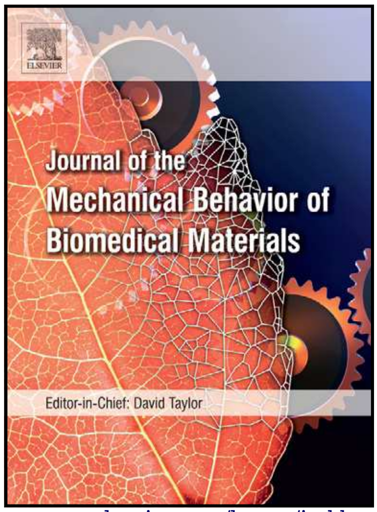
Article:

Nogiwa-Valdez, AA, Rainforth, WM and Stewart, TD (2014) Wear and degradation on retrieved zirconia femoral heads. Journal of the Mechanical Behavior of Biomedical Materials, 31. 145 - 151. ISSN 1751-6161

https://doi.org/10.1016/j.jmbbm.2013.09.019



www.elsevier.com/locate/jmbbm

Wear and degradation on retrieved zirconia femoral heads

A.A. Nogiwa-Valdez, W.M. Rainforth, T.D. Stewart

PII: S1751-6161(13)00320-2
DOI: http://dx.doi.org/10.1016/j.jmbbm.2013.09.019
Reference: JMBBM977

To appear in: *Journal of the Mechanical Behavior of Biomedical Materials*

Received date: 26 March 2012
Revised date: 24 April 2013
Accepted date: 11 September 2013

Cite this article as: A.A. Nogiwa-Valdez, W.M. Rainforth, T.D. Stewart, Wear and degradation on retrieved zirconia femoral heads, *Journal of the Mechanical Behavior of Biomedical Materials,* http://dx.doi.org/10.1016/j.jmbbm.2013.09.019

Wear and degradation on retrieved zirconia femoral heads

A. A. Nogiwa-Valdez[a], W. M. Rainforth[a], T. D. Stewart[b]
[a]Department of Materials Science and Engineering, University of Sheffield, UK
[b]Institute of Medical and Biological Engineering, University of Leeds, UK

Corresponding Author

A. A. Nogiwa-Valdez

University of Sheffield, Department of Materials Science and Engineering, Sir Robert Hadfield Building, Mappin Street, S1 3JD, Sheffield, UK, Tel. +44 (0) 114-222-5934, Fax: +44 (0) 114-222-5943, e-mail: a.nogiwa@sheffield.ac.uk

Abstract

Zirconia femoral heads retrieved from patients after different implantation periods (up to 13 years) were analysed using vertical scanning interferometry, atomic force microscopy and Raman microspectroscopy. A range of topographical and compositional changes on the surface of the retrievals are reported in this work. The study revealed that changes in roughness are the result of a combination of factors, i.e. scratching, surface upheaval due to transformation to the monoclinic phase and grain pull-out. Clusters of transformed monoclinic grains were observed on heads implanted for more than 3 years. The phase composition of these clusters was confirmed by Raman microspectroscopy. Increased abrasive wear and a higher monoclinic phase content concentrated on the pole of the femoral heads, confirming that the tetragonal to monoclinic phase transformation was not only induced by the tetragonal phase metastability and environmental conditions but mechanical and tribological factors, also affected the transformation kinetics. Additionally, the head implanted for 13 years showed evidence of a self-polishing mechanism leading to a considerable smoothening of the surface. These observations provide an insight into the interrelated mechanisms underlying the wear and transformation process on zirconia ceramics during implantation.

1. Introduction

The interest in zirconia for load bearing applications can be traced back to 1975 when Garvie et al. (1975) described it as “ceramic steel” due to the transformation toughening mechanism that conferred the material outstanding fracture toughness amongst ceramics. In the mid-eighties, zirconia ceramics were introduced to the orthopaedic prostheses market as a promising alternative to the well established alumina femoral heads for total hip replacement (Christel et al., 1988). It was expected that zirconia, with two to three times higher flexural strength than alumina, would be an improvement on the higher fracture incidence of the alumina implants (Clarke et al., 2003; Piconi et al., 2003). However, even though some reports indicated that zirconia exhibited an exceptionally low fracture incidence of 0.002% (*i.e.* 1:46,000), other zirconia heads produced by the same manufacturer had a disastrous performance (Clarke et al., 2003). In 2001, more than 350 zirconia femoral heads from St. Gobain Desmarquest (France) were retrieved from patients due to an unexpectedly high fracture rate (Chevalier, 2006; Chevalier et al., 2007; FDA, 2001). The company named an external scientific advisory committee intended to understand the failure causes. They concluded that the combination of a new sintering process in a tunnel furnace and the subsequent machining operations yielded a more unstable surface prone to the accelerated transformation that caused the fractures (Clarke et al., 2003).

