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Leading Opinion

# What future for zirconia as a biomaterial?☆

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**Abstract**

The failure events of Prozyr® femoral heads in 2001–2002 have opened a strong, controversial issue on the future of zirconia as a biomaterial. The aim of this paper is to review and analyze the current knowledge on ageing process and on its effect on the long term performance of implants in order to distinguish between scientific facts and speculation. Current state of the art shows the strong variability of zirconia to in vivo degradation, as a consequence of the strong influence of processing on ageing process. As different zirconia from different vendors have different process related microstructure, there is a need to assess their ageing sensitivity with advanced and accurate techniques, and ISO standards should be modified, especially to gain confidence from clinicians. There is a trend today to develop alumina–zirconia composites as an alternative to monolithic alumina and zirconia: the issue of ageing is also discussed for these composites.
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*Keywords:* Zirconia; Ageing; Explant analysis; Orthopedics

## 1. Introduction

Among the materials for orthopedics, biomedical grade zirconia is maybe the one for which there is the largest controversy among scientists, industrials or clinicians. Biomedical grade zirconia was introduced 20 years ago to solve the problem of alumina brittleness and the consequent potential failure of implants [1]. Today, more than 600 000 zirconia femoral heads have been implanted worldwide, mainly in the US and in Europe. On the one hand, biomedical grade zirconia exhibits the best mechanical properties of oxide ceramics: this is the consequence of phase transformation toughening, which increases its crack propagation resistance. The stress-induced phase transformation involves the transformation of metastable tetragonal grains to the monoclinic phase at the crack tip, which, accompanied by volume expansion, induces compressive stresses [2]. On the other hand, due to this metastability, zirconia is prone to ageing in the presence of water [3]. Zirconia manufacturers claimed that this problem was limited under in vivo situation until year 2001 when roughly 400 femoral heads failed in a very short period [4]. The failure origin is now associated to an accelerated ageing in two particular batches of the leader Prozyr® product [5]. Even if limited in time and number, and clearly identified to be process controlled, these events have had a catastrophic impact for the use of zirconia, some surgeons going back to other solutions. Some still claim that zirconia alone allows the use of a larger range of designs (cf. Fig. 1), for example 22 mm heads that fail with alumina, more brittle. They also rightly claim that the failure rate before 2001 was exceptionally low and that ageing

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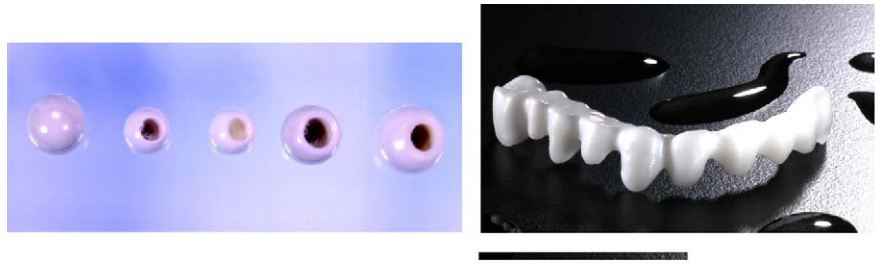

Fig. 1. Range of femoral heads dimensions allowed with zirconia (courtesy HTI, Decines, France) and example of a zirconia dental bridge (courtesy Diatomic, Louey, France).

sensitivity can be controlled and decreased by a careful control of process. Others, also at right, claim that it is unsatisfactory to implant a material in the body, which is not fully stable. There is a dearth of clinical retrieval studies to really assess this issue. Part of the answer should appear in the next years with the revision of thousands of implants, related or not to this aspect. Up to date clinical reports appear to be again somewhat opposite: some results show excellent behavior of some heads after several years in vivo [6], while others show poor follow up results [7], with severe wear and osteolysis around the implant. Few case studies report surface degradation of zirconia implants, which could be related to ageing [8,9]. However, there is a clear lack today of correlation between ageing and clinical failures. So, why did some zirconia heads behave well while other show problematic results?

The orthopedic community is thus confronted to a dilemma concerning zirconia, and the market sale has decreased of more than 90% between 2001 and 2002 (end of Prozyr® activity) with no evidence of a clear renew. At the same time, and quite surprisingly, the dental community is 'discovering' the aesthetical and mechanical benefits of using zirconia (see Fig. 1) and seems not to be so concerned by ageing problems. For these dental applications, zirconia market increases of more than 12% per year.

