

X-ray diffraction and atomic force microscopy study in aged zirconia-toughened alumina composite with dispersion of *m*-ZrO₂ nanoparticles

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ARTICLE INFO

Article history:

Received 12 April 2012

Accepted 25 June 2012

Keywords:

Zirconia toughened alumina

Aging

Grain size

Monoclinic phase transformation

Topography

ABSTRACT

X-ray diffraction (XRD) and atomic force microscopy (AFM) were utilized to investigate the aging behavior of pressureless sintered monolithic ZrO₂ (TZ-3Y) and zirconia-toughened alumina composite with additions of 2 wt% *m*-ZrO₂ nanoparticles at 1520 °C for 1 h. Results show that TZ-3Y exhibited significant aging in water steam at 134 °C under pressure 2 bar compared to zirconia toughened alumina (ZTA) composite. The maximum fraction of monoclinic polymorph resulted after 10 and 15 h of aging for monolithic TZ-3Y (~85%) and ZTA (~2.3%) composite, respectively. The homogeneous dispersion of zirconia into the matrix and its fine grain size as well as the high Young's modulus of the Al₂O₃ matrix which can provide a constraining effect on the zirconia could partially inhibit the phase transformation. In terms of monoclinic phase content, our ZTA composite fulfil ISO 1336–2008 requirements for implants for surgery, being thus an interesting alternative in this field.

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1. Introduction

As was pointed out by Lawson in their excellent review [1], “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 to monoclinic phase transformation around propagating crack fronts.” This makes it of great benefit for use in the orthopedic field and as superior dental material for crown and bridges, for example Ref. [2]. Nevertheless, there is a major drawback with Y-TZP ceramics which is referred as aging, hydrothermal degradation or low temperature degradation (LTD) [3–5] accompanied by intergranular micro-cracking resulting in the loss of mechanical properties. This degradation (commonly between 150 and 400 °C) is time dependent and can be accelerated by water or water vapor from the surface to the bulk of zirconia and was first observed by Kobayashi et al. [6] limiting therefore, the application in ceramic implants [7,8]. Although this phenomenon has been extensively documented, there are conflicting views concerning to aging mechanism. For example, the aging was found to be strongly dependent on the grain size of the ceramic [9] and when zirconia ceramics were aged in air, critical grain size for the tetragonal (*t*) to monoclinic (*m*) phase transformation was reported to increase from 0.2 to 0.6 μm for Y₂O₃ content ranging from 2 to 5 mol% according to reported by Watanabe et al. [10].

On the other hand, other factors such as density where the remaining open porosity allows the access of water molecules to the bulk of ceramic

material, homogeneity of phase distribution as well as residual stresses on the surface can influence the *t*→*m* phase transformation and both fracture strength and fracture toughness are greatly reduced [11,12]. In the presence of moisture, the *t*→*m* phase transformation can alternatively occur without the passage of a crack. However, if the transformation is triggered by a propagating crack, then a toughening enhancement can be obtained while the transformation can be triggered chemically by the infusion of water-derived species from the surface [13]. In recent years, it is clear that the hydrothermal degradation is also operative at temperatures lower than 100 °C, even at human corporal temperature in *in vivo* hip prosthetic devices, and it has been the origin of catastrophic failures of femoral heads as can be documented in the excellent review paper by Chevalier et al. [14].

Nowadays, some speculations in order to explain the LTD [15] in zirconia ceramics have been reported. Based on TEM observations, Lange et al. [16] proposed, a reaction of water with Y₂O₃ to form clusters rich in Y(OH)₃ leading to a depletion of the stabilizer in the surrounding zirconia grains which are then free to transform to monoclinic. On the other side, Yoshimura et al. [17] reported that the water vapor attacks the Zr—O bond, breaking it and leading to a stress accumulation due to movement of —OH which in turn generates lattice defects acting as nucleating agents for the subsequent *t*→*m* phase transformation, meanwhile Chevalier et al. [13] postulated that O₂— originating from the dissociation of water, and not OH—, could be responsible for the filling of oxygen vacancies which is probably one of the causes for the destabilization. It is well known that additions of CeO₂ or TiO₂ to Y-TZP may increase the stability of *t*-ZrO₂ [18]. The control of the hydrothermal aging of Y-TZP is nowadays a challenge. However, it has reported that additions of alumina (Al₂O₃) to Y-TZP might inhibit the *t* to *m* phase

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transformation [3,11,19]. No monoclinic phase was found in 3Y-ZrO₂ and 4Y-ZrO₂ alloyed with CeO₂ in excess 10 wt%. On the other side, supplementing the ZrO₂ with 40 wt% Al₂O₃, the *t*→*m* phase transformation rate was decreased. Tsubakino et al. [20] reported *t* to *m* phase transformation to the surface layers with only 1.2–12 wt% Al₂O₃.

In this respect and taking into account that there has not been any systematic and extensive study on the aging behavior of zirconia-toughened alumina (ZTA) with dispersion of *m*-ZrO₂ nanoparticles under hydrothermal conditions, employing XRD and AFM techniques, the aim of this work is to demonstrate by means of these techniques that our TZ-3Y zirconia with additions of Al₂O₃ and dispersion of nanoparticles of *m*-ZrO₂ can undergo much smaller *t*→*m* phase transformation by aging in humid atmospheres than monolithic 3Y-TZP and other ZTA ceramics reported in the open literature which in turn open the door to develop different components for ceramic implants where to avoid or at least reduce the LTD, is of paramount importance.

2. Materials and methods

2.1. Mixture preparation

High purity α-Al₂O₃ (Baikalox SM8, Baikowski, USA; primary particle size 50 nm, purity >99.99%, surface area 10 m² g^{−1}), ZrO₂+3 mol% Y₂O₃ (abridged as TZ-3Y, Tosoh, Japan; primary particle size 75 nm, purity >99.99%, surface area 17 m² g^{−1}) and monoclinic ZrO₂ (Aldrich, USA; primary particle size <50 nm, purity >99.99%, surface area 15–35 m² g^{−1}) powders were employed as starting materials. Homogeneous mixture of Al₂O₃+13 wt% TZ-3Y+2 wt% *m*-ZrO₂ was prepared. The powders were firstly dispersed in 800 mL ethanol with ultrasonic agitation during 60 min to destroy the agglomeration state and subsequently stirring with a magnetic stir bar until most of ethanol evaporated and then the mixture was dried at 100 °C for 24 h. Finally, the dried powder mixture was judiciously ground in an agate mortar.