In order to address the complexity of the accelerated transformation, the crystallographic properties of zirconia must be considered. The manufacture of zirconia components requires high temperature treatments and, during cooling, the crystalline structure changes from cubic to tetragonal to monoclinic symmetry. The tetragonal to monoclinic phase transformation (at approximately 1170°C) is associated with a volume expansion (~4%) that produces extensive microcracking rendering the component useless for any load bearing application. Therefore, the tetragonal phase is stabilized to room temperature by the addition of dopant oxides, such as yttria, magnesia or ceria. However, this tetragonal phase is metastable. This means that under certain conditions it will tend to transform to the more stable monoclinic polymorph. Extensive research has been carried out to understand the mechanisms that control this transformation. It is known that the tetragonal to monoclinic phase transformation (hereafter t→m) is largely related to the presence of water, but also to elevated temperatures, residual stress, grain size, surface roughness, pressure, lubrication and mechanical trauma, amongst others (Brown et al. 2007; Chevalier, 2006; Chevalier et al., 2006; Fukatsu et al. 2009; Lawson, 1995; Masonis et al., 2004).

As highlighted by Clarke et al. (2003) and Chevalier (2006), the behaviour of zirconia ceramics is complicated to describe and thus commonly misunderstood due to the numerous variables that influence its performance. The purpose of the present study is to provide further insight into the interlinking effects of wear and transformation on the coupling surface of zirconia femoral heads by systematically characterizing retrieved implants using high resolution, fast and non-destructive techniques.

2. Materials and Methods

Seventeen retrieved and one unused 22-mm zirconia femoral heads manufactured by Norton Desmarquest (France) were used on this study. The heads were coupled with polyethylene acetabular cups. None of the implants belonged to the batches included in the product recall after the 2001 failure event. Tables 1 and 2 present a summary of the information available on the retrieval cases. Note that, when known, the reason for retrieval was not related to femoral head fracture.

Table 1. Information about patients with retrieved implants.

Age at primary	48±17
Implant time (year)	8.4±3.5
Weight (kg)	77.2±17
Sex	11 female: 6 male

Table 2. Primary surgery and revision reasons.

Primary surgery reason	Findings at revision
Osteoarthritis 8	Loose cup 9
Congenital dislocation of the hip 5	Loose stem and cup 4
Others 4	Other 4

The retrieved heads were analysed using a vertical scanning interferometer (VSI) through a 50x objective in Mirau assembly with white light illumination (Contour GT, Veeco Instruments Inc., USA). The spherical form was removed from images before statistical analysis using the software provided with the interferometer.

Additional high resolution imaging was carried out with atomic force microscopy (Nanoscope IIIA, Veeco Instruments Inc., USA) in contact mode with silicon nitride probes. Images were acquired at a scan rate of 0.5 Hz with a resolution of 512 samples per line and a scan area of 20x20 µm. Image analysis and manipulation were done with the software provided with the equipment (Nanoscope Analysis v1.2, Veeco Instruments Inc., USA).

The compositional analysis was undertaken using Raman microspectroscopy (LabRam HR, Joriba Jobin Yvon, France) with a 532 nm line of HeNe laser through a x50 objective. Spectra were recorded from 100 to 900 cm^{-1} at 1 accumulation of 5 s per point. Commercially available software (LabSpec, Japan) was used to quantify the integrated intensities (I) of the selected isolated bands characteristic of the tetragonal (142 and 256 cm^{-1}) and monoclinic (179 and 190 cm^{-1}) polymorphs. This information was used to calculate the monoclinic phase fraction (f_m) using the approach described by Clarke and Adar (1982):

$$f_m = \frac{I^m_{179} + I^m_{190}}{(I^m_{179} + I^m_{190}) + 0.97(I^t_{142} + I^t_{256})} \qquad \text{Equation 1}$$

3. Results

Figure 1 shows a selection of VSI images of the pole of the retrieved femoral heads after different implantation periods ranging from 0 to 13 years. The surface of the unused implant shows scratches, which most likely were introduced during the manufacturing process. The images suggest that during the first 5 years new deeper multidirectional scratches are formed leading to an increase in surface roughness. The higher concentration of scratches on the top of the head (Figure 2) indicates that the abrasion occurred during operation of the implant by comparison with the unused implant. Further validation would require the analysis of the wear counterpart, i.e. the acetabular cup, and information of the surface topography before implantation. The scratches on the heads implanted for 1 to 5 years are significantly deeper and wider than those observed on the other cases (Figure 3). At longer implantation periods the average size of the scratches is similar to that on the unused head except for the longest term implant (12 years 8 months) in which there is minimal scratching. This observation indicates that a self-polishing mechanism might have taken place.

