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On the fracture of a zirconia ball head

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Y-TZP ball heads were introduced into the market in 1985. Since then these components have had wide diffusion in hip replacements, due to their good mechanical performance and reliability. Namely, only a few papers were published up to year 2000 reporting failures of Y-TZP ball heads. The worldwide recall in August 2001 of some Y-TZP batches changed this situation. This paper analyse the material of a ceramic ball head that fractured *in vivo* 34 months after surgery. The retrieved fragments were submitted for visual inspection, fractographic analysis by optical microscopy, X-ray diffractometry, and FEG-SEM ceramography analysis. The results obtained show that the hydrothermal stability of the material had only a secondary role in the fracture. The literature reporting on failures of THR making use of Y-TZP ball heads is discussed.

Introduction

Ceramic ball heads in clinical use today are manufactured from two oxide ceramics, alumina (Aluminium Oxide Al_2O_3, α-alumina a.k.a. corundum) and zirconia (Zirconium Dioxide ZrO_2, mostly stabilized by Yttria Y_2O_3, a.k.a. Yttria-stabilised Tetragonal Zirconia Polycrystals, Y-TZP). THRs using ceramic ball heads have a wide diffusion, especially in some European countries, as shown in Table I. The introduction of Y-TZP in clinical practice during the mid-1980s [1] allowed to put at surgeons disposal, and to the disposal of their patients, a ceramic biomaterial characterised by toughness and strength better than the ones of the ceramics in use at that time. The properties and the technology of Y-TZP in biomedical engineering was the object of some comprehensive reviews [2–5] taking into account all the aspects of the technology and of the clinical use of this ceramic biomaterial. The properties of Y-TZP ceramics as required for clinical applications are stated in the standard ISO 13356 [6]. A non exhaustive list of manufacturers of Y-TZP ball heads is given in Table II: the main manufacturer worldwide, Saint Gobain Céramiques Avancées Desmarquest (SGCA Desmarquest, formerly Céramiques Techniques Desmarquest, then Norton Desmarquest, simply Desmarquest in the following of this paper) made about 400.000 ball heads up to 2002.

The excellent mechanical properties of Y-TZP (see Table III) are depending on the transformation toughening mechanism [7]. Briefly, the Y-TZP microstructure is mainly constituted by homogeneous and fine tetragonal grains that are metastable in nature. Grains remain in the tetragonal phase depending on three parameters, namely: (1) the constraint of the matrix, say the constraint that the grains act on their neighbours; (2) the size of the grains; (3) the concentration (and the distribution) of the stabilizing oxide. If the matrix constraint is relieved by an advancing crack, the tetragonal grains may transform into monoclinic. This implies a small increase in volume (3–4%Vol) depending on grain size and concentration of the stabilizing oxide. Fracture energy is dissipated by the T-M transformation. Moreover, the crack must overcome the compressive stress due to the matrix expansion to continue its progress. These mechanisms constitute the basis for the toughness of the material, e.g. its ability to dissipate fracture energy.

As tetragonal grains are metastable in nature, they may spontaneously shift to monoclinic. This behaviour is well known at temperature between 100 and 200 °C in wet environment, and its consequences are the decrease in density, strength and toughness of the ceramic [8]. However, the transformation rate can be reduced in several ways thus maintaining excellent strength levels

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TABLE I Use of ceramic ball head in total hip replacements in selected countries. (Based on data from Ref. [4])

Country	Ceramic ball heads (%)	% Alumina	% Zirconia
Austria	80	95	5
France	50	50	50
Germany	40	95	5
Switzerland	60	90	10
Japan	<10	20	80
USA	<10	10	90

TABLE II Manufacturers of Zirconia ball heads

Manufacturer	Country	Brand name
SGCA Desmarquest	F	Prozyr®
Morgan Matroc	UK	Zyranox®
Ceraver	F	
Cerasiv	D	Ziolox®
HTI Technologies	F	Biozyr®
Metoxit	CH	TZP BioHIP®
Kyocera	J	Bioceram®
NGK	J	
Kobelco	J	
Astromet	USA	
Xylon	USA	

for a time compatible with the lifetime of the prosthetic device. This may be achieved acting on the distribution of the stabilizing oxide, as ceramic based on yttia-coated powders show little phase transition in comparison to ceramic based on coprecipitated powders [9], or by the introduction of small quantities of Ceria or Alumina into the powders before firing [8–11].

The applications of Y-TZP in biomedical engineering are manifold: Y-TZP allowed the design and manufacture of innovative ceramic components for hip arthroplasty, like ∅ 22,22 mm (7/8 in) ball heads and ball heads with extra neck length, and the study of new wear couples based on the use of Y-TZP ball heads and alumina sockets [12]. Other medical devices made from Y-TZP are in different development stages or already in clinical use, e.g. zirconia condylar components for knee replacements [13] or interposition arthroplasty of carpometacarpal joints [14], and many dental applications have been developed [15–20]. Taking into account the widespread use of Y-TZP as a biomaterial, the detailed investigation of the fracture of a zirconia ball head, that took place in atraumatic conditions after 34 months of clinical use is a quite interesting task.

Figure 1 XR showing the evidence of the ball head fracture. The Y-TZP ball head fractured after 36 months, in atraumatic conditions.

Materials and methods

The ceramic fragments retrieved belong to a ball head that fractured *in vivo* 36 months after surgery. The clinical case was already described elsewhere [21]. Revision surgery was performed two months after the fracture, felt by the patients as a sudden and loud noise in the operated hip. Two months later, due to pain and ROM limitations, he underwent an RX control, that put in evidence the situation shown in Fig. 1.

TABLE III Properties of Zirconia ceramics for biomedical applications

Characteristic	Unit	ISO 13356	SGCA Desmarquest (Ref. [38])	Metoxit (Ref. [4])	Kyocera (Ref. [40])
Density	g/cm^3	≥6	>6.08	6.08	6.08
Ave. Grain size	μm	≤0.6	<0.5	0.4	0.2
Young Modulus	GPa	n.s.	n.s.	210	210
Bending strength	MPa	>800	>1500	1200	1200
Fracture toughness	Mpa $m^{-1/2}$	n.s.	8–10	8	5
Hardness	GPa	n.s.	n.s.	12	13

(n.s.: not specified)

During surgery the fragments of the ceramic head were collected. Some of the fragments went lost. The fragments were submitted to visual inspection by optical microscopy to analyze the fracture pattern, then selected samples were analysed by FEG-SEM (LEO 1530, Oberkochen, Germany) equipped with backscattered CENTAURUS® detector. Sections were cut by a diamond saw in oil in order to avoid Subcritical Crack Growth during cutting. After embedding in epoxy resin cured at 80 °C, samples were ground by diamond disks (20 μm, then 6 μm), polished by diamond paste on nylon cloth (6 μm, then 3 μm), then underwent final polishing by 1 μm diamond paste on silk cloth.

