HYDROTHERMAL AGEING OF CRACKED 3Y-TZP

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RESUMEN

En la circona dopada con 3% molar de itria, el vapor de agua puede inducir la transformación de la fase tetragonal a monoclínica en la superficie. Dicha transformación se extiende hacia el interior acompañada por la aparición de microfisuras, lo que induce una pérdida de la integridad estructural. Este fenómeno de degradación a baja temperatura (LTD) es una clara desventaja para la utilización del material en atmósferas húmedas. Sin embargo, el efecto del agua sobre grietas de indentación no ha sido estudiado. Este trabajo estudia la influencia de LTD en la resistencia mecánica de dichas grietas. Los resultados muestran sorprendentemente un incremento de la resistencia mecánica en probetas indentadas sometidas a largos tiempos de degradación; al contrario del comportamiento en probetas sin indentar. Para explicar este comportamiento, se ha evaluado también la influencia de las tensiones residuales y el tratamiento de recocido adecuado para eliminarlas. Finalmente, se plantean los mecanismos que explican el aumento de la resistencia mecánica observado.

ABSTRACT

In zirconia stabilised with 3% molar of yttria, the water vapour can induce the transformation from tetragonal to monoclinic phase at the surface. This transformation propagates to the bulk with the apparition of microcracks; which induce a loss in the structural integrity. This low temperature degradation (LTD) is a clear disadvantage for the application of the material in humid environments. On the other hand, the effect of the water on indentation-induced cracks has not been previously studied. This work studies the change in mechanical strength of indentation cracks submitted to water vapour. The results show how, after long degradation times, there is surprisingly an increase in mechanical strength. This is the opposite behaviour as the one expected in normal specimens which are not indented. To explain the observed behaviour here, the influence of the residual tensions was evaluated included annealing treatments. Finally, the mechanisms explaining the observed increase in strength are discussed.

PALABRAS CLAVE: Cerámicas, Resistencia, Biomateriales

1. INTRODUCTION

Tetragonal zirconia polycrystals stabilised with 3% molar of yttria (3Y-TZP) have been widely used in the past in orthopaedics; and in currently are used in dental restorations because of their high mechanical strength (~1000MPa), wear resistance and excellent biocompatibility. Additionally, this ceramic has moderate fracture toughness of ~5MPam$^{1/2}$; which is caused by a transformation toughening mechanism from tetragonal (t) to monoclinic (m) phase. This t-m transformation takes place in the vicinity of the crack front and is accompanied by a volume increase of about 4% resulting in shielding of the crack tip as the extension takes place [1].

Kobayashi *et al* [2] first observed in 1981 the t-m transformation can also initiate by ageing at low temperature in humid environment. In this case, the phase change is activated by water at the surface and progresses into the bulk. Thus, TZP ceramics stabilized with yttria, ceria, calcia or magnesia are susceptible in a variable degree to water vapour and aqueous fluids [3]. This phenomenon is frequently referred to as hydrothermal degradation or low temperature degradation (LTD) [3], [4]. Currently, it is accepted that LTD is produced by diffusion of water species (oxygen, hydrogen or hydroxyls) inside the zirconia lattice by a mechanism of oxygen vacancies, which induces tensile stresses because of change in lattice parameters and activate t-m transformation [5], [6], [7]. The kinetics of transformation depends on many parameters such as the specific alloying element and its concentration, grain size, etc.

Recently, it has been shown that LTD degradation may occur at human body temperature in the presence of body fluids in femoral heads made of 3Y-TZP [3], [8]. Although the strength may not practically change after several years *in vivo*, LTD may produce roughening of the surface and a subsequent grain pull out under contact loading. Nowadays, this degradation

phenomenon represents a serious factor to consider for the applications of 3Y-TZP in medical implants under contact loading.

It is important to understand the interaction of water vapour with the natural defects of the material. One simple way to study this is by producing artificial cracks in the ceramic and exposing them to water. Although there have been many studies [9] of environmental crack growth in 3Y-TZP in the presence of humidity, there has been hardly any study on the effect of hydrothermal ageing on cracks.

