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Low-temperature ageing degradation of 2.5Y-TZP heat-treated at 1650 °C

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Abstract

Low temperature ageing degradation at 250 °C in air of 2.5 mol% Y-TZP with various grain sizes has been investigated by using specimens in the form of discs of 8 mm diameter and 1 mm in thickness. The increase in tetragonal grain size, as well as some cubic phase, were attained by heat-treating 0.3 μm fine grain size Y-TZP at 1650 °C for different times. XRD and Raman spectroscopy analysis were used to evaluate the amount of tetragonal to monoclinic (t–m) phase transformation after different ageing times at 250 °C in air up to 900 h and its effect on strength was measured by using the biaxial ball-on-three-balls test. It is shown that transformability under ageing conditions at 250 °C increases with tetragonal grain size. Raman analysis was done punctually at various distances form the edge of the aged samples and it is shown that the nucleation of monoclinic sites begins at the edge of the samples and that the depth of the transformation zone varies with the distance from the edge to the centre of the samples. Biaxial strength always decreases with ageing time and is influenced by the presence of micro and macrocracks formed at the surface centre of the aged samples. This depends strongly on the tetragonal grain size and on the depth of the transformed layer at the central part of the discs.

Keywords: Grain size; Toughness and toughenning; ZrO_2; Ageing; TZP

1. Introduction

Zirconia ceramics present a good combination of fracture toughness (4–15 MPa $m^{1/2}$) and mechanical strength (500–1000 MPa) which makes these materials good candidates for structural applications.[1] These properties are related to the stress-induced phase transformation of tetragonal zirconia into monoclinic symmetry (t–m). It is well known that such phase transformation is accompanied by an increase in volume of ∼4% that may induce compressive stresses in the crack wake.[2] The tendency of the tetragonal phase to transform to monoclinic crystallographic structure depends on the amount of stabilising oxide (Y_2O_3, CeO_2, MgO, etc.) that is incorporated into the crystalline unit cell of zirconia for stabilising the tetragonal form at room temperature.[1] By adding small amounts of Y_2O_3 to pure zirconia, about 2–3 mol%, a well-known family of ceramics, called yttria-tetragonal zirconia polycrystals (Y-TZP), is obtained. The Y-TZP microstructure is mainly formed by fine tetragonal grains of about 0.2–0.5 μm of average grain diameter. On the other hand, if a large amount of stabiliser is added, another family, called PSZ (partially stabilised zirconia) ceramics, is formed, and which is characterised by fine precipitates embedded in a coarse cubic matrix.

It is well known that the strength of Y-TZP may decrease drastically during ageing in air at temperatures between 100 and 400 °C.[3–6] At these temperatures, the t–m phase transformation is activated by the environment and the volume expansion that takes place can generate microcracks in the transformed surface, thereby degrading the strength and surface properties of the material. There are many mechanisms that have been put forward to explain the low-temperature ageing phenomenon of zirconia ceramics.[7–9] It is worthy mentioning the mechanism proposed by Lange et al.[8] and confirmed later by Li et al.[9] using XPS analysis. These authors proposed that there is a reaction

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between water molecules and Y_2O_3 at the surface of Y-TZP resulting in the formation of small crystallites of $Y(OH)_3$ of nanometric size (20–50 nm). Thus, a tetragonal surface grain is destabilised and transforms to the monoclinic structure when water vapour draws out a sufficient amount of yttrium. After this, growth of monoclinic sites can continue spontaneously without further yttrium diffusion.

Recently Guo and He[10] has observed that 8 mol% Y_2O_3 doped cubic-ZrO_2 pellets cracked after exposing to 2.6×10^{-2} atm. water vapour at 250 °C during 2 years. XRD and TEM analyses have shown the presence of a small amount of m-phase. The explanation given by the authors is that during ageing, c-ZrO_2 transforms to t-ZrO_2 and then to m-ZrO_2 because of the annihilation of the oxygen vacancies.

It is now well established that this low temperature ageing degradation is characterised by: (a) t–m transformation proceeds from the surface to the interior; (b) when degradation occurs in air, from all constituents of air, only water vapour is responsible; (c) increasing the amount of stabilising oxide (i.e. increasing oxygen vacancies) or decreasing the tetragonal grain size, can retard the degradation.