Specimen were analysed without any coating. To measure grain size specimen were thermally etched at 1200 °C × 1 h (heating rate 600 °C/h). Grain size were measured in conformity to standard EN 623-1 [22] and by SEM-coupled computerized image analysis. Phase composition was investigated by XRD (D8Advance, Bucker AXS, Madison, WI, USA, coupled to software DIFFRAC®).

Density was determined by the Archimedes' method.

Results

Visual inspection

The ceramic fragments retrieved are shown in Fig. 2. It is not possible to detect marks allowing to identify the ball head manufacturer, as during gait for two months secondary fragmentation and abrasion is likely to have occurred. The reconstruction of the ball head evidence that many fragments are missing (Fig. 3(a) and (b)).

Density

The density of the ceramic was measured on several parts. The value measured (6,089 g/cm^3) complies with the specifications of the ISO standard 13356 [6] on Y-TZP for surgical implants.

Analysis of the fracture pattern

The fracture pattern was analyzed by optical microscopy. Many information that would have been useful for failure analysis went lost, as the fragments have been rubbing against each other for two months before revision surgery, and it can be assumed that in this time further fragmentation and chipping may have occurred.

The overall fracture pattern may indicate that the first fracture must have started between fragment n.6 (Fig. 3(a) and (b)) and one of the adjacent fragments. On the other hand, the fracture surface of fragment n.1 shows a fracture surface almost plane which extends parallel to the ball head axis (Fig. 4). This feature is the characteristics of the surface of a primary ball head fracture as it is known from laboratory experiments [23].

Only one of the primary fracture surfaces is available for investigation (fragment n.1), as the counterpart was lost. On this fragment the edge of the fracture surface adjacent to the conical bore got lost by a large chip and the surface structures remaining are worn to a large extent. As a consequence, it is not possible to exactly determine the origin of the fracture nor to make an estimate on the fracture stress by applying the fracture mirror calculation, but the existing indications show that the crack propagated from the conical bore in outward direction.

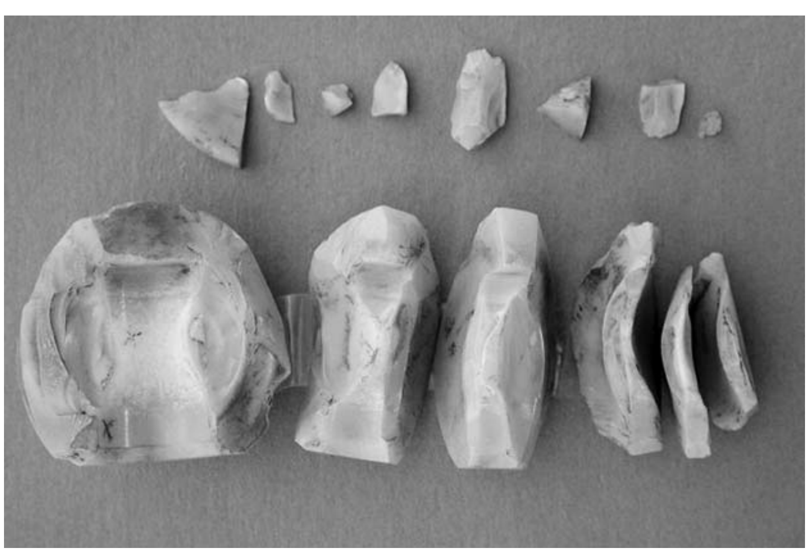
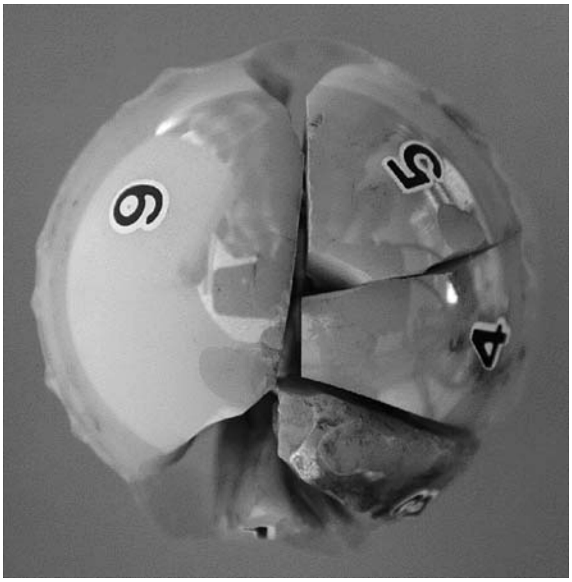
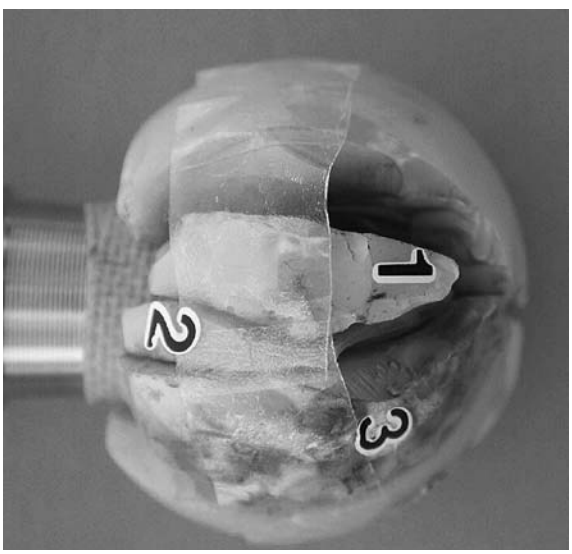


Figure 2 Ceramic fragments collected during revision surgery.



(a)



(b)

Figure 3 Reconstitution of the fractured ball head. Note the many parts that are missing. (a) top view, (b) lateral view.

On most fragments the surface of the conical bore was damaged as observed in fragment n.1. Also on the largest fragment the conical bore surface is completely destroyed by severe wear indicating the degradation of material properties in the central zone of the ball head.

The other fragments have warped fracture surfaces which are not parallel to the ball head axis. In addition, two fragments have fracture surface structures consisting in part of "fracture lances", a feature characteristic of a fracture which does not extend by tensile stresses alone but also by superimposed shear stresses. This superposition condition is not given at the moment of the primary fracture, that under regular conditions is initiated by the hoop stress arising for the press fit connection between stem and ball head.

