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Comparative ageing behaviour of commercial, unworn and worn 3Y-TZP and zirconia-toughened alumina hip joint heads

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Abstract

There is a trend today to develop zirconia toughened alumina (ZTA) composites for orthopaedic applications. So far, there is limited data concerning their sensitivity to ageing, especially considering tests performed on implants produced on an industrial scale. Here, complementary tools were used to assess the ageing resistance of ZTA femoral heads. The results were compared to femoral heads processed under the same industrial process with monolithic 3Y-TZP. As expected, monolithic 3Y-TZP implants exhibited significant ageing. In contrast ZTA femoral head showed no sign of degradation even over a period equivalent to that of a human life. The potential impact of coupling effects between wear and ageing is assessed. Monolithic zirconia and ZTA femoral heads were thus first worn in a hip joint simulator, and then aged in autoclave. The kinetics of transformation of the worn monolithic zirconia implants is accelerated while that of worn ZTA femoral heads remains almost unchanged.

Keywords: Lifetime; Al_2O_3; ZrO_2; Biomedical applications; Composites

1. Introduction

High purity alumina has been widely used for orthopaedic applications for several decades with well-documented clinical follow up.[1] But due to its modest fracture toughness and despite improved processing, only a limited number of designs can be conceivable with this particular material. For example, alumina hip balls are restricted to sizes greater than or equal to 28 mm.

Zirconia presents several allotropic forms. At room temperature and atmospheric pressure, pure zirconia is monoclinic (m) whereas zirconia alloyed with some oxides (i.e. yttria) can be retained in the cubic (c) or tetragonal (t) form. This last crystallographic form benefits from a transformation toughening mechanism that acts to resist crack propagation. The stress-induced phase transformation involves the transformation of metastable t-ZrO_2 crystallites to the m phase at the crack tip, which, accompanied by a volumetric expansion, induces compressive stresses and slows down the propagation. Therefore yttria-stabilized tetragonal zirconia polycrystal (3Y-TZP) was proposed in the 90s as an alternative to the more brittle alumina.[2] However, it was soon realized that this grade of structural ceramic exhibited a low temperature degradation (LTD), also called ageing, when in contact with body fluid.[3] This instability results in a t–m undesirable transformation with time, even at body temperature. The initiation mechanism of this transformation, which takes place on the surface, is still under discussion but is linked with the diffusion of water species through the lattice.[4] The first stage of the transformation results in the formation of monoclinic spots at the surface. The formation of microcracks related to the transformation allows water to penetrate into the material, so that the size of the monoclinic spot increases. Thus, the extension of this ageing follows a nucleation and growth mechanism and can even reach dramatically the core of the implant (see 4 for the detailed steps of the LTD process). The wear performance of the bearing material is lost as

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roughening, micro cracks and pullouts are generated. This may lead to aseptic loosening, caused by osteolysis and adverse tissue reactions to the particles. The critical events of Saint Gobain Desmarquest have shown that such transformation was relevant in vivo and may lead to failure of implants after short duration.[4–6]

The kinetics of the transformation is process controlled.[4–6] Some crucial parameters are density (open porosity offers water molecules easy access to the bulk of the material), grain size (finer grain size increase the resistance to transformation), homogeneity of the phase distribution (negative effect of residual cubic phase) and residual stress on the surface. Unfortunately, in 3Y-TZP, the presence of numerous vacancies due to the trivalent character of yttrium makes the diffusion rate of water higher than in other zirconia ceramics.[4] Fortunately, there are powder choices and process conditions for which LTD can be limited. Also, during the past decade, improved techniques have been developed to monitor and predict the long-term in vivo environmental resistance of t-ZrO_2.[7] Therefore, it is now possible to assess the sensitivity against ageing of biomedical grade zirconia prior to surgery. Because the transformation is thermally activated, autoclave accelerated ageing tests can be performed. It has been calculated for example that 1 h of autoclave treatment at 134 °C has theoretically the same effect as some years in vivo at 37 °C.[3] Depending on the value of the apparent activation taken for extrapolating LTD kinetics performed at moderately low temperature, it is calculated that 1 h of autoclave at 134 °C is roughly equivalent to 1–4 years in vivo. Such accelerated ageing tests however do not take into account the possible effect of wear and implant loading on the ageing kinetics in vivo. Such effect seems to have been neglected so far.

