintering at 1550°C for 2, 5, and 10 h, was 0·55, 0·69, and 0·85 μm, respectively. After annealing in air, the concentration of m-ZrO_2 in the specimens sintered for 2 h, 5 h, and 10 h was 10%, 44%, and 64%, respectively. As the same specimens were aged in the dry air, the m-ZrO_2 contents decreased to 0%, 0%, and 32%. This demonstrates that the moisture becomes less influential as the residual stress in 3Y-TZP, which scales with the grain size,[20] increases. None of the 3Y-TZPs in Figs 4(a) and 4(b) exhibited m-ZrO_2 after aging for 30 h at 220°C under vacuum.

A probable involvement of the $Y(OH)_3$ formation in LTD has been examined by a subsequent aging of 3Y-TZP, which was previously aged at 220°C and then annealed at 1200°C to reverse the transformed m-ZrO_2 to t-ZrO_2.[11] The observation that the amount of m-ZrO_2 on the specimen treated at 1200°C was less than that on the as-sintered specimen excluded the involvement of the Y_2O_3 depletion during low-temperature aging. Thus, neither the bond breakage nor the hydrate formation model can precisely account for LTD of 3Y-TZP alloyed with 1·5 mol% Nb_2O_5 under the vacuum environment in Fig. 3(c).

At ambient temperature t-ZrO_2 is internally strained by the fact that the size of Zr^{4+} is too small to be coordinated to eight oxygen ions in the fluorite structure.[21] In the system ZrO_2–Y_2O_3, the stabilization of t-ZrO_2 is achieved by the substitution of Y^{3+}, whose ionic radius is larger than that of Zr^{4+}, for Zr^{4+}. The substitution leads to the formation of oxygen vacancies and ZrO_7 oxygen polyhedron due to the lower valency of

Y^{3+} than Zr^{4+}. In the ZrO_2-Y_2O_3-$Ta(Nb)_2O_5$ systems, the internal strain in t-ZrO_2 depends on the tetragonality which decreases and increases with rising concentrations of Y_2O_3 and pentavalent oxides, respectively.[12] Another source of the internal strain is the thermal expansion anisotropy which governs the grain size dependence of transformability of t-ZrO_2.[20] LTD of TZPs is probably related to a relaxation of the internally strained lattice by a thermally activated oxygen vacancy diffusion as indicated by the isothermal transformation in Fig. 2. For 3Y-TZP, the activation enthalpy for the oxygen vacancy diffusion was determined to be 88–89 kJ/mol from the bulk ionic conductivity measurements at temperatures below 500°C.[22,23] This value is close to the activation energy for the low-temperature degradation of the 3Y-TZPs alloyed with Nb_2O_5 in air, which

