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ScienceDirect
Journal of the European Ceramic Society 27 (2007) 1547–1552
www.elsevier.com/locate/jeurceramsoc

Key role of processing to avoid low temperature ageing in alumina zirconia composites for orthopaedic application

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Available online 14 June 2006

Abstract

Zirconia toughened alumina (ZTA) composites are considered today as promising materials for orthopaedic applications, since they offer a higher crack resistance than alumina and zirconia monoliths. However, despite the presence of zirconia in the material, there is lack in literature concerning the crucial question of ageing. In particular, the role of the quality of the dispersion of zirconia in the alumina matrix has never been discussed. In this work, the dispersion behaviour of alumina and zirconia powder is studied. Using an optimal dispersion at pH 4.5, homogeneous ZTA are obtained. Neither alumina nor zirconia aggregates are present in the final microstructure. Ageing experiments are conducted on ZTA of different compositions for both yttria stabilized and unstabilized zirconia. The results are compared with previous works where aggregates are present in the final materials. The ageing kinetics show a drastic difference between ZTA with or without aggregates. For ZTA containing unstabilized zirconia, aggregates are transformed during cooling, giving rise to an ageing sensitivity, even for low zirconia content (i.e. 10 vol.%). For ZTA containing yttria stabilized zirconia, aggregates transformation occurs during the first stages of ageing. On the other hand, no transformation at all is observed for materials without aggregates, provided that the zirconia content is kept below the percolation threshold (16 vol.%).

Keywords: Ageing; Composite; Al_2O_3; ZrO_2; Biomedical application

1. Introduction

Ceramic materials used in femoral heads for total hip replacement have to combine good mechanical and tribological properties, associated with perfect in vivo stability. Alumina and yttria stabilized zirconia (Y-TZP) are considered as premium choices today.

Y-TZP ceramics exhibit superior toughness and strength as compared to alumina. However, Y-TZP can undergo a low temperature degradation (ageing). Ageing occurs at the surface by a slow tetragonal-to-monoclinic phase transformation of grains in contact with water[1] or body fluid. It begins by the transformation of isolated grains at the surface and propagates to the neighbouring grains by a nucleation-growth mechanism.[2] This transformation leads to surface roughening,[2] grain pull out and micro-cracking.[3] A consequence of implant roughening is an increased wear of hip components, which can cause premature failure and require early revision. To avoid early ageing of zirconia implants during sterilisation procedure, the U.S. Food and Drug Administration (FDA) cautions today against steam sterilisation of such implants. More important, in 2001, the FDA[4] and the Australian Therapeutic Goods Administration (TGA) announced that series of Y-TZP hip prostheses were recalled due to a fracture risk. According to the concerned zirconia ceramic manufacturer, the failures origin was an accelerated tetragonal to monoclinic phase transformation of zirconia on particular batches, which induced severe micro-cracking.[5] This event, although limited in duration and number (only two batches were affected by the failure episode) has had a major effect on the use of zirconia in orthopaedics. It has lead surgeons to return to less competitive but apparently safer solutions. Among these, metallic femoral heads (inox, CoCr alloys) on ultra high molecular weight polyethylene (UHMWPE) or metallic acetabular insert are widely used. Unfortunately, these alternative solutions produce polymeric or metallic wear particles, which are at the origin of osteolytic and/or allergic reactions.[6–8] In the same way, alumina femoral heads, more brittle than zirconia heads, are currently used despite their inferior crack resistance.[9]

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doi:10.1016/j.jeurceramsoc.2006.04.123

Table 1
Materials processing conditions

Designation	Zirconia level	Sintering conditions	HIP conditions	Final density (%)
A5Z3Y	5 vol.% 3Y-TZP	1520 °C, 2 h	1520 °C, 2 h, 200 MPa	99.8
A10Z3Y	10 vol.% 3Y-TZP	1520 °C, 2 h	1520 °C, 2 h, 200 MPa	99.8
A13Z3Y-1600	13 vol.% 3Y-TZP	1600 °C, 2 h	No HIP	99.6
A15Z3Y	15 vol.% 3Y-TZP	1520 °C, 2 h	1520 °C, 2 h, 200 MPa	99.9
A25Z3Y	25 vol.% 3Y-TZP	1520 °C, 2 h	1520 °C, 2 h, 200 MPa	99.9
A5Z0Y	5 vol.% pure ZrO_2	1520 °C, 2 h	1520 °C, 2 h, 200 MPa	99.8
A10Z0Y	10 vol.% pure ZrO_2	1520 °C, 2 h	1520 °C, 2 h, 200 MPa	99.8
A10Z0Y-1600	10 vol.% pure ZrO2	1600 °C, 2 h	No HIP	99.6
A15Z0Y	15 vol.% pureZrO2	1520 °C, 2 h	1520 °C, 2 h, 200 MPa	99.5