Most of the metal transfer layers are found on the spherical surface of the ball head and on fracture surfaces. These metal transfer layers obviously were generated after the primary fracture and consequently do not provide information on the cause of the fracture.

TABLE IV Summary of the results of XRD analysis

Ball head region	vol% M-phase
Polished surface	4
Fractured surface	21
White region in the taper	36
Grey region near the cone taper bottom	61

XRD analysis

The monoclinic phase composition of the material was measured in different locations on the surface of the ball head fragments. The results show that maximum of about 60% monoclinic phase is present in the inner cone near the chamfer, while in the outer polished surface only 3% monoclinic phase is present. The results obtained are summarised in Table IV. Additional measurements performed on the polished surface of a section transversal to the ball head axis near the median plane of fragment n.5, show that the interior of the component completely consists of tetragonal grains (Fig. 5).

SEM examinations

SEM put in evidence that the retrieved specimens are characterised by two different microstructures. The zone near to the surface of the taper, in the core of the ball head, is constituted by a inhomogeneous structure formed by dense agglomerates of Y-TZP grains, about 10 μm in diameter, within a matrix of lower density, appearing dark in the SEM images due to organics used in the preparation (Fig. 6(a) and (b)). The preparation effect becomes evident in thermally etched sections (Fig. 7). Agglomerates in size as above and cracks were identified also in the surface of the fragment corresponding to the inner part of the taper (Fig. 8). The cracks in the inner surface are infiltrated by residuals of organic liquids (Fig. 9) indicating that environment-enhanced Subcritical Crack Growth took place.

A crack network originates from the above mentioned inhomogeneous zone, and extends through the outer part of the sample which consists of well densified material (Fig. 10). The grain size of ceramic in the agglomerates dispersed in the low density inner part (0.301 $\pm$ 0.007 S.D μm) is the same as that of the fully dense

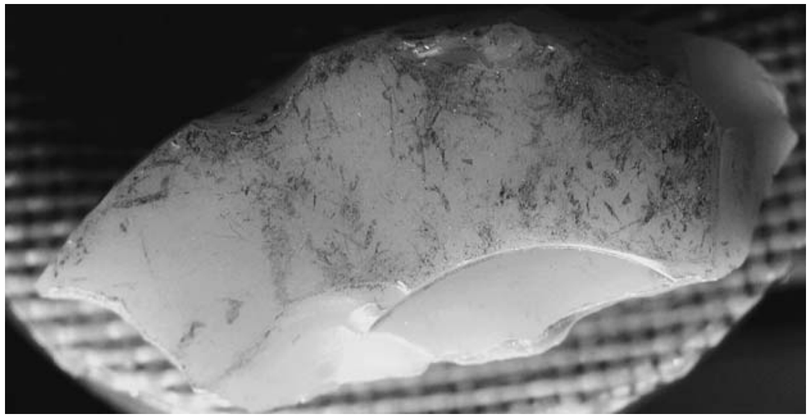


Figure 4 Primary fracture surface in fragment n.1.

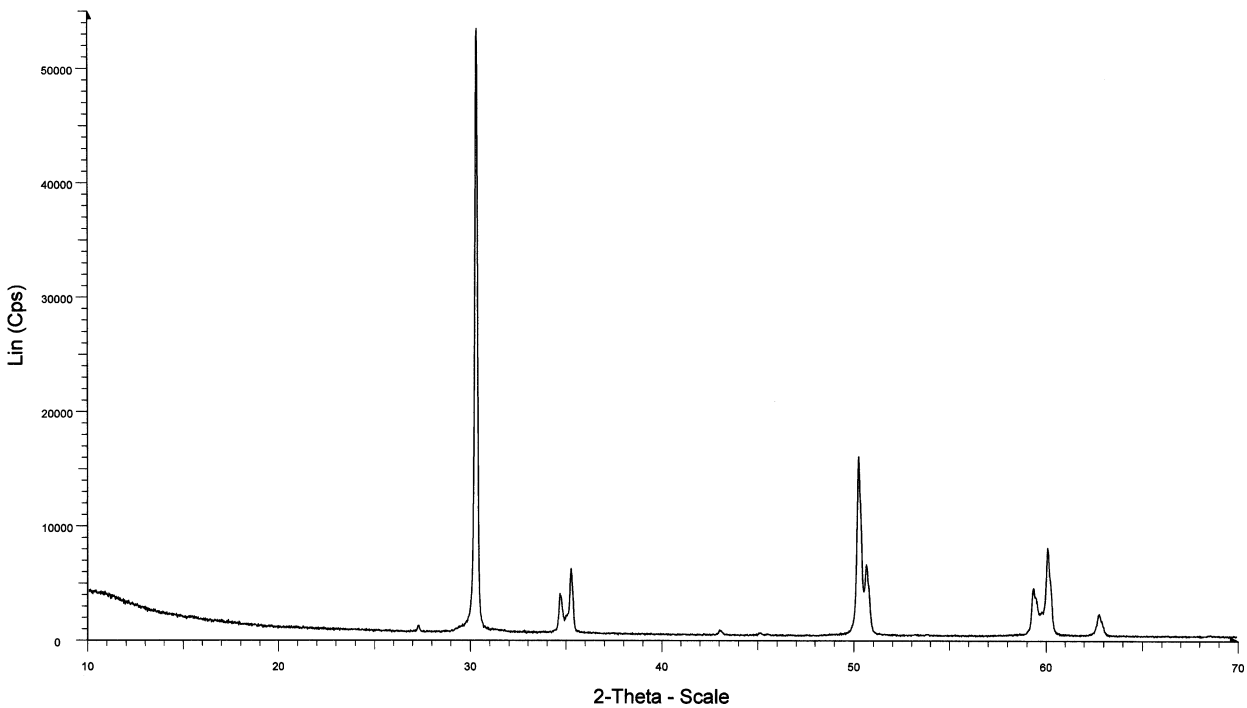


Figure 5 XRD spectrum measured in the transverse section of Fragment 5, after polishing.