2.2. Compaction and sintering

The mixed powders were uniaxially pressed in steel die 16 mm in diameter and 5 mm height applying a pressure of 50 MPa using an Elvec Hydraulic Press with a load rate of 0.39 MPa s^{−1}. Green samples were placed into an alumina crucible with ZrO₂+Al₂O₃ bed powders and sintered at 1520 °C for 1 h in air at a heating rate of 10 °C min^{−1}. After sintering, the furnace was shut off and it was allowed to cool down. The sintered density was measured using geometric method. The samples were ground and polished through SiC paper in sequence of # 800 and # 1200, and then polished by diamond pastes of both 0.5 and 0.25 μm. A monolithic TZ-3Y sample was also prepared by comparison following the same procedure as for ZTA. The initial surface roughness was 5.5 and 20 nm for the ZTA composite and monolithic TZ-3Y, respectively. Then, the samples were thermally etched in air for 30 min at 1475 °C.

2.3. Accelerated aging

The LTD was evaluated by performing accelerated aging tests in water steam at a temperature of 134 °C, 2×10⁵ Pa (2 bar) water vapor partial pressure (according to ISO standard 13356 related to ceramic implants based on 3Y-TZP for surgery). The samples were placed on an Al₂O₃ ceramic disk in an autoclave made of stainless steel in order to avoid some possible corrosion that may occur during aging process. The aging treatments were carried out under these conditions for 1.5, 5, 10, 15, 20, 30, and 40 h.

2.4. X-ray diffraction

The tetragonal (*t*) to monoclinic (*m*) phase transformation was followed by measuring the phase fraction evolution using XRD. XRD data were collected with a θ–2θ diffractometer (Model X' Pert Pro, by

PANalytical, The Netherlands) equipped with Cu Kα monochromatic radiation. All diffractograms were obtained from 20° to 80° at 2θ intervals of 0.05° using a step-counting time of 10 s. The Rietveld refinement method was used to obtain the volumetric fraction of monoclinic phase in each aged sample.

2.5. Samples characterization

The polished and thermally etched surfaces of the ZTA composites and pure TZ-3Y were observed by Scanning Electron Microscopy (SEM: JEOL JSM 5800 LV, Japan, and FEG SEM: JEOL JSM 7000F, Tokyo, Japan) using an accelerating voltage of 2 kV. The changes in surface topography after aging were examined by AFM. The AFM (Multimode Nanoscope IVa, Veeco Instruments from Broker AXS, USA) was implemented in contact mode with an average scanning speed of 10 μm s^{−1}. The vertical resolution of AFM allows us to follow the transformation-induced relief very precisely. Digital images were obtained for each surface and the nano-roughness *R*_a was automatically assessed by the specific software WsXM 4.0 Beta 5.0 [21] and mean image roughness was obtained.

3. Results

Typical microstructures of the starting ceramics are shown in Fig. 1. Pure TZ-3Y zirconia presented an average grain size of 0.46 μm (Fig. 1a). On the other hand, the grain sizes of Al₂O₃ and TZ-3Y in the ZTA composite were 0.74 and 0.23 μm, respectively (Fig. 1b). Likewise, the sintered densities for monolithic TZ-3Y and ZTA composite were 98.8 and 94.9 %TD, respectively.

Fig. 2 illustrates the XRD patterns of pure TZ-3Y and ZTA composite before aging treatment. As can be observed, the monoclinic ZrO₂ presence, characterized by diffraction peaks at 2θ=28.1° and 2θ=31.3° was not noticed; only the tetragonal ZrO₂ phase appeared in the monolithic TZ-3Y ceramic. On the other side, in the pattern corresponding to ZTA composites, the monoclinic ZrO₂ phase content was estimated to be approximately 2% suggesting an almost stabilizing of the tetragonal phase during cooling.

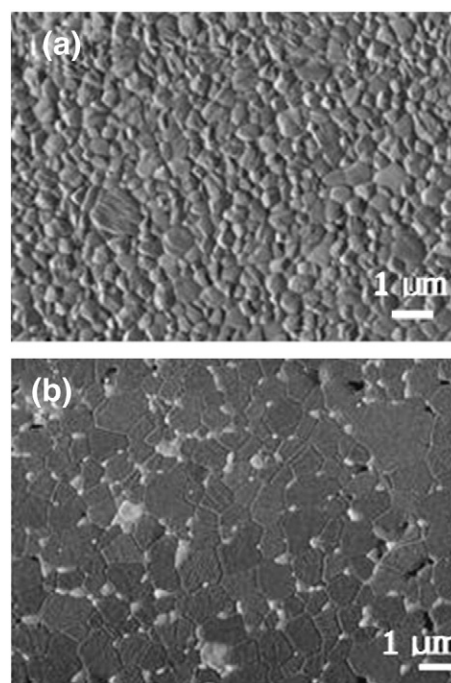


Fig. 1. SEM micrographs of thermally etched surface (a) pure TZ-3Y and (b) ZTA composite.

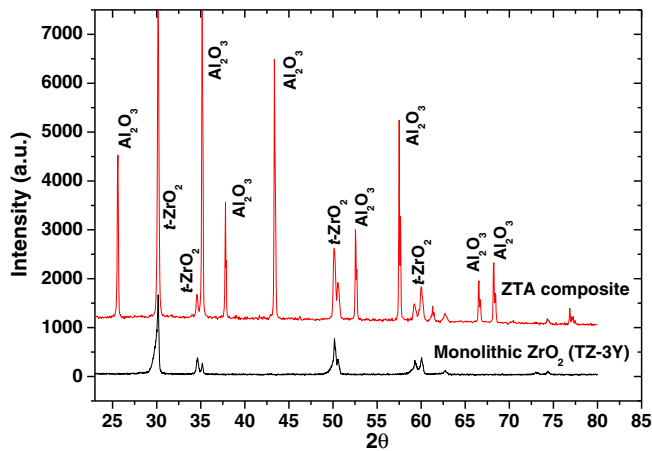


Fig. 2. XRD patterns of monolithic TZ-3Y specimen and ZTA composites sintered at 1520 °C for 1 h before aging treatment.