In the present work, a large effect of hydrothermal ageing on strength is reported. For doing so, first is necessary to determine the strength of indented 3Y-TZP, the influence of residual stresses, the annealing treatment for removing residual stresses without crack healing and the shape of indentation cracks. All these points are addressed here with the main objective of investigate the change in strength of indented specimens exposed to water vapour.

2. EXPERIMENTAL

The material studied was 3Y-TZP in the form of cylindrical rods produced by Kyocera Corp. (Japan) with a diameter of 8 mm and 65 mm in length. The microstructure and mechanical properties have been reported elsewhere [10]. Briefly, the average grain size is 300 nm, the hardness HV1= 12.5 GPa and the strength is close to 1 GPa with a Weibull modulus around 10.

It is well known that Vickers indentation cracks in 3Y-TZP, under usual indentation loads, are Palmqvist cracks (see figure 1). One of the most used equations for the indentation fracture toughness has been proposed by Niihara [11]:

$$K_{IC}^{ind} = \beta\left(\frac{PH}{8c_{ind}}\right)^{1/2};\beta=\left(\frac{E}{H}\right)^{0.4};\ 0.0251\le\frac{2c_{ind}}{(d/2)}\le 2.5 \quad (1)$$

Where P is the indentation load, d is the diagonal of the indentation, $2c_{ind}$ is the length of the Palmqvist crack at the surface, H here is taken as the indentation load divided by the indentation projected area, $H=P/2a^2$ and E is the Young modulus. From this equation, it is possible to estimate the indentation fracture toughness, K_{IC}^{ind} from the length of a Palmqvist crack, in an indentation test.

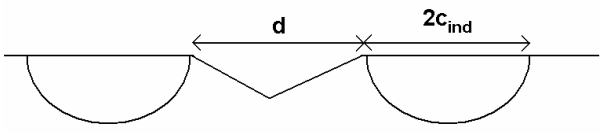

Figure 1. Palmqvist cracks with definition of lengths.

Indentations for measuring the fracture toughness were done on polished discs obtained from the rods. The indentation loads used were 5, 10, 30 and 40 kg. The lengths of the cracks emanating from the corners of the imprints were measured in order to estimate K_{IC} values by using equation (1).

Indentations were also done on the cylindrical rods using loads of 1, 2, 3, 5, 10, 30 and 40 kg. The indenter was oriented in such a way that one of the imprint diagonals was perpendicular to the rod length. The flexural strength of the indented rods was determined by four point bending in air with inner and outer spans of L_i=30 and L=60 mm, respectively. The load was applied in a servohydraulic fatigue testing machine Instron 8562 with a loading rate of 200 N/s. Maximum tensile stress at the indented surface was calculated by the following expression:

$$\sigma=\frac{8F(L-L_i)}{\pi D^3} \quad (2)$$

where D is the rod diameter and F the maximum applied load. The temperature selected to anneal the indented specimens, 1200°C, is commonly used to anneal 3Y-TZP. The dwell time was determined in order to ensure the removal of residual stresses and to avoid crack healing. To study the effect of annealing on the strength, an indentation load of 5 kg was used for all the rod specimens.

Finally, the effect of hydrothermal aging on indentation cracks was studied. The hydrothermal aging test consisted in the exposure of 10 kg indented specimens to 131ºC water vapour in autoclave for several periods of time.

3. RESULTS

The growth of the indentation crack length with indentation load is shown in figure 2. For loads smaller than 2 kg, cracks are not clearly observed and equation (1) is not valid because their length does not satisfy the condition established in the equation. The indentation crack length increases linearly with the applied load as expected from equation (1) in the range of c_{ind} studied here. From the slope of this dependency, the indentation fracture toughness in air was estimated as 5.1 MPam$^{1/2}$.