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, and different types of zirconia (stabilized or not with yttria) have been proposed.[8]

Zirconia-rich composites still exhibit a certain degree of ageing.[9] In contrast, some have demonstrated that ZTA ceramics, even containing yttria, can exhibit much better ageing resistance than monolithic 3Y-TZP,[10,11] provided the volume percent of zirconia is kept low enough (below the percolation threshold being a must) and the microstructure homogenous, free of aggregates.

Some alumina–zirconia composites are already implanted or developed by companies (Biolox delta® by Ceramtec being an improved version of these composites, with SrO and Cr_2O_3 additions and alumina grains with platelet-like morphology). As expected, they show significant improvement in ageing resistance as compared to 3Y-TZP, and excellent crack resistance.[12] In these commercial composites, the zirconia content is around the percolation threshold and stabilization is achieved partly by 1.3 mol.% yttria additions. So ageing occurs, although the consequences are not critical as it was the case for 3Y-TZP[13]: even long ageing treatments do not lead to a critical degradation of structural integrity.

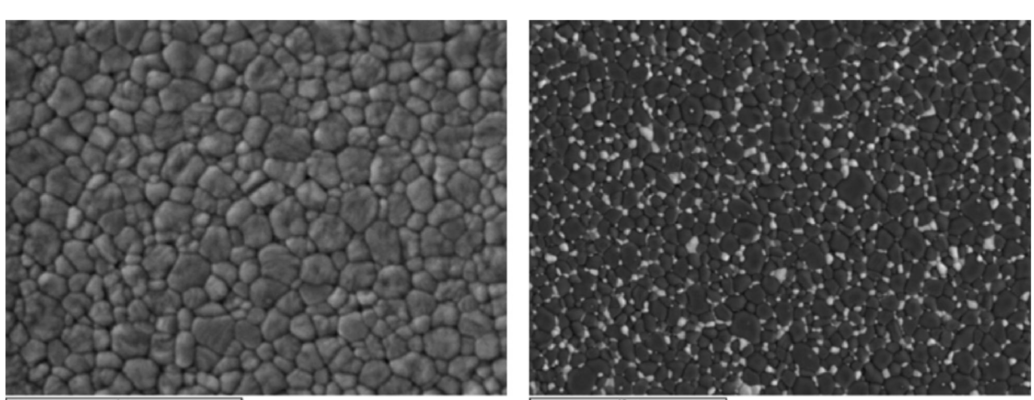
These previous studies devoted to ageing in alumina–zirconia systems show that, even if limited, some degree of degradation can be observed, depending on microstructural features. They show also that process and machining can play a major role on the overall behaviour of a zirconia-based component. In this respect, there is only little information on the ageing behaviour of ZTA femoral heads processed at the industrial scale. Last but not least, the couplings between wear and ageing have never been described, and seems to be under-emphasised so far.

This observation led us to perform the present study the aim of which was to examine the ageing resistance of alumina–zirconia femoral heads processed at the industrial scale and the potential impact of ageing on surface state and mechanical performance. The ageing resistance of these heads will be compared to that of monolith zirconia femoral heads processed by the same company and same processing methods. The influence of wear produced with a hip joint simulator on the kinetics of ageing will also be discussed.

2. Materials and methods

2.1. Materials

The initial surface state after grinding/polishing and residual stresses strongly influence the ageing sensitivity of zirconia.[14] Therefore, the study was conducted on commercial ZTA femoral



(a) (b)

Fig. 1. SEM images taken at the surface of thermally etched femoral heads (a) monolithic 3Y-TZP and (b) ZTA (Vitox® AMC).

heads (28 mm diameter) provided by Morgan Technical Ceramics Ltd, under the trade name Vitox® AMC. The performance of the Vitox® AMC heads was compared directly with high purity 3Y-TZP zirconia heads produced using similar manufacturing processing route. The Vitox® AMC is a composite material composed of 80 wt% high purity alumina and a maximum of 20 wt% 3Y-TZP (i.e. 13.4 vol.%). Typical microstructures of the two materials are given in Fig. 1. Monolithic 3Y-TZP exhibits an average grain size of 0.6 μm. 3Y-TZP and alumina grains in Vitox® AMC exhibit an average size of 0.45 μm and 1.4 μm, respectively. The generic manufacturing process used to produce the femoral heads and cups for this research involved the pressing of blanks from the approved composite material. The blanks were then green machined to specified dimension, and sintered. Post-sintered products were ground and polished to drawing specification. Prior to release for sterilisation, all products underwent stringent inspection procedures and a cleaning operation to remove process residue.

