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Review

Environmental Degradation of Zirconia Ceramics.

Simon Lawson

School of Engineering & Advanced Technology, University of Sunderland, Sunderland SR1 3SD UK

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Abstract

This paper critically reviews the existing published experimental evidence for ageing mechanisms in zirconia ceramics. The first part of the paper is concerned with the material and environmental variables affecting the kinetics of the transformation. The current ageing mechanisms are presented and discussed and attention is drawn to the contradictions between the theories. Finally, techniques to retard or prevent the tetragonal–monoclinic phase transformation are presented.

1 Introduction

Partially stabilized zirconia (PSZ), and in particular tetragonal zirconia polycrystalline (TZP) ceramics have excellent mechanical properties such as bending strength and fracture toughness, which are associated with the tetragonal–monoclinic phase transformation around propagating crack fronts. However, a serious limitation to their use, e.g. as cutting tools for microsurgery,[1] is the phenomenon of poor, relatively low-temperature ageing resistance first observed by Kobayashi *et al.*,[2] where surface phase transformations occur and mechanical properties rapidly deteriorate. This phenomenon is widely documented in the literature although there are conflicting views as to the likely ageing mechanism.

Zirconia ceramics stabilized with yttria, ceria, calcia or magnesia are susceptible to various environments such as humid air, water vapour and other aqueous fluids over a temperature range of 65–500°C, but in aqueous solutions the effect is more catastrophic at lower temperatures and in shorter times. It should be noted that hydrothermal corrosion over the same temperature range has been observed in silicon nitride ceramics.[3]

During ageing the degradation of properties is associated with the transformation of metastable tetragonal crystals to the stable monoclinic structure.[4] It has been shown under certain circumstances that almost total strength recovery can occur when aged specimens are annealed, thus re-transforming the monoclinic grains back to the tetragonal phase.[5] It is therefore feasible to use Y–TZPs at higher temperatures or under thermal cycling conditions above the critical ageing temperature regime.

The tetragonal–monoclinic transformation during ageing can benefit certain types of Y–TZP due to the creation of a compressive surface layer of monoclinic phase on the ceramic.[6,7] This layer can, therefore, actually improve mechanical properties, although there is a narrow range between improvement and destruction of mechanical properties, as further ageing results in property deterioration.

The experimental observations on ageing have been summarised by Yoshimura[8] as follows:

1. The degradation proceeds most rapidly at temperatures of 200–300°C and is time dependent.
2. The degradation is caused by the tetragonal–monoclinic transformation accompanied by micro- and macro-cracking.
3. The transformation progresses from the surface to the interior of the specimen.
4. Water or water vapour enhances the transformation.
5. A decrease in grain size and an increase in stabilizer content retards the transformation.

The main variables influencing the stability of the tetragonal zirconia grains are dealt with in the following section.

2 Experimental Observations

The experimental observations of hydrothermal degradation are divided into two main sections, the material variables, and the test conditions under which the zirconia ceramics are examined.

2.1 Material variables

2.1.1 Grain size

One of the principal factors in anti-degradation behaviour is the critical tetragonal grain size which is Y_2O_3 dependent. When the grain size exceeds a critical value for tetragonal phase retention, the monoclinic phase content increases with ageing, as shown in Fig. 1.[9] Tsukuma *et al.*[9] reported that grains larger than 1 μm exhibited a large amount of tetragonal–monoclinic transformation, together with a remarkable decrease in strength. On the other hand, grains of $<0{\cdot}4$ μm showed no significant change of phase content and strength.

Below a critical tetragonal grain size, it is reported that no tetragonal–monoclinic transformation can occur. Watanabe *et al.*[4] estimated the critical grain size for tetragonal phase retention as a function of Y_2O_3 content as shown in Fig. 2. The critical grain size, D_c, increases from 0·2 to 0·6 μm as the Y_2O_3 content increases from 2 to 5 mol%. Tsubakino *et al.* however, found tetragonal grains with sizes lower than the critical grain size were also subject to ageing induced transformation.[10]

Winnubst and Burggraaf[11] found that a 3·5 mol% Y–TZP with a grain size of 0·1 μm was resistant to the ageing-induced phase transformation, although a 2 mol% Y–TZP with identical grain size was susceptible to the phase transformation. They also found yttrium enrichment at the surface which, therefore, resulted in depletion of the grain interior of yttrium. To compensate for the yttrium loss the critical grain size must be smaller than reported elsewhere for a uniform yttrium distribution. This could perhaps account for Tsubakino's results. Watanabe also found the presence of c-ZrO_2, and that the grain size and c-ZrO_2 content increases with increasing Y_2O_3 content, but the mean t-ZrO_2 grain size remained almost independent of Y_2O_3 content for a given sintering temperature.

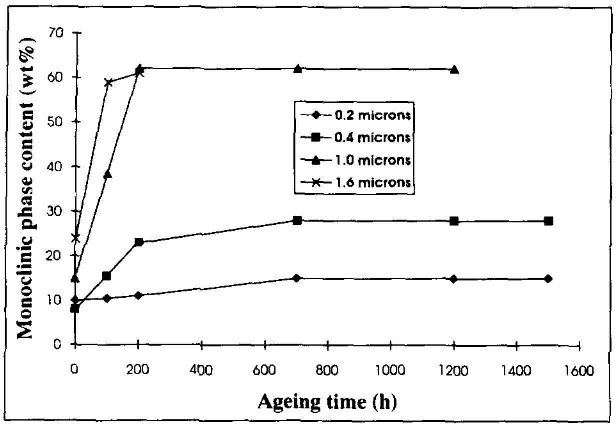


Fig. 1. Grain-size dependence of surface phase transformation on a 3Y–TZP aged at 230°C in air. (After Tsukuma *et al.*[9]).

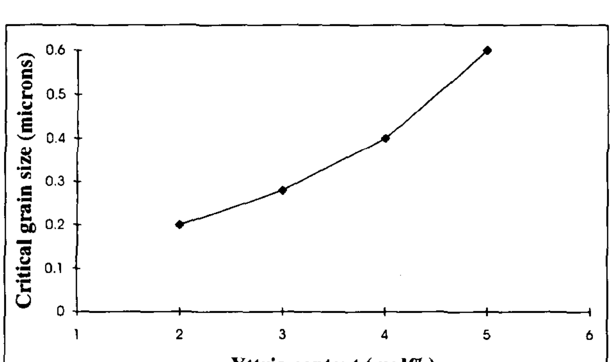


Fig. 2. Critical grain size as a function of yttria content when aged in air at 300°C for 1000 h. (After Watanabe *et al.*[4]).

There have been numerous reports on the stress-states of the tetragonal grains and grain-boundaries, and the effects of grain size and intergranular glassy phases on the residual stresses.[12–15] Schmauder and Schubert[12] used finite element analysis to determine the stress distribution in grains of different sizes. They found that for smaller grains the stresses created by thermal expansion anisotropy decrease more rapidly into the grain than for larger grains. Therefore at a fixed depth into a grain the average stress is higher for larger grains which are, therefore, less stable. Grain-shape also affects the stress levels. Spherical grains exhibit a homogeneous stress level, whereas faceted grains show singularities at the edges. Grains with rounded edges (i.e. when a glassy phase is present) have lower stresses than in perfectly sharp-edged grains. Mecartney[16] investigated the effects of glass content on the ageing resistance and found that materials with the greater glass content degraded the least. This infers that either the glassy phase reduces the residual stresses surrounding the grains, or the glassy phase protects the grain-boundaries from water attack by coating the grains.

Grain size control is normally exercised through the use of ultra fine powders and lowering the sintering temperature. The effect of calcination temperature on the powder crystallite size, the sintered grain size, and hence ageing properties has been investigated by Arai *et al.*[17] They found that of the combinations of calcination and sintering temperatures investigated, only compositions that had been calcined at the lowest temperature (800°C) survived ageing in air and water (200°C in an autoclave).