is about 83 kJ/mol regardless of Nb_2O_5 content.[11] Theoretical estimates of lattice defect energies also suggested an activation energy of 82 kJ/mol for the migration of an oxygen vacancy in the presence of Y^{3+} in cubic zirconia.[24] The diffusion rate is governed by internal stress in t-ZrO_2.[11,19] Assuming that oxygen vacancies migrate from the sample surface into the interior, Zr^{4+}, previously bonded to eight oxygens in the interior, would be 7-coordinated and consequently the internal strain would be relieved. Concurrently, the fraction of the ZrO_8 polyhedron on the surface increases, resulting in the cation network being strained and the oxygen ions being overcrowded. Since the strained network and overcrowding correspond to the instability of t-ZrO_2,[25] t-ZrO_2 on the surface becomes unstable as a consequence of the oxygen vacancy diffusion. As the accumulation of residual
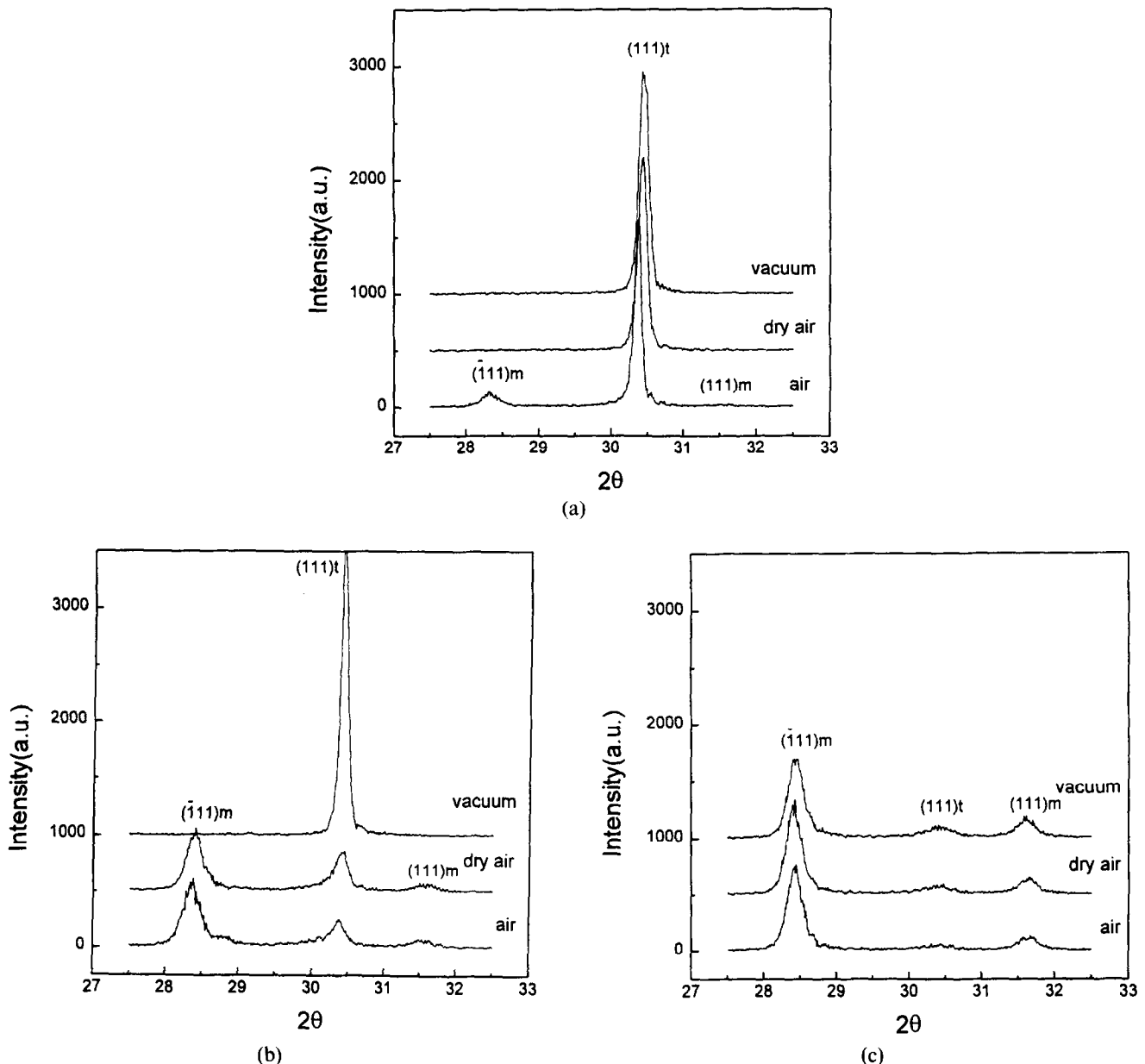

Fig. 3. Influence of aging environment on the extent of degradation of 3Y-TZP containing (a) 0·5 mol%, (b) 1·0 mol%, and (c) 1·5 mol% Nb_2O_5 after aging for 30 h at 220°C. The dryness of dry air was 0·005 mg H_2O/litre and the pressure of vacuum was 2–3 × 10^{-5} torr. The specimens were prepared by sintering for 1 h at 1500°C.

stress on the surface is sufficient to overcome the nucleation barrier for m-ZrO$_2$ formation with the lapse of aging time, the t → m transformation proceeds and consequently LTD occurs. As the Nb$_2$O$_5$ content and the grain size increase, a critical stress can be accumulated in a shorter period of time.