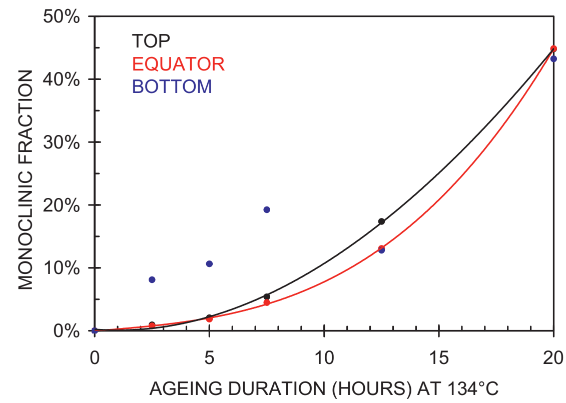


Fig. 2. Evolution of the XRD monoclinic fraction versus ageing time in autoclave measured on a 3Y-TZP femoral head. Indicative lines added for Top and Equator.

2.2. Methods

2.2.1. Accelerated ageing tests

The LTD kinetics were evaluated by performing accelerated ageing tests in water steam at 134 °C, 2 bars (i.e. under the conditions prescribed by the ISO standard 13356 related to ceramic implants based on 3Y-TZP for surgery). Samples were located on a grid in the autoclave (Fisher Bioblock Scientific, Illkirch, France) so that they were not soaked in water during ageing, but only subjected to steam atmosphere. Before increasing the temperature up to 134 °C, enclosure was left open to evacuate the air atmosphere initially present in the steam autoclave, thus ensuring a 100% humidity atmosphere during ageing.