It is well known that the aging investigations allow obtaining an important analogy to the stability of zirconia-based ceramics when they are used as implants in human bodies. Therefore, an accelerated aging study gives us in short time the amount of phase transformation that

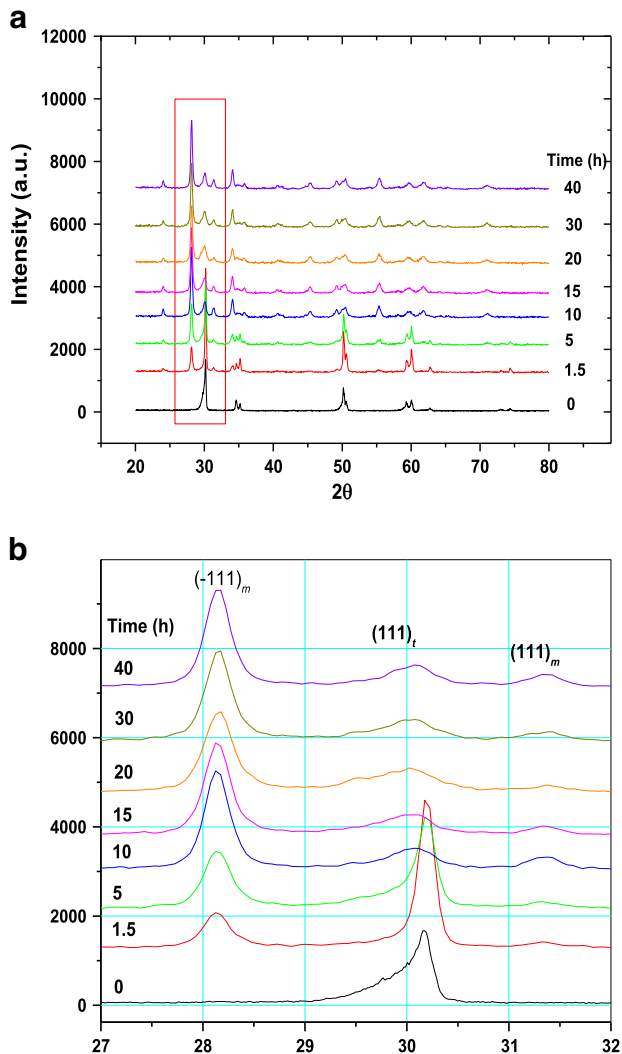


Fig. 3. XRD diffractograms of TZ-3Y degraded in autoclave at 134 °C and 2×10^5 Pa (2 bar), (a). High magnification of square in (a) is shown in (b). Note the stabilization of monoclinic zirconia phase at times greater than 15 h.

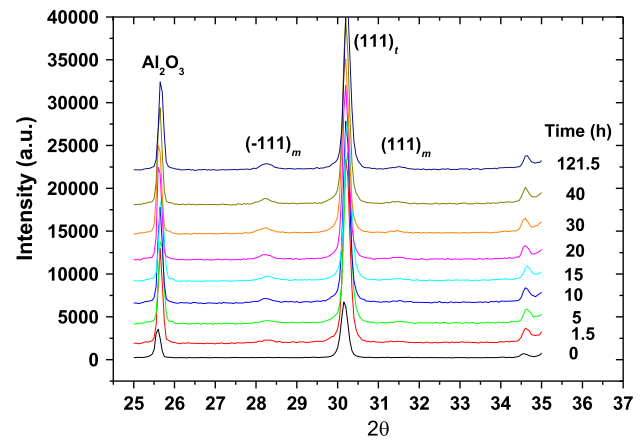


Fig. 4. XRD patterns of ZTA composite aging in autoclave at 134 °C and 2×10^5 Pa (2 bar).

might take place in human bodies over several years (approximately 30–40 years). Figs. 3 and 4 show the XRD patterns obtained on aged pure TZ-3Y and ZTA composites, respectively, in water steam at 134 °C for different times at 2×10^5 Pa (2 bar). For the monolithic TZ-3Y (Fig. 3a), as aging time increased from 0 to 15 h, the monoclinic ZrO₂ phase increased continuously as well (see Fig. 5). The monoclinic phase content was higher than 80% (see Fig. 5) and was also saturated for aging times higher than 15 h (see also Fig. 3b). A similar behavior was obtained for ZTA composite (Fig. 4) where the stabilization of monoclinic phase was observed for aging times higher than 10 h (~2.3%). However, a slight increase in *m*-ZrO₂ phase (not shown here) was found for an aging time of 125 h (which can be equivalent to ~375 years in vivo performance [22]). Undoubtedly, under same aging conditions, ZTA composite is more resistant to degradation than pure ZrO₂. A summary of monoclinic phase content (obtained by Rietveld refinement method) before and after aging treatment for monolithic zirconia TZ-3Y and ZTA composites, is presented in Tables 1 and 2, respectively.

AFM was conducted with the aim to investigate the surface damage induced by phase transformation. Representative AFM images of monolithic TZ-3Y zirconia and ZTA composites surfaces after 0, 15 and 40 h exposure in autoclave at 134 °C are shown in Figs. 6 and 7, respectively. The arithmetic average of the roughness (R_a) assessed as a numeric value (in nanometers) with specific software [21] has been inlayed in the images. For more clarity, these average roughness values were plotted in Fig. 8

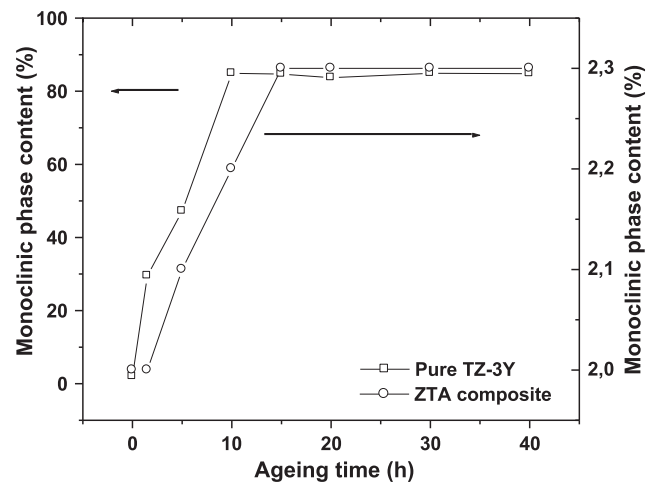


Fig. 5. Monoclinic fraction measured by Rietveld analysis on the θ -2 θ XRD data of the samples degraded at 134 °C and a pressure of water vapor partial pressure of 2×10^5 Pa (2 bar).