2.1.2 Stabilizer content

The level of stabilizing oxide also has a profound effect on ageing resistance. The higher the Y_2O_3 level, the more resistant to the ageing-induced tetragonal–monoclinic phase transformation are the Y–TZP ceramics,[9] and this is clearly demonstrated in Fig. 3 (the tetragonal grain sizes of all

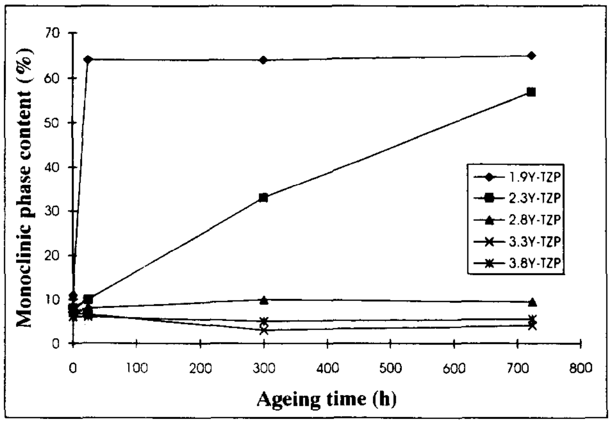


Fig. 3. Phase transformation dependence on yttria content for TZPs (grain size of ~0·4 μm) aged in air at 300°C. (After Tsukuma *et al.*[9]).

the specimens were almost the same ≈0·4 μm). The higher the Y_2O_3 content, then the larger the critical particle size for tetragonal phase retention. Watanabe *et al.*[4] found that as the Y_2O_3 content was raised from 2 to 5 mol%, then the critical particle size for tetragonal phase retention increased from 0·2 to 0·6 μm.

Sato *et al.*[18,19] showed that with increasing levels of Y_2O_3, increasing levels of *c*-ZrO_2 were formed, at the expense of the tetragonal phase. Upon ageing, the level of transformed *m*-ZrO_2 decreased with decreasing initial tetragonal content and in purely *c*-ZrO_2 (6 mol%) no monoclinic phase was detected after ageing. Therefore, they concluded that the monoclinic layer is formed from transformation of the metastable tetragonal phase and not the more stable cubic phase. Yoshimura *et al.*[20] confirmed that the monoclinic phase was a result of the tetragonal–monoclinic phase transformation, and in addition these monoclinic grains had an expanded lattice when compared to the initial lattice, whereas the cubic phase changed neither in content nor lattice parameter, therefore the transformation rate was proportional to the concentration of *t*-ZrO_2 on the surface. They also showed that the final amount of *m*-ZrO_2 decreased with increasing concentration of yttria, but the normalised transformation rate (normalised to the original tetragonal phase content) was almost constant, i.e. increasing the yttria content results in more cubic phase. Nakajima *et al.*[21] assumes that the saturated monoclinic fraction of each specimen is the transformed fraction of the metastable tetragonal phase under the test conditions. It should be borne in mind that the 'nontransformable' fraction of the tetragonal phase is actually *c*-ZrO_2 or *t*'-ZrO_2. Lawson[22,23] has shown that an increase in Y_2O_3 content (2–4 mol %) does not necessarily result in an increase in phase stability and can be detrimental to the ageing resistance of the zirconia.

It is usually thought that only Y–TZP ceramics exhibit the ageing phenomenon. However, Garvie *et al.*,[24] Swain,[25] Sato *et al.*,[26] Hecht *et al.*[27] and Drennan *et al.*[28] have shown that Mg–PSZs are also susceptible to hydrothermal degradation and exhibit the characteristic tetragonal–monoclinic phase transformation accompanied by a reduction in MOR, and Sato *et al.* observed the dissolution of Mg^{2+} ion in water above 200°C. Furthermore, Sato *et al.*[29] aged Ce–TZP in air and water vapour and found an increase in surface monoclinic content with <10 mol% CeO_2. They showed that the rate of transformation decreased with increasing CeO_2 content and smaller grain sizes, and that water vapour accelerated the transformation. The rate of change was slower than for Y–TZP, but the activation energies for transformation were almost identical. Leach and Khan[30] confirmed that <10 mol% CeO_2 exhibited the ageing-induced transformation. Tsukuma's[31] and Matsumoto's[32] results show that 12 mol% Ce–TZPs are highly resistant to the ageing-induced phase transformation. Pampuch *et al.*[33] fabricated Ca–TZP ceramics with sintered densities > 97% theoretical which were aged in air, water vapour (various temperatures) and in an autoclave (230°C). They found that samples of 4·3 mol% CaO sintered at 1300°C (grain size of 0·11 μm) were susceptible to the ageing-induced phase transformation. Samples sintered at lower temperatures were however resistant to degradation. This resistance is attributed to the smaller grain size, 0·09 μm.

Schmauder and Schubert *et al.*[12] showed that stresses caused by anisotropy of thermal expansion are Y_2O_3 dependent. By finite element analysis they showed that the higher anisotropy of the 2 mol% material resulted in higher shear stresses than 3 mol% materials. These stresses are shown schematically in Fig. 4. This figure shows that the stresses in a protruding gram decrease very rapidly

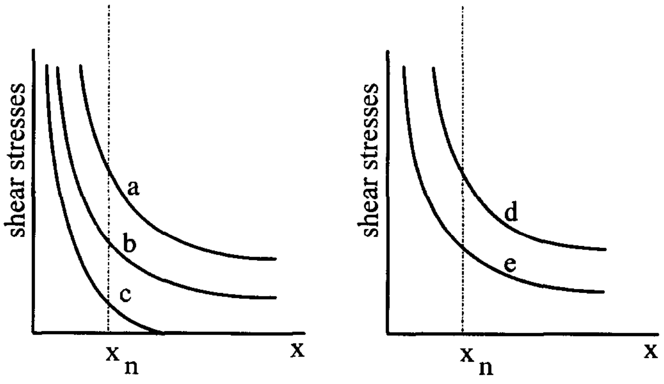


Fig. 4. Maximum shear stresses in the vicinity, *X*, of a grain corner for Y–TZPs. Curve (a) an included grain, 2 mol% Y_2O_3 (position 1 in Fig. 13); (b) an included grain, 3 mol% Y_2O_3 (position 1 in Fig. 13); (c) a protruding grain (position 4 in Fig. 13); (d) a large included grain; (e) a small included grain. (After Schmauder & Schubert[12]).

to zero, that is, these grains relax simply by changing their shape. Also, the stresses in large grains were found to be higher than those in smaller ones. The authors correlate the difference in free energy with various stresses (such as undercooling, residual and transformation stresses) and any increase in internal stresses will decrease the difference in free energy and hence reduce the activation barrier for transformation.

The Y_2O_3 content influences the free energy change of the t-ZrO_2 in two ways:

1. Undercooling is smaller for higher yttria contents,
2. Stresses due to thermal expansion anisotropy increase strongly with reduced yttria content.

Schmauder and Schubert also attach great importance to yttria distribution, and argue that inhomogeneous distribution is detrimental to the ageing resistance. They suggest the existence of a critical composition X_{cr}. For grains with a lower yttria content than X_{cr}, the stresses in the surrounding matrix will be so high as to cause micro cracking. Schubert's results suggest the critical composition X_{cr} for a 0·3 μm average grain size is between 2·2 and 2·8 mol% (4 and 5 wt%) Y_2O_3. It is obvious that the critical composition, X_{cr} will also be controlled by the average grain size of the zirconia ceramics.

The importance of the yttria distribution on stability is shown in Fig 5. The narrow grain size distribution can be achieved by low-temperature sintering. However, a narrow yttria distribution can only be reached with a homogeneous powder. Wang and Stevens[6] also state that a chemically homogeneous TZP will lead to few nucleation events and therefore less opportunity for transformation initiation. Ruhle *et al.* examined and compared commercial Y–TZP ceramics in the TEM[34] and suspected that a higher Y_2O_3 content and thinner grain-boundary layer may retard transformation. They suggest that either a stress corrosion mechanism is in operation at the specimen surface, or a surface-nucleated isothermal martensitic transformation. It is noticeable from their results that the powder which has the greatest inhomogeneous yttria distribution, is readily transformable, and is more resistant to the ageing-induced phase transformation than the other powders evaluated, and has recently been demonstrated by Lawson *et al.*[22,35] and Burger *et al.*[36]

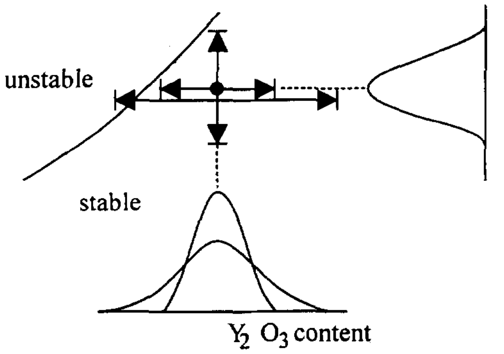


Fig. 5. Schematic of the relationships between grain size and yttria distribution, showing a stable and an unstable region. (After Schubert & Petzow[15]).

Cubic stabilized zirconia (8 mol% Y_2O_3) has been widely accepted as ageing resistant, however recent results obtained by Gibson *et al.*[37] show that such a fully cubic stabilized zirconia ceramic aged in boiling water for 24 h exhibited degradation and a phase change from the stable cubic phase to the monoclinic phase. This could possibly create problems on the use of fully stabilized zirconia in fuel cell applications.