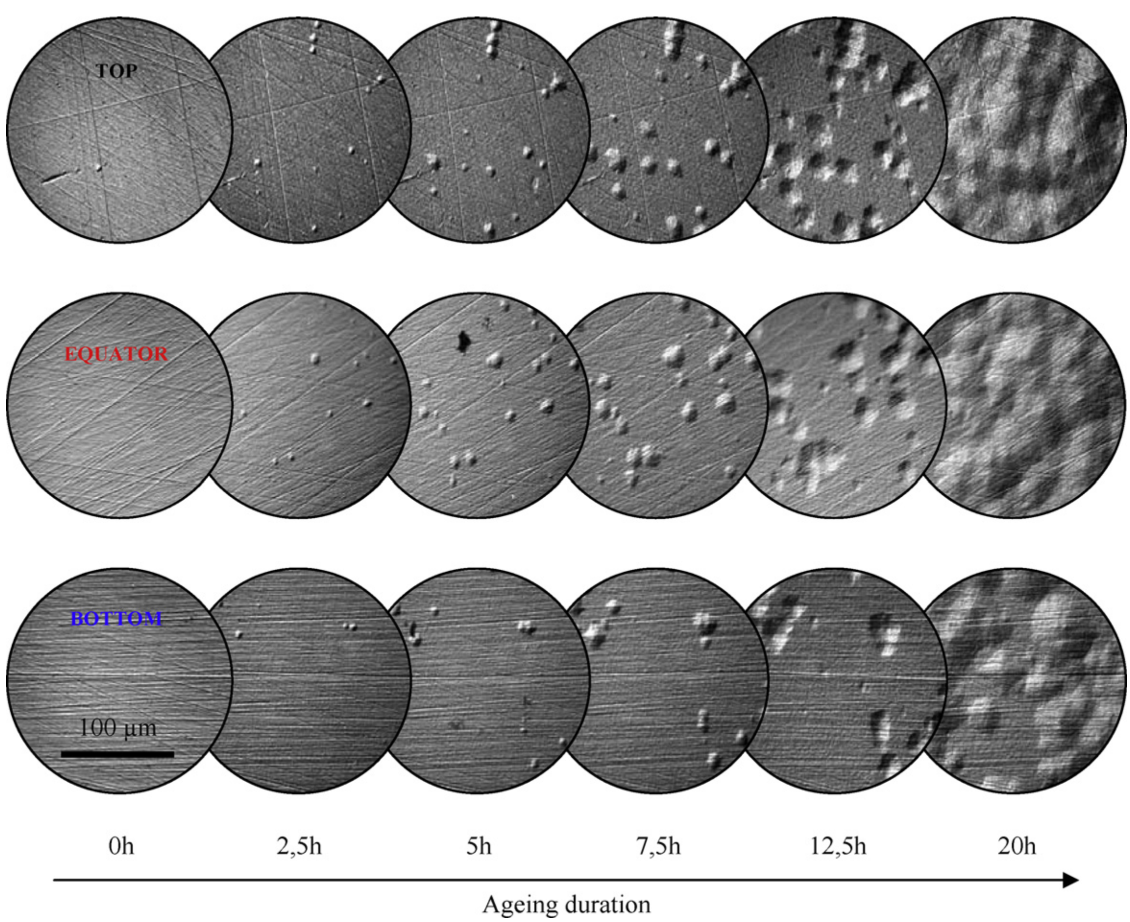


Fig. 3. Nucleation and growth process of the monoclinic spot periodically observed by reflected light DIC microscopy for three locations of the 3Y-TZP femoral head.

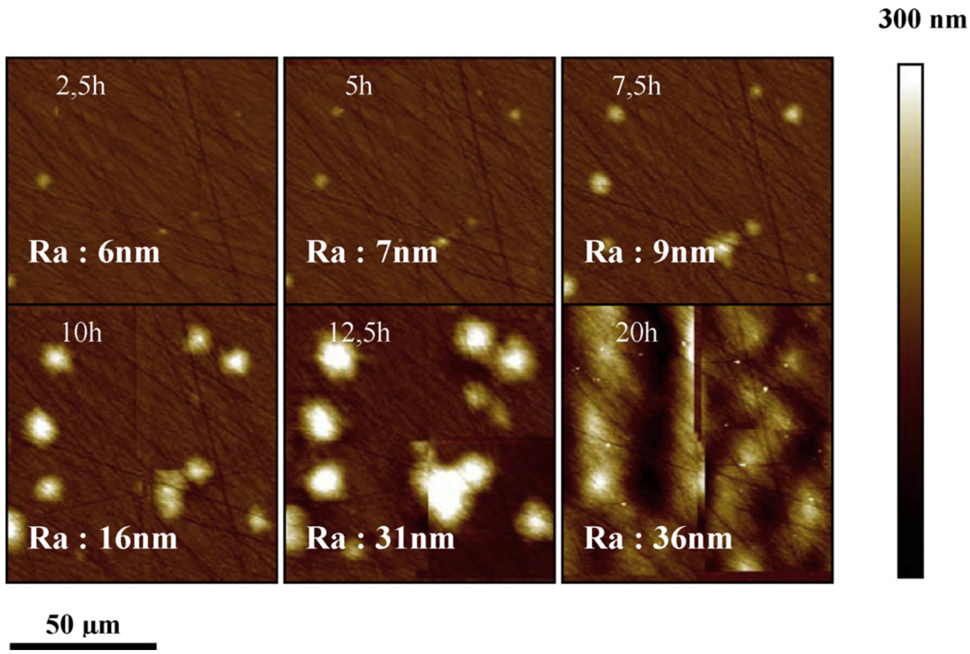


Fig. 4. AFM micrographs (height image) of the progressive nucleation and growth of monoclinic phase as function of the exposure time in hydrothermal environment, at the top of a 3Y-TZP head (similar behaviour was observed at the equator and at the bottom). Ageing duration and Ra are inlayed in the images.