Table 1

Monoclinic (*m*) phase content in monolithic zirconia TZ-3Y before and after aging at 134 °C under 2 bar pressure. (The number in parentheses corresponds to the error of the last number.)

Aging time (h)	(<i>t</i>) Phase	(<i>m</i>) Phase
0	98.0(1)	2.0(1)
1.5	70.5(1)	29.5(1)
5	52.8(2)	47.2(1)
10	15.1(1)	84.9(1)
15	15.3(1)	84.7(1)
20	16.3(9)	83.7(4)
30	15.1(2)	84.9(1)
40	15.2(1)	84.8(1)

as a function of the aging time. One depth profile corresponding to topography along an arbitrarily selected horizontal line for each figure was plotted for better visualization on the right side of each map. From Figs. 6 and 7, the various features of the surface relief (bright parts) induced by the tetragonal to monoclinic phase transformation, as well as the scratches induced during polishing procedure, which appears as dark lines on the micrographs (arrow marks in Figs. 6a, b and 7c) are clearly observed. An apparent coalescence of the grains in monolithic TZ-3Y degraded at 40 h (Fig. 6c) is also clearly observed suggesting a transformation along grain boundaries. Representative SEM micrographs of the ZTA composites aged at 134 °C during 40 and 125 h showing surface reliefs characteristic of a martensitic-type transformation are shown in Figs. 9 and 10, respectively. On the other hand, it is noteworthy that the topographic maps revealed that with increasing aging time, the *t*→*m* phase transformation proceeded according to increases in heights for pure zirconia (Fig. 6a–c) and ZTA composites (Fig. 7a–c). However, it is very important to note that the biggest differences in height as well as roughness (*R_a*) were detected for monolithic ZrO₂ suggesting a major degradation during exposure to water vapor.

4. Discussion

Taking into account that materials based on yttria stabilized tetragonal zirconia (*t*-ZrO₂) stand out among ceramic materials and are sensitive to their surrounding environment, particularly in aqueous medium that cause evident degradation due to the transformation of metastable *t*-ZrO₂ to monoclinic phase (*m*-ZrO₂) at low temperatures (commonly between 150 and 400 °C), the aim of this work was to study and to compare the LTD in pure TZ-3Y zirconia and in ZTA composite with dispersion of *m*-ZrO₂ nanoparticles by means of XRD and ATM. XRD analysis revealed for monolithic TZ-3Y (see Fig. 3) a decreasing of the peak corresponding to the plane (111)*t* of the tetragonal phase at 30.2° (2θ) with the increasing time of degradation up to 10 h, when the monoclinic fraction reaches a plateau, while there is an increase in the peaks corresponding to monoclinic phase. For times longer than 15 h, the monoclinic phase remains almost constant. Under same aging time in ZTA composite, it was observed (Table 2) that the fraction of

tetragonal zirconia decreased from 13.0 to 12.7%, i.e. less than 0.3% of *t*-ZrO₂ transform into *m*-ZrO₂ (see Figs. 4 and 5) which could be 20 times less than in the case of the same ceramic material but without alumina content according to reported by Sato and Shimada [23]. The low transformed tetragonal phase into monoclinic one indicates that the ZTA composite exhibited significantly enhanced hydrothermal stability. This behavior can be due to the constraining force of the harder alumina matrix [24] where the tetragonal ZrO₂ particles need overcome a critical stress in order to trigger the phase transformation. On the other side, the stability of tetragonal zirconia is increased by the higher Young's modulus of the Al₂O₃. Our results are in agreement with observations by Tang et al. [7]. Evidently, the high monoclinic phase present in the monolithic TZ-3Y (Fig. 5) can also be due to its larger grain size (0.46 μm, Fig. 1a) compared to 0.23 μm measured in the ZrO₂ grains within the alumina matrix (Fig. 1b). It is therefore clear that the grain size plays an important role in the degree of tetragonal phase transformation [25].

The relationship between the amount of monoclinic phase and aging time for monolithic TZ-3Y and ZTA composite (see Fig. 5) revealed that although the rate of transformation was much faster in TZ-3Y compared to ZTA composite, the maximum concentration of monoclinic phase formed in both ceramics (obtained values by means of Rietveld analysis conducted on the θ -2θ XRD data) was found at 10 and 15 h aging time for TZ-3Y and ZTA composites, respectively. According to Chevalier et al. [22] the observed difference in transformation rates is of paramount importance for the first stage of transformation where nucleation of the new monoclinic phase is predominant. The sigmoid shape of the curves in Fig. 5 could be characteristic of a nucleation-and-growth (N-G) process and therefore, the LTD kinetics can be described using Mehl–Avrami–Johnson's law [3]:

$$X_m = 1 - \exp[-(bt)^n] \quad (1)$$

where *X_m* corresponds to the monoclinic fraction and *t* the aging time. *b* and *n* are parameters describing the apparent activation energy and the nucleation-and-growth mechanisms. The nucleation and growth process which characterizes hydrothermal degradation of zirconia has been extensively studied in previous publications [14] where is accepted that during hydrothermal degradation, water species as OH[−] ions diffuse into the material filling oxygen vacancies, destabilizing the tetragonal grains and promoting the tetragonal to monoclinic phase transformation according to Wada and Yokoyama [26] and Muñoz-Tabares et al. [27]. The nucleation arises at grains which are less stable than average [28]. On the other hand, the great difference in monoclinic phase content at 10–15 h of aging could be related to the overall grain size (0.46 μm for TZ-3Y and 0.26 μm for TZ-3Y in the composite) where if the transformed grain is less than the critical size, then nucleation, growth, and thus transformation of subsurface grains will be limited by long-range diffusion of yttrium to the surface. Conversely, if the transformed grain is larger than the critical size, then microcracks will form and open up subsurface grains and subsequently water vapor attack [1].