In this context, there is a clear need of ceramics combining superior mechanical properties and ageing resistance. ZTA composites, with improved microstructures, should be able to realise this compromise. Numerous studies have shown that ZTA composites exhibit high mechanical properties: fracture toughness ranging from 5.5 to 10.5 MPa $m^{1/2}$ is reported in the literature.[9–14] However, very few studies have focused on their resistance to ageing. Some studies[15–17] claim that no decrease in bending strength is observed after ageing experiments on alumina–zirconia composites, compared to the detrimental effect observed on the strength of aged Y-TZP. However, a decrease in bending strength only occurs after extensive t–m transformation. The transformation itself must be completely avoided in order to ensure the perfect stability of the material in vivo and avoid the detrimental consequences. The addition of alumina to zirconia limits the ageing process.[15] However, it is clearly impossible to completely avoid the transformation in a material where zirconia is the main phase.[18] Moreover, it has been shown that the zirconia level should be lower than the percolation threshold (16 vol.%) to avoid ageing propagation from grain to grain.[18,19] At last, even under the percolation threshold, significant transformation level can be observed at the beginning of some ageing experiments.[19] Zirconia aggregates are suggested to be responsible for this transformation, but no study assessed clearly this issue.

The aim of this study is thus to provide more information on the effect of processing conditions – and consequently the effect of microstructure – on the ageing sensitivity of ZTA. The effect of composition (zirconia and yttria content) is also examined, and particular attention is paid to the critical role of zirconia dispersion. Several methods are available to obtain evenly dispersed zirconia particles in alumina matrices. Some powder synthesis techniques such as sol–gel[20] or alcoxide routes[21] enable small, sometimes nano-sized zirconia particles with narrow particle size distributions and thus optimised microstructures free of zirconia aggregates.[10] However, these techniques are difficult to industrialise, since the synthesis of large, reproducible, batches is still difficult. This is why a simple powder mixing technique was preferred in this work. A key aspect of this method is to avoid the presence of aggregates with optimal dispersion conditions, which are studied here.

2. Experimental procedure

2.1. Materials processing and microstructure characterization

Alumina and zirconia starting powders following ISO 6474 and ISO 13356 standards respectively were used. These standards give specifications for alumina and zirconia implants subjected to high loads (femoral heads for example), in terms of purity, chemical composition and size distribution. Alumina powder was containing 300 ppm of MgO as a sintering additive. Zirconia powders were either stabilized with 3 mol% of Y_2O_3 (3Y-TZP) or free of stabiliser ('unstabilized zirconia').[1] ZTA composites were processed by a conventional powder mixing technique. The powders were mixed in appropriate amounts in water and electrostatic dispersion was used to prepare stable slurries. Ball milling was then performed using high purity alumina balls in a plastic jar for 24 h. These dispersed slurries were spray dried using an ultrasonic spray drier (20 kHz, SODEVA, Chambery, France). Spray dried granules were pressed uniaxially (150 MPa) and isostatically (300 MPa) in order to obtained small cylinders of 10 mm diameter and 3 mm thickness. Most of the samples were then sintered in air at 1520 °C for 2 h, and then post treated by HIP (Hot Isostatic Pressing) at 1520 °C for 1 h, with a pressure of 200 MPa. In some specific occasions, some specimens were sintered at 1600 °C for 2 h without post-HIP, in order to compare with existing literature. The main characteristics of the final products are given in Table 1. All the samples reached full density. Samples were mirror-polished using diamond suspensions (BULHER, Lyon, France), down to 3 μm. All the samples processed here can be considered as biomedical grade ceramics.