2.2.2. *Hip joint simulator wear-testing*

The wear tests were conducted using the Durham University Mark II hip joint wear simulator, in which six joints (3 Y-TZP Zirconia and 3 Vitox® AMC) were mounted at 33° to the horizontal plane against UHMWPE in the case of zirconia heads and against Vitox® AMC cups in the case of the Vitox® AMC heads and subjected to a dynamic loading cycles. The stations allowed the flexion/extension (F/E) motion of the femoral component and the internal/external (I/E) motion of the acetabular cup at 1 Hz. The load was applied using a pneumatic actuator and proportional valve for each station. Simplified loading profiles were employed, which varied in the range of 250–2800 N. The lubricant used was diluted bovine serum, which was 25% in volume concentration and had the protein content in 18 g/L (ISO 14242-1:2002E). An antibacterial agent (0.2% sodium azide (NaN_3)) was added to inhibit bacterial growth, and additives (EDTA) to prevent calcium deposition.

The hip simulator stopped every 500,000 cycles (approximately 5 days and 19 h). The hip prostheses were cleaned following the cleaning/drying protocol for further analysis of the wear particles produced. At each half-million-cycle test the fresh lubricant was re-filled. The tests were performed up to 5 million cycles. Wear rates and surface monitoring with time will be the subject of another paper. In the present study, the aim was to use these heads that had worn against polyethylene for 5 Mc for subsequent ageing tests.

2.3. *Follow up of surface modifications*

Ageing effects were monitored periodically using non-destructive reflected light differential interference contrast (DIC) microscopy, atomic force microscopy (AFM) and X-ray diffraction (XRD) analysis. Such methods have been successfully used in previous works to investigate the t–m transformation (XRD) and its consequence on surface topography (DIC, AFM).[7]

Reflected light differential interference contrast (DIC) microscopy is an optical microscopy illumination technique, which uses interference of polarized light wave fronts to enhance contrast. The image created in reflected light DIC can often be interpreted as a pseudo three-dimensional representation of the surface geometry. If it is not suitable for accurate measurement of actual heights and depths, this technique is very efficient to qualitatively follow the evolution of monoclinic uplifts when their area reaches a few microns. Our DIC examinations were performed with a Zeiss Axiophot microscope.

To quantitatively follow the surface degradation kinetics at a nanoscopic scale, AFM was implemented in *contact mode* (Dimension V Scanning Probe Microscope – Veeco). As

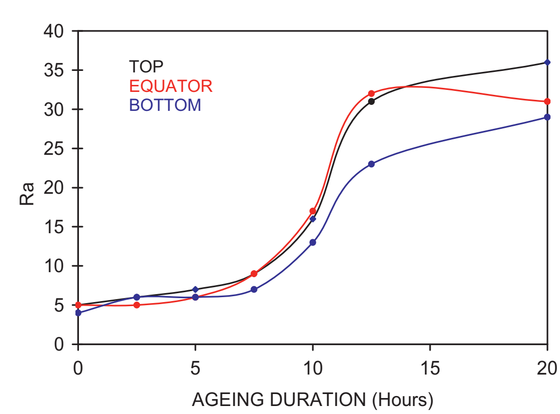


Fig. 5. Evolution of the arithmetic average of the roughness profile (Ra) versus ageing time in autoclave measured by AFM, for a 3Y-TZP head and at three locations.