With regard to the last point, it should be noticed that the study of the influence of tetragonal grain size on the mechanical behaviour of Y-TZP has been often conducted by changing the amount of stabiliser in order to obtain a larger stable tetragonal grain size at room temperature. Thus, according to the work of Lange[11] the critical tetragonal grain size for t–m transformation increases with Y_2O_3 content, being about 0.5 μm for 2.5 mol% Y_2O_3. However, as reported by Ruiz and Readey[12] and Casellas et al.[13] a larger and stable tetragonal grain size, as well some small amount of cubic phase, can also be obtained by heat-treating Y-TZP at high temperature without recurring to increase the yttria content. The average tetragonal grain size that results is surprisingly nearly three times larger than this critical value. This has the additional benefit of an increase in the fracture toughness without decreasing the fracture strength.[13] Thus, the fracture toughness (K_{Ic}) increases from 4.4 MPa $\mathrm{m}^{1/2}$ (2.5Y-TZP) to 7.4 MPa $\mathrm{m}^{1/2}$ after 2 h of annealing at 1650 °C. This enhancement of K_{Ic} is rationalised by the higher transformation capability of the microstructure. The transformability of a tetragonal grain is quoted by a critical diameter, D_{CR}, which is affected by the amount and type of stabiliser as well as by internal stresses.[11] The presence of large tetragonal grains that are stable at room temperature has been associated to the presence of cubic phase that results in an increase in D_{CR} because the level of internal stresses is reduced.[12,13]

The increase in transformability of larger tetragonal grains in the heat-treated samples was analysed by Raman spectroscopy in a previous work.[14] It was found that the height of the transformation zone around a crack induced by Vickers indentation in heat-treated samples was ranging from 16 to 28 μm, which are clearly larger than those measured in the starting Y-TZP (∼3 μm).

Unfortunately, this high transformation capability due to the presence of large tetragonal grains may induce a strong degradation when exposed at low temperatures during large periods of time. Therefore, the main objective of this paper is to investigate the ageing behaviour of Y-TZP with different tetragonal grain sizes, between 0.30 and 1.37 μm. These are obtained by heat-treating Y-TZP samples at 1650 °C during 1 and 2 h without modifying the overall amount of stabilising oxide (Y_2O_3) in the microstructure.

2. Experimental procedure

The starting material was Y-TZP stabilised with 2.5 mol% Y_2O_3 in the form of rods of 8 mm in diameter. Its microstructure consisted of tetragonal phase (volume fraction >99%) with 0.3 μm mean size. Slices in the form of discs of 8 mm in diameter and about 1 mm in thickness were cut from the rods and they were polished using diamond pastes of 30 and 6 μm. The discs were then heat-treated in air at 1650 °C during 1 and 2 h and the resulting materials were referred to as 1H and 2H, respectively. Then, the samples were aged at 250 °C in air during periods of time up to 900 h. The microstructural analysis was conducted by using scanning electron microscopy (SEM) and X-ray diffraction (XRD). Atomic force microscopy (AFM) analysis where also done at the surface of tetragonal and cubic zirconia grains after ageing experiments. This technique may be useful to analyse the presence of monoclinic twins that are formed during ageing due to t–m transformation.

The amount of monoclinic phase at the surface of the aged samples has been evaluated as a function of the XRD intensities of (1 1 1) tetragonal peak and (1 1 1) and (1 1 $\bar{1}$) monoclinic peaks according to:[15]

$$\%\mathrm{m} = \frac{\mathrm{m}(1\,1\,1) + \mathrm{m}(1\,1\,\bar{1})}{\mathrm{t}(1\,1\,1) + \mathrm{m}(1\,1\,1) + \mathrm{m}(1\,1\,\bar{1})} \quad (1)$$

Raman microprobe spectroscopy technique was used in order to study the t–m transformation at the surface and at various depths on some of the aged samples. A Jobin Ivon T64000 Raman spectroscope with an Ar laser with a wavelength of 632 nm was used. The diameter of the zone analysed varies between 1 and 10 μm for the depth and surface studies, respectively. The amount of monoclinic phase determined by using this technique was calculated by taking into account the area of the tetragonal bands at 148 and 264 cm^{-1} and of the monoclinic doublet at 181 and 192 cm^{-1} according to:[14]

$$V_{\mathrm{m}} = 0.65 + 0.39 \log \left(\frac{I_{\mathrm{m}}^{181,192}}{I_{\mathrm{m}}^{181,192} + I_{\mathrm{t}}^{148} + I_{\mathrm{t}}^{264}} \right) \quad (2)$$

The mechanical strength was evaluated by using the biaxial ball-on-three-balls method. In this test the samples were supported on three tungsten carbide balls positioned at 120° one from each other. The load was applied in the centre of the opposite side by using another ball. The support of the samples was on a circumference of radius equal to 3 mm. The radius of the balls was of 1 mm. The load was applied with a crosshead speed of 200 N/s. The biaxial strength at the centre of the discs was calculated by an equation proposed by Börger et al.:[16]

$$\sigma = f\frac{P}{t^2} \tag{3}$$

where P is the load, t is the thickness of the sample and f is a factor given by:

$$f\left(\frac{t}{R}, \frac{R_a}{R}, \nu\right) = c_0 + \frac{(c_1 + c_2 t/R + c_3(t/R)^2 + c_4(t/R)^3)}{1 + c_5 t/R} \left(1 + c_6\frac{R_a}{R}\right) \tag{4}$$