Microstructural observations were carried out using a high resolution scanning electron microscope (SEM) (FEI, ESEM, XL30). Before observation, specimens were thermally etched at 1400 °C for 12 min in order to reveal the microstructure, and gold-coated to avoid any surface charging effect. Particle size distribution of zirconia grains was obtained thanks to image analysis (Imaq Vision Builder 6.0) of SEM pictures: pictures were

[1] For confidential reasons from our industrial partners, the tradenames of the powders are not indicated.

binarised in order to separate alumina and zirconia particles, which present very different contrasts.

2.2. Dispersion characterization

Viscosity and Zeta potential measurements were performed on alumina and zirconia slurries (35 wt.% solid loading) in order to get insight on their respective dispersion behaviour. Viscosity measurements were conducted with a Couette rheometer (HAAKE VT 501, Villebon, France) at different shear velocities, from 0 to 1500 s^{-1} and for different pH. Zeta potential measurements were performed using the acoustophoresis technique (acoustosizer Iis, Colloidal Dynamics, Sydney, Australia). This method allows the qualification of concentrated suspensions which are more representative of industrial processing of ceramics.

2.3. Ageing experiment

Ageing experiments were carried out in steam at 134 °C under 2-bar pressure, in a steam autoclave (Fisher Bioblock Scientific, Illkirch, France). This temperature corresponds to classical sterilisation procedures and is often chosen for ageing experiments on biomedical grade zirconia based materials. One hour of this treatment applied to 3Y-TZP corresponds roughly to 3–4 years in vivo.[22]

The evolution of zirconia monoclinic content was measured versus sterilisation duration, by means of X-ray diffraction (XRD) using Cu Kα radiation. Monoclinic content was calculated from the modified Garvie and Nicholson equation.[23] Diffractometer scans were obtained from 27° to 33° at a scan speed of 0.5°/min and a step size of 0.05°.

3. Results

3.1. Slurry preparation

Electrostatic dispersion was conducted first with alumina and 3Y-TZP zirconia separately. Fig. 1 shows the zeta potential and the viscosity versus pH for both suspensions, measured for the same solid loading content.

A high zeta potential is measured for both alumina and zirconia powders in the acidic region (respectively 80 and 60 mV at pH 4.5), corresponding, in Fig. 1b, to very low viscosity (about 5 mPa s for the three tested powders). These high zeta potentials, associated to low viscosity, indicate that suspensions are very well dispersed. The iso-electric point is 9.5 for alumina and 10 for zirconia. These pH values correspond to the maximal viscosities. In the basic area (above pH 11), the alumina can be well dispersed, but the zirconia suspension floculates, as we can see in Fig. 1b. As a consequence, the best working pH to obtain a good powder dispersion of both alumina and zirconia is the acidic pH.

3.2. Microstructures

Typical microstructures of sintered compacts are shown in Fig. 2 (micrographs presented for A10Z3Y and A25Z3Y for Fig. 2a and b, respectively). Zirconia is well dispersed in the alumina matrix. No aggregates are present. The distribution of zirconia grain size is similar for all compositions, for the same sintering temperature. As an example, Fig. 3 shows the zirconia grain size distribution for A10Z3Y and A25Z3Y compositions (mean grain size 0.62 ± 0.14 and 0.66 ± 0.18 μm, respectively). Therefore, any difference in ageing cannot be related to a change in grain size from a composition to another. When zirconia level is above the percolation threshold (theoretically 16 vol.%), i.e. for A25Z3Y, zirconia grains form an interconnected network, which should define a path for transformation propagation.[18,19]

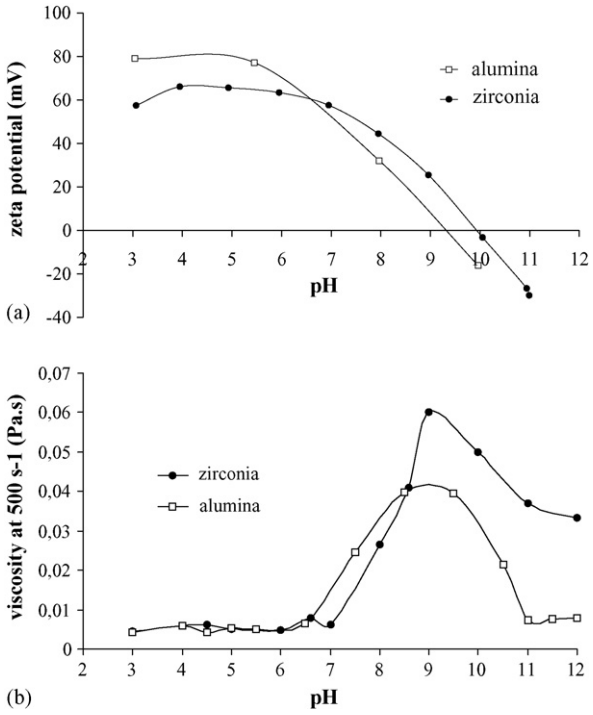

Fig. 1. Zeta potential (a) and viscosity (b) of 35 wt.% alumina and zirconia slurries vs. pH.