For 3Y-TZP containing 1·5 mol% Nb$_2$O$_5$, the internal stress is so high that LTD is observed regardless of the presence of H$_2$O (Fig. 3(c)). The high internal stress is attributed to annihilation of a large number of oxygen vacancies in 3Y-TZP and increase in the tetragonality by the alloying of 1·5 mol% Nb$_2$O$_5$. When the accumulated stress is not that large but moderate, the m-ZrO$_2$ formation will be achieved by the reaction between the strained Zr-O bonds, exposed on the specimen surface, and OH from H$_2$O in air to form the

isolated Zr-OH bonds as proposed by Sato and Shimada.[10] This is the case in Figs 3(a) and 3(b), where the specimens experience the degradation when annealed in air but not under vacuum. If the internal stress is small as in t-ZrO$_2$ having a very fine grain size and/or a high Y$_2$O$_3$ concentration, it takes a long time to observe LTD due to the slow process of oxygen vacancy diffusion.

The vacuum-annealed 3Y-TZPs containing 0, 0·5, and 1·0 mol% Nb$_2$O$_5$, which did not show m-ZrO$_2$ after aging for 30 h at 220°C under vacuum, and the same set of as-sintered specimens were annealed for 5 h at 220°C in air to clarify the effect of humidity on the degradation. The grain
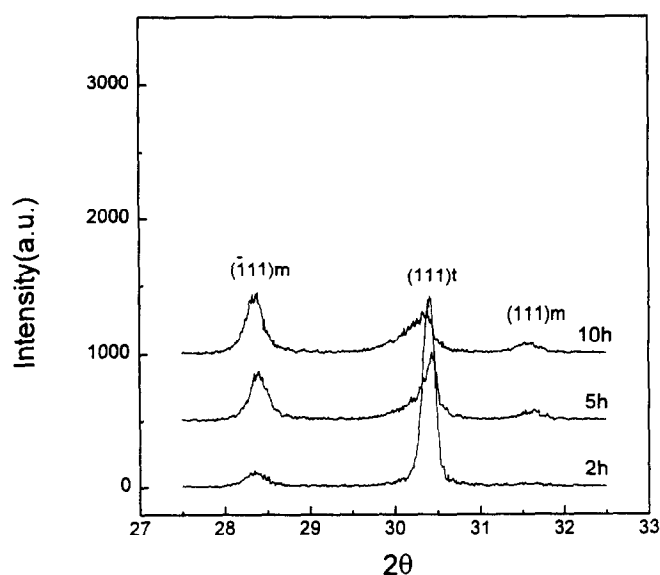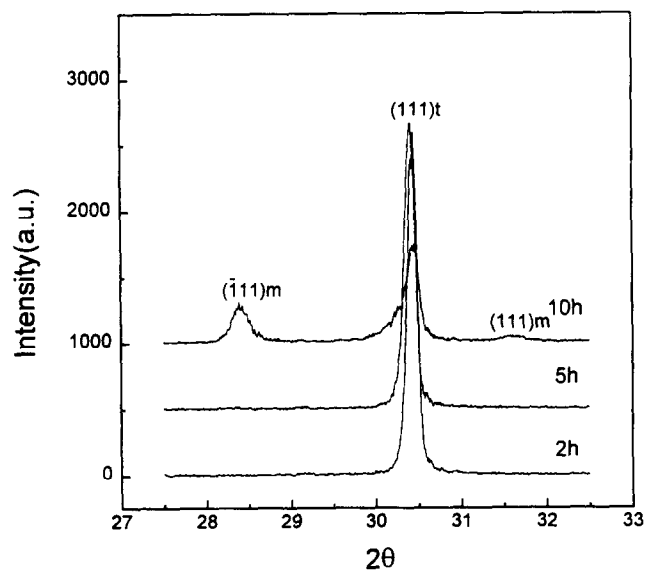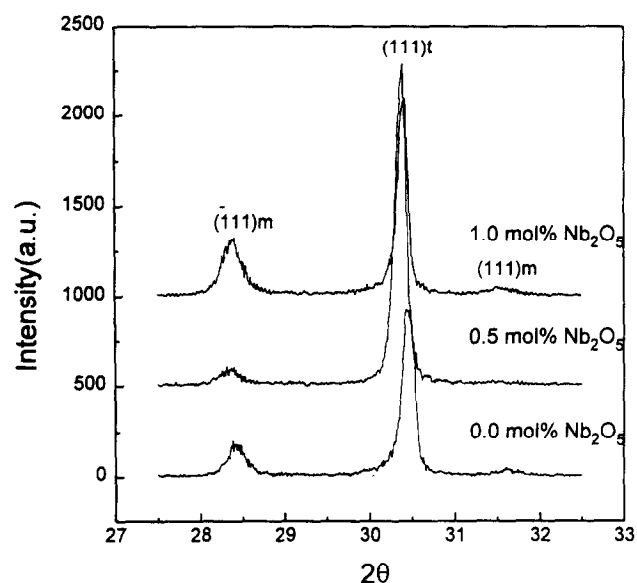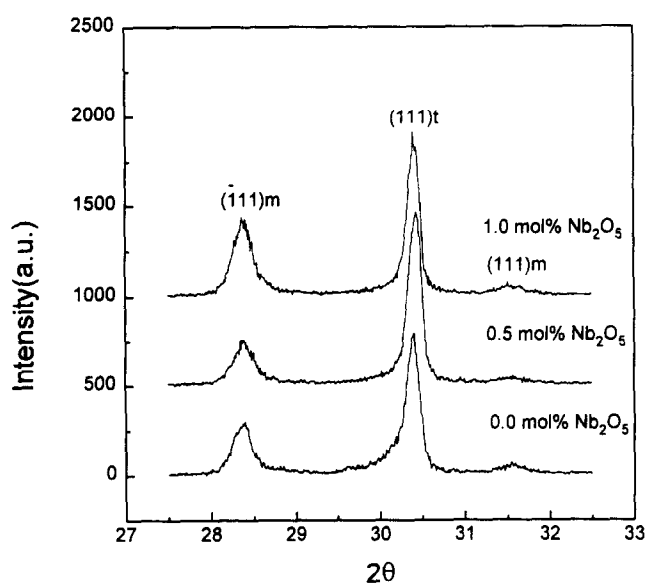

Fig. 4. XRD peak profiles of 3Y-TZP, prepared by sintering for 2, 5, and 10 h at 1550°C, after aging for 30 h at 220°C in (a) air and (b) dry air of 0·005 mg H$_2$O/litre.

Fig. 5. Influence of pre-annealing in vacuum on the extent of degradation of tetragonal zirconia alloys after aging for 5 h at 220°C in air: (a) as-sintered and (b) pre-annealed for 30 h at 220°C under vacuum of 2–3 × 10^{-5} torr. 3Y-TZP only was sintered for 10 h at 1550°C and the specimens containing Nb$_2$O$_5$ were prepared by sintering for 1 h at 1500°C.