The values for the parameters c_i (i = 1, . . . ,6) are given in terms of Poisson coefficient of the tested samples.[16]

3. Results

3.1. Microstructural evolution during ageing at 250 °C

The microstructure of the samples resulting from the heat-treatments at 1650 °C is shown in Fig. 1. The average grain sizes of tetragonal and cubic phases, their volume fractions and maximum tetragonal grain size are given in Table 1. It is important to note that heat-treatment at 1650 °C during 1 and 2 h of Y-TZP results in an increase in tetragonal grain size (from 0.3 to 1.4 μm for 2 h) and also in a small increase in the amount of cubic phase. TEM analysis revealed that the large cubic grains contain small tetragonal precipitates as shown in previous work.[17] These tetragonal precipitates are formed during cooling from the annealing temperature because the cubic grains become less stable and tend to decompose in tetragonal ones. The volume fraction of the tetragonal precipitates present in the cubic matrix was quantified as cubic phase, since the amount of cubic phase was determined from observations of the size of the grains at the surface of polished specimens. The presence of large tetragonal grains (up to 3 μm) which are stable at room temperature might be related to the presence of cubic phase, which can reduce the level of internal stresses associated with thermally induced mismatches.[12]

In Fig. 2 it is shown the change in the amount of monoclinic phase detected by XRD at the surface of the aged specimens, and it can be seen that the amount of monoclinic phase increases with ageing time. In the case of the starting Y-TZP, the monoclinic fraction reaches a saturation value of about 12% after 150 h. Heat-treated samples (1H and 2H) show a rapid increase in the amount of monoclinic phase at

Table 1
Average grain size of tetragonal (D_t) and cubic (D_c) grains, maximum D_t ($D_{t,max}$) and volumetric fraction of cubic phase (V_c)

Material	D_t (μm)	D_c (μm)	$D_{t,max}$ (μm)	V_c
Y-TZP	0.30 ± 0.01	–	0.50	0
1 h at 1650 °C (1H)	1.05 ± 0.02	3.45 ± 0.08	1.84	0.19
2 h at 1650 °C (2H)	1.37 ± 0.02	3.84 ± 0.10	2.97	0.24

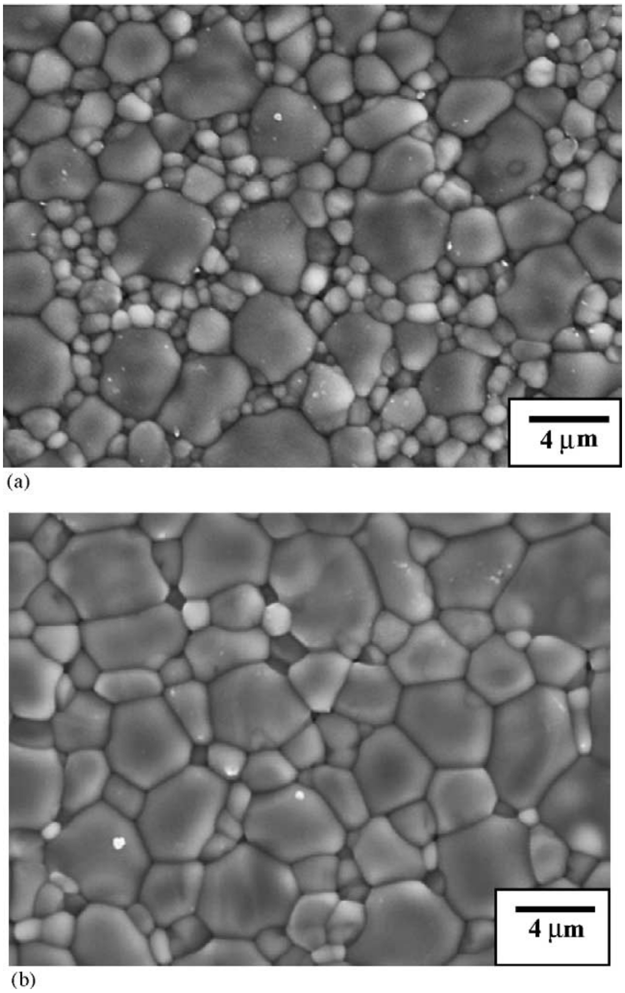

Fig. 1. Microstructures of Y-TZP samples after the heat-treatments at 1650 °C during 1 h (a) and 2 h (b).