3.3. Ageing results

Ageing kinetics of ZTA composites processed with 3Y-TZP and with unstabilized zirconia are presented in Figs. 4 and 5, respectively.

The initial monoclinic fraction in 3Y-TZP based ZTA is close to zero. During autoclave treatments, A25Z3Y exhibits significant ageing, in contrast with the other compositions where no significant variations of the monoclinic fraction can be measured (variability around ± 2% for low zirconia content). These results are in agreement with the previous work of Deville et al.[19]: the percolation threshold (16 vol.%[18]), defines a critical zirconia content above which the tetragonal to monoclinic transformation can propagate from one grain to its neighbours. Below this content, transformation can begin for some grains at the surface, but cannot propagate to the other grains.

In unstabilized zirconia based ZTA, the tetragonal content retained after processing depends on zirconia level. This point will be discussed later. In agreement with the percolation the-

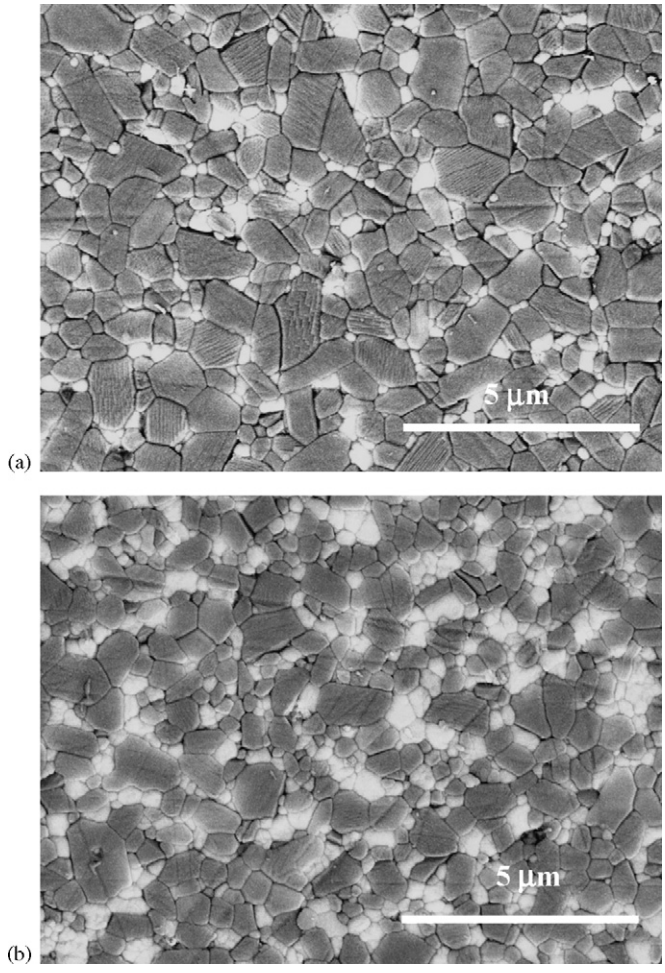

Fig. 2. Typical microstructure of sintered compacts (a) A10Z3Y and (b) A25Z3Y. Bar = 5 μm.

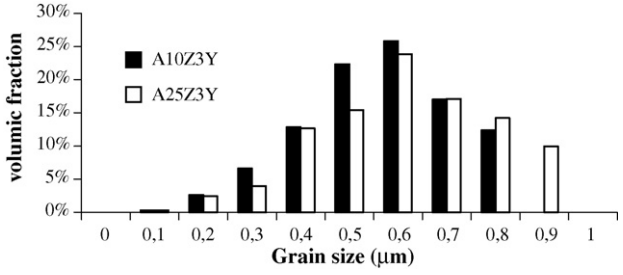

Fig. 3. Zirconia grain size distribution for A10Z3Y and A25Z3Y.

ory, no ageing is observed, since all zirconia contents are below 16 vol.%.