The strength of specimens which have been indented with 5 kg and annealed at 1200°C for different times present relatively large scatter (see figure 3), but it can be appreciated that the strength is practically independent of the annealing time in the range studied. Therefore, annealing for 1 hour was considered a sufficiently long period for the removal of the indentation residual stresses and to ensure that the crack is not completely closed, since the strength is not affected after annealing in the range 1 to 4 hours.

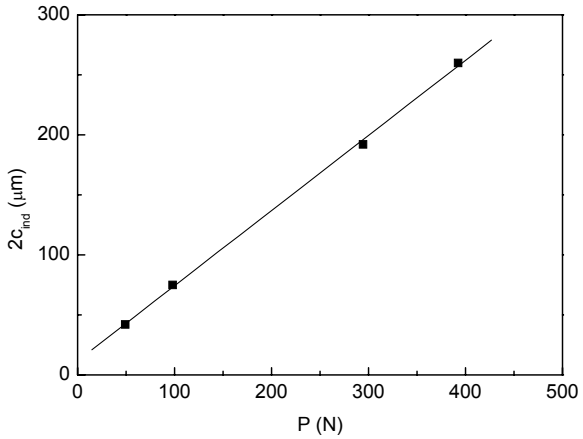

Figure 2. Surface crack length in terms of indentation load in 3Y-TZP.

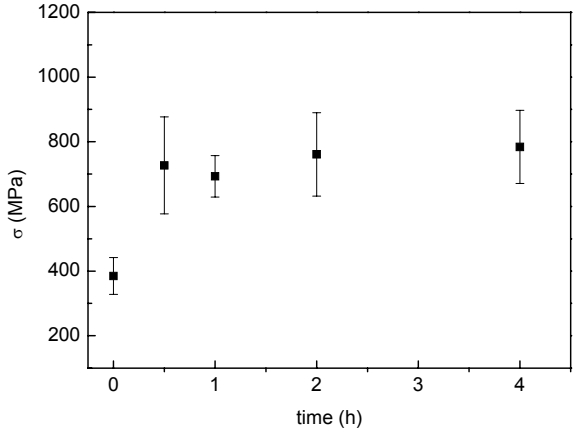

Figure 3. Bending strength of specimens indented with 5 kg in terms of time of annealing at 1200°C. Ten specimens were tested for each heat treatment.

The strength of indented (I) and indented + annealed (I+A) specimens is represented in figure 4 in terms of Vickers indentation load. It is clear that annealing increases the strength of indented specimens. Figure 5 illustrates the change of the flexural strength of indented HV10 rods after being subjected to hydrothermal ageing. It can be noticed that there is a spectacular rise in the fracture strength after 200 hours of aging (it doubles).

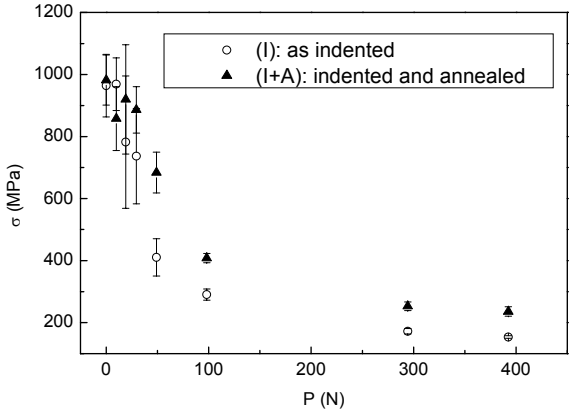

Figure 4. Bending strength in terms of indentation load.

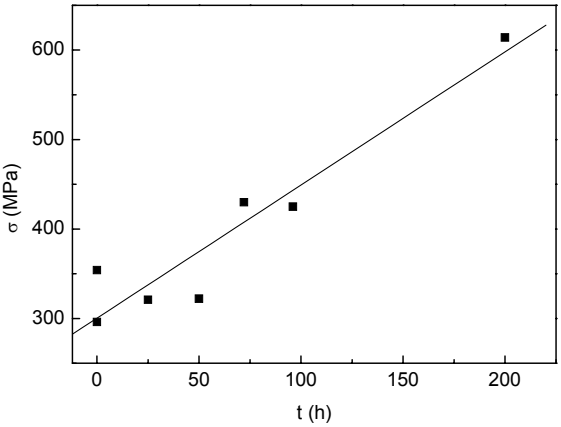

Figure 5. Bending strength in terms of ageing time for bars indented with a Vickers load of 10 kg.