2.1.3 Composition

The composition of the base powders is also of importance to the ageing behaviour of Y–TZP ceramics. Comparisons of commercial powders[34–36,38–41] have been made and the results show that test pieces of equivalent stabilizing oxide, behave differently under hydrothermal conditions. It is an accepted view that a homogeneous yttria distribution and small grain size distribution lead to TZPs with superior anti-degradation performance[12,42] but recent results challenge this view[35,36]

Differences in anti-degradation behaviour occur due to the technique used for incorporating yttria, i.e. co-precipitation, co-coating or milling. The purity of base materials can be of importance and Lange *et al.*[43] investigated the effects of SiO_2 impurities. They found that the intergranular glassy phase does not play a major role in the ageing process, so disproving their initial hypothesis that ageing behaviour is a result of a stress-corrosion type reaction (water vapour reacting with a glassy silicate grain-boundary phase).

Mecartney[16] investigated the effects of intergranular glassy phases on the sintering and mechanical properties of 2·5Y–TZP. She states that the 'omnipresent' glassy phase is due to contamination from two sources: SiO_2 from the powder precursor ($ZrSiO_4$) and SiO_2 and Al_2O_3 from milling media. Mecartney found that an increase in glassy phase content improved the ageing resistance. This behaviour was accounted for by a reduction in the thermal expansion mismatch stresses, and the rounding of grains, thus eliminating the stress concentrations associated with the corners of sharply faceted grains.[12]

Masaki *et al.*[44] state that high purity powders are effective transformation inhibitors. They also conclude that impurities which do not form solid solutions with ZrO_2 or additives such as TiO_2,

Fe_2O_3 and Al_2O_3 can cause strain and thermal stresses which act as transformation nucleation points along grain-boundaries. Masaki goes on to say:

> *"On the other hand these oxides [TiO_2, Fe_2O_3 and Al_2O_3] act as sintering aids, and hence different results will occur depending on their amount. This problem is important subject to be studied in the future."*

2.2 Test conditions

2.2.1 Ageing temperature

It has been found by many researchers that low temperature ageing occurs within the temperature range 65–500°C,[19] with the maximum rate at ≈250°C, and typical results are shown in Figs 6 and 7. The figures show that mechanical properties decrease[45] over the critical temperature range and are accompanied by an increase in the surface monoclinic content.[46]

The temperature limits of the ageing phenomenon are described by Sato *et al.*[47] The upper limit is due to thermodynamic constraints (stabilizer levels, grain size and thermal anisotropy), and the lower limit is due to the kinetics of the transformation. Kim and Jung[13] attribute the lower temperature limit to the onset of thermally activated dipole reorientation.

Sato *et al.*[46] found that the critical temperature below which m-ZrO_2 was formed decreased with decreasing sintering temperature. This may be due to the effect of the surface energy of the smaller grains; the resistance to the phase transformation increases with decreasing grain size. Kim and Jung[13] deliberately added destabilizing oxides (Ta_2O_5 and Nb_2O_5 which have little effect on the grain size) to 3Y–TZP in order to study the kinetics of ageing-induced phase transformations. They found that increasing destabilizer levels from 0 to 1·5 mol% increased the monoclinic content and raised the upper temperature limit for no transformation to occur from 250 to 500°C, the lower temperature limit being 80°C regardless of composition.

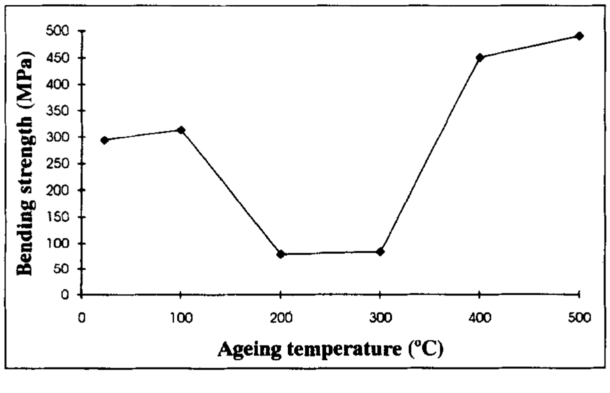


Fig. 6. Relationship between the ageing temperature and bending strength of PSZ ceramics aged in air. (After Miyazawa *et al.*[45]).

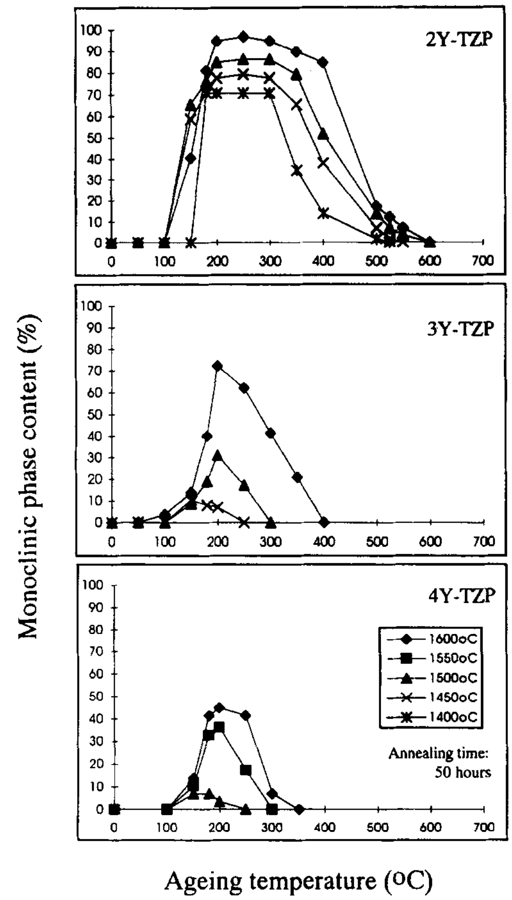


Fig. 7. Relationship between the amount of surface monoclinic phase and the ageing temperature, for a range of Y–TZPs sintered from 1400 to 1600°C and aged for 50 h in air. (After Sato & Shimada[46]).

2.2.2 Test environment

Ageing environments used to study the effects of low-temperature degradation in zirconia ceramics vary from the relatively mild, ageing in humid air (for periods in excess of 3 years[48]), to the much more aggressive autoclave conditions.[34] Generally the autoclave contains water, is heated to temperature (and corresponding pressure) and the test undertaken. The first reported autoclave results were obtained by Nakajima *et al.*[21] who aged a range of Y–PSZs in water from 100 to 180°C. At 180°C the saturation phenomenon was observed in <5 h. They also dipped the Y–PSZ specimens into sulphuric acid, nitric acid, and caustic soda and found that the phase transformation increased with dipping time.

Sato *et al.*[47] aged specimens in air and in water vapour, and concluded that the water vapour accelerated the rate of reaction, but did not change the reaction equilibrium. The water vapour pressure was also altered and it was found that the monoclinic content increased with increasing vapour pressure. They also aged specimens under a vacuum and they found that only a trace of monoclinic phase was formed. Sato *et al.*[19] also examined the effect of ageing in various solvents. It was concluded that aqueous solutions and non-aqueous solvents with a molecular structure containing a lone-pair electron orbital opposite a proton donor site also accelerates the tetragonal–monoclinic phase transformation.

The effect of water vapour pressure was investigated by Sato and Shimada[49,50] who found that as the vapour pressure was increased, then the rate of transformation also increased, but the saturation level remained constant. Also, ageing only occurred in water vapour and ammonia gas and not at all in vacuum or carbon dioxide atmospheres. Yoshimura *et al.*[51] investigated the effects of high pressure water (5 to 100 MPa) on the ageing behaviour, and found that transformation proceeds quicker under increasing pressure and over a greater temperature range than for lower pressures.

Perhaps the most interesting observation on the effects of ageing atmosphere was seen by Kuroda *et al.*[52] and is shown in Fig. 8. A sample was aged at 300°C in dry air for 24 h, then subsequently aged at 300°C for 72 h in a dynamic vacuum. The resultant profile (profile 4) was very similar to the one obtained for 96 h at 300°C in dry air (profile 2). Yet when they aged samples in a dynamic vacuum at 300°C they effectively saw no transformation. Therefore, once the transformation had been initiated by the water vapour, autocatalytic propagation then occurs without further chemical attack required.