4. Discussion

4.1. Dispersion conditions

Aggregates, and especially zirconia aggregates, is the most commonly reported problem with the conventional powder mixing technique. In this work, a special attention was paid to the dispersion conditions, in order to avoid the presence of such aggregates. Deville et al.[19] reported, for the same type of ZTA,

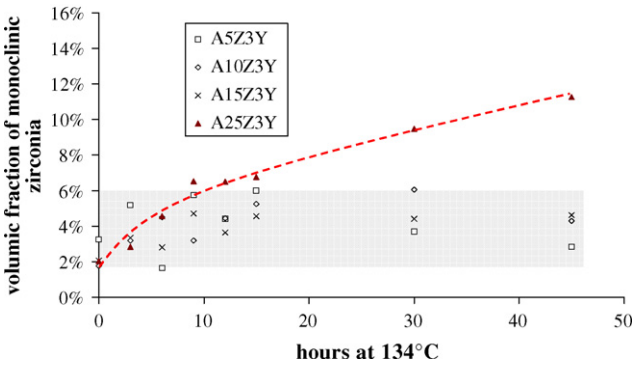

Fig. 4. Variation of monoclinic volumic fraction of zirconia vs. ageing time: case of 3Y-TZP based ZTA.

that 30 vol.% of the zirconia is located in aggregates measuring up to 10 μm. In this previous work, electrosteric dispersion was used, with Dolapix C64 as dispersing agent. Maybe this polyelectrolyte (or the amount of this polyelectrolyte) was appropriate for the dispersion of alumina, but not to disperse zirconia. Another study[24] reports this type of problem with electrosteric dispersion of ZTA: the polyelectrolyte was selected for optimum dispersion of zirconia, and alumina aggregates larger than 20 μm were present in the ZTA. These aggregates were often at the origin of fractures. Some preliminary results (not presented here) confirm this issue: it appears very difficult to correctly disperse both alumina and zirconia particles by electrosteric way. Anyway, aggregates definitely have to be avoided in order to optimise ZTA characteristics, especially for orthopaedic applications (aggregates being at the origin of fracture and ageing). Electrostatic way allows this optimal dispersion of both powders thanks to their high zeta potential at acidic pH. Consequences on ageing behaviour are presented below.

4.2. Role of aggregates on ageing kinetics

To clearly assess the role of aggregates on ageing kinetics, an additional batch was prepared using the electrostatic dispersion with the composition A13Z3Y. This batch was sintered under the same conditions used by Deville et al.,[19] i.e. at a temperature of 1600 °C, without HIP, in order to compare with their results, the difference between our two studies lying only in the presence or

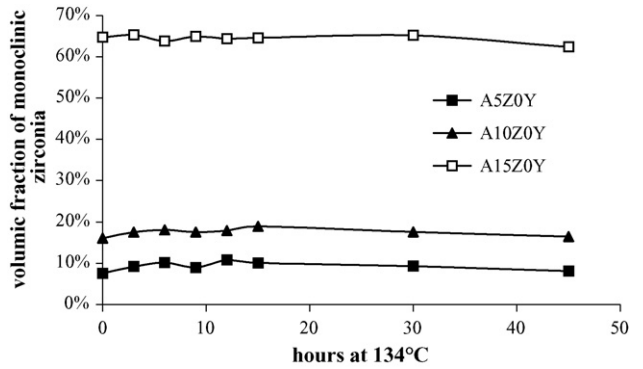

Fig. 5. Variation of monoclinic volumic fraction of zirconia vs. ageing time: case of unstabilized zirconia based ZTA.