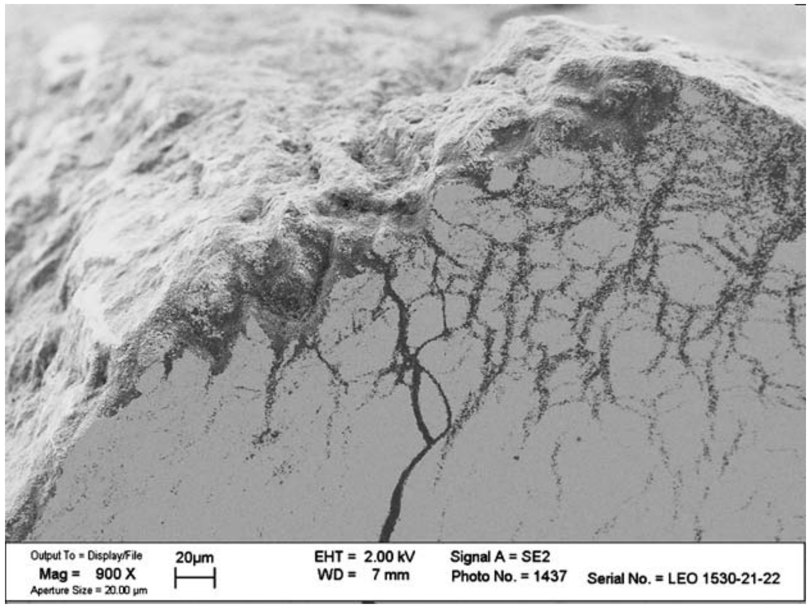
material of the outer part (0.292 ± 0.013 S.D. μm). The microstructure of both zones are reported in Fig. 11(a) and (b) respectively.

Discussion

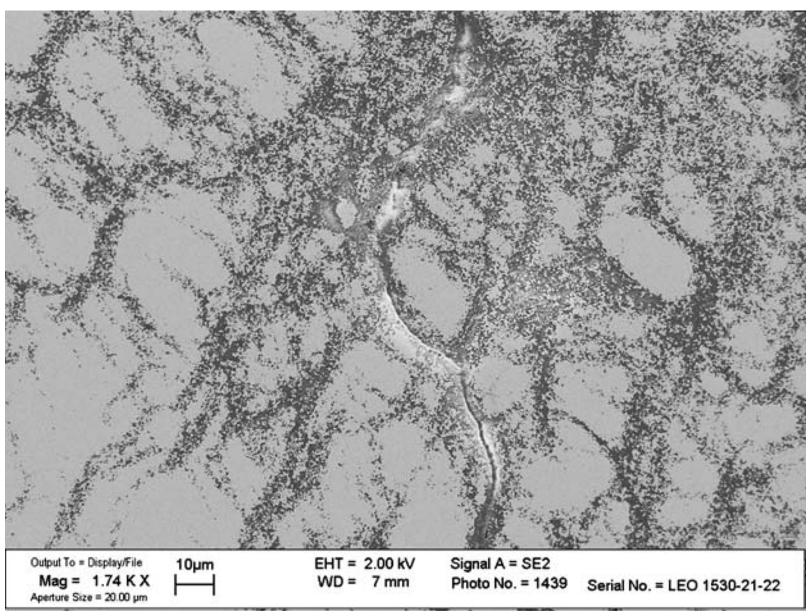
The reported failures of THR with zirconia femural heads are related to UHMWPE wear, surface degradation that in some reports was associated to the degradation of the surface of the ceramic, either to head fractures that took place rarely up to 2001.

Zirconia surface degradation

Most of the reports concerning high wear of UHMWPE cups coupled to zirconia ball heads, sometimes associated with the evidence of surface degradation of the ceramic, are dealing with materials manufactured before 1995. This feature was reported for the fist time by Haragouchi *et al.* [24] that observed the increase in roughness of the bearing surface of zirconia heads in correspondence with the increase in monoclinic content from 1% to mean 30% (min 23,2%, max 36,6%). There is a remarkable correspondence between these findings and the ones reported by Hernigou and Bahrami [25] that measured concentration up to 30% on the surface of retrieved zirconia heads. Santos *et al.* [26] measured the monoclinic content in the bearing surface of zirconia heads made by three different manufacturers, and found a concentration depending on the implantation time. Although the mean value (21,5%) remains in



(a)



(b)

Figure 6 Low magnification SEM images (a, b) of the zone of fragment 5 near the taper surface.

the range of concentration already reported, they measured concentration up to 70% in some samples. The tetragonal-to monoclinic phase transformation on the surface of retrieved zirconia heads was reported also in the exhaustive paper by Clarke *et al*. [27]. The decrease in surface nanohardness related to tetragonal to monoclinic phase transition in retrieved zirconia heads was reported by Catledge *et al*. [28] who observed that the extent of transformation was higher in heads that had longer clinical use.

High clinical wear of zirconia-polyethylene bearings was reported by Allain *et al*. [29] who made the comparison in survival rate at ten years of two series of THA performed from 1988 to 1991 using the same implant but ceramic heads in alumina or zirconia. The survival rate of implants with alumina head was 96,1%, while it was only 63% in implants with zirconia head. The increase of clinical wear of UHMWPE coupled with zirconia heads was reported also by Langlais *et al*. [30] and by Hammadouche *et al*. [31] who observed moderate osteolysis 2–4 years after surgery in about 35% of the implants with zirconia heads in a series implanted from 1997 to 1999. Jenny *et al*. [32] in the survival analysis of a series of 1200 THR with different type

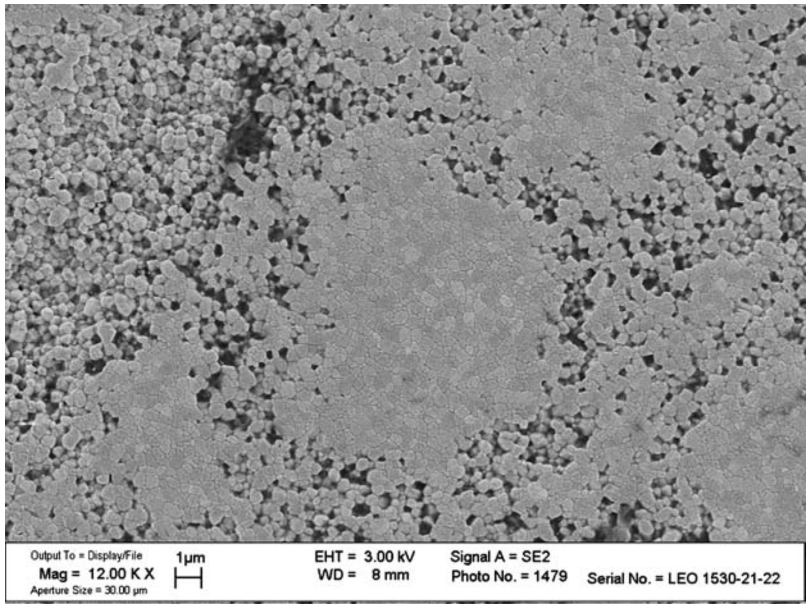


Figure 7 Detail of the same zone shown in Fig. 6, after thermal etching at 1200 °C X 1 h, showing agglomerates within the low density matrix.

of bearings reported the worse survival at seven years for the zirconia-UHMWPE bearing. Opposite results were obtained by Wroblewski *et al*. [33] in the 4,3 year (mean) follow-up of 373 THA with 22,22 mm zirconia heads. The characterisation of the bearing surface of some of these implants show the absence of significant increase in roughness or in monoclinic content [34].