For 3 mol% Y₂O₃-TZP ceramics of relatively larger grain size, low-temperature aging degradation can only be prevented at temperatures below 80 °C or alternatively, at a much higher temperature than 500 °C due to the high martensitic start temperature (*M_s*) according to reported by Chen et al. [9]. Likewise, the final surface condition (roughness) that might contain microstructural defects (residual stresses, scratches or alternatively residual pores (see for example circle in Figs. 6b and 7c)) could act as nucleation sites for the monoclinic phase during all aging treatment. This, in turn, would lead to an increase in the tetragonal to monoclinic phase transformation, considering that the tetragonal to monoclinic transformation always initiates at the sample surface with propagation into bulk of the ceramic. This observation was also reported by Elshazly et al. [2]. For medical applications such as orthopedic and dental applications where the selected materials must meet an

Table 2

Monoclinic (*m*) phase content in ZTA composite before and after aging at 134 °C under 2 bar pressure. (The number in parentheses corresponds to the error of the last number.)

Aging time (h)	(<i>t</i>) Phase	(<i>m</i>) Phase	Al ₂ O ₃
0	13.0(1)	2.0(2)	85.0
1.5	13.0(1)	2.0(1)	85.0
5	12.9(1)	2.1(1)	85.0
10	12.8(2)	2.2(1)	85.0
15	12.7(1)	2.3(1)	85.0
20	12.7(1)	2.3(3)	85.0
30	12.7(1)	2.3(1)	85.0
40	12.7(1)	2.3(2)	85.0
125	12.4(1)	2.6(2)	85.0

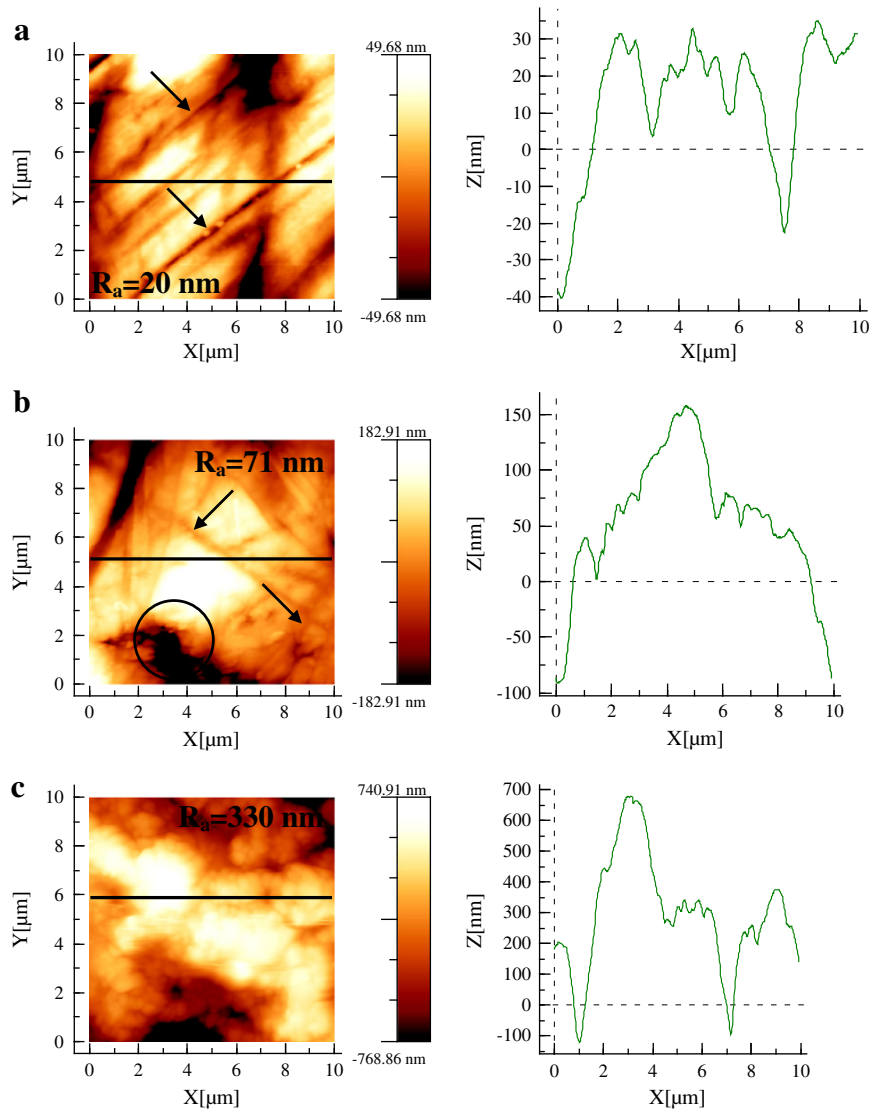


Fig. 6. AFM observation (height image) of the TZ-3Y after aging at 134 °C, 2 bar of pressure. (a) 0 h ("as sintered"), (b) 15 h, and (c) 40 h. In each image, a horizontal line was arbitrarily selected to show a typical depth profile on right side each figure. Note the preferential transformation (bright areas). Arrow marks and circle are explained in text.

important combination of both biocompatibility and mechanical properties, and with the purpose to avoid or to minimize the wear phenomenon and particle release in the body, it is important to keep in mind that a surface roughness as low as possible has always been a primordial objective for prosthesis manufacturers [29].

It is well known that for polycrystalline ceramics where the tetragonal phase is retained, the transformation is mechanically constrained under metastable conditions [13]. Therefore, taking into account studies carried out by Lange [30], the tetragonal-to-monoclinic phase transformation can be expressed in terms of the different energy contributions to the overall energy [11,13]. Then, the free energy change of the tetragonal-to-monoclinic transformation ($\Delta G_{t \rightarrow m}$) can be described by:

$$\Delta G_{t \rightarrow m} = \Delta G_c + \Delta U_{SE} + \Delta U_S \quad (2)$$

where ΔG_c , ΔU_{SE} , and ΔU_S are the chemical free energies (<0 at temperatures below the equilibrium M_s temperature), the strain free energies associated with the transformation of particles (>0), and the surface free energies (>0) in the monoclinic and tetragonal phases, respectively. Under these conditions, the particle remains in its tetragonal state if the overall thermodynamic driving force is $\Delta G_{t \rightarrow m} > 0$, $|\Delta G_c| < \Delta U_{SE} + \Delta U_S$. The transformation of $t \rightarrow m$ occurs when

$\Delta G_{t \rightarrow m}$ becomes negative. In reason of this, the tetragonal-to-monoclinic phase transformation can be controlled increasing ΔG_c , ΔU_{SE} , and ΔU_S . Y_2O_3 , CeO_2 , for example, can increase ΔG_c inasmuch as it lowers the transformation temperature drastically [31]. On the other side, since ΔU_{SE} is dependent on the elastic properties of the transformed inclusion and surrounding matrix, ΔU_{SE} is therefore increased with the increasing elastic modulus of the constraining matrix (having the matrix of a stiffer material such as Al_2O_3) [11,30], stabilizing the tetragonal phase. However, as was pointed out by Chevalier et al. [13], the driving force for the $t \rightarrow m$ phase transformation will not be the same inside the bulk and on its surface because neither ΔU_{SE} nor ΔU_S is the same. It is also important to stress that just as a critical size exists for the $t \rightarrow m$ phase transformation exists in powders [32], it may well be modified on the surface [33] or alternatively in the bulk [30]. Eichler et al. [34] reported a critical size for bulk transformation on the order to 1 μm , whereas around 1 nm at the surface.