There have been numerous studies on the effect of *in vitro* and *in vivo* environments on the ageing resistance of Y–TZP. Garvie *et al.*[24] aged Mg–PSZ in Ringer's solution and found that there was a slight decrease in strength and MOR. Their *in vivo* experiments showed that there had been no degradation after 6 months. Drummond found that YSZ ceramics aged in water, saline, and Ringer's solution at 37°C gave a reduction in strength with ageing time,[53] and that autoclaving in water slightly reduced the strength of Mg–PSZ.[54] Thompson and Rawlings found that ageing in Ringer's solution promoted phase transformation and MOR decrease with TZP and ZTA materials.[55]

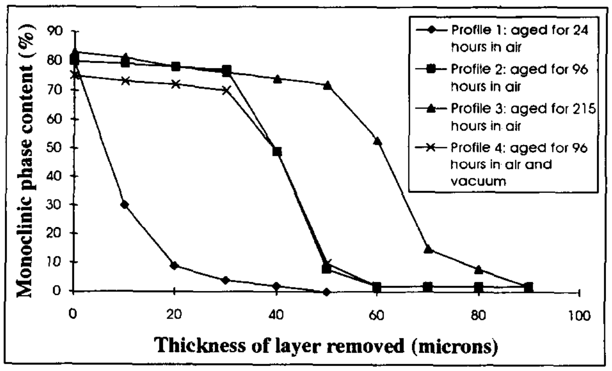


Fig. 8. Relationship between the amount of monoclinic phase and thickness of transformed layer removed for a 2Y–TZP aged in air or vacuum at 300°C. (After Kuroda *et al.*[52]).

Surprisingly, there is little data available on the effect of ageing on the wear behaviour of zirconia which is clearly of commercial significance. Preliminary results obtained at the University of Sunderland[56,57] clearly show that wear tests undertaken on aged material exhibit enhanced wear rates.

3 Ageing mechanisms

There are many conflicting and confusing mechanisms for modelling the ageing behaviour of Y–TZP. Ageing observations have been explained using various mechanical and chemical degradation mechanisms. In the former, stress corrosion cracking of the amorphous intergranular glassy phase or of the *t*-ZrO_2 grains has been considered, whilst in the latter, the role of water has been suggested to form OH^- by the chemisorption at the surface of Y–TZP grains,[19] or to form $Y(OH)_3$[14,43] perhaps leading to the depletion of yttrium.[43] Part 2 of this paper will present a new ageing mechanism that accommodates all of the experimental observations.[58] The most significant ageing mechanisms are described in the following sections.

It is important, however, to firstly discuss the nature of the monoclinic layer and its kinetics. Tsukuma *et al.*[9] found that the transformation proceeds from the grain boundaries to the grain centres with time. He also suggests that the surface tetragonal grains are more unstable than those in the bulk. Therefore, thermal stability is dependent upon the surrounding grains. However, Schmauder and Schubert[12] observed that unconstrained surface grains were resistant to the ageing-induced phase transformation.

Miyazawa *et al.*[59] polished away the transformed surface layer and measured the monoclinic content with penetration depth for various samples. They found that the monoclinic content decreases with depth from the surface and that penetration depth increases with ageing time as shown in Fig. 9.

These results suggest that there is a gradual decrease in the monoclinic content with depth into the sample. However this is not the case, as the transformed layer has a fixed saturation level[21] dependent on the initial tetragonal and cubic contents of Y–TZPs. Optical microscopy clearly shows that there is a distinct transformed layer boundary with the tetragonal bulk material as shown in Fig. 10[60].

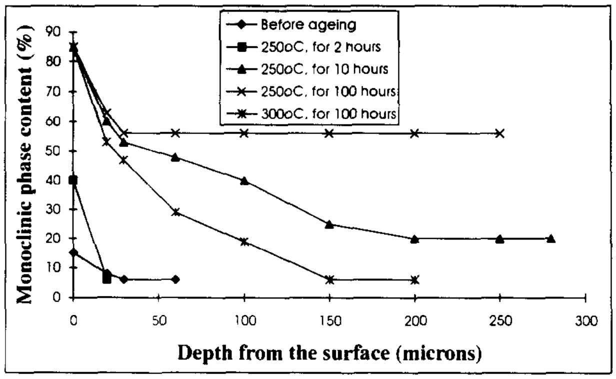


Fig. 9. Relationships between the amount of transformed monoclinic phase as a function of distance from the sample surface for a 5Y–PSZ aged in air. (After Miyazawa *et al.*[59]).

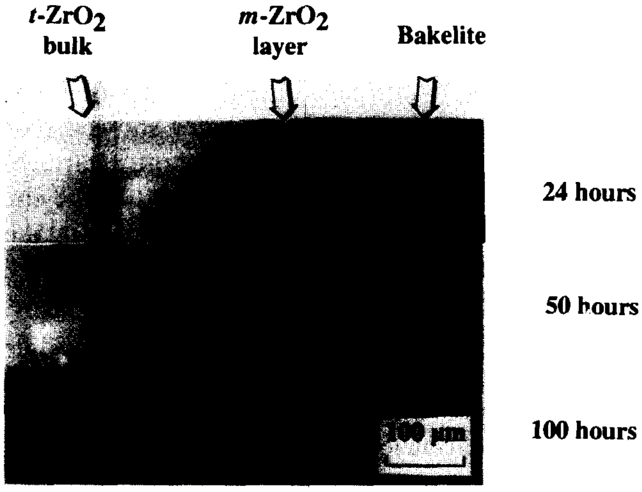


Fig. 10. Optical micrograph showing the growth of the surface monoclinic layer with ageing time for 2·5Y–TZP aged at 180°C in an autoclave containing superheated water (1MPa pressure). (After Lawson *et al.*[22]).

Tsubakino *et al.*,[10,61] Lawson[22] and Zhu *et al.*[62,63] showed that the relationship between the amount of transformation and the ageing time can be expressed by the Johnson–Mehl–Avrami equation:

$$f = 1 - e^{-bt^n} \qquad (1)$$

where f is the transformation fraction, t is the time, and b and n are constants.

The value of n obtained was 0·7–1·0 irrespective of grain size or ageing environment. They also show that cracks accompanying the transformation propagate along grain-boundaries. Therefore, an increase in the cohesion of grain boundaries will probably be the most important factor in preventing the propagation of the tetragonal–monoclinic transformation from the surface to the interior.

Sintering aids that promote liquid phase formation do not enhance cohesion, but they help to prevent crack initiation. Kimura *et al.*[64] suggests the

> "*...presence of dopant in grain boundaries [acts] as a protective coating of [the] ZrO$_2$ grains against water (moisture) attack.*" which will therefore prevent OH$^-$ attack on the grain surfaces.

Chen and co-workers[65–68] identified an incubation region on the kinetic plots of monoclinic content versus ageing time. The first derivative of these kinetic curves shows that generally the rate of transformation gradually increases to a maximum and then decreases. Lu and Chen extrapolated the plot of maximum rate of transformation versus grain size and deduced a critical grain size of 0·37 µm, below which degradation does not occur. Mäntylä *et al.*,[69–71] Lilley[42] and Lawson *et al.*[22,60,72] have shown that there is no incubation time and that the rate of transformation is constant, i.e. the phase transformation reaches saturation immediately and grows inwards linearly with time. Lawson *et al.* found that for 2·5Y–TZP the monoclinic transformation rate was 2–3 µm/h (0·2–0·4 µm grain size respectively) in superheated water in an autoclave at 180°C.

3.1 Corrosion mechanisms

Sato and Shimada[19] based their ageing model on the mechanism of stress corrosion in vitreous silica exposed to water.[73] The authors dismissed the dissolution of yttria or zirconia into the solutions by analysing the solvents used, and also no weight change of the aged specimen was observed. The reaction between water and Zr–O–Zr bonds at the crack tip is shown in Fig. 11. The strain which acts to stabilize the tetragonal phase[74,75] may be released on the surface (due to the reaction in Fig. 11), along with the growth of pre-existing flaws, so inducing the phase transformation.

Sato *et al.*[29] explained the reaction between water and zirconia on the basis of activation energies for transformation in Y– and Ce–ZrO$_2$. These studies gave similar values for both stabilizers (72·8–93·8 kJ/mol), therefore indicating that the water reacted primarily with Zr–O–Zr bonds on

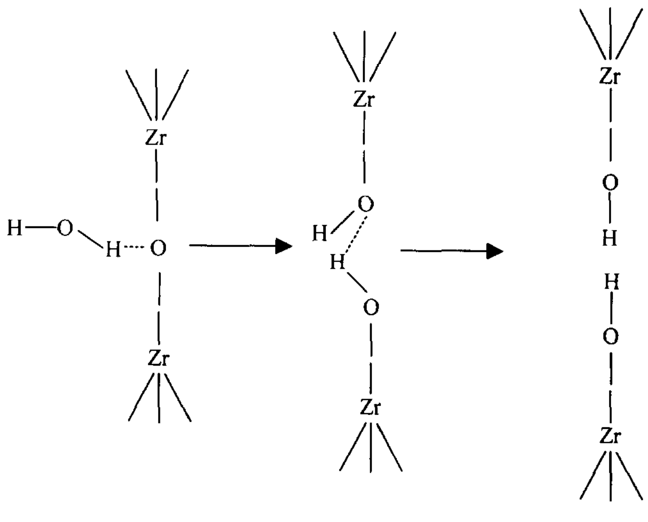


Fig. 11. Reaction scheme expected for the reaction between water and Zr–O–Zr bonds at the crack tip. (After Sato & Shimada[19]).

the surface and not the stabilizing oxide. They also expect solvent environments with a molecular structure containing a lone-pair electron orbital opposite a proton donor site to strongly affect crack growth. Investigation of various solutions[19] lead the authors to conclude that solutions which accelerate crack growth have the greatest effect on the tetragonal–monoclinic transformation.