On these basis one can conclude that it is confirmed that phase transition leading to surface degradation and polyethylene wear is a behaviour that is not shown by all the zirconia ceramics [8–11], and that can be controlled by improvements in the manufacturing process, as reported e.g. by Nakamura *et al*. [35].

Head fractures

Up to the year 2001 when the sudden and unexpected high number of failures caused the worldwide product recall of several batches of zirconia ball heads [36], the zirconia fractures reported (see Table V) were very little in number. Two cases of fractures were reported by Hummer *et al*. [37], one of them related to a traumatic accident. The failure of ten ∅ 22.22 mm ball heads was reported by Arnaud [38] in the retrospective analysis of a series of more than 3000 implants. Calés [39] reported 28 failures, observed between 1987 and 1993, ten of them taking place on ball heads implanted in revision surgeries on presumably damaged tapers and five fractured in traumatic conditions. Oonishi et al, [40] did not observe fractures in the follow up of 1484

TABLE V Summary of follow-ups of Zirconia ball head

Ref.	Author (s)	n. of cases	n. of Fractures	head ∅ (mm)	Follow-up period
33	Wroblewski et al	373	0	22,225	Mean 52 months. (min 0, max 96)
37	Hummer *et al*.	189	2	28	
38	Arnaud *et al*.	3233	10	22,22	Mean 40 months. (min 12, max 84)
39	Càles	280.000	1	32	1985–1996
			25	28	
			2	26	
40	Oonishi *et al*.	1484	0	22,22	1989–1997
		149	0	26	1996–1997
41	Ueno *et al*.	73	0	22	1989–1993
		6855	0	22	1995–1999
		1854	0	26	1996–1999
42	Caton and Bouraly	600	0	22,2	1996–2000

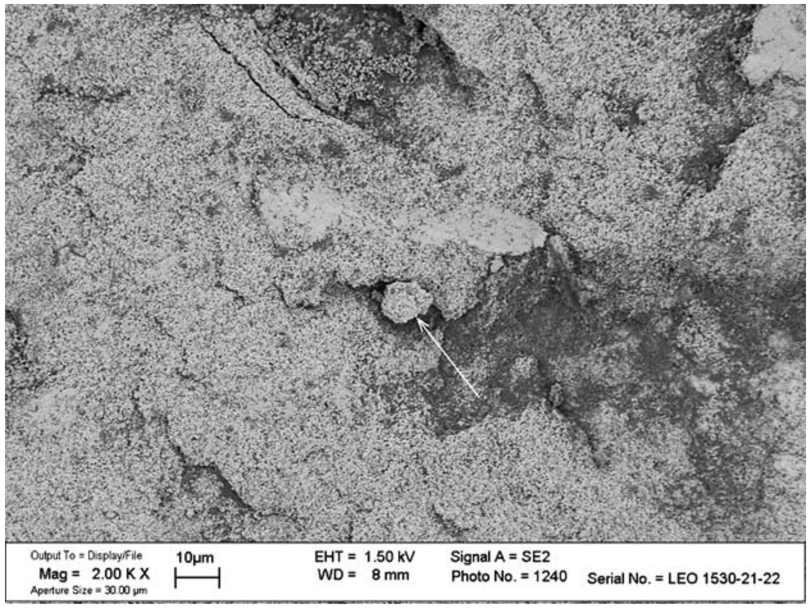


Figure 8 Low magnification SEM image of the inner surface of the taper, showing agglomerates and cracks.

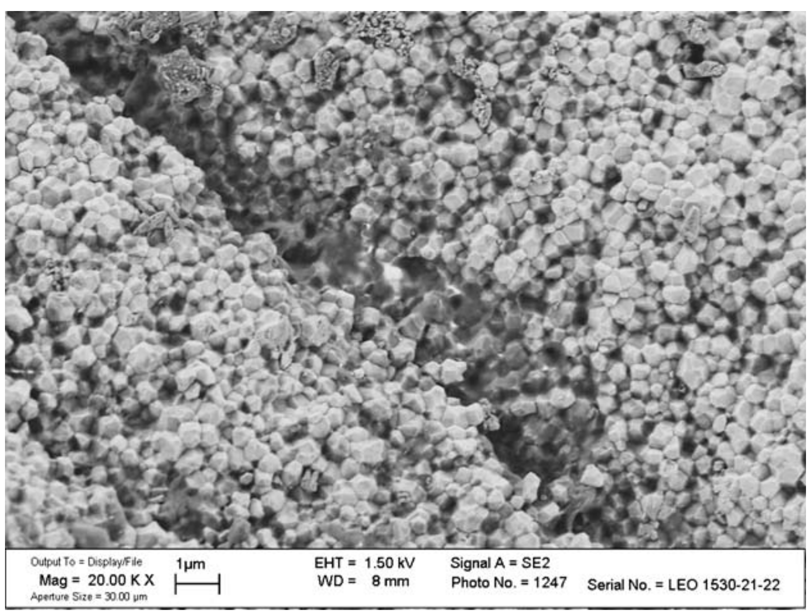


Figure 9 Cracks in the transversal section showing residuals of organic liquids within the crack.

Y-TZP ∅22 mm zirconia ball heads from 1989 to 1997, nor in 149 Y-TZP ∅ 26 mm ball heads implanted from 1996 to 1997. Also Ueno et al. [41] reported no fractures in 8782 ball heads implanted from 1989 to 1999. Similar results were reported by Caton and Bouraly [42] in a series of more than 600 ACORA THR with ∅22,22 mm ball heads as well as by Wroblewski *et al.* [33].