As underlined recently by Clarke et al. [10], the history of zirconia has been the subject of misleading interpretations and confusions, mainly due to an absence of rigorous scientific clarifications on ageing. The purpose of the present paper is to bring recent highlights on the ageing mechanism to analyze deeper some recent retrieval studies. This could help the readers to distinguish between scientific facts and speculations. The 400 failures of 2001 have also shown that ISO standard [11] should be modified, at least taking into account ageing, in order to avoid any new dramatic event of that kind. This paper aims at showing the main changes necessary to the ISO standards in the future.

At last, another source of confusion can be associated to the present tendency to develop zirconia-toughened alumina composite [12]. Is it possible indeed that zirconia grains inside these composites could be affected by ageing and lead to potential problems as it was the case for monolithic zirconia? This paper tries to define some rules to be followed for future developments of zirconia-based products.

## 2. Ageing process and methods for assessing the ageing sensitivity of zirconia ceramics

The main issue concerning zirconia ceramics, not only in orthopedics, is their sensitivity to low temperature degradation (LTD). LTD has been associated to the roughening of the implants after steam sterilization [13] and more recently to the failure events of Prozyr® heads [4]. Giving a comprehensive review of the ageing mechanism would considerably extent the scope of the present paper. The readers not familiar with this field can refer to the excellent review of Lawson [3]. The monoclinic phase is the stable structure of zirconia ceramics at room temperature. When stabilized with yttria, zirconia ceramics can retain their high temperature tetragonal structure, which is metastable at room temperature. Ageing occurs by a slow surface transformation to the stable monoclinic phase in the presence of water or water vapor. Transformation starts first in isolated grains on the surface by a stress corrosion type mechanism. For a femoral head, surface means the polished wearing surface, but also the interior of the cone, in contact with the metallic taper. This surface was somewhat 'forgotten' before the failure events of Prozyr® heads. The initial transformation of specific grains can be related to their disequilibrium state, i.e. either to a larger size [3], a lower yttria content [3], a specific orientation from the surface [14], the presence of residual stresses [15] or even the presence of cubic phase [16], that has been underestimated in most of the existing literature. As schematically described in Fig. 2, this nucleation of the transformation leads then to a cascade of events occurring neighbor to neighbor: the transformation of one grain leads to a volume increase stressing up the neighboring grains and to microcraking. This offers a path for the water to penetrate down into

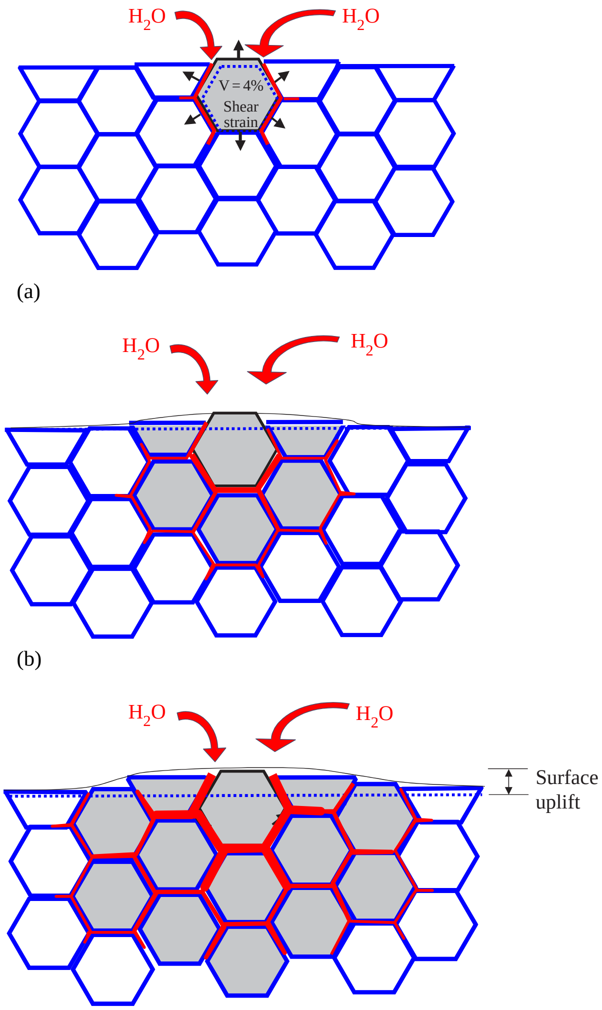


Fig. 2. Scheme of the ageing process occurring in a cross section, showing the transformation neighbor to neighbor. (a) Nucleation on a particular grain at the surface, leading to microcracking and stresses to the neighbors. (b) Growth of the transformed zone, leading to extensive microcracking and surface roughening. Transformed grains are gray. Red path represents the penetration of water due to microcracking around the transformed grains.