4. DISCUSSION

It is well known [12] that in ceramics with half-penny indentation cracks and without R-curve, a logarithmic plot of the strength versus indentation load gives a straight line with a slope equal to -1/3. Zhang and Lawn [13] have shown that this is also the case for 3Y-TZP even for cracks of Palmqvist type. These authors included in this plot small indentation loads for which cracks are either not visible or very small. For these small loads there is large uncertainty in the slope because of large scatter in the strength. Here, the study has been restricted to the range where cracks are clearly visible and larger than the imprint semidiagonal (that is, in the range where equation (1) is valid). In this range, the scatter in strength is nearly an order of magnitude lower and the plot also follows a straight line with similar slopes of (-0.48±0.01) and (-0.55±0.07) for both (I) and (I+A) specimens, respectively. In fact, it will be shown below that a slope of -1/2 is to be expected if the cracks are Palmqvist instead of half-penny cracks and equation (1) is obeyed.

There is a severe drop in strength for indentation loads higher than 5 kg (see figure 4). For smaller loads, natural defects have a similar size as compared to indentation cracks, so the failure may occur either by natural defects or by indentation cracks smaller than the semi-diagonals of the imprint in which case equation (1) is not obeyed. In the as-indented specimens, indentation cracks control fracture only for loads higher than 2 kg, while in I+A specimens it occurs for indentation loads higher than 3 kg. This means that the removal of the residual stress by annealing, specimens indented with 2 and 3 kg did not left critical size defects larger than natural defects, so their fracture strength is practically the same as for non-indented specimens.

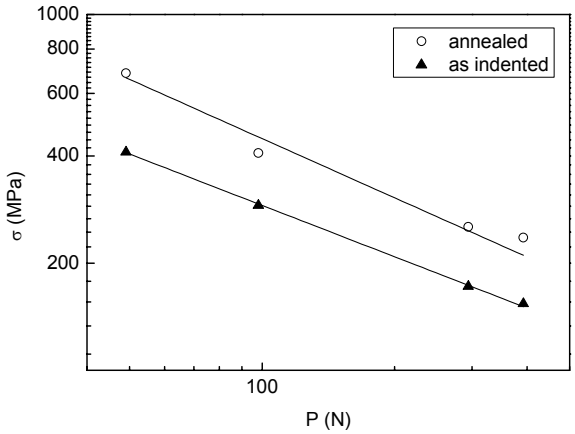

Figure 6. Logarithmic plot of strength versus indentation load

If σ is the applied strength on the surface of the specimen in four point bending test, the total stress intensity factor of a Palmqvist crack, *K*, is given by adding the stress intensity factors of the external applied stress for a semicircular surface crack that corresponds to the indentation residual stress (equation 1):

$$K = \psi_c \sigma \sqrt{c} + \beta \left(\frac{PH}{8c} \right)^{1/2} \qquad (3)$$

Unstable fracture takes places when the two following conditions are simultaneously obeyed:

$$K_I = K_{Ic}\,, \qquad \frac{dK_I}{dc} = 0 \qquad (4)$$

By imposing these conditions to equation (3) we obtain the crack length, $c_{I,unstable}$ and the strength, σ_I, for which the crack becomes unstable and catastrophic fracture occurs:

$$c_{I,unstable} = \frac{\beta (PH)^{1/2}}{2\sqrt{2}\psi_c \sigma_I} \qquad (5)$$

$$\sigma_I = \frac{K_{Ic}^2}{\sqrt{2}\beta\psi_c (PH)^{1/2}} \qquad (6)$$

Therefore, by plotting the strength versus the indentation load in a logarithmic scale, a straight line should result with a slope of -1/2. As shown before, the value found for the slope is equal to -0.48±0.01 (see figure 6).