The lower monoclinic content after degradation of the ZTA composites at different times (Fig. 5) compared to monolithic TZ-3Y can be due to the presence of Al_2O_3 (Young's modulus around 400 GPa) since its dispersion into zirconia favors the stability of the tetragonal phase under moisture environments. Although the dispersion of Al_2O_3 into TZ-3Y decreases the $t \rightarrow m$ phase transformation, it was not prevented totally. Tsukuma and Shimada [35] also found a reduction of monoclinic content

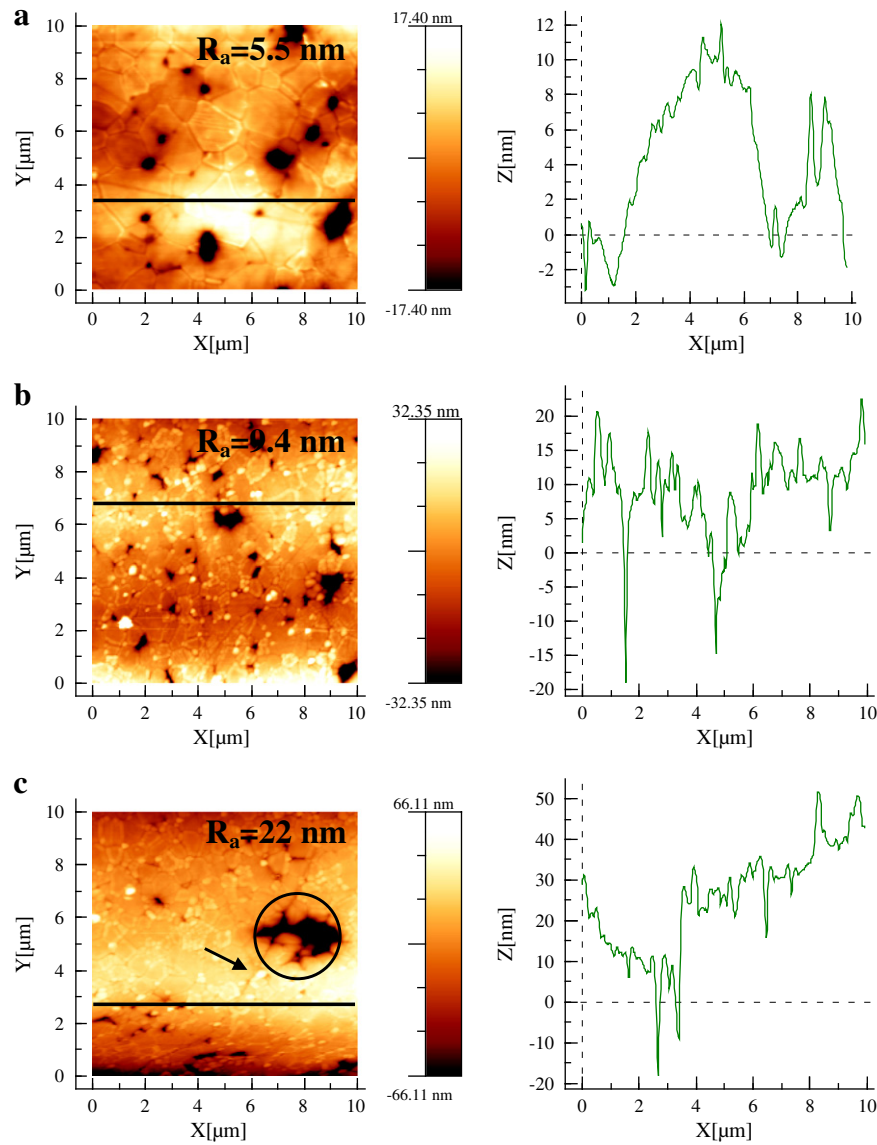


Fig. 7. AFM observation (height image) of the ZTA composite after aging treatment at 134 °C, 2 bar of pressure. (a) 0 h ("as sintered"), (b) 15 h, and (c) 40 h. In each image, a horizontal line was arbitrarily selected to show a typical depth profile on right side each figure. Note the preferential transformation (bright areas). Arrow mark and circle are explained in text.

with Al_2O_3 additions and they reported that 40 wt% alumina almost perfectly restrained the transformation. Keeping in mind that a two-phase alumina zirconia material is currently marketed for orthopedic applications and that alumina containing a small concentration of zirconia is also exceptionally resistant to LTD, it is useful to distinguish between these two types of composites (ZTA and ATZ) depending on the continuous phase [13]. Considering that the explanation for the slower LTD kinetics in zirconia containing small additions of alumina is unclear, there is a consent in terms that the explanation for the retarded kinetics is perhaps clearer in the ceramic materials where the majority phase is the alumina (commonly denominated as ZTA) [36] considering that if the zirconia phase is not microstructurally continuous, then there is not a pathway for diffusion of the moisture into the ceramic and so the degradation could not past the surface and deep into the material. However, if the percolation threshold is not exceeded, transformation to monoclinic does not occur [37]. It has been reported that zirconia content inside alumina matrix corresponding to the percolation threshold is 10 wt% (16.7 vol%) in order to avoid aging degradation [38].