The role of the water molecule on degradation in Y–TZPs has been investigated by Yoshimura *et al.*[20,51,76] The ageing-induced phase transformation was accompanied by an increase in the crystal lattice. The initial lattice parameters could be restored and a weight loss detected if the aged sample was annealed (400°C for 6 h in vacuum or 1300°C for 1 h in air). This reversible expansion and contraction of the monoclinic lattice seems to be caused by the inclusion and exclusion of OH^- in the lattice. The authors feel that if yttrium depletion by $Y(OH)_3$ formation or by Y^{3+} dissolution had occurred, such a reversible lattice recovery would not be observed at low temperatures and/or in a short period of time. Infrared spectroscopy clearly showed the introduction of OH^- on ageing (also confirmed by Raman spectroscopy) and its subsequent exclusion on annealing.

Yoshimura *et al.* calculate that approximately 60% of oxygen vacancies were occupied by OH^- ions, and that these OH^- ions would migrate faster than O^{2-} because of less charge and similar size. The slow diffusion of Y^{3+} to form $Y(OH)_3$ is thought unlikely by Yoshimura *et al.* and dissolution of Y^{3+} during the hydrothermal dissolution of yttria-stabilized zirconia, YSZ[76] does not occur. Based upon the arguments for anion diffusion, the OH^- ion trigger mechanism was proposed by Yoshimura *et al.*[20,51,76] is described below and shown schematically in Fig. 12.

Step 1 Chemical adsorption of H_2O at the surface.

Step 2 The formation of Zr–OH and/or Y–OH bonds at the surface, at which points stressed sites are created.

Step 3 The accumulation of strain by the migration of OH^- ions at the surface and in the lattice, to prepare nucleating defects.

Step 4 The nucleaton of monoclinic phase in the tetragonal grains: then the tetragonal–monoclinic transformation yields micro- and macro-cracking.

Further investigations[51] into the effect of high-temperature and high pressure-water showed that the activation energy remained constant regardless of temperature or pressure and seemed to be the activation energy for the diffusion of OH^- in the Y–TZP lattice, which further suggests that the degradation is controlled by OH^- diffusion. This model is based upon the accumulation of strains to exceed a critical value, i.e. the energy barrier from tetragonal–monoclinic formation. Therefore the transformation becomes barrierless, and spontaneous nucleation of monoclinic domains occurs.

The mechanism proposed by Sato *et al.*[19] also suggests the formation of Zr–OH at the surface. Sato however, assumes the formation of OH^- causes the release of strain which act to stabilize the t-ZrO_2 whereas Yoshimura *et al.* think that

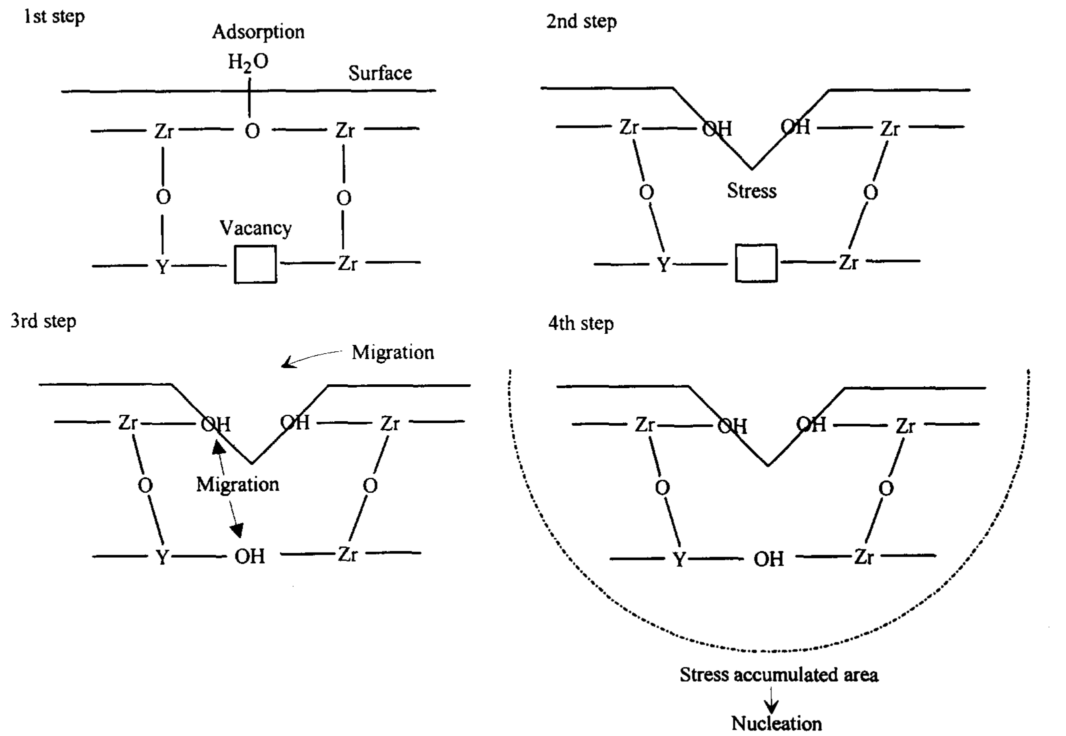


Fig. 12. Proposed degradation process of Y–TZP by the OH^- trigger mechanism. (After Yoshimura *et al.*[20]).

Zr–OH (Y–OH) creates a stressed site. Yoshimura also suggests that the mechanical stresses caused by thermal expansion mismatch as proposed by Schubert *et al.*[12,14,15] also play a role in triggering the tetragonal–monoclinic phase transformation. This mechanism is also supported by Masaki[44] who then proposes that the transformation develops along grain-boundaries causing zirconia particles to lose coherency with the matrix, therefore resulting in great loss in MOR. Masaki attributes inhibition behaviour to higher densities, therefore decreasing the number of cracks and defects for water attack.

Lepisto and Mäntylä have shown by the use of IRS and XPS,[69] that OH^- ions exist on the surface of Y–TZP, but they have also found that the OH^- ions do not extend throughout the transformed layer.[70] It is therefore considered that hydroxide formation throughout the transformed layer is not possible. However it would appear that Zr–OH formation at the specimen surface nucleates the phase transformation which then proceeds autocatalytically, without the requirement of continued hydroxyl ion involvement. Evidence for this mechanism is shown in Fig. 8[52] which shows that the transformation is nucleated in the presence of water vapour and then proceeds at the same rate under a dynamic vacuum.

3.2 Destabilization mechanism

Lange *et al.*[43] initially hypothesized that the ageing phenomenon was a result of a stress–corrosion type reaction, water vapour reacting with a glassy silicate grain-boundary phase. Using specimens with and without silica additions/impurities they found that the presence of a glassy phase at the grain-boundaries had no effect on the ageing behaviour of Y–TZP, which is also supported by Mecartney.[16] Nakajima[21] examined a range of Y–TZP ceramics in the TEM and found no evidence of an intergranular glassy phase. Aged specimens exhibited twinning within grains, and cracks along the grain-boundaries. These cracks seemed to initiate from the triple points and grow along the grain-boundaries. Nakajima attributed these cracks not only to the transformation, but also to corrosion.

TEM studies by Lange *et al.* on a 6·6 mol% specimen (consisting primarily of large cubic grains) before and after ageing revealed an additional microstructural feature that was not present before ageing. Clusters of small yttrium-rich crystallites (20–50 nm) bridged gaps in the TEM foils and were frequently adjacent to the transformed m-ZrO_2 grains as well as the cubic grains. Lange *et al.* found that the crystallites were α-$Y(OH)_3$. In addition, the glassy intergranular phase remained intact and so disproved their initial hypothesis. These crystallites have not been observed by any of the other TEM studies of aged Y–TZP.

Lange *et al.* propose that the tetragonal–monoclinic phase transformation will occur when water vapour draws out an amount of yttrium from a small volume element on the surface of the grain, thus destabilizing this small volume element. As this monoclinic nucleus grows by further yttrium depletion, it will achieve a critical size whereby spontaneous growth can occur without the need for further yttrium diffusion to completely transform the tetragonal grain in which it was growing.