The decrease in the extent of the scratching coincided with the first detection of the monoclinic phase formation by VSI. The brighter areas on the VSI images correspond to the surface upheaval resulting from the volume expansion associated with the t→m transformation. Initially the t→m transformation creates small isolated clusters of monoclinic grains that slightly protrude from the surface. The first monoclinic clusters were observed on the pole of the head, correlating with the higher concentration of scratches on earlier retrievals. As implantation time increased, the number and size of monoclinic clusters increased. The t→m transformation propagated autocatalytically enlarging the size of the existing monoclinic clusters while the formation of new monoclinic nuclei occurred on untransformed areas. Eventually, the whole surface was covered with monoclinic phase, as shown in Figure 1e. Figure 4 gives the monoclinic phase surface fraction, calculated from Raman microspectroscopy spectra, plotted against implantation period. Even though each retrieved head represents unique “experimental” conditions, it is possible to infer from the graph a sigmoidal trend characteristic of nucleation and growth mechanisms. The monoclinic phase is first detected by Raman microspectroscopy on heads implanted for 3 and 5 years, in line with the small amount of isolated monoclinic clusters observed by VSI. The intensity of the monoclinic phase Raman signal increases until reaching a maximum on the heads implanted for 12-13 years. At this stage, the monoclinic clusters have coalesced and covered the surface at the pole and equator and most of the lower hemisphere of the femoral head (Figure 2). Additionally, grain boundary microcracking and grain pull out is observed after the longer implantation periods.

The three kinds of surface features observed, i.e. scratches, upheaval due to monoclinic phase formation and grain pull-out, have an effect on the topographical measurements (Figure 2). Heads retrieved earlier than 5 years showed a continuous increase in roughness with implantation time associated with the formation of scratches. The increase in monoclinic clusters was associated with an initial decrease in roughness. However, the roughness increased again as more monoclinic clusters grew on the surface. Finally, a decrease in roughness was observed on heads implanted >12 years. For example, a roughness of 16-19 nm was measured on the surface of the heads implanted for 1, 8 and 12 years. From the VSI and AFM images it is evident that the same roughness value results from very different topological characteristics. Thus, it is important to utilize other statistical measurements, such as skewness and kurtosis, to fully describe the surface (Hall et al., 1996, Pezzotti et al. 2011). Skewness (Ssk) is a measure of the symmetry of the surface heights about the mean plane. Ssk>0 indicates a surface where peaks predominate over valleys. The opposite is true in a surface with Ssk<0. Kurtosis (Sku) is an indicator of the presence of inordinately high peaks or low valleys (Sku>3). If the surface heights follow a Gaussian distribution, then Ssk=0 and Sku=3. Figure 5 shows plots of surface roughness (Sa), skewness (Ssk) and kurtosis (Sku) against implanted period. In the present study, scratches and pores are described as valleys and monoclinic clusters as peaks. The unused head shows the lowest roughness Sa=12 nm, Ssk≈0 and Sku≈3. These values describe a relatively smooth surface where neither peaks nor valleys prevail. The heads retrieved between 0 and 5 years have increasingly rougher surfaces (from 12 nm to 42 nm). At the same time, the skewness value decreases indicating that valleys were the predominating feature on the surface. The high kurtosis also confirms that there is a large incidence of inordinately low valleys, in agreement with the observation of deep scratches on the surface. The nucleation of monoclinic phase and the associated volume expansion creates peaks on the surface (*i.e.* monoclinic clusters). Rather than roughen the surface, the initial formation of monoclinic clusters results in a roughness decrease. Low positive skewness and kurtosis just above 3 indicate that the surface is slightly dominated by monoclinic clusters but these peaks were not significantly higher than the mean surface. With the growth of more monoclinic clusters, lower skewness and kurtosis values were observed in association to increased roughness. Comparing the unused head and the 11 years retrieval, similar skewness and kurtosis values were observed as well as significant roughening. This is explained by the increasing height difference between the lowest and highest points on the surface, averaging out higher roughness values. The final topography change observed is a considerable surface smoothening and simultaneous grain pull-out as observed on the head retrieved after 12 years and 8 months. The smoothening reached such an extent that allowed resolving grain boundaries by AFM (Figure 3c). In this case, the skewness is negative meaning that valleys predominate over peaks, and the considerably large kurtosis indicates infrequent but extreme deviations from the mean. As observed in Figure 3c, these parameters describe an area with a few pores on an otherwise smooth surface.

4. Discussion

The overall *in vivo* wear and transformation process on the zirconia femoral heads studied can be described as three overlapping and interrelated stages: 1) surface scratching, 2) nucleation and growth of monoclinic phase, and 3) surface smoothening. It is assumed that the surface scratches were not present before implantation and were not introduced during handling and surgery. Thus, they were caused by hard particles entrapped in the interface between the head and the acetabular cup. Previously, the origin of such hard particles has been traced back to the polishing material used on the head manufacture (e.g. alumina)