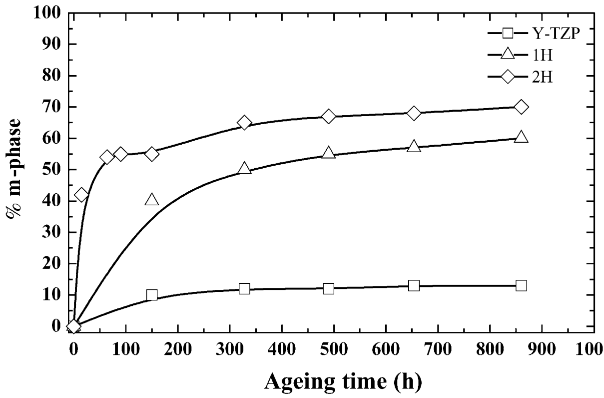

Fig. 2. m-Phase content evaluated by XRD at the surface of the samples as a function of ageing time.

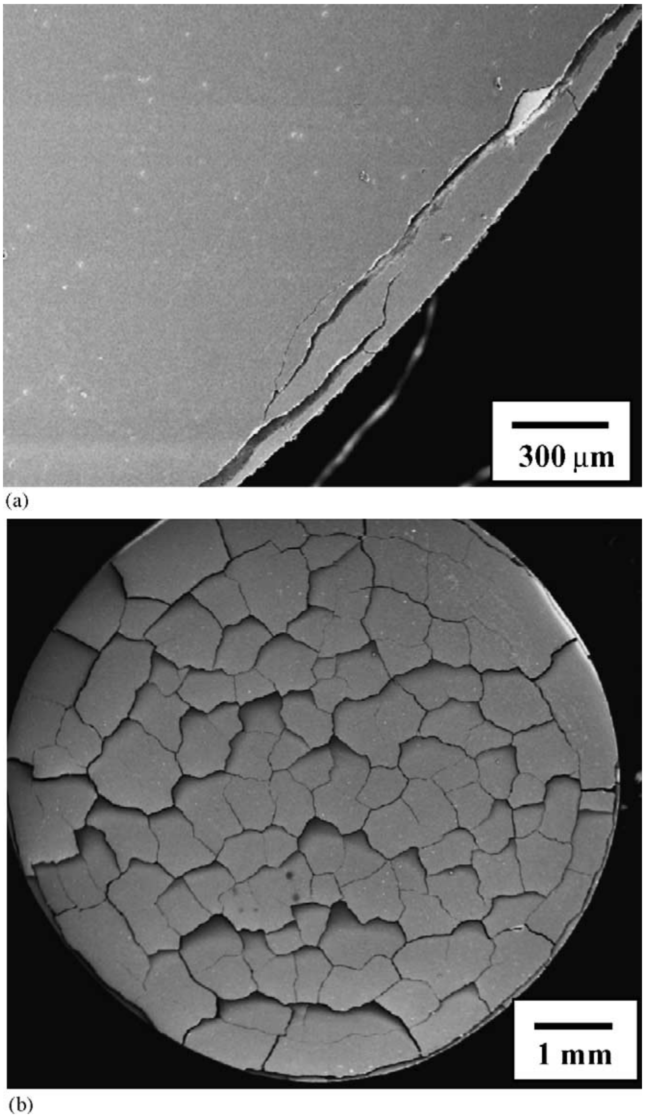

Fig. 3. SEM micrographs at the surface of 1H (a) and 2H (b) after 150 h of ageing.

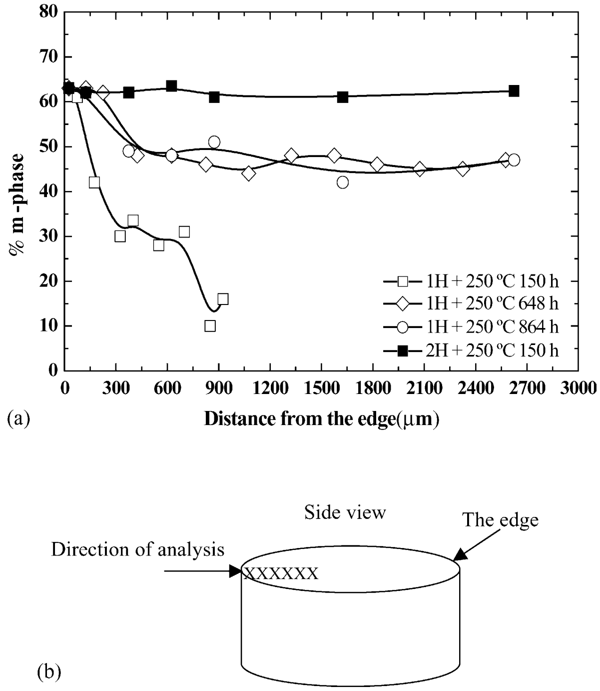

Fig. 4. Evolution of m-phase evaluated by Raman spectroscopy at the surface at a various distances from the edge of the 1H and 2H samples for different ageing times (a) like the scheme in (b).

the surface reaching also saturation levels after times longer than 150 and 90 h, respectively.