The volume expansion and shear strain associated with the transformation will produce a microcrack if the grain size is greater than a critical value. If the transformed grain is less than the critical size required for microcracking, then nucleation, growth, and thus transformation of subsurface grains will be limited by long-range diffusion of yttrium to the surface. If the transformed grain is larger than the critical size, then microcracks will form and open up subsurface grains to further water vapour attack. Lange comments that only short-range diffusion of the yttrium is required and that this mechanism also explains why transformation only occurs above a critical particle size. However, Tsubakino *et al.*[10] showed that grains smaller than the critical size which should be 'stable' tetragonal grains, do transform when aged under hydrothermal conditions. Yoshimura *et al.*[20] have criticized $Y(OH)_3$ crystallite formation on account of the slow diffusion of yttrium in zirconia.

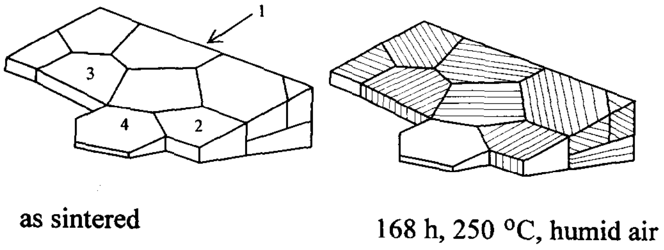
Winnubst and Burggraaf[11] also favour the formation of α-$Y(OH)_3$. Water reacts with yttrium from the Y–TZP surface grains to form yttrium hydroxide. This results in an yttrium-rich surface layer (observed by AES) and an yttrium depleted region close to the enriched surface. When a critical composition and grain size are reached then the tetragonal–monoclinic transformation will be initiated. Recent work by Azzoni *et al.*[77] who have studied the degradation mechanism using electron paramagnetic resonance (EPR) clearly supports the formation of α-$Y(OH)_3$. Additionally, Kruse *et al.*[78] studied the role of water on the ageing mechanism of Y–TZP using elastic recoil detection analyser (ERDA) and found that hydrogen penetrates deep into 3Y–TZP during ageing, while no penetration was observed for an ageing resistant Y–TZP. This experimental evidence has been used by Boutz[79] as clear confirmation that Y–OH bond formation and diffusion of OH^- into the degrading material occurs. However, Hughes *et al.*[80] who also studied the role of water on the ageing of Y–TZP, concluded that hydroxides of yttrium are only observed after severe treatment and are therefore symptomatic of the ageing process rather than initiators of the transformation.

Hernandez *et al.*[81] investigated the surfaces of aged Y–TZP using XPS and deduced that water molecules dissociate and are adsorbed at the surface. Reaction of OH^- ions with Y_2O_3 leads to formation of an oxyhydroxide, YO(OH), species. Simultaneously, tetragonal zirconia embryos form, grow and then transform when their size exceeds a critical value. Microcracking and spalling can then occur opening up new Y–TZP surfaces for continued attack.

3.3 Stress-induced transformation

The effects of internal stresses on the ageing behaviour of Y–TZP ceramics has been extensively investigated by Schubert *et al.*[12,14,15] and also more recently by Kim and Jung.[13] Schmauder and Schubert's[12] experiments were conducted on a 2 mol% Y–TZP, sintered at 1500°C for 2 h and prepared for TEM analysis. The sample was photographed in the TEM, then removed and annealed in air at 250°C for 0·5–168 h, and then remounted in the TEM with the same orientation as before.

The result was that only unconstrained, faceted grains in a protruding position (position 4), Fig. 13, were stable against environmental attack. Grains in positions 2 and 4 have the same surface area in contact with the water and should have the same surface energy. However, if the surface energy determined the stability, these grains would behave in the same way. The observation that the constrained grains behave differently than protruding ones indicates that the stress situation of the grains is the dominant factor governing grain stability. It is known that shear and tensile stresses are destabilizing, whereas compressive stresses stabilize the grains. The shear component is normally the largest and therefore nucleates, or controls, the transformation. They attribute these stresses to the anisotropy of the thermal expansion; the stresses increase with cooling.



as sintered

168 h, 250 °C, humid air

TEM experiment: unconstrained grains did not transform during degradation test.

Fig. 13. Schematic showing the effect of ageing for 168 h, at 250°C in humid air, on constrained and unconstrained grains in 2Y–TZP. (After Schmauder & Schubert[12]).

Schmauder and Schubert propose that the instability of the constrained surface grains is due to stress corrosion attack of these grains by water vapour. They favour the formation of yttrium hydroxide, not however, by diffusion of Y^{3+}, but by the self diffusion of water. The argument is based on the anion vacancies of the distorted fluorite structure coupled with the high anion mobility as a possible path for an uncharged species to diffuse into the lattice. The water molecule is smaller than the O^{2-} ion and could fit therefore into the vacancies. Migration into the lattice is dependent on substitution with an oxygen ion or a vacancy. Schubert calculated that the self diffusion coefficients for the motion of vacancies and for oxygen ions are similar to the linear diffusion coefficient of the transport mechanism for hydroxide formation. Therefore stress–corrosion attack of surface grains by water vapour results in $Y(OH)_3$ formation. The depleted area acts as a monoclinic nucleus which then grows under the influence of thermal expansion anisotropy stresses and propagates autocatalytically and is further aided by water attack via microcracks caused by the volume expansion of transforming grains.

These tensile stresses obviously increase with increasing grain size, and therefore a small grain size is required to prevent microcracking and hence transformation propagation. Schubert also attaches great importance on yttria distribution and attributes an inhomogeneous yttria distribution with reduced ageing performance. An interesting observation by Matsui *et al.*[82] on a 3Y–TZP aged sample with one face in tension and the other in compression, showed that the face in tension had nearly 100% transformation, whereas the rate of change on the other face was lower. Similar studies by Drennan *et al.*[28] on Mg–PSZ also show this behaviour.

The work of Kim and Jung[13] also mentions internal stresses caused by thermal expansion anisotropy, but in this case evidence from the literature points towards relaxation of these internal stresses by dipole rearrangement, which then create localised strains initiating the transformation. Dipole reorientation is a thermally activated process and so according to Kim's mechanism ageing-induced phase transformations would occur in dry air or vacuum. This is not experimentally observed and so this mechanism is not complete without the effect of water vapour taken into account. However, internal friction through dipole rearrangement is a plausible mechanism for aiding ageing-induced transformation initiation and propagation.

Lu *et al.*[65,67] studied the kinetics of the ageing behaviour of Y–TZP and showed that in air the

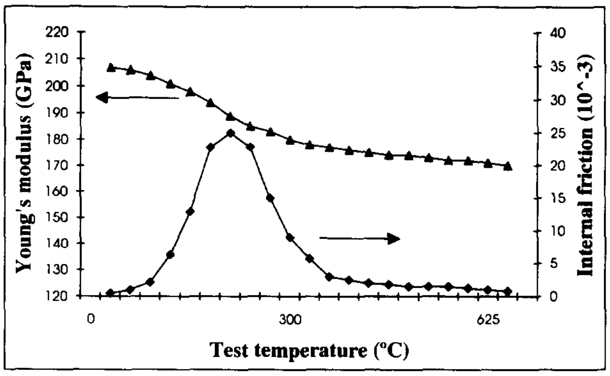


Fig. 14. Temperature dependence of Young's modulus and internal friction in 3Y–TZP. (After Shimada *et al.*[83]).

kinetic curves were sigmoidal, whereas in water they exhibited a linear logarithmic relationship. The sigmoidal kinetic relationship in air was split into three segments; an incubation time, an increase in the rate of transformation, and a reduction in transformation rate with the reaction levelling off. This premise is flawed however, as the sigmoidal shape is simply due to the monoclinic surface layer increasing in thickness until it exceeds the X-ray penetration depth.[22]

They consider that water catalyses the tetragonal–monoclinic transformation by reducing the incubation time. As the more the transformation is induced by the transformation strain, the easier it could be for water to catalyse the phase transformation when it diffuses through microcracks to the interior. Consequently the acceleration of the phase transformation is enhanced by a combination of water-vapour catalysis and subsequent autocatalytic reaction.

3.3.1 Internal friction

An initial reference to the ageing temperature regime and a similar temperature dependence of internal friction was made by Matsui *et al.*[83] Matsui referred to the work of Larsen and Adams[84] who plotted internal friction versus temperature and obtained similar results to Shimada *et al.*[85] and Weller and Schubert.[86] Matsui's results suggest that the tetragonal–monoclinic phase transformation proceeds most rapidly at ≈200°C, which coincides with the optimum internal friction temperature in Larsen's work and is suggested to be due to twin motion in *m*-ZrO_2.[85]

The temperature dependence of Young's modulus and internal friction for various engineering ceramics was studied by Shimada *et al.*[85] They found that for Y-PSZ the internal friction increased rapidly with temperature to a maximum at 200°C then decreased rapidly with temperature up to 400°C where it was a similar value to the room temperature figure. The Young's modulus decreased with decreasing temperature, but an anomolous sudden change was observed accompanied by the internal friction peak. Above 400°C the Young's modulus decreased linearly with increasing temperature up to 650°C and is shown in Fig. 14.