Now, the metastability of the tetragonal zirconia plays an important role in the ZTA composites because if zirconia grains are likely to

be in net tensile stress after processing as a result of thermal expansion mismatch, the transformation is therefore hindered by the much

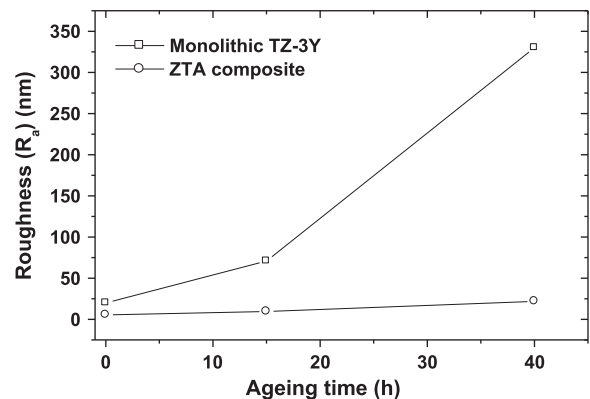


Fig. 8. Average arithmetic roughness profile (R_a) as a function of aging time in autoclave measured in TZ-3Y and ZTA composite.

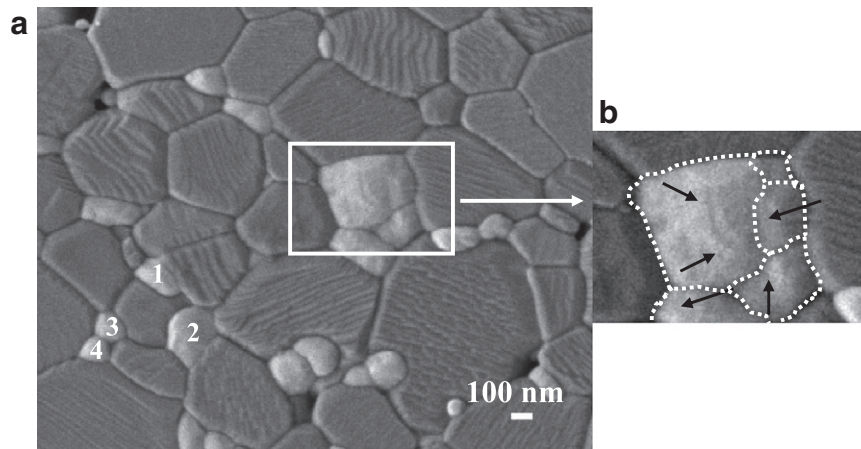


Fig. 9. SEM micrograph of ZTA composite aged at 134 °C during 40 h (a). Magnification of square in (a) is shown in (b). Dotted line in (b) represents the grain boundaries in the TZ-3Y grains. Arrow marks and numbers in (a) are explained in text.

stiffer alumina matrix. For our ZTA composites pressureless sintered at 1520 °C during 1 h it seems that the retarded phase transformation is produced thanks to the dispersion of Al_2O_3 particles as well as smaller grain size in ZrO_2 . ZrO_2 nanoparticles well-dispersed at grain boundaries prevents the grains closing during densification resulting in nanocomposites with fine grain size by grain pinning retarding notably the transformation. Indeed, it is clearly impossible to completely avoid the transformation in a ceramic material where the zirconia is the main phase [37]. The lowering of the ZrO_2 content down to 2.5 wt% leads to a further decreasing of the monoclinic zirconia volume according to appreciations by Affatato et al. [38]. Nonetheless, the monoclinic zirconia content at 40 h of aging in our ZTA composite displayed significantly lower values (2.3%) as compared to that measured in TZ-3Y (84.8%) for the same time and temperature. On the other hand, Pezzotti et al. [39] reported ~10% of monoclinic phase in a 80 vol% Al_2O_3 –17 vol% ZrO_2 –3 vol% strontium aluminate composite aged at 134 °C during 40 h, Gutknecht et al. [36] obtained ~11% m - ZrO_2 in the case of Al_2O_3 + 25 vol% 3Y-TZP after aging at 134 °C for 40 h, and Deville et al. [40] have reported approximately 13%, 15%, and 22% of monoclinic phase for alumina with additions of 10 vol%, 17 vol% and 20 vol% 3Y-TZP content, respectively, aged at 140 °C during 40 h. From these results, we argue that the ZTA composite reported here effectively can be a promising material for orthopedic applications due to the lower monoclinic zirconia phase present and

considering specially that 40 h of aging at 134 °C corresponds to approximately 120–140 years in vivo, being much more than life expectancy of the patient. Nonetheless, although the mechanical properties must be evaluated after aging treatment, this theme is the objective of another paper.

With regard to the topographical studies, AFM was conducted to investigate the possible surface degradation induced by phase transformation in TZ-3Y and ZTA composites inasmuch as this technique is more sensitive to the early stages of aging treatment and provides important information on the topological changes accompanying the tetragonal-to-monoclinic phase transformation. The roughness (R_a) before and after aging treatment in TZ-3Y and ZTA is shown in the Fig. 8. The initial roughness was about 5.5 and 20 nm for TZ-3Y and ZTA, respectively. As can be seen in this Fig. 8, the roughness increased until a maximum of 330 and 21.8 nm for TZ-3Y and ZTA composite as consequence of the $t \rightarrow m$ transformation suggesting that during hydrothermal degradation treatment, TZ-3Y exhibited a significant and abrupt aging in contrast with ZTA composite where the degradation was lower. The great surface damage in monolithic TZ-3Y is the result of volume increasing during the phase transformation an holes were unquestionably created as can be in Fig. 6b, for example (indicated by circle). This transformation has induced a height increase modifying therefore the AFM contrast which is reflected by the brightening up of the transformed grains. The volume increases due to the

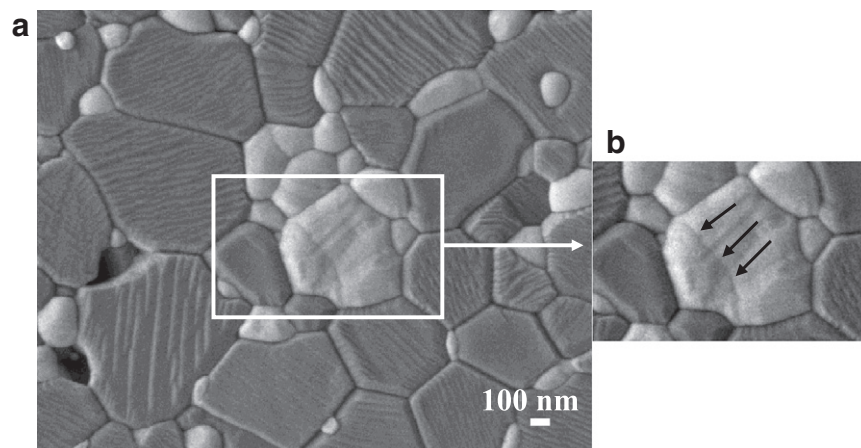


Fig. 10. SEM micrograph of ZTA composite aged at 134 °C during 125 h (a). Magnification of square in (a) is shown in (b). Arrow marks and numbers in (a) are explained in text. The observed relief is undoubtedly a characteristic of a martensitic transformation.

transformation leads to that monoclinic spots appear brighter. Similar observations were reported by Deville et al. [40]. The higher the local surface relief, the brighter the image. These increases in height are much more intense in TZ-3Y ceramics as consequence of higher monoclinic phase than ZTA composite (see depth profile in the right side of each map in Figs. 6 and 7).