(Bohler et al,. 2002; Reinisch et al., 2003) to ceramic debris produced by head wear (Hasegawa et al., 2011) and to PMMA cement (Hall et al. 1996; Howie et al., 2005). The particles either embed in the polyethylene cup or roll loose in the articular interface (Hasegawa et al., 2011; Wang and Essner, 2001). In this abrasive wear situation, removal of material can occur by ploughing and wedge formation (Bhushan, 1999; Lee et al., 2009). Figure 3b evidences the formation of a ridge along the groove (i.e. ploughing) and the accumulation of removed material as a wedge at the end of the scratch. These ridges and wedges flatten and eventually fracture with continued load and unload cycles (Bhushan, 1999). This is in agreement with the observation of shallower and ridge-less scratches on the late retrievals (Figures 1 and 3). A second source of debris is the grain pull-out produced by wear and intensified by the intergranular fracture resulting from the t→m phase transformation. If fine wear debris (<1 μm) circulates on the sliding interface, it can contribute to self-polishing of the surface (Denape and Lamon, 1990) as observed on the surface of the head retrieved after 12 years 8 months. *In vivo* self-polishing has been investigated for metals (Joyce et al., 2011) but there are only a few mentions of the phenomenon on ceramic prostheses (Cales, 2000; Shishido et al., 2006).

The behaviour of the t→m transformation followed by Raman microspectroscopy can be fitted by the Mehl-Avrami-Johnson laws of nucleation and growth mechanisms (Chevalier et al., 2007; Christian, 1975). This model denotes that the formation of monoclinic phase nuclei begins with an apparent incubation time followed by a period of growth driven transformation until saturation is reached. The incubation period might be an artefact of the limited sensitivity of the characterization technique being used. In the present study, the monoclinic phase doublet in the Raman spectra (179 and 190 cm^{-1}) can be resolved on the analysis of heads implanted for 3 and 5 years, but only few isolated monoclinic clusters were seen by VSI on the head implanted for 3 years. However, the sensitivity of these techniques is inadequate to detect the early stages of phase transformation, and therefore the apparent incubation time may just be that the extent of transformation was below the detection limit of Raman spectroscopy or VSI. The surface monoclinic fraction on the heads implanted for 12-13 years was approximately 35%. This is comparable with the monoclinic fraction associated with nucleation saturation on *in vitro* (130°C in water steam) degraded 3Y-TZP ceramics reported by Chevalier et al. (2007). This means that from this point onwards the t→m transformation is driven predominantly by growth and since the surface is already covered by monoclinic phase (Figure 1), the transformation propagates from the surface into the bulk of the material given a continued exposure to water. Moreover, the transformation generates a region of accumulated compressive stresses in the surroundings of transformed monoclinic grains. The stress is relieved through grain boundary microcracking and results in grain pull out as observed on Figure 3c and 3d. This is consistent with laboratory based studies of hydrothermal degradation mechanisms in zirconia in pressurised water at 180°C (Nogiwa-Valdez and Rainforth, 2009; Nogiwa-Valdez et al., 2013).

It is not possible to independently describe the wear process without considering the phase transformation since they are closely interrelated, particularly in *in vivo* scenarios. As the surface undergoes physical deformation, the chemical structure of the material also changes.

While the t→m transformation is notably induced by the presence of water, other factors have been found to play an important role, including temperature, severe mechanical trauma, loading, lubrication, friction and manufacturing route (Brown et al., 2007; Chevalier et al., 2007). The results in the present study show that the t→m transformation initiates in the load bearing areas around the pole of the femoral head. Longer implantation periods allow the monoclinic phase to nucleate and grow also in low load bearing areas (Figure 2). The head pole is also the area where tribological effects are intensified. This zone exhibited the highest concentration of scratches and was also the first area to present smoothing. Moreover, it is possible that the self-polishing mechanism is aided by the grains pulled out after transformation induced grain boundary microcracking. Thus, in addition to the inherent metastability of the tetragonal phase and the environmental conditions, also the inclusion of mechanical and tribological factors influences the t→m transformation. However, it is interesting to note that the the explants from 12 years 8 months and 13 years, which showed the highest surface monoclinic zirconia contents, exhibited the smoothest surfaces (Figures 4 and 5). AFM (Figure 3 b) showed that the grain structure could be seen, suggesting an etching effect. This is similar to observations on alumina zirconia composites, which is believed to be associated with a tribochemical effect, which can in itself result in significant wear rates (Ma and Rainforth, 2012).

5. Conclusions

1) Examination of retrieved zirconia femoral heads implanted for 1-13 years shows simultaneous damage from wear and phase transformation, the extent of which depended on implantation time.
2) Phase transformation of tetragonal to monoclinic zirconia was first observed after 3 years implantation, occurring primarily at the pole of the head. The amount of transformation followed an approximately sigmoidal behaviour with a peak of 38% observed from the head retrieved after 12 years 8 months. This suggests that transformation kinetics are similar to that observed from accelerated *in vitro* investigations.
3) For the first five years, the majority of surface damage arose from abrasion, resulting in more widespread surface scratching. A peak in surface roughness (combined with marked skewness and kurtosis) was observed for the implant retrieved after 5 years 1 month.
4) The head retrieved after 6 years 11 months exhibited a roughness similar to that of the unused implant, although the surface was different as a result of transformation of tetragonal to monoclinic zirconia in the explanted head. The roughness increased in implants with greater life up to a maximum at 11 years. This roughness was associated with a greater amount of transformation of tetragonal to monoclinic zirconia that caused surface uplift. Surprisingly, the explants from 12 years 8 months and 13 years, which showed the highest surface monoclinic zirconia contents, exhibited the smoothest surfaces. AFM demonstrated that the grain structure could be revealed, suggesting some chemical aspect to the wear.