the specimen. The transformation occurs therefore by a nucleation and growth process, well described by Mehl–Avrami–Johnson laws [17] (Fig. 3). The growth stage again depends of several microstructure patterns: porosity, residual stresses, grain size, etc. It is quite clear at this stage that both nucleation and growth will be highly process related. Table 1 summarizes the potential effect of different process stages on microstructure of zirconia and consequently on ageing. During the short—20 years—story of zirconia, we have seen black/white zirconia, HIPed heads, non-HIPed heads, etc., all these differences affecting LTD resistance. As different zirconia from different vendors (or even from different processes for a given vendor) will have different microstructural characteristics, there is a need to assess

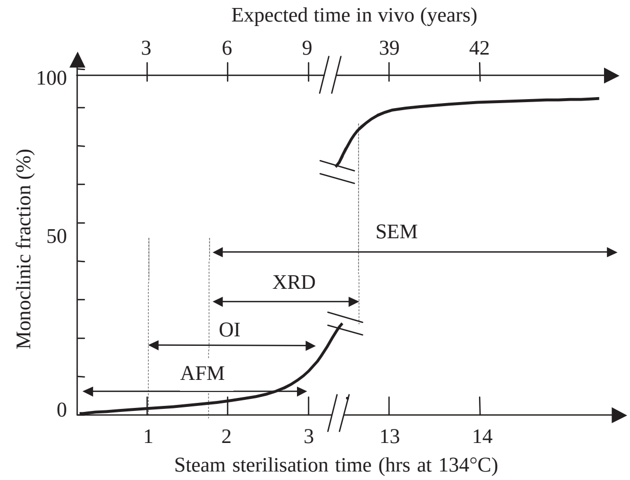


Fig. 3. Relevance domains of experimental techniques, as a function of the transformation stage.

the ageing sensitivity of each with advanced and accurate techniques. This can be done via accelerated tests in vitro and from the analysis of in vivo femoral heads explanted for any reason after a given duration (we will review some existing retrieval studies further in the text). Ageing being thermally activated [17], accelerated tests can be performed at temperatures higher than 37 °C, in the framework of the classical time–temperature equivalence principle. The standard, now forbidden, steam sterilization procedure at 134 °C was proven to induce some degree of ageing. It was therefore a good basis to propose an accelerated test. It was thus calculated that 1 h of autoclave treatment at 134 °C had theoretically the same effect as 3–4 years in vivo [17]. If proved to be accurate, this should avoid heavy and long experiments to assess the ageing sensitivity of a given zirconia prior to commercialization. A critical comparison of methods for the determination of the ageing sensitivity of biomedical grade zirconia can be found in Ref. [18]. X-ray diffraction (XRD) analysis was traditionally used to follow quantitatively the transformation. However, this technique suffers some limits such as a poor precision during the first stages of ageing (when the monoclinic content measured by XRD is typically less than 5%), and the absence of local information on ageing process. However, due to its simplicity, this technique can be considered as a first step to investigate the ageing sensitivity of a particular zirconia. Scanning Electron Microscopy (SEM) has been used to investigate the potential impact of ageing on the surface degradation. However, SEM suffers poor vertical resolution and can be also inadequate to investigate the first stages of ageing. It should be preferred to follow the transformation in the bulk or the effect of ageing on surface grain pull out. Moreover, SEM, especially on cross sections, requires specific preparation that can modify the observed surface. Some