High frequencies of zirconia heads fractures were reported first by Calés [43], The highest frequencies of fractures were observed in two batches processed by a tunnel furnace, while the batches processed by batch kilns remained unaffected. The Author puts in correspondence the failures with the low density achieved after pre-sintering. Masonis *et al.* [44] analysed five heads fractured 12 to 32 months after surgery. The content of monoclinic phase in the bearing surface of these implants was in the range 2,8% to 5,7%, while the monoclinic concentration in the bore surface was 68%. Tong *et al.* [45] investigated the monoclinic content of retrieved fractured zirconia heads and of uniplanted heads aged in-vitro. In the retrieved heads they found that the concentration of monoclinic phase in the bearing surface was in the range 2–6%, in agreement with the previously cited Authors [44] and with our findings, while it was in the range 17–30% in the fractured surfaces. In

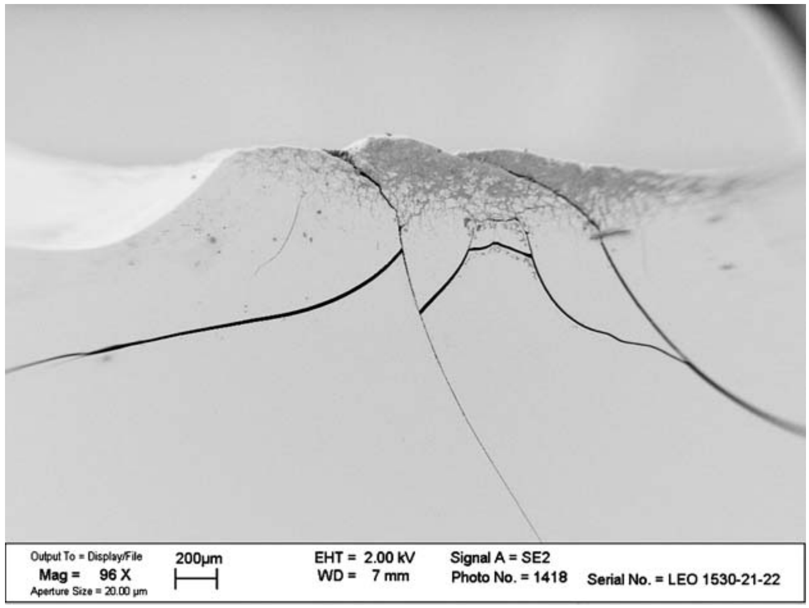


Figure 10 SEM image of the transversal section of fragment 4, showing the crack network starting from the inner inhomogeneous zone.

heads aged *in vitro* they identified a zone rich in monoclinic phase and prone to microcracking in proximity of the taper bore, a feature that we too observed in our specimens.

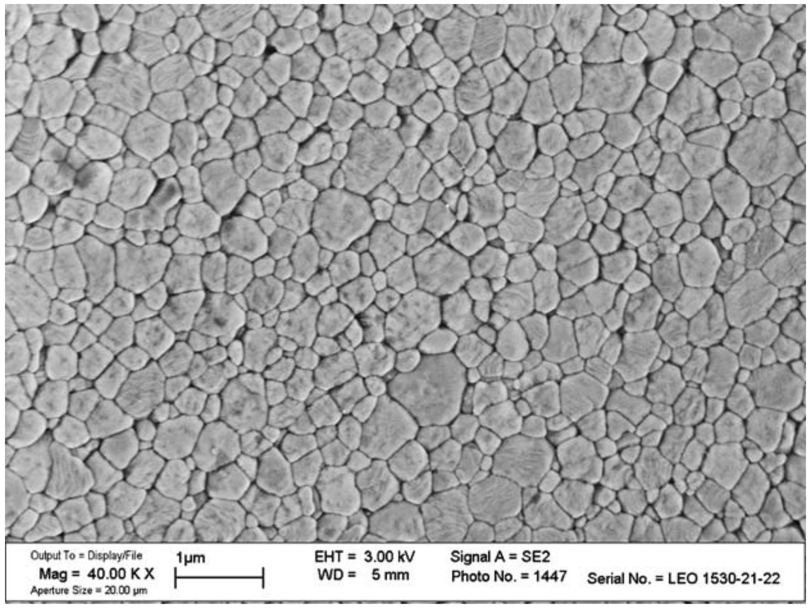
In the case discussed in this paper only little monoclinic phase was measured in the bearing surface, while tetragonal phase only was found in the bulk of the ball head. High contents of monoclinic phase were detected on the surface that were subject to rubbing after the fracture. If the nucleation of the monoclinic phase have been initiated by spontaneous hydrothermal tetragonal-monoclinic phase transformation, an higher monoclinic concentration could be expected on the bearing surface, as previously reported [24–27].

In the bulk of the retrieved samples, no monoclinic phase was detectable. The high amount of monoclinic phase on the inner surface of the conical bore may be ascribed to the rubbing of fragments in wet environment during the two months period between the fracture and the revision surgery.

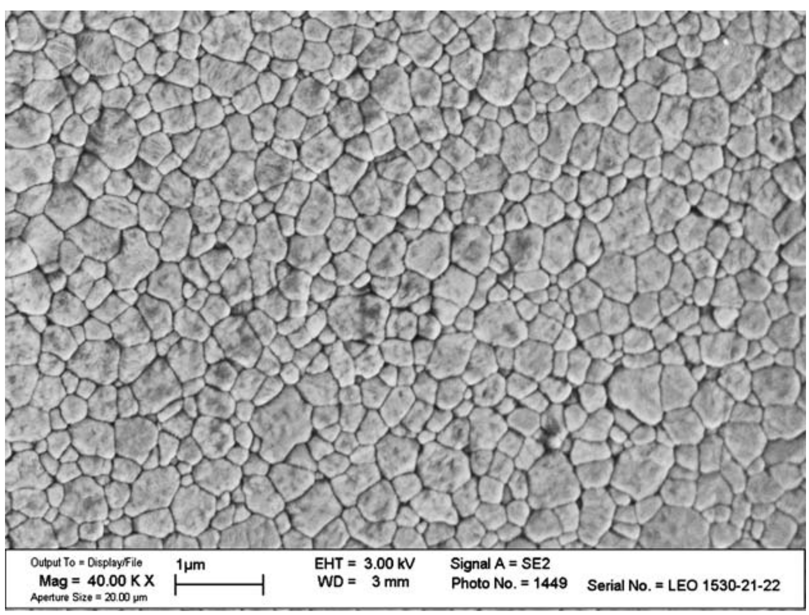
In analysing our case we would like to focus our attention on the crack network observed in the inner part of the ball head, and on the uneven distribution of density in the ball head zone close to the taper surface evidenced by SEM and already observed by other Authors [44, 45] in retrieved zirconia heads. To explain the presence of the above features, it will be worthwhile to analyse a typical flow sheet used in the production of YTZP heads (Fig. 12) as described elsewhere [3, 4, 43]. The process starts by blending additives (binders, lubricants, sintering aids, etc.) to ceramic powders. This is usually made by mixing the different components in a slurry, which is then transformed by spray-drying into a granulate of homogenous composition and size, thus increasing also the flowability of submicron-size powders in feeding the pressing dyes where the granulate is compacted in the shape of a ball. The balls then undergo a first thermal treatment (pre-sintering) that may take place or in a batch furnace (a kiln), or in a continuous (tunnel) furnace. The full density is achieved by a further treatment by hot isostatic pressing (HIP) in gas under high pressure. Then the fully densified ceramic balls are polished and finally the conical bore is hard machined within the ball, e.g. by ultrasonic drilling.