Assuming that the annealing treatment does not heal any part of the indentation crack surface, the strength of I+A specimens is given by:

$$\sigma_A = \frac{K_{Ic}}{\psi_c \sqrt{c_{annealed}}} \qquad (7)$$

The ratio between the strengths of I+A and I specimens is given by dividing equations (7) and (6):

$$\frac{\sigma_{annealed}}{\sigma_I} = \sqrt{2}\,\frac{K_{IC}^{ind}}{K_{Ic}} \sqrt{\frac{c_{ind}}{c_{annealed}}} \qquad (8)$$

Here $c_{annealed}$ and c_{ind} are the lengths of the cracks after annealing and after indentation, respectively. These should be the same if no healing of the crack occurs. So, if crack healing is insignificant and there is not slow crack growth during indentation or during the bending test, then the ratio between crack lengths of equation (8) can be considered approximately equal to 1. In fact, the possibility of crack healing may be ruled out by the observation that the strength does not change between 1 and 4 hours of annealing. K_{IC}^{ind} and K_{Ic} are, respectively, the fracture toughness measured by indentation and the true fracture toughness. If K_{IC}^{ind} / K_{Ic} is practically equal to 1, then the ratio of equation (8) is constant and close to √2. This would imply that the strength of a specimen with a Palmqvist crack increases about 40 % after removal of the residual stresses by annealing. In the present work, it was seen (figure 6) that this simple relationship is fairly obeyed. In fact, this is rather surprising in view of the number of assumptions made for deriving equations (6) and (7). Small deviations could be related to slight different fracture toughness for as indented specimens (R-curve in the saturation stage) and for annealed specimens (with initially unshielded cracks).

It can be noticed that in the formulation of equation (3) it has been assumed that K_{Ic} is a constant and this is in agreement with the linear dependence found (figure 2). However, this is contrary to the assumed mechanism of transformation toughening of 3Y-TZP, which gives rise to an R-curve behaviour.

This can be explained if it is considered that the R-curve in 3Y-TZP is restricted only to the first few microns of crack extension. For example, if the R-curve characterized by an exponential equation often used to describe R-curve behaviour [15]:

$$K_R = K_{\max} - (K_{\max} - K_0) \exp\left(\frac{c_{ind}}{\lambda} \right) \qquad (9)$$

$K_{\max}$ stands for the maximum fracture toughness, K_0 represents the intrinsic fracture toughness and λ is a parameter that characterizes the rate of increase of fracture toughness with crack extension. If the length of the indentation crack is much larger than λ, K_R is practically constant and equal to $K_{\max}$, see equation (9). This is the case for 3Y-TZP with small grain size[1]. Therefore, indentation cracks had already developed their full R-curve in I-specimens when tested, while I+A specimens have cracks without any initial

transformation on the wake so that in this case the effect of the presence of an R-curve should be considered. The effect of the R-curve would be to decrease the calculated strength since in the calculation it was assumed that the cracks had reached saturation toughness so that the maximum value of fracture toughness of 5.1 MPa√m was assumed.

For I+A specimens it is possible to estimate the absolute value of the strength if K_{IC} and the dimensions of the cracks are known. The observation of the fracture surfaces reveals that the length of the crack at the surface, *2c*, is roughly equal to its depth, *a*, so that *a/c* ~2 (figure 7). For this configuration, the stress intensity factor at the surface is larger than at the deepest point, so that fracture will start at the surface (figure 8). As the crack grows at the surface, the stress intensity factor both at the surface and at the deepest point increase as *a/c* diminishes, so that the crack will not stop. Under these assumptions, the strength necessary to start fracture of I+A specimens is given by:

$$\sigma_{annealed} = \frac{K_{Ic}}{\psi_a(\phi = 0, a/c = 2)\sqrt{a}} \qquad (10)$$

Taking a/c=2, $\psi_a(\phi = 0, a/c = 2) \sim 1.17$, a=85μm, K_{Ic}=5.1MPa√m, $\sigma_{annealed}$ =474 MPa which is in good concordance with the experimental value (461±44).