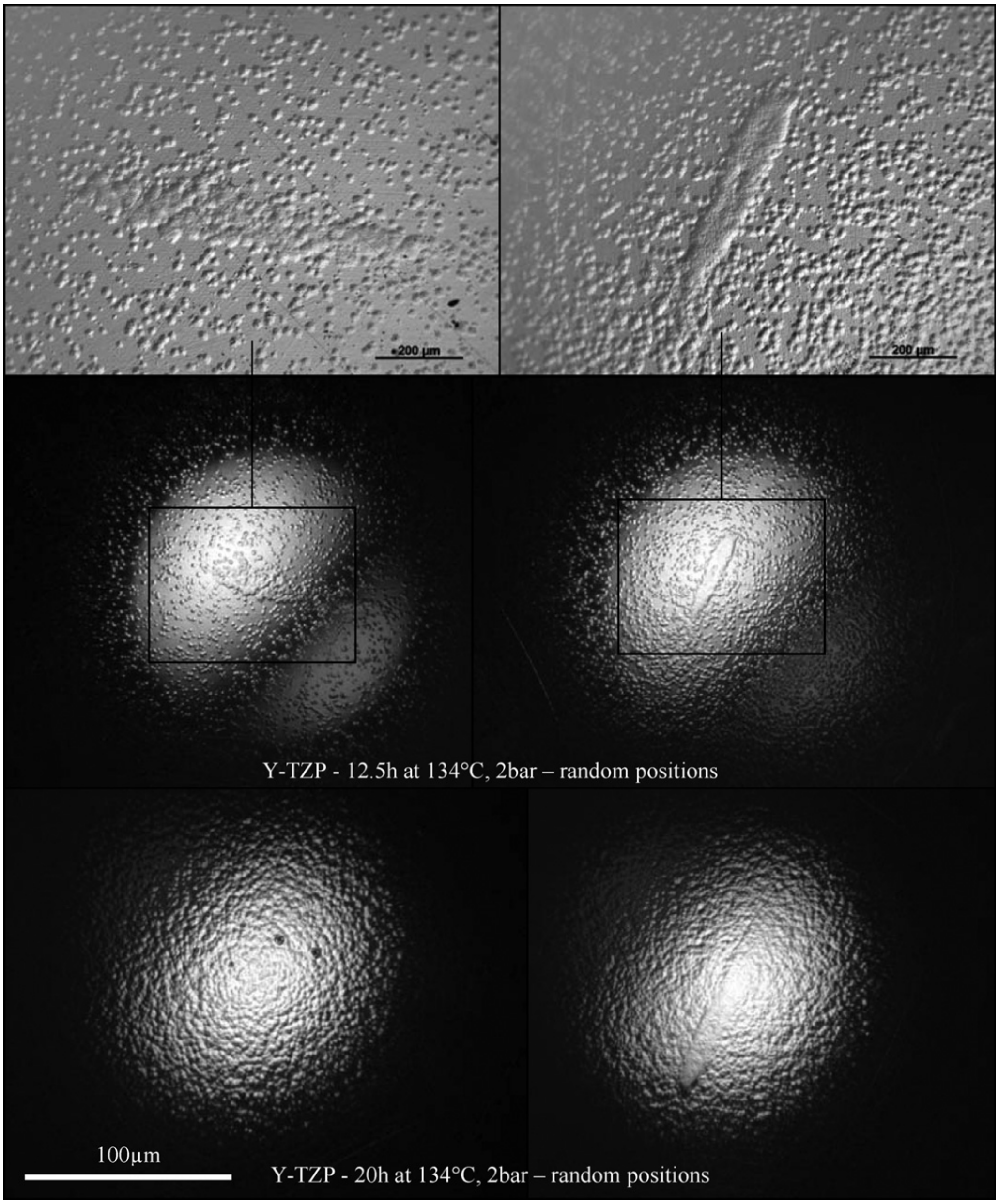


Fig. 6. Stripes formed by local coalescence of the monoclinic uplifts observed by reflected light DIC microscopy for random locations of the 3Y-TZP femoral head after ageing.

compared with reflected DIC microscopy, this surface imaging technique also gives access to topological changes but this time, it provides a true three-dimensional surface profile. AFM offers a vertical resolution as low as atomic scale thanks to piezoelectric scanner sensitivity. Lateral resolution depends not only from the probe tip size but also from the numerical image sampling. Here we used 1024 pixels to describe 50 µm so as to have *X–Y* numerical resolution close to 50 nm. The experiments were carried out using oxide sharpened silicon nitride probes whose tips radius was about 20 nm (Nanosensor, CONT-R model) and a scan rate of 1 Hz. The AFM depth of field (given by the axial travel of the piezoelectric tube) is limited to a few micrometers, making difficult its use on non-flat samples such as femoral heads. Therefore, only small areas (typically 50 µm × 50 µm) can be observed with our configuration. So, to make statistical analysis more acceptable, we tried to collect 4 adjacent fields of 50 µm × 50 µm for each monitored location of the femoral heads. The roughnesses were deducted after the AFM images have been subjected to *second-order flattening* (excluding the monoclinic protuberance) with the *Nanoscope 7.20 software* (Vecco).