size of the Nb$_2$O$_5$-free 3Y-TZP, prepared by sintering for 10 h at 1550°C, was 0·85 µm and those of 3Y-TZP alloyed with 0·5 and 1·0 mol% Nb$_2$O$_5$ were 0·47 and 0·49 µm, respectively, after sintering for 1 h at 1500°C. For the as-sintered specimens alloyed with 0, 0·5, and 1·0 mol% Nb$_2$O$_5$, the m-ZrO$_2$ concentrations were 15, 8, and 23%, respectively (Fig. 5(a)). For the specimens preannealed under vacuum, the values were 21, 19, and 33% (Fig. 5(b)). The higher m-ZrO$_2$ content on 3Y-TZP than on 3Y–0·5Nb–TZP is due to the fact that the influence of the grain size on LTD is more pronounced compared to that of the alloying in this particular combination of the grain sizes and the compositions. Nevertheless, it is noteworthy that the extent of LTD in the vacuum-annealed specimens is consistently higher than in the as-sintered specimens. If only the reaction of H$_2$O with t-ZrO$_2$ governs the extent, the m-ZrO$_2$ fractions on the vacuum-annealed and the as-sintered specimens should be identical since the specimens were exposed for the same period of time in air. The higher m-ZrO$_2$ concentration indicates that the t-ZrO$_2$ lattice on the specimen surface has been already strained during the vacuum annealing and the strained Zr–O–Zr bonds are more favorable to the reaction with H$_2$O than those in the as-sintered specimens. The results in Figs 3(c) and 5(a) and 5(b) suggest that the existence of H$_2$O is not a prerequisite to LTD but the amount of residual stress in t-ZrO$_2$, which is probably accumulated by the diffusion of oxygen vacancies, plays an important role in LTD.

4 Conclusion

Unlike the martensitic stress-induced t → m phase transformation, the low-temperature degradation is characterized by isothermal and diffusion-controlled process. It is proposed that the limiting step for LTD is the diffusion of oxygen vacancies which results in an accumulation of residual stress on specimen surface. The diffusion of the vacancies from the sample surface into the interior during aging at low temperatures distorts the Zr–O bonds on the surface, which facilitates the tetragonal to monoclinic transformation and the reaction between Zr–O–Zr bond and H$_2$O.