The internal friction, dielectric loss, and ionic conductivity of 3Y–TZP has been studied by Weller and Schuber.[86] Their results were similar to the ones shown in Fig. 14. Mechanical or dielectric loss resulting from reorientation of atomic defects by application of mechanical stress or an electric field, is proportional to the concentration of defects. The experimental results show that the activation enthalpy for mechanical and dielectric relaxation is the same (87 kJ/mol), which is similar to the activation energies calculated for ageing-induced phase transformation by Sato *et al.*[29] and Lawson.[22] They conclude that the mechanical and dielectric relaxation is caused by thermally activated reorientation of the same anisotropic defects.

Weller and Schubert propose the following atomistic model for mechanical and dielectric loss in TZP ceramics. During the formation of *c*- and *t*-ZrO_2 solid solutions, substitution of Y^{3+} for Zr^{4+} is accompanied by the introduction of oxygen-ion vacancies (for charge neutrality) in fluorite and distorted fluorite respectively. The coulomb interaction between substituted Y'_{Zr} and oxygen-ion vacancy, V''_{o}, produces $(Y'_{Zr}V''_{o})$ complexes. This complex behaves as an anisotropic electric and elastic dipole, which reorients upon application of an electric or elastic field. It is assumed that dipoles are oriented parallel to [111] lattice direction as in *c*-ZrO_2. The reorientation is caused by oxygen vacancies jumping around the Y'_{Zr} ions for electrical and mechanical fields.

Kim and Jung[13] argue that these dipoles may reorient when residual stresses are relieved due to annealing above the lower temperature limit for ageing. This reorientation produces small localised strains along the [111] direction. When a critical value of strain is reached, the locally strained lattice becomes mechanically unstable, causing nucleation of *m*-ZrO_2. This relaxation temperature is not necessarily sensitive to additive levels or grain size.

The effect of Al_2O_3 additions to 3Y–TZP on the temperature dependence of internal friction were investigated by Ono *et al.*[87] Their results are comparable with those of Weller and Schubert for low Al_2O_3 additions. As the dopant content increased then the internal friction peak became lower and occurred at higher temperatures. They also found that the internal friction peak was accompanied by an inflection point in the Young's modulus.

They conclude that the relaxation phenomenon was concerned with the Y_2O_3 and not ZrO_2.

Nishiyama *et al.*[88] measured internal friction and modulus changes with temperature, and found similar results to those reported above. They attribute the internal friction peak to dipole relaxation (according to Weller and Schubert), to a stress-induced phase transformation, and to water initiated phase transformation (hydrothermal ageing).

3.4 Alternative mechanisms

Lepisto and Mäntylä[69] suggest that zirconia reduction and oxygen vacancy annealing was responsible for the degradation. Zirconia dissolution is initiated at grain-boundaries where the reaction proceeds deeper into the material.

$$Zr_s^{4+} + 2O_s^{2-} + 2V''_o + 4H^+ + 4e^- + 2O^{2-} \rightarrow Zr + 2H_2O$$

The dissolution at grain-boundaries relieves the internal stresses stabilizing the tetragonal structure and thus triggers the phase transformation to monoclinic symmetry.

Kuroda *et al.* suggest that the oxygen anions are responsible for the chemical attack.[52] It is proposed that thermally activated oxygen exchanges take place between the environment and the surface. Oxygen anions occupy monoclinic sites rather than the tetragonal ones, since monoclinic zirconia is thermodynamically more stable at low temperatures. As a result cations shift and therefore cause the tetragonal–monoclinic phase transformation.

Further investigations by this group on the application of an electric potential to induce the tetragonal–monoclinic phase transformation,[89] showed that the surface monoclinic content of the anode and cathode had increased. The reactions at the cathode are as follows:

$$O_2 + 4e^- \rightarrow 2O^{2-} \text{ (in the presence of oxygen)}$$
$$H_2O + 2e^- \rightarrow H_2\uparrow + O^{2-} \text{ (in the presence of water)}$$

Once the above reaction occurs only the oxygen ions can diffuse into the bulk. Oxygen ions then trigger the transformation as explained in the opening paragraph. As the tetragonal grains in the bulk are constrained by the matrix then transformation does not occur despite oxygen ion motion. They conclude that the gas–solid reaction at the surface rather than the anion diffusion through the bulk is essential for the transformation to nucleate.

4 Transformation Inhibition

The free energy change ($\Delta G_{t\text{-}m}$) of the tetragonal–monoclinic phase transformation on cooling through the transformation temperature in absence of an applied stress field is given by:[90]

$$\Delta G_{t\text{-}m} = (G_c^m - G_c^t) + (G_{se}^m - G_{se}^t) + (G_s^m - G_s^t) \quad (2)$$

where G_c is the chemical free energy, G_{se} the (dilational) strain free energy, and G_s the surface free energy. Superscripts t and m denote tetragonal and monoclinic phases respectively.

Heuer and Lenz, and Heuer *et al.* have modified eqn (2) by taking into account bulk residual shear strains from twinning, interfacial contributions from twin boundaries and particle-matrix microcracking,[91] and an extra nucleation term[92] respectively. The influence of important parameters, however can still be assessed using eqn 2.

The metastable tetragonal phase can only exist when $\Delta G_{t\text{-}m} > 0$. The chemical free energy term is always negative, but the addition of stabilizing oxides will make this term less so. The strain free energy term is also negative, and is influenced by the matrix stress according to.[93]

$$G_{se} = 1/2\ \sigma_{ij}\epsilon_{ij}V_{mol} \quad (3)$$

where σ_{ij} is the stress tensor, ϵ_{ij} the strain tensor and V_{mol} the molar volume.

Therefore in the presence of a tensile stress the strain free energy term is negative, making the tetragonal phase less stable. When compressive stresses are present, the tetragonal phase is more stable. Without the presence of compressive stresses, or in general strain contributions, stabilization will only occur when the surface free energy term in eqn 2 is positive and larger than the sum of the first two terms.

Generally speaking, and with reference to eqn 2, the control of the tetragonal–monoclinic phase transformation can be achieved by:

1. An increase in the chemical free energy change by alloying with another stabilizing oxide, e.g. CeO_2.
2. An increase in the strain free energy change by dispersion of a second phase, e.g. Al_2O_3.
3. By increasing the surface free energy change, e.g. reduction in grain size.
4. Coating.
5. Surface microstructural engineering.

It should be noted though that an increased thermal stability by methods 1 and 2 above generally results in a decrease in mechanical properties through over-stabilization of the *t*-ZrO_2 phase.

4.1 Chemical free energy increase

An increase in the chemical free energy can be achieved quite simply by increasing the yttria content. However this over-stabilization of the *t*-ZrO_2 phase (and probable *c*-ZrO_2 phase formation) leads to a sharp reduction in the mechanical properties of Y–TZP.

An alternative method of increasing the thermal stability of Y–TZP is to alloy with another stabilizing oxide. Sato and Shimada[29,49,94–96] examined the effects of various oxide additions to Y–PSZ. They found that CeO_2 was an effective additive for eliminating degradation, without any reduction in mechanical properties and actually increased the elastic modulus. The authors feel that the effect of CeO_2 may be to increase the size of the transformation zone in the vicinity of a crack front. TiO_2 did reduce the phase transformation but at a cost of increased grain size and reductions in relative density, hardness and fracture toughness. The other oxides evaluated (CaO and MgO) did decrease the surface monoclinic content, but only because of increased cubic formation, which obviously lowered the fracture toughness.

Duh and Wu[97] alloyed 1, 3 and 4 mol% Y–TZPs with 10 mol% CeO_2 and showed that the tetragonal phase could be retained in water at 300°C for up to 1 month. A similar result was obtained by Hirano and Inada[98] but they only alloyed with up to 5·5 mol% CeO_2. Further work by Duh and Wan[99] showed that 9·5 mol% CeO_2 alloyed with 1·5 mol% Y–TZP is required to inhibit ageing.