Table 1
Potential effect of the different process stages on the microstructure of zirconia ceramics

| Process stage | Potential effect on microstructure |
|---|---|
| Initial powder | Yttria content and distribution, presence of additives (leading to secondary phases) |
| Forming | Pore distribution of green compacts, and consequently porosity of final components |
| Sintering temperature and duration | Density, grain size, amount of cubic phase |
| Cooling rate after sintering | Phase partitioning, residual stresses |
| Hot isostatic pressing | Density, phase assemblage, increase of oxygen vacancies content, residual stresses |
| Whitening | Decrease of oxygen vacancies, modification of residual stresses |
| Grinding and machining | Surface roughness, residual stresses, initial monoclinic content |
| Cleaning, sterilization | Initial monoclinic content |

care should be taken on reports revealing an apparent poor initial density of damaged monoclinic zones with some SEM analyses. Indeed, microcraked zones can lead to extensive pull out during the preparation of the samples. More recent methods, such as optical interferometer (OI) and Atomic Force Microscopy (AFM) can provide valuable insights on the nucleation and growth process, especially during the very first stages of ageing, when SEM and XRD lack precision. Fig. 3 represents the relevance domains of the experimental techniques as a function of the transformation stage. The combination of each technique provides a wide range of characterization, that will inevitably validate or not a given batch of zirconia for future in vivo situation.

## 3. Current state of the art concerning retrieval studies: some different stories

Some retrieval studies give positive clinical experiences with zirconia [6], while others show surface degradation of zirconia implants and in some occasions severe wear and/or osteolysis around the implant [7].

The consequences of ageing process on the long term performance of zirconia implants can be twofold: ageing is associated (a) to roughening—this will lead to increased wear, (b) to microcracking—this will lead to grain pull-out and generation of particle debris and possibly premature failure when the microcracked, damaged zone reaches the critical size for slow crack growth to proceed. These two effects are poorly documented in the existing literature: despite 20 years of use and several thousands of implanted heads, only few reports have detailed retrieval analysis, often with no attention dedicated to microstructural features and structural modification. Recent studies give a first scenario of the ageing of zirconia in the body, and its effect on the biomechanical performance of the implants [8–10,19].

At this stage, we must come back and separate between 'normal' and 'unusual' ageing in typical batches of Prozyr® heads. The two case reports from Maccauro et al. [19] and from Varner et al. (in Ref. [10]) deal with a batch in which fracture rates could be as high as 42%. In these series, fracture occurred after 21–46 months after surgery. It was said by the manufacturer that failure occurred via 'unexpected' and accelerated ageing in some batches [5]. It is clear today that these failures were indeed attributed to an accelerated ageing of the ceramic, in the cone region [10,19]. Due to a change in the processing technique (change from batch to tunnel furnace) the microstructure was varied so that the ageing resistance was poor in this region. We might suppose that such changes in process may have similar dramatic events in any materials. These two reports, and the crisis of 2001, emphasis the importance of accuracy in process control, but should not conduct to any conclusion on the normal behavior of zirconia in the body.

Maybe more critical are the reports which show, under 'normal' situation, surface degradation of zirconia implants, or strong osteolysis associated with the use of zirconia heads. Haraguchi et al. [8] reported for the first time two cases of surface degradation (roughening and microcracking) caused by phase transformation. The zirconia used in this work, presumably processed by Kiocera followed ISO criteria. They measured monoclinic contents of 20% and 30% in both heads, after only 3 or 6 years respectively, associated with a strong increase of roughness (from 6 to 120 nm). From the photomicrographs provided by the authors, small surface domes, of some dozen of microns, were present on the pole of the heads. They were likely to be monoclinic 'spots', which were observed in previous works with accelerated, in vitro tests [17]. Craters of the same size were visible at the equator (region of wear contact). They should correspond to the same monoclinic spots, but worn out, i.e. inducing large amount of pull out. This gives us the scenario of surface degradation, due to the combination of LTD and wear, as schematically described in Fig. 4. More recent paper from Shane et al. [9] confirms the degradation of surface properties for some zirconia heads, by means of nano-indentation hardness measurements on explanted heads that had

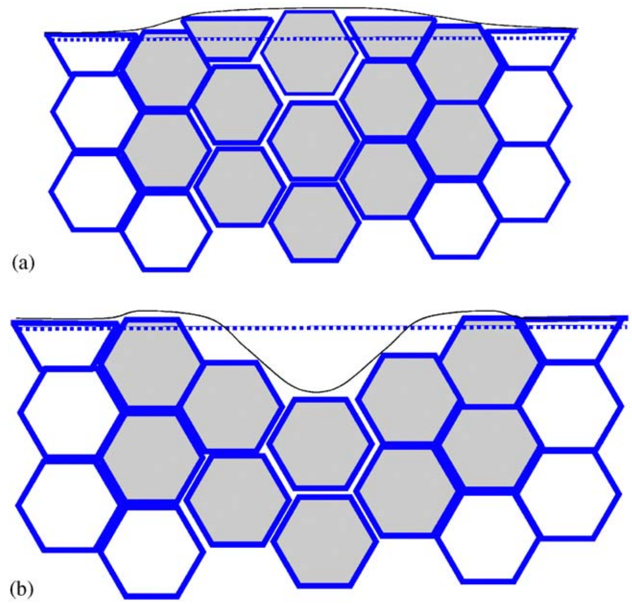

Fig. 4. Scheme of the surface degradation of zirconia hip prostheses due to the combination of ageing and wear. (a) Surface roughening and microcracking on a surface not subjected to wear (i.e. pole of the head). (b) Grain pull-out induced by wear, leading to craters at the surface (i.e. equator of the head).