References

Bhushan, B., 1999. Principles and Applications of Tribology, John Wiley and Sons, New York.

Böhler, M., Kanz, F., Schwarz, B., Steffan, I., Walter, A., Plenk Jr, H., Knahr, K., 2002. Adverse tissue reactions to wear particles from Co-alloy articulations, increased by alumina-blasting particle contamination from cementless Ti-based total hip implants. J. Bone Joint Surg. Br. 84B(1), 128-136.

Brown, S. S., Green, D. D., Pezzotti, G., Donaldson, T. K., Clarke, I. C., 2007. Possible triggers for phase transformation in zirconia hip balls. J Biomed. Mater. Res. Part B: Appl. Biomater., 85B, 444-452.

Chevalier, J., 2006. What future for zirconia as a biomaterial? Biomaterials, 27(4), 535-543.

Chevalier, J., Gremillard, L., Deville, S., 2007. Low-temperature degradation of zirconia and its implications for biomedical implants, Annu. Rev. Mater. Res. 37(3), 1-32.

Christel, P., Meunier, J.M., Dorlot, J. M., Crolet, J. M., Witvoet, J., Sedel, P., Boutin, P., 1988. Ann. NY Acad. Sci., Biomechanical compatibility and design of ceramic implants for orthopaedic surgery.

Christian, J.W., 1975. The Theory of Transformations in Metals and Alloys, Part I Equilibrium and General Kinetic Theory, second ed. Pergamon Press, Oxford.

Clarke, D. R., Adar, F., 1982. Measurement of the crystallographically transformed zone produced by fracture ceramics containing tetragonal zirconia. J. Amer. Ceram. Soc., 65(6), 284-288.

Clarke, I. C., Manaka, M., Green, D.D., Williams, P., Pezzotti, G., Kim, Y.H., Ries, M., Sugano, N., Sedel, L., Delauney, C., Ben Nissan, B., Donaldson, T., Gustafson, G.A., 2003. Current status of zirconia used in total hip implants. J. Bone Joint Surg., 85, 73-84.

FDA, 2001. Enforcement Story., Chapter 2 Center for Devices and Radiological Health, http://www.fda.gov/ICECI/EnforcementActions/EnforcementStory/EnforcementStoryArchive/ucm106947.htm#orth, accessed February 2012.

Fukatsu, K., Pezzotti, G., Hayaishi, Y., Sugano, N., 2009. Evaluation of phase stability in zirconia femoral heads from different manufacturers after in vitro testing or in vivo retrieval. J. Arthroplasty, 24(8), 1225-1230.

Hall, R.M., Unsworth, A., Siney, P., Wroblewski, B.M., The surface topography of retrieved femoral heads. J. Mater. Sci. Mater. M., 7(12), 739-744.

Hasegawa, Y., Sheng, P., Kanoh, T., Seki, T., Matsuoka, A., 2012. A polyethylene liner scratch after revision hip arthroplasty performed to repair ceramic fracture. J. Arthroplasty, 27(5), 820.e17-820.e19.

Garvie, R.C., Hannink, R. H., Pascoe, R.T., 1975, Ceramic steel? Nature, 258, 703-704.

Lawson, S., 1995. Environmental degradation of zirconia ceramics, J. Eur. Ceram. Soc., 15, 485-502.

Ma, L., Rainforth, W.M., 2012. The effect of lubrication on the friction and wear of Biolox® delta, Acta Biomater., 8, 2348–2359.

Najjar, D., Bigerelle, M., Migaud, H., Lost, A., 2005. Identification of scratch mechanisms on a retrieved metallic femoral head. Wear, 258(1-4), 240-250.

Nogiwa-Valdez, A.A., Rainforth, W.M., 2009. Hydrothermal Degradation of Zirconia Bioceramics: Effect of Ternary Oxide Additions, Key Engineering Materials, 396-398, 145-148.

Nogiwa-Valdez, A.A., Zeng, P., Ross, I.M., Rainforth, W.M., 2013. Deceleration of hydrothermal degradation of 3Y-TZP by alumina and lanthana co-doping. Acta Biomater., 9(4), 6226-6235.

Piconi, C., Maccauro, G., Muratori, F., Brach del Prever, E., 2003. Alumina and zirconia ceramics in joint replacements. J. App. Biomater. Biomech., 1, 19-32.