SEM micrographs of the surface of the 1H and 2H samples are displayed in Fig. 3 after ageing for 150 h. It can be noticed the presence of macro-cracks that are the result of the increase in volume (∼4%) that accompanies t–m phase transformation. The amount of cracking is larger in 2H probably because of the higher transformability of tetragonal grains, and it takes place rapidly during the first 90 h (see Fig. 2). On the contrary, the surface of the starting Y-TZP is free from cracks after periods of ageing up to 900 h despite of the amount of monoclinic phase (∼12%) detected by XRD. This is explained by the presence of small tetragonal grains (∼0.3 μm) in the microstructure, which are more stable against t–m phase transformation. It can also be noted that cracking starts around the edge of the discs, as can be seen in 1H discs in Fig. 3a, that is, in this zone the transformation is easier than at the centre of the discs.

The cracks observed by SEM around the border of 1H samples (see Fig. 3a) indicate that the t–m transformation during ageing initiates in this zone. This may be due to a higher transformability of the grains near the edge in comparison with those in the central area of the disc. In order to analyse this possibility, Raman microprobe spectroscopy analysis was carried out at various distances from the circumferential edge of 1H aged discs (Fig. 4). Raman analysis clearly shows that the nucleation and growth of monoclinic sites begin at the edge of the samples and grow to the centre with ageing time. It can be seen that the maximum amount of monoclinic phase is reached at the edge after 150 h in both 1H and 2H samples. So, in this zone the kinetics of t–m transformation is more rapid than at the centre of the discs.

Carefully polished transversal sections of the aged samples were also observed by optical microscopy (Fig. 5a) and Raman analysis was carried out at various depths and distances from the edges (Fig. 5b and c). It is found that the thickness of the transformed layer also varies with the distance from the edge. Thus, for 1H samples after 150 h, the depth of the transformed layer at 50 μm from the edge is ∼200 μm, meanwhile at a distance of 175 μm from the edge, this depth diminishes to ∼60 μm and it is relatively homogeneous at the centre. After ageing for 864 h, the depth of the transformed layer in the same type of sample was larger and less inhomogeneous varying from 250 μm, at a distance