XRD is a nondestructive technique allowing crystallographic characterization on a typical depth of a few micrometers. So, XRD was performed to assess the volume fraction of monoclinic phase associated to the ageing process. Measurements were conducted with a classical Bragg–Brentano geometry, with Cu (K_α) radiation and using a BRUKER AXS D8 ADVANCE diffractometer and a one-dimensional LYNXEYE detector (collection on an angular area of 3° – 192 strips). The diffractograms were obtained between 27° and 33° (2θ) at a scan speed of 2 s/point and a step size of 0.01°. The volume fraction of monoclinic phase was calculated using the empirical relationship established by Toraya et al.[15] expressing ν_m versus the ratio of reflection intensities X_m:

$$X_m = \frac{I_m(\bar{1}\ 1\,1) + I_m(1\,1\,1)}{I_m(\bar{1}\,1\,1) + I_m(1\,1\,1) + I_t(1\,0\,1)}$$

$$\nu_m = \frac{1.311 X_m}{1 + 1.311 X_m} \qquad (1)$$

where $I_x(h\,k\,l)$ denotes the integrated intensity (or area) of the peak associated to the plane $(h\,k\,l)$ of phase X (m for monoclinic and t tetragonal).

For one as received femoral head of each kind (one monolithic zirconia and one alumina–zirconia), ageing was monitored at three locations of the head: top, equator and bottom. This was repeated on femoral heads worn on the hip joint simulator.

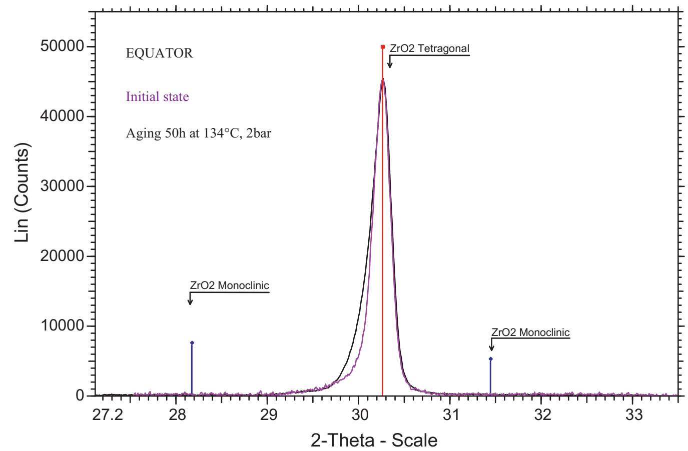


Fig. 7. Superposed X-ray diffractograms before and after an ageing of 50 h at 134 °C, 2 bar of a ZTA femoral head. No presence of the monoclinic structure is detected.