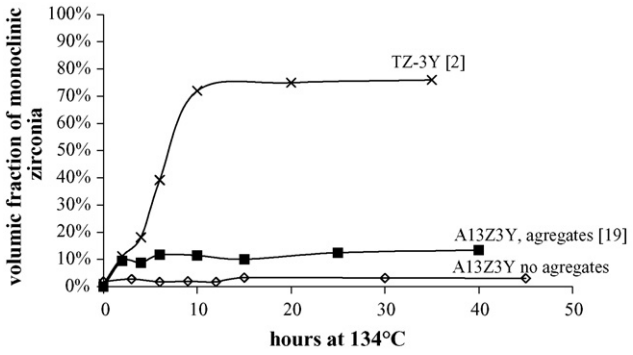

Fig. 6. Influence of zirconia aggregates on ageing kinetics of ZTA: aggregates are transformed like monolithic zirconia during the first 2 h in autoclave.

not of aggregates. The ageing kinetics are presented in Fig. 6, together with results obtained for a pure 3Y-TZP.[2]

The aggregate-free ZTA does not exhibit any ageing, in agreement with the results reported above, in contrast with the ZTA presenting aggregates, where ageing is observed especially during the first two hours of autoclave treatment. Interestingly, the kinetic of ageing is consistent with that of pure 3Y-TZP. This is quite logical, since zirconia grains present inside aggregates should exhibit the same behaviour than inside a monolithic zirconia. This easier transformation of grains surrounded by other zirconia grains (compared to zirconia grains surrounded by alumina) is due to the lower constraining effect (lower elastic modulus of zirconia). Zirconia grains inside aggregates can then transform by the commonly accepted nucleation-growth mechanism occurring in pure 3Y-TZP. It should be noted, however, that not all zirconia grains present in aggregates (30 vol.%) transform to the monoclinic form. Indeed, it can be anticipated that the transformation of grains at, or near the interface with the alumina matrix is hindered by the constraining effect of alumina.

The same conclusion can be drawn from Fig. 7, where the results of A10Z0Y from this study are compared to the same composition of Deville's study[19] (A10Z0Y with aggregates). It was shown that alumina zirconia composites processed from unstabilized zirconia could exhibit ageing, even below the percolation threshold. This was related to extensive microcracking during cooling, leading to an interconnected network of cracks allowing water to penetrate inside the component. Microcracking was reported extensively in the literature, for concentrations around 10 vol.% zirconia.[25] This microcracking can be avoided by an optimal dispersion. Here we show that the ZTA composite processed with no aggregate does not exhibit any ageing. It could be argued that this difference could be linked to HIP. In order to assess this point, additional specimens were processed, by sintering at 1600 °C for 2 h, without HIP, i.e. under the same conditions as the previous work (except, again, the absence of aggregates). The initial monoclinic content is higher than for the specimen sintered at 1520 °C, followed by HIP. This is due to the higher zirconia grain size (Figs. 8 and 9). The mean

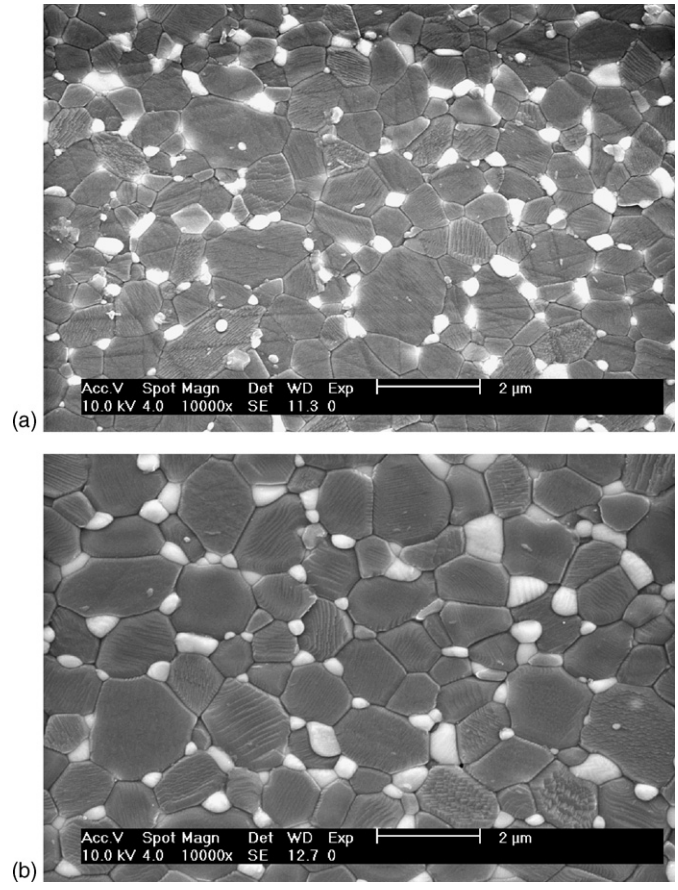

Fig. 8. Microstructures of A10Z0Y (a) and A10Z0Y-1600 (b).