For low zirconia contents (present work), the grains can be homogeneous distributed in the Al_2O_3 matrix and the agglomeration fraction could be low suggesting therefore that, the majority of zirconia grains are really isolated in the all alumina matrix. With this background, it is believed that if a zirconia grain is transforming, this transformation eventually will not propagate to surrounding zirconia grains taking into account the presence of alumina grains in between. Then near-to-near propagation of the transformation is therefore not possible [41]. This can be supported in Fig. 9a for ZTA composite aged during 40 h in autoclave at 134 °C. In Fig. 9a it is shown that if the ZrO_2 grains 1 and 2 transform, the transformation can not be propagated to surrounding zirconia grain 3 by the presence of Al_2O_3 grain in between. On the other hand, if zirconia grain 3 transforms, the transformation only can be propagated to surrounding zirconia grain 4. A detailed zone in Fig. 9a is zoomed in Fig. 9b in order to visualize the martensitic variations within the several zirconia adjacent grains (arrow marks). On the other side, Fig. 10b shows the enlarged square in Fig. 10a where the arrow marks indicate a transgranular martensitic variant in ZTA composite aged at 134 °C during 125 h confirming that the transformation in that zone has been propagated to surrounding zirconia grains. In the same Fig. 10a, fine zirconia particles with size lower than 100 nm located in grain boundaries can also be observed which could suggest that transformation does not occur inasmuch as the critical grain size has not been achieved. (It is worth noticing that the rippled surface induced by the thermal etching treatment according to its crystallographic orientation to the surface [41] shown in Figs. 9 and 10 on the alumina grains is limited at ~10 nm, while the surface increase after transformation observed on zirconia grains in the ZTA composites is more much than 10 nm (approximately 20 nm) suggesting therefore that the transformation-induced relief is clearly more important than the relief produced by the thermal etching. As an example, more details can be seen in Supplementary Fig. S1 for ZTA composite aged for 20 h). Kelly and Francis Rose [42], Hayakawa et al. [43] and Deville and Chevalier [44] theoretically have shown that, under certain crystallographic conditions of the original tetragonal (*t*) zirconia phase, the transformed martensitic variant could traverse several tetragonal domains explaining the observed feature in Fig. 10b. Judging for the SEM images (Figs. 9 and 10) we could argue that there will be therefore a tendency toward the growth stage as mentioned earlier (propagation of transformation). This observation is in agreement with results of Deville et al. [41]. Nevertheless, in our ZTA composites this phenomenon of propagation of transformation can be very limited considering the low zirconia content into the Al_2O_3 matrix. ZTA nanocomposites containing up to 10 vol% ZrO_2 nanoparticles (ZTA nanocomposite presented here contained 2 wt% ZrO_2 nanoparticles (<50 nm)) were found to suffer low or no deterioration of the ZrO_2 phase after more than 40 h of aging under 134 °C. Our results are in agreement with this appreciation [44,45] indicating a suitable stability of the composites. Although in terms of monoclinic phase content after accelerated aging, our ZTA composites fulfil the requirements of the ISO 1336–2008 for Implants for surgery – Ceramic materials based on yttria-stabilized tetragonal zirconia (Y-TZP), more detailed works are needed regarding the combination of LTD with the mechanical properties in order to obtain stability when the ZTA composites are applied both dental and orthopedic applications. A study on aged ZTA composites is in progress with the aim to provide more reliable information concerning its mechanical response after hydrothermal degradation.

5. Conclusions

TZ-3Y and ZTA composites containing *m*- ZrO_2 nanoparticles were manufactured by pressureless sintering; the monoclinic phase content

and topological features after hydrothermal aging in water steam at 134 °C for 0, 1.5, 5, 10, 15, 20, 30, and 40 h was evaluated by XRD and AFM, respectively. The following results were obtained:

1. TZ-3Y ceramic was very susceptible to LTD in comparison to ZTA composite which presented a lower tetragonal-to-monoclinic phase transformation. The maximum monoclinic phase content in TZ-3Y after aging 10 h was higher than 80% meanwhile for the same aging time, the monoclinic phase present in ZTA composite was only 2.3%.
2. The excellent LTD resistance of the ZTA composite can be attributed to increased constraining force on the zirconia grains dispersed into the alumina matrix suggesting an increase in Young's modulus of the matrix by the presence of Al_2O_3 . In addition, the fine zirconia grain size (approximately 0.23 μm) also contributed to the aging resistance. A homogeneous dispersion of zirconia in the alumina matrix facilitates the no propagation of the transformation by the presence of Al_2O_3 grains between zirconia ones.
3. It is possible to control the tetragonal-monoclinic phase transformation increasing the strain free energy change by the dispersion of a second phase, e.g. Al_2O_3 . Likewise, by increasing the surface free energy change (reduction in grain size) it is also possible to control the phase transformation. In this context, it seems to be that the ZTA composites reported here followed these general rules.
4. The *t* → *m* phase transformation followed a sigmoid shape up to 40 h of aging suggesting probably the existence of a nucleation-and-growth (N-G) process being predominant the nucleation process.
5. Three-dimensional AFM images provide us more information than SEM inasmuch as important quantitative information about topography of the surface of the ceramics can be obtained not only on the atomic scale but also on the nanometer to micron level.
6. Much more and detailed work in developing aging resistant ZTA ceramic composites with remarkable mechanical properties must be undertaken studying also carefully the aging kinetics. However, the present investigation experimentally proves the great possibility to develop a ZTA composite which could be applied in biomedical applications taking into account, at the moment, its lower monoclinic phase content after aging for longer times.

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.ijrmhm.2012.06.009>.

Acknowledgments

The authors sincerely thank Wilber Antunez for SEM assistance.

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