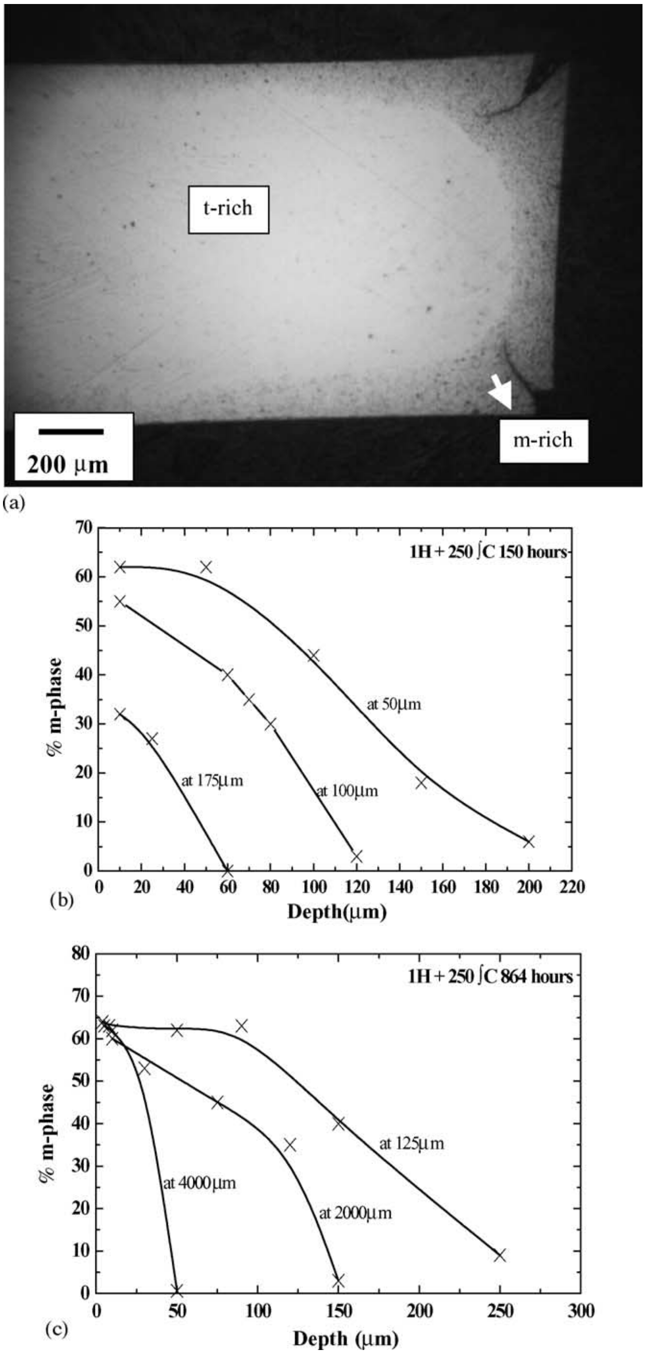

Fig. 5. Optical photograph of a polished cross-section of a aged 1H disc (a) and the evolution of m-phase calculated by Raman spectroscopy in the polished cross-sections of the aged samples at various depths and distances from the edge for the 1H samples aged during 150 h (b) and 864 h (c).

of 125 μm from the edge, to 50 μm at the centre of the disc. Thus, the Raman results indicate that the t–m transformation during ageing is not activated homogeneously at the surface so that the energy to activate this transformation depends on the position of the grains in the microstructure. The macrocracks that are formed during ageing facilitate the water vapour to penetrate inside the samples, in this way promoting the activation of t–m phase transformation inside the volume.

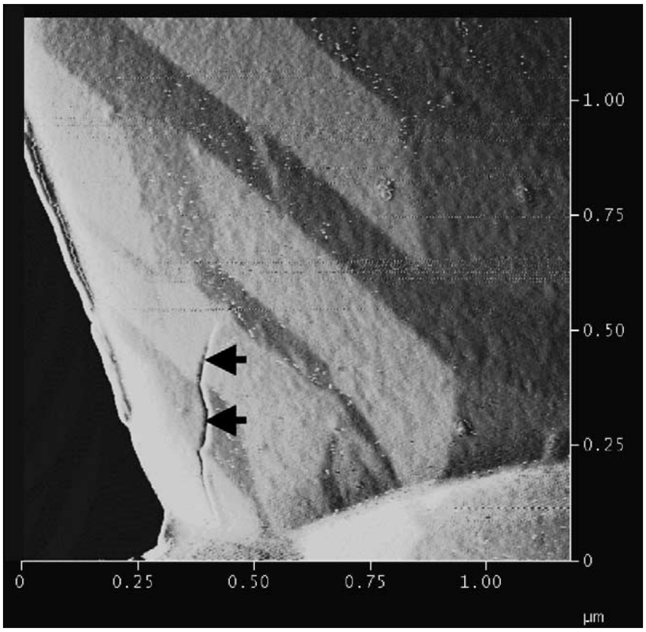

Fig. 6. AFM observations of a transformed tetragonal grain at the surface of 2H sample aged during 648 h.

In the case of as received Y-TZP specimens, Raman analysis can not detect the presence of m-phase because of the little amount of phase transformation inside the layer penetrated by the Raman signal. The t–m transformation in these samples occurred only in the outer surface grains but the propagation into the underlying grains was difficult because of the subcritical grain size of this material.

To explain the presence of microcracks along the surface in the aged samples we should recall that according to Lange,[11] the volume expansion associated with t–m transformation and the corresponding shear strains induced by twinning will produce a microcrack if the grain size is greater than a critical value. For Y-TZP samples there is not cracking at the surface of the aged specimens. The tetragonal grain size (~0.3 μm) in Y-TZP is too small to produce the sufficient stresses for initiating microcracking. On the contrary, the microcracks observed at the surface of samples 1H and 2H (see Fig. 3) are related to the large shear strains produced by twinning during t–m transformation. The larger is the tetragonal grain size, the larger are the stresses associated with twinning and the higher is the probability to initiate microcracks inside the tetragonal grain. This hypothesis is supported by AFM observations made at a twinned tetragonal surface grain of 2H samples aged during 648 h (Fig. 6). The stresses associated with the formation of the twins should be higher in a larger tetragonal grain,[11] and, consequently, microcracks are formed (marked by arrow). Then, by increasing the ageing time, microcracks can propagate and coalesce, resulting in the formation of macrocracks observed in Fig. 3.

To explain the results obtained in this work we have to take into account various factors which may influence the transformability of the tetragonal phase in heat-treated Y-TZP.