undergone various degrees of phase transformation in service (ranging from 0 to ≈78% monoclinic content[1]). The hardness dropped from 18 to 11 GPa for high transformation ratios, which indicates extensive microcracking on the transformation sites. Little information was given on the origin of the heads, their microstructural features and on their clinical history, making an extended analysis of the results difficult. However, it should be noted that one heads exhibited about 78% of monoclinic phase after 62 months of implantation.

Contrasting with these bad clinical experiences, some results still show good, at least middle term follow up [6]. For instance, 22 mm diameter zirconia heads after 45 months showed less than 10% monoclinic content, with apparently neither increase in roughness nor grain pull out. Explanted heads from the same team should be regarded with special interest, since LTD occurs by nucleation and growth and may be at the nucleation stage (small but significant monoclinic content).

These different clinical experiences seem to confirm the strong variability of zirconia heads as regard to LTD resistance. Many processing factors may affect LTD resistance (Table 1) and it seems that, even in the framework of ISO standards, some heads behave well while other show catastrophic behavior. There is, thus, a great need of more advanced studies on zirconia implants, with a deeper correlation between microstructure and LTD resistance in vivo. We recently performed a retrieval analysis of two heads that supports the large variability of zirconia heads to LTD, and in consequence to in vivo situation. Two independent surgeons provided the retrieved heads. One was retrieved after 8 years, the origin of revision being other than related to failure or aseptic loosening. This head was processed by Saint Gobain Desmarquest within the year 1996 (Prozyr® laser marking). The second head was retrieved due to breakage of the zirconia femoral head after only 4.5 years in vivo. The femoral head was broken into four pieces. No information could be obtained on the fabrication, since no trade-name Laser marking was visible in the head. The retrieved heads were first analyzed at different locations on the surface via XRD in order to estimate the amount of phase transformation in vivo. SEM and AFM were conducted in order to investigate possible surface degradation induced by phase transformation. The explants were then cut in parts in order to obtain sections at the core of the heads free of any surface transformation, i.e. not in contact with body fluid. These sections were polished at a laboratory scale with diamond pastes down to 1 μm grain size, leading to surface roughness of about 2 nm. On one polished section of each head, ageing kinetics were performed at 134 °C, 2 bars in autoclave in order to get insight into the expected kinetics at 37 °C for each head, and to compare with results obtained experimentally at the surface in contact with body fluid. On another polished section of each head, thermal etching at 1300 °C, for 30 min was conducted so as to get information on grain size. Density and composition were also checked in agreement with the ISO standard.

Table 2 summarizes the grain size (intercept dimension), density and chemical composition of the two heads, in comparison to ISO standard. XRD monoclinic content at the surface (including measurements at different locations) and approximate size of monoclinic spots visible at the surface via AFM are included. Both heads follow the ISO recommendations. The major difference lies in the grain size, in the upper limit of the norm for the second head. This probably traduces differences in the sintering process (temperature, time, etc.), which may have a strong influence on ageing kinetics. This may be the major origin for the strong difference lying in monoclinic content: about 10% after 8 years for the first one, and 20% after only 4.5 years for the latter. This leads to large surface degradation on the second head, with the occurrence of large damaged zones appearing like 'craters' (Fig. 5a), which have to be related to monoclinic nuclei formed by ageing [17]. In comparison the surface of the present Prozyr® head after 8 years exhibited minor topographic changes. Only AFM could reveal the presence of transformed zones (Fig. 5b). No craters were observed.

[1]Values re-calculated from intensity ratios given on the paper.