The point whether equation (1) gives the true fracture toughness for a specific material is not clear because of the limitations of indentation [16]. However, in the case of biomedical standard 3Y-TZP of 300 nm grain size, this equation gives reasonable values when compared to the values obtained from the strength of I+A specimens or from the strength of I specimens. It should be noticed that this is in spite of the sensitivity of 3Y-TZP to moisture and in spite of the existent of a short R-curve.

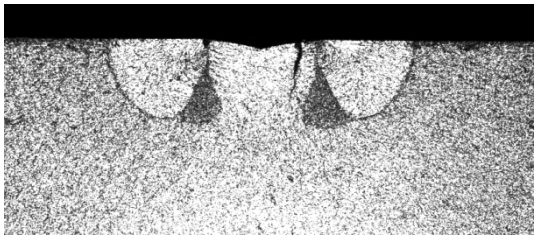

Figure 7. Fracture surface with a pair of Palmqvist cracks induced by Vickers indentation.

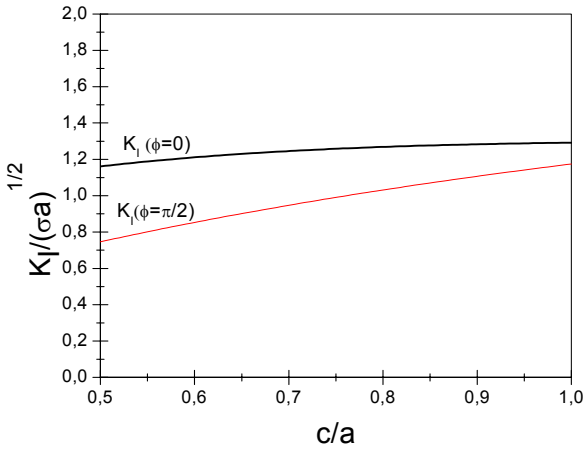

Figure 8. Stress intensity factor in terms of c/a at the surface, ϕ=0, and at the deepest point, ϕ=π/2.

Moisture may induce environmental slow crack growth of indentation cracks in air, so that K_{IC}^{res} in air may be smaller than the true fracture toughness in vacuum. In the present case, the cracks were measured in air so that the values obtained for K_{IC}^{res} may be sub-estimated. Additionally, subcritical crack growth during the application of load in all fracture tests could affect the results. It is then surprising that good estimations can be achieved without considering effects of R-curve and slow crack growth.

It is also worthwhile pointing out that even if residual stresses were relaxed in the hydrothermal degradation treatment, this could not explain the observed rise in strength that takes place after hydrothermal ageing (figure 5). The reason is simply that when residual stresses are truly removed by very high temperature annealing, the increase in strength of indented specimens is much smaller than the reported increase after hydrothermal ageing.

Recently, some additional experiments have been carried out by testing large numbers of specimens in the I and I+A conditions, after degradation for 200 hours. In both cases, similar increase in the strength has been observed. Therefore, this effect cannot be related to a decrease in residual stresses in indented specimens, instead a mechanism of interaction between water vapour and the crack tip is being considered.

5. CONCLUSIONS

The flexural strength of indented 3Y-TZP with Palmqvist cracks has been analysed by four point bending in the as indented condition, after an annealing heat treatment to remove the indentation residual stresses, and after hydrothermal ageing. The main conclusions can be summarised as follows:

- The strength of as indented specimens varies as $1/\sqrt{c}$ as expected from a residual stress intensity factor that has a $1/\sqrt{c}$ dependence on crack length.

- The strength of indented plus annealed specimens can be predicted within 10% from the fracture toughness determined by indentation by using the profile of the indentation crack measured from the fracture surfaces. The combined effect of the R-curve and the subcritical crack growth on the strength for annealed specimens with unshielded cracks is very small.

- A strong increase in strength is reported for the first time in indented specimens after hydrothermal treatment which is related to the interaction between the water vapour and the crack tip.

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