Reinisch, G., Judmann, K. P., Lhotka, C., Lintner, F., Zweymüller, K. A., 2003. Retrieval study of uncemented metal-metal hip prostheses revised for early loosening. Biomaterials, 24(6), 1081-1091.

Wang, A., Essner, W., 2001. Three-body wear of UHMWPE acetabular cups by PMMA particles against CoCr, alumina and zirconia heads in a hip joint simulator. Wear, 250, 212-216.

Figure captions

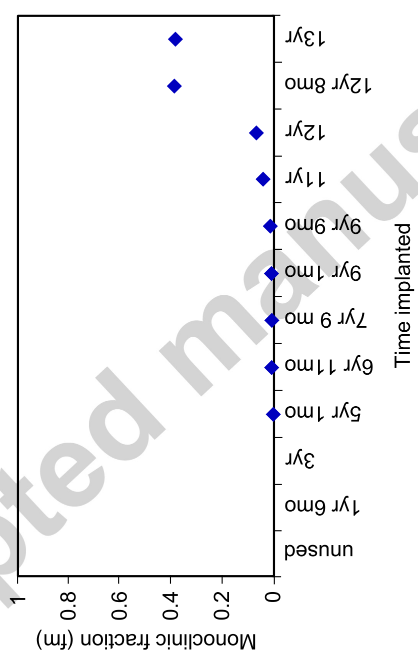
Figure 1. VSI images of the surface of retrieved femoral heads after different implantation periods: a) unused, b) 1 year 6 months, c) 5 years 1 month, d) 9 years 1 month, e) 11 years and f) 12 years 8 months.

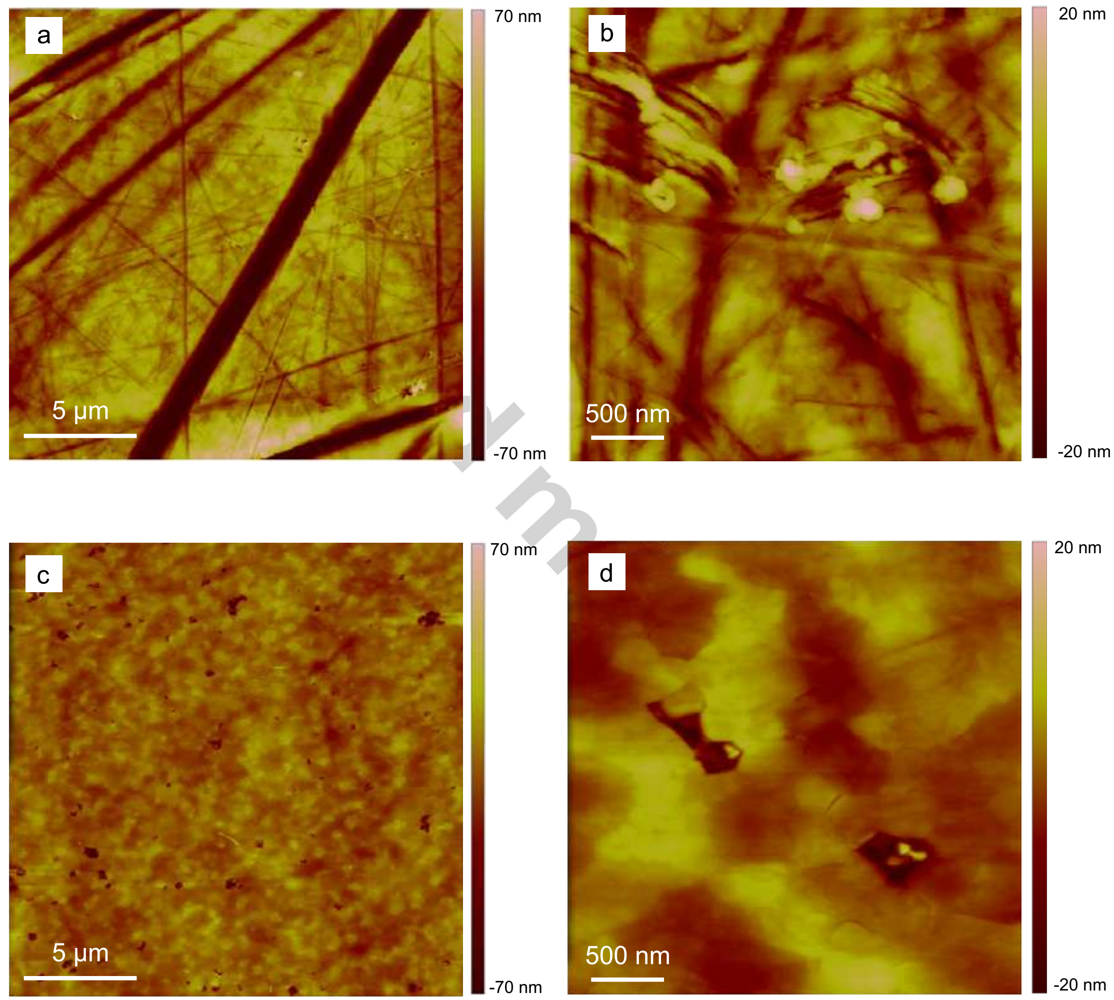
Figure 2. VSI images from different locations on the surface of femoral heads retrieved after: a) 5 years 1 month, b) 9 years 1 month and c) 12 years 8 months. Position 0° corresponds to the pole of the head.