Table 2
Physico-chemical characteristics of the two retrieved heads of the present study, together with measured XRD monoclinic content and monoclinic spots mean diameter

| | Prozyr® head after 8 years in vivo | Second head after 4.5 years in vivo | ISO 13356 |
|---|---|---|---|
| Density | $6.08 \pm 0.2\,g/cm^3$ | $6.05 \pm 0.2\,g/cm^3$ | $> 6\,g/cm^3$ |
| Grain size (intercept dimension) | $0.42 \pm 0.04\,\mu m$ | $0.67 \pm 0.07\,\mu m$ | $< 0.6\,\mu m$ |
| Chemical composition | | | |
| $ZrO_2 + HfO_2$ | $94.4\% \pm 1$ | $94\% \pm 1$ | $> 94\%$ |
| $HfO_2$ | $\leqslant 1\%$ (non-detected) | $\leqslant 1\%$ (non-detected) | $< 5\%$ |
| $Y_2O_3$ | $5.6\% \pm 1$ | $6.0\% \pm 1$ | $5\% \pm 0.5$ |
| $Al_2O_3$ | $\leqslant 1\%$ (non-detected) | $\leqslant 1\%$ (non-detected) | $< 0.5\%$ |
| XRD monoclinic content | 7–10% | 18–23% | |
| Monoclinic spots diameter | $\sim 6\,\mu m$ | $\sim 15\,\mu m$ | |

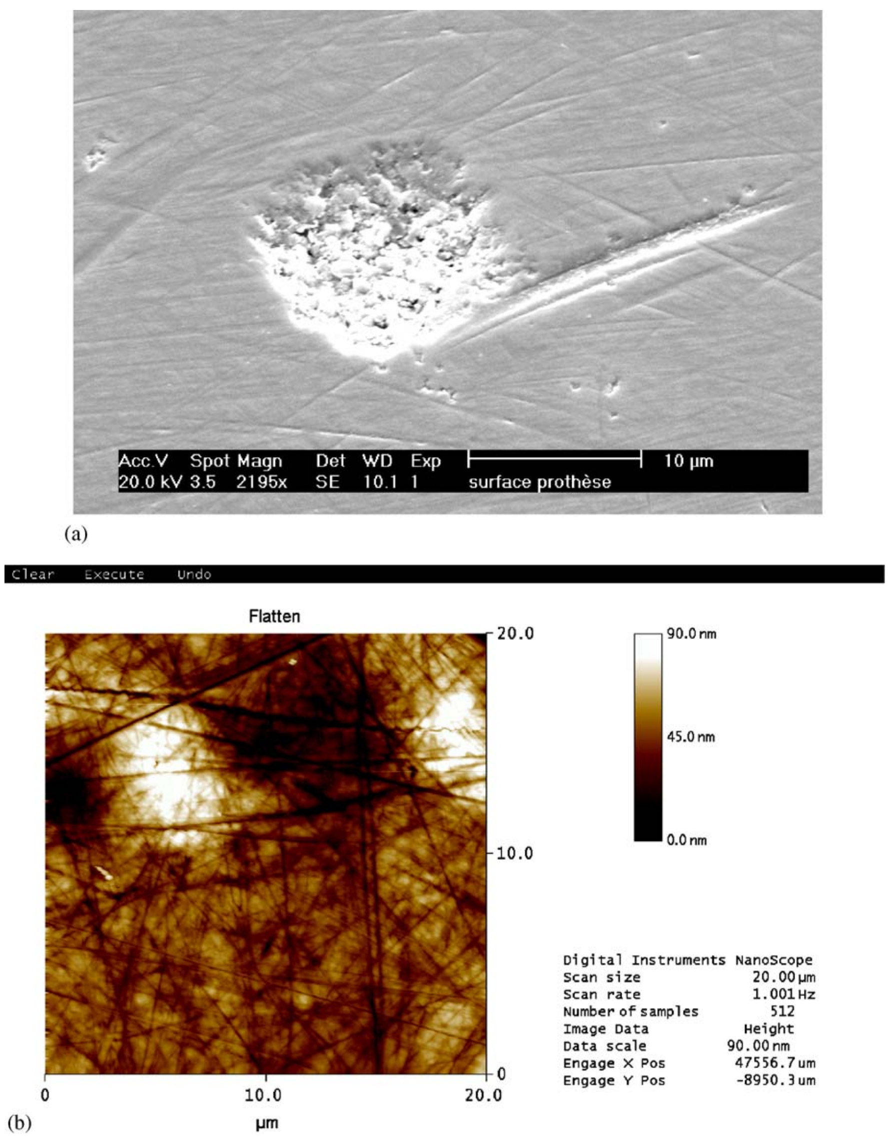


Fig. 5. (a) SEM picture of one retrieved head ('second' head in the text) after 4.5 years. Note the large crater at the surface, induced by ageing associated to wear. (b) AFM picture (height image) of the Prozyr® after 8 years. The transformed zone does not lead yet to grain pull out.