Firstly, the results indicate that by increasing the tetragonal grain size and the amount of cubic phase by heat-treating 2.5Y-TZP, the stability against t–m transformation assisted by the environment decreases. This phenomenon may be related to the amount of stabilising oxide and its distribution inside the tetragonal and cubic grains. According to the Y_2O_3–ZrO_2 phase diagram proposed by Scott,[18] by increasing the annealing temperature there is a migration of Y^{3-} ions from one grain to another resulting in the formation of rich yttria cubic phase and poor yttria tetragonal phase. Thus, the tetragonal grains which are in contact with cubic ones are more susceptible to transform to monoclinic phase because of the decrease in yttria content at the boundaries.[19]

On the other hand, the amount of monoclinic phase detected by XRD in 1H and 2H aged samples (see. Fig. 2) indicates that, when cubic regions increase (with increasing annealing time), the Y_2O_3 concentration of the tetragonal regions decrease because of the continuous diffusion of yttrium ions to the cubic regions. Thus, an increased annealing time results in a small increase of the amount of cubic phase which is equivalent with a decrease of the stability of the surrounding tetragonal grains. These results are in good agreement with those obtained recently by Chevalier et al.[19]

Therefore, the knowledge of the yttria amount and distribution inside and along the grain boundary is very important for the design of zirconia ceramics with high stability in presence of the air humidity. As it may be seen in Fig. 1, 2H samples which are characterised by a grain size coarser than 1H, have tetragonal grains in contact with more cubic ones than 1H. This means that a tetragonal grain in 2H is less stable because of the decreased yttria amount at the t/c boundaries. By contrast, in 1H samples, there are more t/t grain boundaries which mean that the tetragonal grain in this type of samples is more stable against t–m transformation.

The influence of yttria distribution and tetragonal grain size on the ageing of Y-TZP was analysed previously by various authors.[3,7] Li and Watanabe[7] have shown that increasing the tetragonal grain size from 0.51 to 0.96 μm by increasing the sintering time of 2 mol% Y-TZP from 2 to 100 h results in an increase in the resistance to t–m transformation activated by water between 80 and 120 °C. The explanation for this behaviour was given in terms of yttria distribution at grain boundaries. These authors propose that the effect of grain size on transformation induced directly by water results in a "U"-type relationship between the amount of transformation and grain size. In addition, Tsukuma et al.[3] have studied the influence of tetragonal grain size on the transformability of Y-TZP by increasing the amount of stabiliser oxide from 2 to 6 mol%. They found that increasing the tetragonal grain size decreases the resistance against t–m transformation during ageing at 200–300 °C. Thus, the sintered bodies with tetragonal grain size greater than 1 μm showed a large amount of transformation and a remarkable decrease in strength. But, on the other hand, samples which contained grains of average size less than 0.4 μm showed no significant change of monoclinic phase content and strength even after 1500 h.

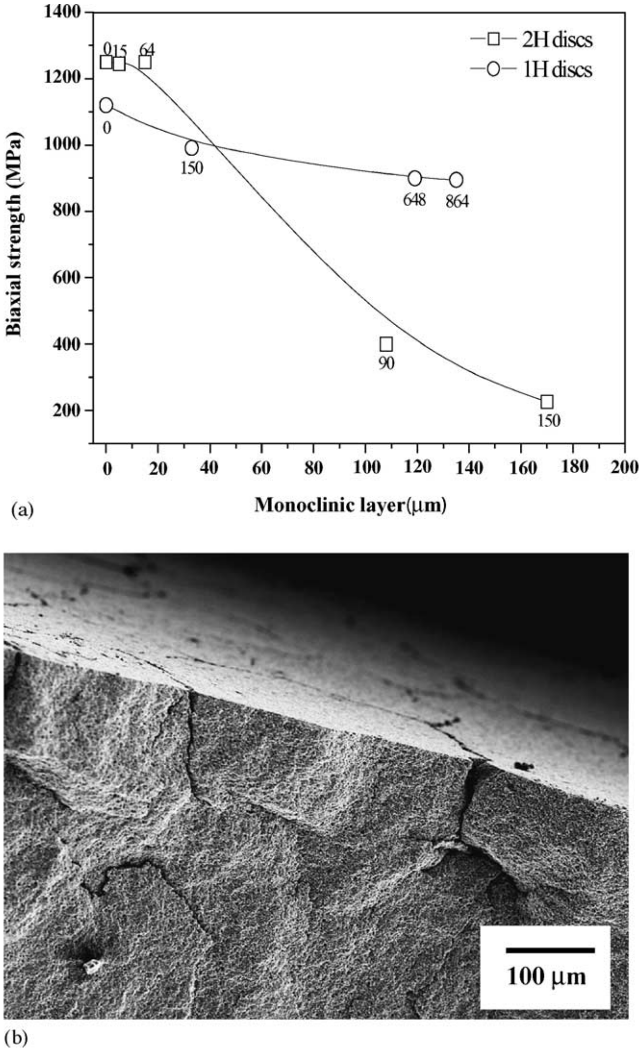

Fig. 7. Evolution of biaxial strength as a function of the depth of monoclinic layer and of the ageing time marked at each point (a) and a fracture surface of a 2H sample aged during 150 h (b).