Due to the size of the agglomerates detected by the SEM (Fig. 7), it may be concluded that they are residual traces of spray drying. These are either extremely fine secondary grains coming from the spray-drying process itself or particles that have been difficult to be de-formed during pressing. Taking into account the operation of pressing a ball, probably there was a density gradient from the surface to the centre of the pressed part. If pressing these secondary grains caused problems, it may be assumed that a similar event took place also in the outer part of the sample, thus causing gaps within the green body.

It sounds then suitable that in the pre-sintering step the overall bulk density required has been achieved [43], whereas some open channels remained due to the gaps. Pre-sintering is combined with the shrinkage of the green body. However, a gap in the body will develop further during pre-sintering allowing the gas to enter during the hot isostatic treatment at elevated temperatures (HIPing). As a consequence, one would obtain the identical microstructure in the different “dense microparts”, as we observed by SEM in our samples, but the gaps will remain.



(a)



(b)

Figure 11 Ceramography of inner (a) and outer (b) high density sections of fragment 5, after thermal etching. No significant difference in grain size is detectable.

It has to be stated that, depending on the size of the gaps, there may be an healing effect if sintering is performed under controlled conditions in a long term sintering cycle, e.g. as usually made in batch furnaces. Tunnel- and roller kilns, which are designed for fast sintering regimes, may not show this healing effect due to the short sintering time [44], finally resulting in leaving "open channels" after pre-sintering.

In order to densify these kind of "open channels" a glassy coating would be necessary before HIPing. However under economic aspects it is more effective to reach a real closed porosity during pre-sintering before the HIPing cycle takes place.

From above explanations it becomes evident why the microstructure in the bulk material and in the inner agglomerates do not show any difference. If there are any cracks caused by pressing or pre-sintering defects, such kind of defects do not influence the remaining overall bulk density and it may be expected that even short term burst strength properties may not directly be influenced. This is in agreement with previously quoted Authors [43] that reported high fracture rates

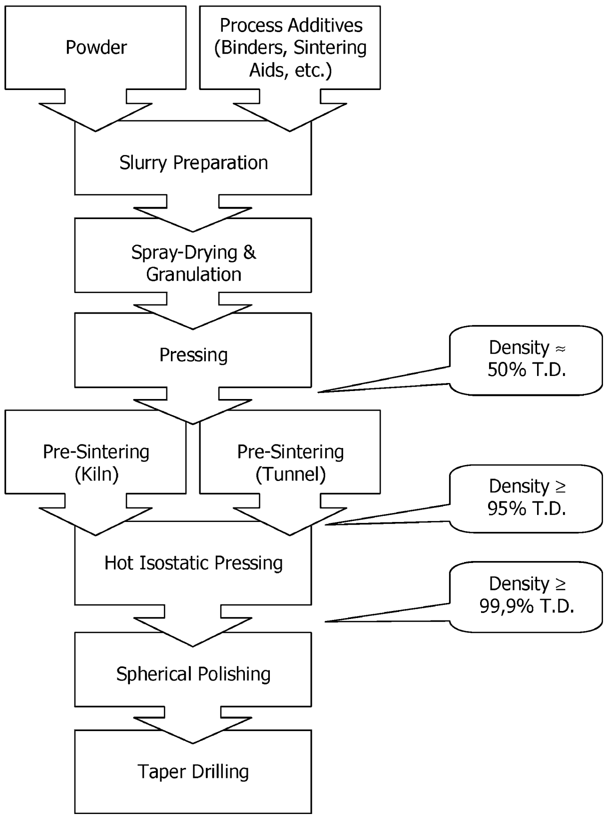


Figure 12 Typical flow sheet used in production of Y-TZP ball heads. Based on data from Refs. [3, 4, 43].

in batches of zirconia heads showing low density after pre-sintering.

Another aspect, which has to be taken into account is the drilling of the conical bore into the ball head. The drilling of the conical bore in presence of sintering defects produced by the processing procedures described above may develop subcritical microcracks, which however may not affect the short term mechanical properties. Since the bore surface is under tensile stress once the ball head is fixed onto the stem, and in presence of the wet environment due to body fluid, subcritical crack growth (SCG) can start and spontaneous transformation of unconstrained Y-TZP grains may take place leading eventually to fracture.

Such a mechanism explains the time elapsed between the surgery and the fracture in the case that we reported, as well as in the cases reported by other Authors [43–45].

Conclusions

The conclusion concerning the analysis of the retrieved fragments of the ball head, described in the present paper, may be summarised as follows:

– The crack that lead to the fracture started from the inner part of the ball head, e.g. from the inhomogeneous zone at the metal-ceramic interface.

– The initiator of fracture is the presence of a low density zone containing dispersed high density agglomerates in the inner part of the ball head.

– The presence of low density material in the innermost part of the ball head is likely due to process control.

– Due to the lack of matrix constraint, and due to the lack of continuity between agglomerates, slow crack nucleation and growth took place in the low density material, enhanced by the exposition to the physiological wet environment under cyclic loading.

– Tetragonal-to-monoclinic transition detected on the surfaces corresponding to the inner part of the ball head had a secondary role on the fracture of the component.

– Overall results of the examination of the retrieved fragments show the relevance of accuracy in process control and validation for the production of high-tech ceramic materials.

– It can be expected that the behaviour of components based on zirconia ceramics designed, processed and installed correctly remain unaffected by in-service fracture phenomena due to SCG.