Fig. 6 shows the ageing kinetics exhibited by the two materials, measured by XRD at 134 °C. The kinetics are given versus time at this reference temperature and expected at 37 °C from the time–temperature equivalence discussed above. Also included are the experimental data obtained at the surface of the retrieved heads in contact with body fluids. The results show an excellent agreement between prediction at 37 °C from the accelerated test and experimental measurements at the surface in contact with body fluid performed before. This shows that accelerated tests can accurately predict in vivo behavior of a given zirconia and should be used as a quality control test before any commercialization. This shows also how slight variations in the process of zirconia can lead to difference in LTD resistance. Among difference things it also shows that the hypothesis of significant elevation of the temperature of the surface during motion in vivo [8] seems not valid and may be an artifact of hip joint simulators [20].

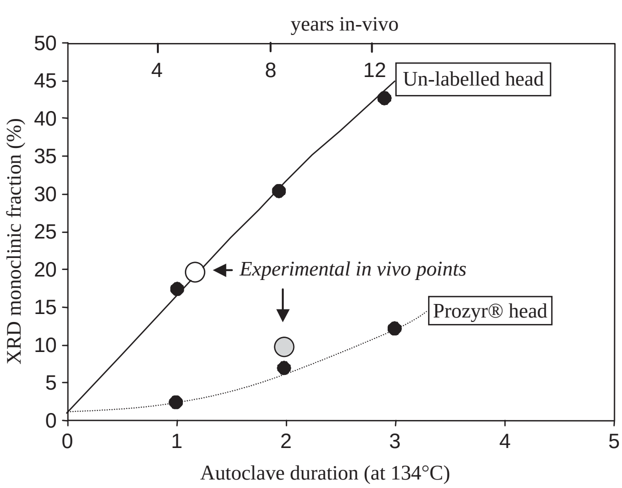


Fig. 6. Kinetics measured on polished 'non-aged' (see text) sections of the two heads at 134 °C, calculated at 37 °C from apparent activation energy, and compared with experimental in vivo points.

## 4. The future of zirconia?

### 4.1. A need for advanced specifications for ISO standards

The tendency of zirconia to ageing both in vitro and in vivo, and the differences observed from one zirconia to another lead us to come back to the crucial question of the title 'what future for zirconia as a biomaterial?'. Indeed, from their inception 20 years ago, the performance of zirconia ceramic heads has been controversial, mainly because of a lack of accurate standards and specifications giving emphasis on LTD. To gain the confidence of surgeons community, a revision of current specifications on zirconia is mandatory. How is it possible that no reference to ageing is made after 20 years experience in the orthopedic community, and much more for other fields? Why is it still possible to process 3Y-TZP with a real grain size approaching 1 μm (the ISO standard referring to a linear intersection distance of 0.6 μm), while a number of studies clearly show dramatic decrease of ageing resistance for a real grain size above 0.6 μm [21] (i.e. linear intersect distance of 0.38 μm)? Table 3 summarizes actual ISO 13356 requirements for a given number of parameters (which clearly affect long term behavior of zirconia materials) and necessary changes to be adopted. In particular, accelerated tests in steam, for a given batch of products or after a change in the process or even in the development of new 'ageing free' zirconia ceramics are the key for gaining confidence in the future.

### 4.2. A need for 'ageing free' zirconia materials

The differences observed under in vitro and in vivo situations have shown that zirconia products could behave well. It is difficult to talk about 'ageing free' zirconia since the transformation occurring upon ageing consists in a 'natural' return back to the monoclinic equilibrium state. However, the transformation kinetics can be much affected by microstructural issues. Some solutions were proposed in the literature, but were