In the case at hand, it has been shown that by increasing tetragonal grain size combined with a slow increasing of the amount of cubic phase, a decrease in the stability of Y-TZP tetragonal phase in presence of humidity occurs.

4. Evolution of biaxial strength

The increase in the amount of monoclinic fraction and microcracks after ageing resulting from t–m transformation may affect the mechanical strength of the aged samples. In the Fig. 7a it is shown the variation of the biaxial strength as a function of the depth of the monoclinic layer measured by Raman in the cross sections of the aged specimens. It can be seen that the biaxial strength in 2H samples is reduced strongly for the depths of monoclinic layer inferiors to that of 1H samples. This demonstrated that the reduction in strength depends principally on the tetragonal

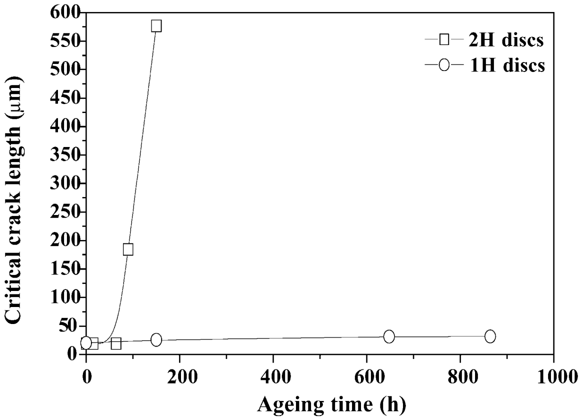

Fig. 8. Variation of the critical crack length calculated by using the Eq. (5) as a function of the ageing time.

grain size which influences the microcracking during ageing.

The fracture surface of a 2H sample aged during 650 h is shown in Fig. 7b. The t–m transformation during ageing has formed macrocracks which are large enough to strongly reduce the biaxial strength.

The biaxial strength of 1H does not decrease drastically despite of the presence of microcracks observed by SEM (see Fig. 3). The reason may lie in the fact that in the strength test used here the maximum stress is reached in a very small zone at the centre of the discs, which is just the place where the transformed layer is thinnest as has been shown previously for 1H and 150 h of ageing. This could be the reason for the relatively small degradation in strength (∼25%) in 1H, which is similar to that observed in the starting Y-TZP. After ageing for 864 h, the drop in strength of 1H is not important, which is consistent with the fact that the biaxial strength of the aged specimens are dependent on the grain size of the tetragonal phase that transforms during ageing. If the tetragonal grain size is below a critical value, the stresses formed during t–m transformation are not sufficient to produce enough microcracks to strongly reduce the strength.

By knowing the fracture toughness value of 1H and 2H samples (6.48 and 7.4 MPa $\mathrm{m}^{1/2}$, respectively) and also the maximum strength, we can make a rough estimation for the maximum length for a microcrack that are formed during t–m transformation by considering the well known equation:

$$K_{\mathrm{Ic}} = Y\sigma\sqrt{c} \tag{5}$$

$$c = \left(\frac{K_{\mathrm{Ic}}}{Y\sigma}\right)^2 \tag{6}$$

where Y is a constant depending on the geometry of the crack (for simplification we are considering that the crack is semicircular and $Y = 1.29$), σ is the maximum biaxial strength, and c is the crack length.

The evolution of the crack length calculated by the Eq. (5) as a function of the ageing time for 1H and 2H samples is shown in the Fig. 8. The maximum crack length for 1H is much smaller that for 2H. Generally, for 2H samples, it can be observed that the crack length coincides well with the depth of the monoclinic surface layer. This indicates that the cracks are penetrating the whole surface layer due to the high stresses associated to the t–m transformation. By contrast, the lower transformability of 1H tetragonal grains presents microcracking only at the surface. To further open this microcracks, more ageing time is necessary for 1H samples.

5. Conclusions

It has been shown that by heat-treating Y-TZP at 1650 °C by different times, the resistance to low-temperature degradation decreases. This is attributed to the increase in tetragonal grain size as well to the appearance of cubic phase, which increases the tetragonal/cubic boundaries and depletes the neighbouring tetragonal grains.

The growth of monoclinic sites begins rapidly at the edge of the discs studied, and is more slow at the centre, so that the monoclinic layer is very far from approximately uniform.

Microcracks formed on the surface transformed layer are strongly dependent on the tetragonal grain size. By increasing tetragonal grain size, the shear strains associated with the transformation are increased and microcracking occurs because the mechanical accommodation associated with the formation of twins.

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