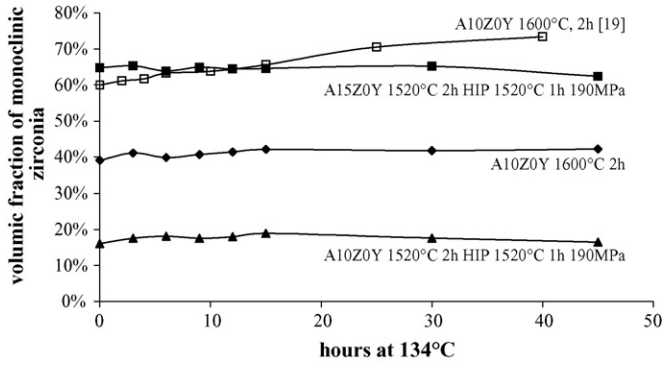

Fig. 7. Ageing kinetics of A15Z0Y sample, and A10Z0Y sintered by different way.

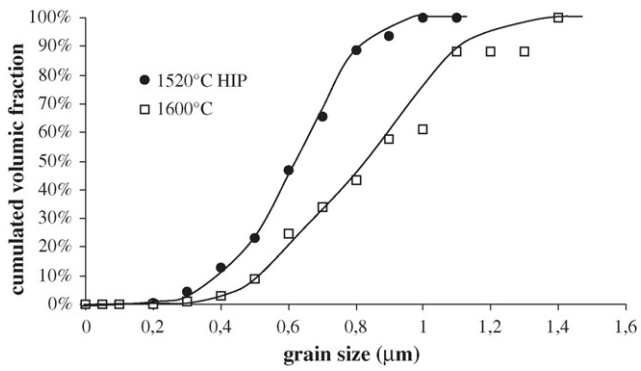

Fig. 9. Cumulative zirconia grain size distribution for A10Z0Y and A10Z0Y-1600.

zirconia grain size is 0.85 μm for A10Z0Y-1600 sample and 0.62 μm for the A10Z0Y-HIP sample. Consequently, a higher level of zirconia is transformed during post sintering cooling in the A10Z0Y-1600 sample. However, no ageing is observed for the A10Z0Y-1600 sample, in contrast with the same material with aggregates. The HIP, performed at a lower temperature than conventional natural sintering, is therefore a key step in the processing to obtain fine grain size materials with full density and consequently low initial amounts of monoclinic phase, but does not account directly in the ageing resistance of ZTA ceramics.

These results prove the possibility to process ageing free unstabilized ZTA with large amounts of zirconia (but still below the percolation threshold), provided that no aggregates are present. The results obtained for the A15Z0Y (without aggregates) confirm this hypothesis: even if the initial monoclinic content is very high (more than 60%), no ageing is observed. This is attributed to the absence of microcracking. Indeed, even after careful SEM observations, no microcracking at all was observed in any specimen. Microcracking occurs in unstabilized zirconia ceramics during cooling, because stresses around transformed particles reach a critical value. In most material combinations where the expansion coefficient of the matrix is larger than that of the second phase, relatively large particles are needed to satisfy the crack extension conditions.[26] In our case, transformation of aggregates is more detrimental to microcracking than transformation of isolated, small, grains.

This demonstrates the critical effect of zirconia aggregates on ageing of ZTA, and the importance of a perfect dispersion, achieved here by electrostatic dispersion.

5. Conclusion

The recent events related to zirconia ageing in orthopaedics show that no ageing can be tolerated for ZTA ceramics. Even apparently low monoclinic content variations with time must be avoided. This work underlines the critical role of processing on zirconia dispersion in alumina matrix, and consequently its influence on ageing resistance. The presence of aggregates is clearly identified as the main factor leading to ageing sensitivity. These aggregates could be avoided by an optimal electrostatic dispersion at acidic pH. This conclusion is only valid for zirconia content below the percolation threshold (i.e. 16 vol.%) above which ageing cannot be avoided.

Acknowledgement

The authors would like to acknowledge the 'Région Rhône Alpes' (Thématiques Prioritaires 2003–2005) for financial support.

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