Table 3
Personal recommendations for modification of ISO 13356 standards

| Current ISO 13356 specifications | Personal recommendations for ISO modifications |
|---|---|
| *Aging*: | |
| No reference to ageing | An accelerated ageing test should be carried out in steam at 134 °C, 2 bars, for 5 h. After this period, the variation of monoclinic content should be lower than 10% (for every surface in contact with body fluids). No strength degradation should be accepted after the test. |
| *Grain size distribution and microstructures*: | |
| Intercept distance < 0.6 μm. | Intercept distance < 0.4 μm, with a standard deviation less than 0.2 μm (large deviation possibly indicating the presence of cubic phase). |
| No reference to initial monoclinic content | Initial monoclinic content less than 20% for every surface in contact with body fluids. |

hardly followed by industrial changes. Among them, the addition of small amounts of silica [22] or the use of Yttria coated instead of co-precipitated powders [23] seem to have a clear benefit to the ageing resistance, while preserving good toughness and strength. These solutions were proposed in the Y-TZP system. It has to be said that the issue of ageing of zirconia medical devices stands to the use of yttria as a dopant. Yttrium, as a trivalent ion, creates oxygen vacancies that help hydroxyl group diffusion in the lattice, generating nucleation of the transformation by stress corrosion type mechanism. Ceria doped zirconia ceramics were almost never considered while they exhibit superior toughness (up to $20\,MPa\sqrt{m}$) and almost no ageing (i.e. non-significant during the lifetime of an implant). There is thus still a door open for zirconia ceramics with improved properties. However, the stop of Prozyr® activity and the new generation of zirconia—alumina composites promoted by major ceramic companies (i.e. Ceramtec or Metoxit) play against further development of such zirconia based products in orthopedics.

### 4.3. *Zirconia toughened alumina composites: the ultimate choice?*

Given the moderate toughness of alumina and the issue of ageing in zirconia, there is a trend today to develop alumina–zirconia composites. This may be the way to benefit from zirconia transformation toughening without the major drawback associated with its transformation under steam or body fluid condition. In the recent literature concerning alumina–zirconia composites for biomedical applications, different compositions have been tested, from the zirconia rich to the alumina rich side [24,25]. Major ceramic companies are developing such materials. A composite material processed with 80% tetragonal zirconia polycrystals ($ZrO_2$-TZP) and 20% alumina ($Al_2O_3$) is reported to have outstanding mechanical and tribological properties. The alumina-toughened zirconia (ATZ) Bio-Hip®, developed by Metoxit AG (Thayngen, Switzerland), has a bending strength of up to 2000 MPa, indicating that it can withstand loads that are four times greater than conventional $Al_2O_3$ implants. This product is still not in the market. At the same time, Ceramtec AG (Plochingen, Germany) recently developed BIOLOX®*delta*, which consists of approximately 75% aluminum oxide, the basis for hardness and wear resistance, and approximately 25% zirconium oxide, for improved mechanical properties. A strength higher than 1150 MPa is reported, associated with a toughness of $8.5\,MPa\sqrt{m}$. This product is now in the market.

The addition of alumina to zirconia clearly hinders ageing, or at least reduces drastically its kinetic. It is shown that strength of Biolox delta® for example does not decrease even when repeatedly steam sterilized. However, 'no decrease in strength' does not mean necessary 'no ageing', since other manifestations of ageing are grain pull out and roughening. Few studies have been devoted to ageing in alumina–zirconia systems, but they show that, even if limited and possibly reduced to zero, some degree of degradation can be observed, depending on microstructural features [26–28]. As an example, we showed in a previous work [26] that ageing could be significant in a 3Y-TZP–alumina composite above 16 vol% zirconia. This critical content was related to the percolation threshold above which a continuous path of zirconia grains allowed transformation to proceed. Any extrapolation to other laboratory scale or industrial composites could be hazardous, but it shows again how ageing must be checked carefully prior to clinical development of a given alumina–zirconia composite. Anyway, the presence of zirconia aggregates, especially if the zirconia is stabilized with yttria, should be avoided.

## 5. Conclusion

The bad story of Prozyr ® femoral heads in 2001, even if dramatic in some aspects, have led the scientific and orthopedic community to deeply study the behavior of zirconia, especially in respect to ageing in vitro and in vivo. Biomedical grade zirconia is by far much deeper understood than ever and powerful tools can be used to assess its sensitivity against ageing. However, given the consequence of the Prozyr® event and some controversial retrieval studies, some of them clearly demonstrating ageing in vivo, further effort will be necessary to gain confidence from the orthopedic community. In this field, it seems that the future, at least for the short and middle term, stands on the combination of alumina and zirconia to obtain advanced composites. However, even if more limited, there is also for these materials a need for more detailed understanding of ageing related issue. The use of zirconia for dental implants is quite young and in development phase. The issue of ageing is still not discussed for these applications.

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