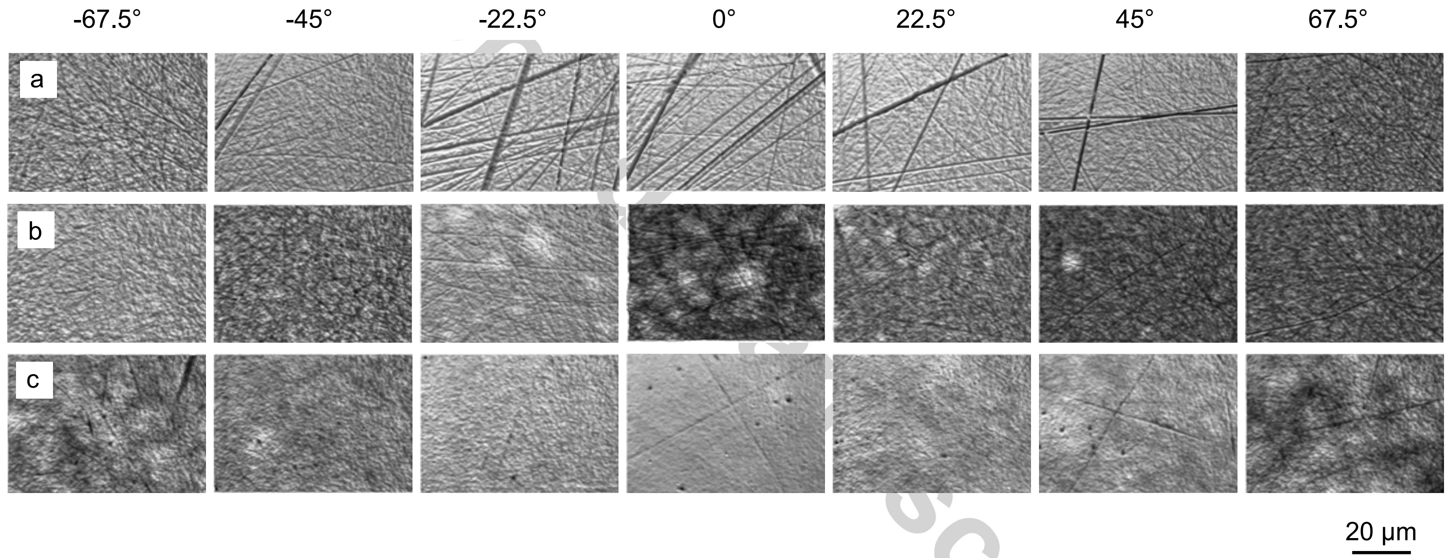
Figure 3. Contact mode AFM images of the surfaces of heads retrieved after: a,b) 5 years 1 month and c,d) 12 years 8 months.

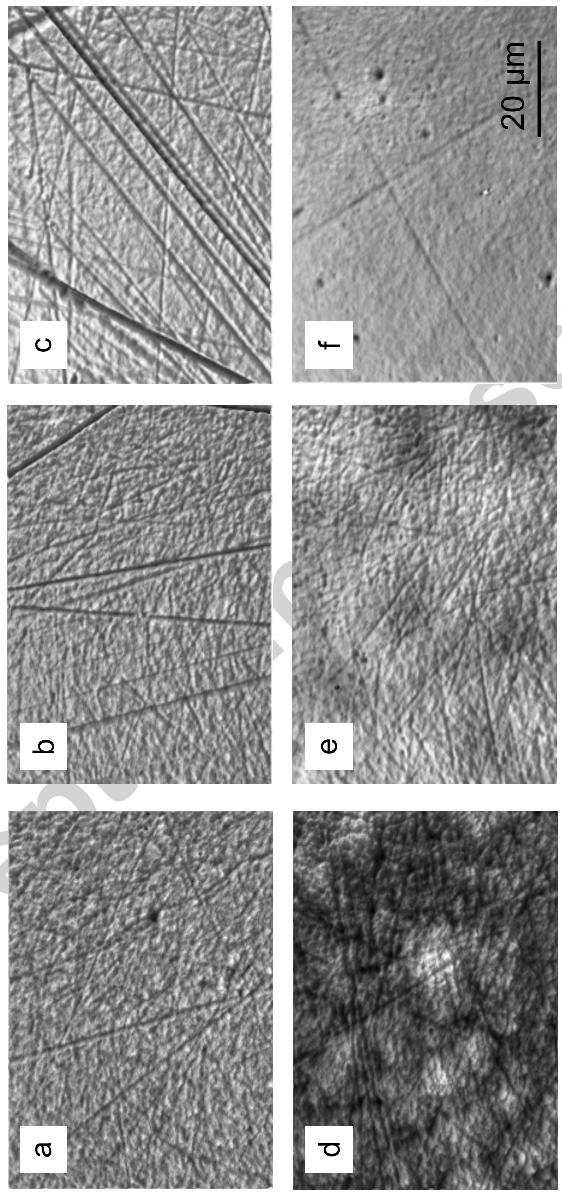
Figure 4. Monoclinic phase fraction on the surface of retrieved femoral heads.