References

1. P. CHRISTEL, A. MEUNIER, J. M. DORLOT, J. M. CROLET, J. WITVOET, L. SEDEL and L. P. BOUTIN, *Annals of N.Y. Academy of Science* **523** (1988) 234.
2. C. PICONI and G. MACCAURO, *Biomater.* **20** (1999) 1.
3. A. DAMBREVILLE, M. PHILIPPE and A. RAY, *Mâitrise Orthop.* **78** (1999) 1.
4. W. RIEGER, in "World Tribology Forum in Arthroplasty", (Hans Huber, Bern, 2001) p. 283.
5. B. CALÉS, *Clin. Orthop. Rel. Res.* **379** (2000) 94.
6. ISO TC 150/SC 1, Implants for Surgery - Ceramic materials based on yttria-stabilized tetragonal zirconia (Y-TZP), ISO 13356, 1997.
7. F. F. LANGE, *J. Mater. Sci.* **17** (1982) 225.
8. T. T. LEPISTÖ and T. A. MÄNTYLA, in "Corrosion of glass, ceramics and ceramics superconductors" (Noyes, Park Ridge, NY, 1992) p. 492.
9. W. BURGER, H. G. RICHTER, C. PICONI, R. VATTERONI, A. CITTADINI and M. BOCCALARI, *J. Mater. Science: Mater. Med.* **8** (1997) 113.
10. L. BLAISE, F. VILLERMAUX and B. CALÈS, *Key Eng. Mater.* **192–195** (2001) 553.
11. H. TSUBAKINO, R. NOZATO and M. HAMAMOTO, *J. Am. Ceram. Soc.* **74** (1991) 440.
12. R. P. PITTO, in Proceedings of the 6th World Biomaterials Congress, Workshop 7, Kamuela, May 2000, the Society for Biomaterials, paper n.11.
13. L. BLAISE, J. D. WEBB, J. M. DROUIN and B. CALÉS, in Proceedings of the 15th ESB Conference, Arcachon, Poster session 3, France, September 1999.
14. J. H. CALANDRUCCIO and M. T. JOBE, *Seminars in Arthop.* **82** (1997) 94.
15. R. J. KOHAL, G. PAPAVASILIOU, P. KAMPOSIORA, A. TRIPODAKIS and J. R. STRUB, *Int. J. Prostodont.* **15** (2002) 189.
16. Y. KAKEHASHI, H. LÜTHY, R. NAEF, A. WOHLWEND and A. SCHÄRER, *Int. J. Periodont. Rest. Dent.* **18** (1998) 587.

17. W. WEBER and W. RIEGER, *Key Eng. Mater.* **192–195** (2000) 841.
18. R. G. LUTHARD, O. SANDKUL and B. REITZ, *Eur. J. Prosthodont. Restor. Dent.* **7** (1999) 113.
19. D. SUTTOR, K. BUNKE, S. HOESCHLER, H. HAUPTMANN and G. HERTLEIN, *Int. J. Comput. Dent.* **4** (2001) 195.
20. A. E. BIANCHI, M. BOSETTI, G. DOLCI JR, M. T. SBERNA, F. SANFILIPPO and M. CANNAS, *J. Appl. Biomat. Biomech.* **2** (2004) 143.
21. G. MACCAURO, C. PICONI, W. BURGER, *et al.*, *J. Bone Joint Surg.* **86-B** (2004) 1192.
22. CEN TC 184 Advanced Technical Ceramics—EN 623 part 1: Grain size measurement
23. H. G. RICHTER, *Key Eng. Mater.* **223** (2002) 157.
24. K. HARAGUCHI, N. SUGANO, T. NISHII, H. MIKI, K. OKA and H. YOSHIKAWA, *J. Bone Joint Surg.* **83-B** (2001) 996.
25. P. HERNIGOU and T. BAHRAMI, *J. Bone Joint Surg.* **85-B** (2003) 504.
26. E. M. SANTOS, S. VOHRA, S. A. CATLEDGE, M. D. MCDENNY, J. LEMONS and K. D. MOORE, *J. Arthroplasty* **19** (2004) 30S2.
27. I. C. CLARKE, M. MANAKA, D. GREEN, *et al.*, *J. Bone Joint Surg.* **85AS4** (2003) 73.
28. S. A. CATLEDGE, M. COOK, Y. K. VOHRA, E. M. SANTOS, M. MCCLENNY and K. D. MOORE, *J. Mater. Sci. Mater. Med.* **14** (2003) 863.
29. J. ALLAIN, S. LE MOUEL, D. GOUTAILLIER and M. C.VOISIN, *J. Bone Joint Surg.* **81-B** (1999) 835.
30. F. LANGLAIS, N. PASSUTTI and P. HERNIGOU, *Ann. Orthop. Ouest* **32** (2000) 305.
31. M. HAMMADOUCHE, F. MADI, L. KERNBOULL, J. P. COURPIED and M. KERNBOULL, in "Bioceramics in Joint Arthroplasty" (Thieme, Stuttgart, 1999) p. 96.
32. J. Y. JENNY, C. BOERI, A. TAVAN and B. SCHLEMMER, *Rev. Chir. Orthop.* **84S1** (1998) 111.
33. B. M. WROBLEWSKI, P. D. SINEY, H. NAGAI and P. A. FLEMING, *J. Orthop. Science* **9** (2004) 253.
34. T. STEWART, N. FLEMMING, P. D. SINEY, B. M. WROBLEWSKI and J. FISHER, 17th Annual Symp. of the International Soc. For Technology in Arthroplasty, Rome, Italy, 21–25 Sept 2004. poster 31.
35. T. NAKAMURA, K. TANAKA, J. TAMURA, *et al.*, *Key Eng. Mater.* **240–242** (2003) 823.
36. Agence Francaise de Securité des Produits de Santé (AFSSAPS). Mise au point sur les ruptures de têtes de prothèses de hanche en céramique de zircone lots TH. http://agmed.sante.gouv.fr/htm/10/zircone/sommaire/htm, 15 Nov 2002.
37. C. D. HUMMER, R. H. ROTHMAN and W. J. HOZACK, *J. Arthoplasty* **10** (1995) 848.
38. J. M. ARNAUD, J. L. CHARISSOUX, D. SETTON, C. PECOUT, J. F. MECHIN and Y. DUNOYER, 30é Meeting de la Societé Othopédique de l'Ouest, Pont l'Aubée (France, June 1997).
39. B. CALES, *Mâitrise Orthop*. **96** (2000) 26.
40. H. OONISHI, H. AMINO, M. UENO and H. YUNOKI, in "Reliability and long-term results of ceramics in orthopaedics", (Thieme, Stuttgart, 1999) p. 7.
41. M. UENO, H. AMINO, M. NISHIDA, S. MASUDA and T. SHIMITOSO, in Proceedings of the 6th World Biomaterials Congress, Workshop 7, Kamuela, May 2000 the Society for Biomaterials, paper n.5.
42. J. CATON and J. P. BOURALY, in Proceedings of the 6th World Biomaterials Congress, Workshop 7, Kamuela, May 2000 the Society for Biomaterials, paper n.9.
43. B. CALES, 4é Jounées d'Orthopedie P Teinturier, Clermont-Ferrand, France, 11–12 Oct. 2002.
44. J. L. MASONIS, R. B. BOURNE, M. D. RIES, R. J. MCCALDEN, A. SALEHI and D. C. KELMAN, *J. Arthroplasty* **19** (2004) 898.
45. W. TONG, D. MCNULTY, T. SMITH and P. LI, *Key Eng. Mater.* **284–286** (2005) 999.

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