Hirano and Inada[100] found that hydrothermal stability could only be achieved by (4Y,4Ce)–TZP–25 wt% Al_2O_3 composites, although (4Y,4Ce)–TZP was resistant to ageing in air. Theunissen *et al.*[101] and Boutz *et al.*[79,102] showed improved ageing resistance with CeO_2 additions under autoclave conditions. Theunissen[103] also examined the effects of TiO_2 additions. They found that some samples aged very quickly and others showed good resistance. This variability was attributed to surface enrichment in TiO_2, for the good ageing resistant samples, that may form a TiO_2 overlayer.

4.2 Strain free energy increase

Sato *et al.*[18] added Al_2O_3 (5–10 wt%) to 3 mol% Y–TZP and found that the surface monoclinic content decreased with increasing concentration of dispersed Al_2O_3. They postulated that the Al_2O_3 grains play a major role in resisting the volume expansion of the zirconia grains accompanying the tetragonal–monoclinic phase transformation. Further investigations by Sato and Shimada[29,49,94–96] showed that Al_2O_3 additions reduced the rate of transformation but did not prevent it totally, and increased the elastic modulus. Schmauder and Schubert[12] however, argue that additions of Al_2O_3 create stresses with the bulk ceramic which are detrimental to the ageing behaviour of TZP. Masaki[44] supports this argument and includes TiO_2 and Fe_2O_3 into this category of stress raisers. However neither Schmauder nor Masaki have presented results to support their argument.

Tsukuma and Shimada[104] also found a reduction in monoclinic content with Al_2O_3 additions, and that 40 wt% Al_2O_3 almost perfectly restrained the transformation. They attributed this improvement in thermal stability of the tetragonal phase to an increase in Young's modulus of the matrix due to the Al_2O_3 additions.[105,106] Additions of Al_2O_3 or TiN to 2–6 mol% Y_2O_3–ZrO_2 have been shown to control the phase transformation and so prevent deterioration in modulus of rupture.[107]

Kim and Jung[13] show that composites of transformable and nontransformable TZPs formed in the ZrO_2–Y_2O_3–$Nb(Ta)_2O_5$ systems can act as lattice relaxation inhibitors (increase the lattice stiffness). This composite basically consists of a metastable tetragonal bulk interspersed with large stable grains. Recent research on the role of second phase additions to zirconia ceramics leading to enhanced ageing resistance has been reported for mullite, spinel and Al_2O_3,[108] MgO and Al_2O_3[109] and tungsten carbide.[48]

4.3 Surface free energy increase

The grain size of Y–TZP can be controlled by reducing the sintering (or calcination) temperature. However, unless the powders are ultra fine and highly reactive, the sintered density will not be very high. Hot-pressed or hot-isostatically pressed powders enable a small grain sized, fully dense Y–TZP to be manufactured.

A much cheaper technique is to use sintering additives to ensure a small grain size through lowering the sintering temperature. The effect of additives on the anti-degradation behaviour of Y–TZP has been investigated by Kimura *et al.*[64] and Lawson *et al.*[22,23,110] Transition metal oxide additives were used as sintering aids and resulted in densification occurring at about 1200°C. The doped 2·5 mol% Y–TZPs had a small grain size, were fully dense and were resistant to degradation in air and boiling water.[64] Similar results were also obtained by Lawson *et al.* who showed that strengths in excess of 1000 MPa could be retained after 1000 h in superheated water in an autoclave at 180°C.

Sato and Shimada[49,95] showed that reducing the grain size of the CeO_2-alloyed Y–TZP reduced the surface monoclinic content and lowered the concentration of CeO_2 required for total inhibition.

4.4 Coating

Iio *et al.*[111] coated Al_2O_3 onto the surface of Y–TZP using CVD. When this sample was aged in air at 300°C they found that the tetragonal–monoclinic phase transformation had been restrained. Any coatings however, must be fully dense and stable against the atmosphere. Such coatings can be produced by CVD but processing is complicated and expensive. If the coating degrades or is fractured in any way, then the susceptible tetragonal grains will be open to water vapour attack.

4.5 Surface engineering

Whalen *et al.* formed a surface layer of very fine-grained tetragonal phase on Y–TZP by surface recrystallization.[112] This had the effect of resisting ageing at 200°C in air for 1000 h. Therefore large grain sized Y–TZP for maximum toughness can be protected from the ageing-induced transformation by simple postsintering treatments.

4.6 Non-transformable tetragonal zirconia (*t*'-ZrO_2)

The effect of *t*'-ZrO_2 on ageing of TZPs has been investigated by Noma *et al.*[76] and by Jue *et al.*[113] Noma found that the *t*'-phase was more resistant to nucleation of the ageing-induced transformation by OH^- trigger mechanism, than a more conventional *t*-ZrO_2. However, once the transformation had begun it proceeded at the same rate as for the *t*-ZrO_2 sample. Jue *et al.* showed that *t*'-ZrO_2 was essentially ageing resistant when it had polished surfaces. However, when surface ground, *t*'-ZrO_2 exhibited very slight transformation (up to 7% monoclinic content) after ageing at 275°C in air.

4.7 Density

Evidence for a density threshold for ageing was reported by Masaki[44] and is shown in Fig. 15. The solid circles and triangles show the sintered materials, the strength of which decreased greatly after ageing (the extent of the black area in each circle corresponds to the degree of strength reduction). The figure also shows lines of critical densities (thresholds) and grain sizes for the Y–TZP compositions after ageing.

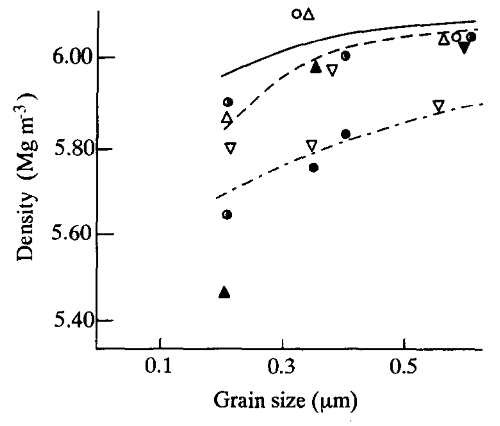


Fig. 15. The interrelation of density and grain size with the degradation of Y-TZPs aged at 200–250°C in air for 2000 h, (O, ——, 2·5 Y_2O_3; Δ, ----, 3 Y_2O_3; ∇, -·-·-, 4 Y_2O_3. (After Masaki[44]).

According to these results if the density is greater than a critical value (Y_2O_3 dependent) then ageing will not occur. The critical density determined by Masaki will however, be an over-estimate, as his specimens were aged and then cut to the required size before the density and MOR were assessed.

4.8 Lattice spacing

An interesting aspect of Kim and Jung's work[13] is the possible existence of a critical value of d_{111}. Figure 16 shows the tetragonal zirconia (111) lattice spacing, d_{111}, and the amount of monoclinic ZrO_2 resulting from various ageing times (at 250°C). These results show that as a critical value of d_{111} is reached, then localised lattice instability occurs and transformation is initiated. Therefore, *t*-ZrO_2 grains whose d_{111} is larger than the critical value, transform.

Yoshimura *et al.*[20] observed a reversible expansion and contraction of the zirconia lattice with ageing and subsequent annealing, and concluded that it was caused by the inclusion and exclusion of OH^- in the lattice. Recent results obtained by Lee and Kim[114] have shown that the transformation is reversible upon annealing above 1200°C. The phase recovery was accompanied by healing of micro-cracks, but the macro-cracks remained to a large extent. Therefore the benefit of annealing severely aged zirconia in order to re-establish the tetragonal phase must be questioned.

5 Summary

The experimental evidence of hydrothermal degradation is well documented and there are compositions and conditions under which ageing will not occur. Much more work in developing ageing resistant zirconia ceramics with good mechanical properties has still to be undertaken. The current ageing models do not accommodate all of the

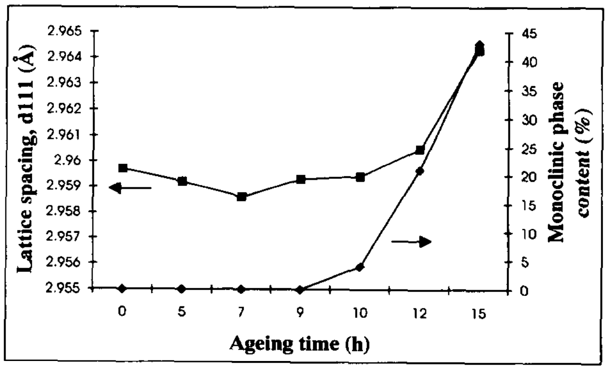


Fig. 16. Monoclinic content and lattice distance vs ageing time for a 3Y–TZP sintered at 1500°C for 5 h and aged in air at 250°C. (After Kim & Jung[13]).

experimental evidence, and there is conflict as to the nature of the attack, and whether there is accumulation or release of strain. The second paper presents a new ageing mechanism which covers all of the published experimental evidence.

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