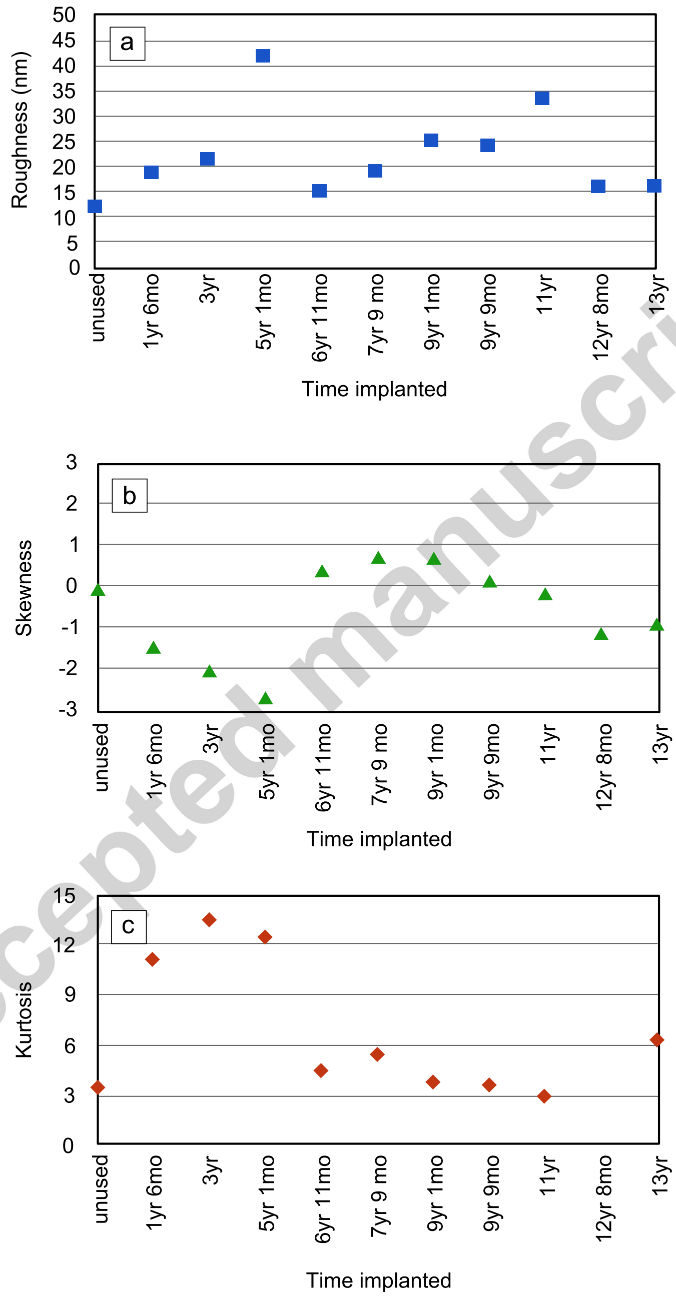
Figure 5. Statistical measurements from VSI images of the pole of retrieved femoral heads: a) average surface roughness (Sa), b) skewness (Ssk) and c) kurtosis (Sku).


Monoclinic fraction (fm)
1
0.8
0.6
0.4
0.2
0
Time implanted
unused
1yr 6mo
3yr
5yr 1mo
6yr 11mo
7yr 9 mo
9yr 1mo
9yr 9mo
11yr
12yr
12yr 8mo
13yr


a
5 µm
70 nm
-70 nm
b
500 nm
20 nm
-20 nm
c
5 µm
70 nm
-70 nm
d
500 nm
20 nm
-20 nm


-67.5°
-45°
-22.5°
0°
22.5°
45°
67.5°
a
b
c
20 µm


a
b
c
d
e
f
20 μm


a
Roughness (nm)
50
45
40
35
30
25
20
15
10
5
0
unused
1yr 6mo
3yr
5yr 1mo
6yr 11mo
7yr 9 mo
9yr 1mo
9yr 9mo
11yr
12yr 8mo
13yr
Time implanted
b
Skewness
3
2
1
0
-1
-2
-3
Time implanted
c
Kurtosis
15
12
9
6
3
0
Time implanted