References

1. Sato, T., Ohtaki, S. and Shimada, M., Transformation of yttria partially stabilized zirconia by low temperature annealing in air. J. Mater. Sci., 1985, 20, 1466–1470.
2. Sato, T. and Shimada M., Transformation of ceria-doped tetragonal zirconia polycrystals by annealing in water. Am. Ceram. Soc. Bull., 1985, 64, 1382–1384.
3. Sato, T., Ohtaki, S., Endo, T. and Shimada M., Improvement of thermal stability of yttria-doped tetragonal zirconia polycrystals by doping CeO$_2$ on the surface. J. Mater. Sci. Lett., 1986, 5, 1140–1142.
4. Sato, T., Ohtaki, S., Endo, T. and Shimada, M., Changes in crystalline phase and microstructure on the surface of yttria-doped tetragonal zirconia polycrystals (Y-TZP) by annealing in humid conditions. In Advances in Ceramics Vol. 24A, Science and Technology of Zirconia III, ed. S. Somiya, N. Yamamoto and H. Yanagida. Am. Ceram. Soc., Columbus, OH, 1988, pp. 501–508.
5. Lange, F. F., Dunlop, G. L. and Davis, B. I., Degradation during aging of transformation-toughened ZrO$_2$–Y$_2$O$_3$ materials at 250°C. J. Am. Ceram. Soc., 1986, 69, 237–240.
6. Schmauder, S. & Schubert, H., Significance of internal stresses for the martensitic transformation in yttria-stabilized tetragonal zirconia polycrystals during degradation. J. Am. Ceram. Soc., 1986, 69, 534–540.
7. Yoshimura, M., Phase stability of zirconia. Am. Ceram. Soc. Bull., 1988, 67, 1950–1955.
8. Lilley, E., Review of low temperature degradation in Y-TZP. In Ceramic Transactions, Vol. 10, Corrosion and Corrosive Degradation of Ceramics, ed. R. Tressler and M. McNallan. Am. Ceram. Soc., Columbus, OH, 1990, pp. 387–407.
9. Jue, J. F. Chen, J. and Virkar, A. V., Low-temperature aging of t'-zirconia: The role of microstructure on phase stability. J. Am. Ceram. Soc., 1991, 74, 1811–1820
10. Sato, T. and Shimada, M., Transformation of yttria-doped tetragonal ZrO$_2$ polycrystals by annealing in water. J. Am. Ceram. Soc., 1985, 68, 356–359.
11. Kim, D.-J., Jung, H.-J. and Cho, D.-H., Phase transformations of Y$_2$O$_3$ and Nb$_2$O$_5$ doped tetragonal zirconia during low temperature aging in air. Solid State Ionics, 1995, 80, 67–73.
12. Kim, D.-J., Effect of Ta$_2$O$_5$, Nb$_2$O$_5$, and HfO$_2$ alloying on the transformability of Y$_2$O$_3$-stabilized tetragonal ZrO$_2$. J. Am. Ceram. Soc., 1990, 73, 115–120.
13. Heuer, A. H., Alloy design in partially stabilized zirconia. In Advances in Ceramics Vol. 3, Science and Technology of Zirconia, ed. A. H. Heuer and L. W. Hobbs. Am. Ceram. Soc., Columbus, OH, 1981, pp. 98–115.
14. Lu, H.-Y. and Chen, S.-Y., Low-temperature aging of t-ZrO$_2$ polycrystals with 3 mol% Y$_2$O$_3$. J. Am. Ceram. Soc., 1987, 70, 537–541.
15. Tsubakino, H., Hamamoto, M. and Nozato, R., Tetragonal-to-monoclinic phase transformation during thermal cycling and isothermal aging in yttria-partially stabilized zirconia. J. Mater. Sci., 1991, 26, 5521–5526.
16. Zhu, W. Z., Lei, T. C. and Zhou, Y., Time-dependent tetragonal to monoclinic transition in hot-pressed zirconia stabilized with 2 mol% yttria. J. Mater. Sci., 1993, 28, 6479–6483.
17. Borg, R. J. and Dienes, G. J., An Introduction to Solid State Diffusion. Academic Press, Inc., San Diego, CA, 1988, pp. 218.
18. Millet, J., Guillou, M. and Palous, S., Electrochemistry of electronic-ionic mixed oxide semiconductors: Zirconium and cerium oxide system. Electrochim. Acta, 1968, 13, 1425–1440.
19. Sergo, V. and Clarke, D. R., Deformation bands in ceria-stabilized tetragonal zirconia/alumina: II, Stress-induced aging at room temperature. J. Am. Ceram. Soc., 1995, 78, 641–644.
20. Becher, P. F., Alexander, K. B., Bleier, A., Waters, S. B.

and Warwick, W. H., Influence of ZrO_2 grain size and content on the transformation response in the Al_2O_3–ZrO_2 (12 mol% CeO_2) system. *J. Am. Ceram. Soc.*, 1993, **76**, 657–663.

21. Ho, S.-M., On the structural chemistry of zirconium oxide. *Mater. Sci. Eng.*, 1982, **54**, 23–29.

22. Weller, M. and Schubert, H., Internal friction, dielectric loss, and ionic conductivity of tetragonal ZrO_2–3% Y_2O_3 (Y-TZP). *J. Am. Ceram. Soc.*, 1986, **69**, 573–577.

23. Badwal, S. P. S., Ceramic superionic conductors. In *Materials Science and Technology Vol. 11, Structure and Properties of Ceramics*, ed. M. V. Swain. VCH, Weinheim, 1994, pp. 567–633.

24. Mackrodt, W. C. and Woodrow, P. M., Theoretical estimates of point defect energies in cubic zirconia. *J. Am. Ceram. Soc.*, 1986, **69**, 277–280.

25. Li, P., Chen, I.-W. and Penner-Hahn, J. E., Effect of dopants on zirconia stabilization – An X-ray absorption study: I, Trivalent dopants. *J. Am. Ceram. Soc.*, 1994, **77**, 118–128.