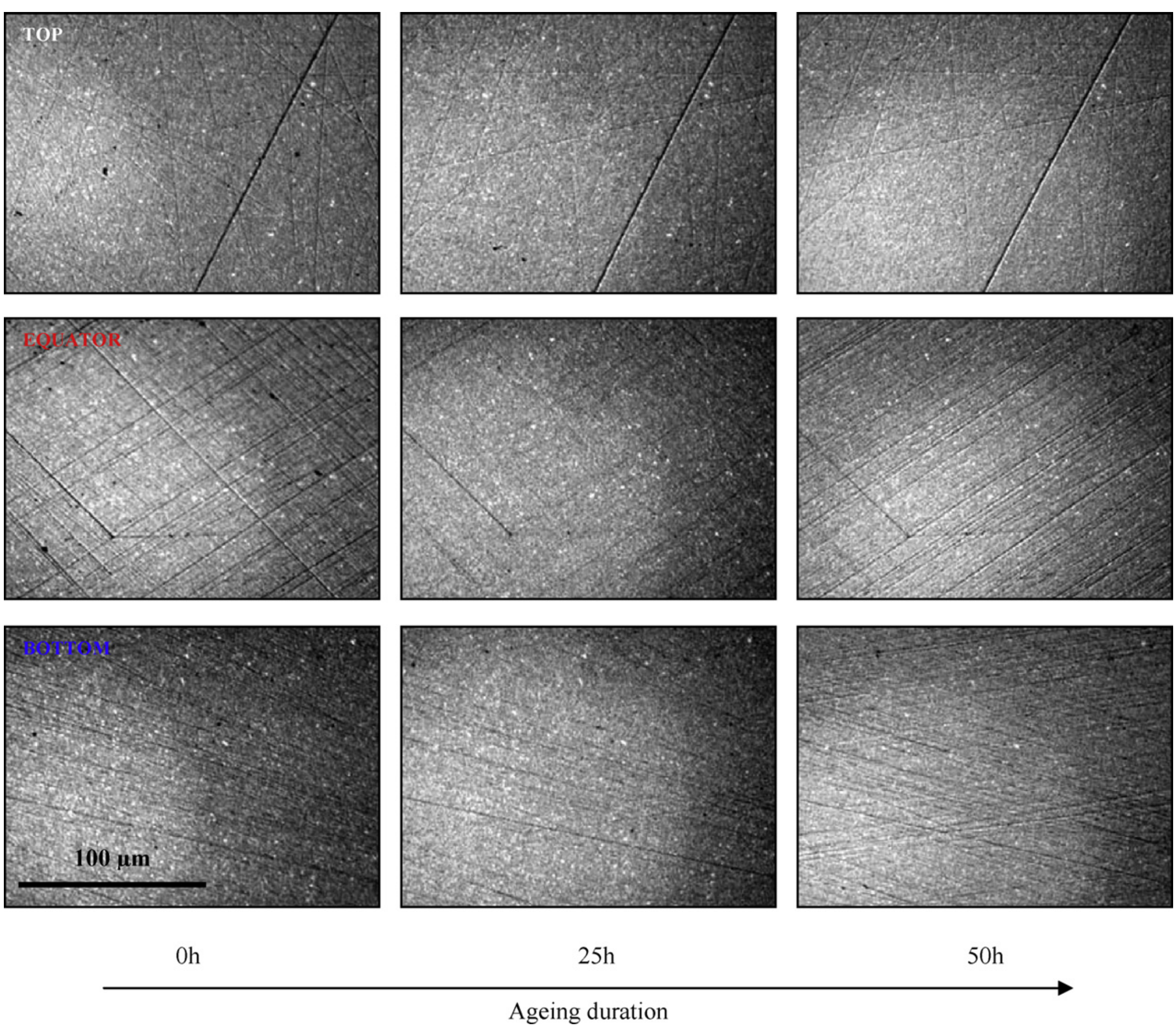


Fig. 8. Reflected light DIC observation of the surface of a ZTA femoral head, for three locations, before and after 25 h and 50 h autoclaving at 134 °C, 2 bars. No evidence of surface change due to t–m transformation is detected.

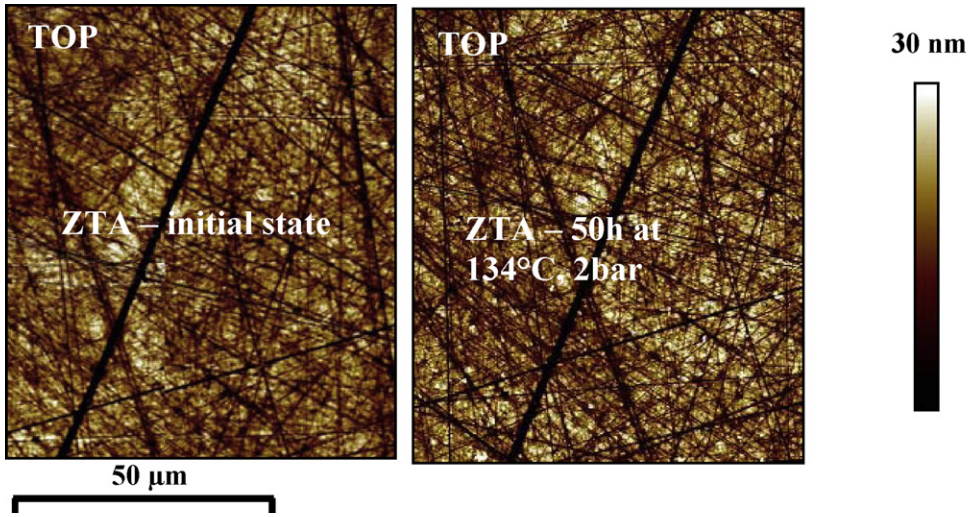


Fig. 9. Atomic force microscopy observations of the same area before and after an ageing of 50 h at 134 °C, 2 bars of a ZTA femoral head. No transformation of the surface is observed (same feature – absence of transformation – at the equator and the bottom).

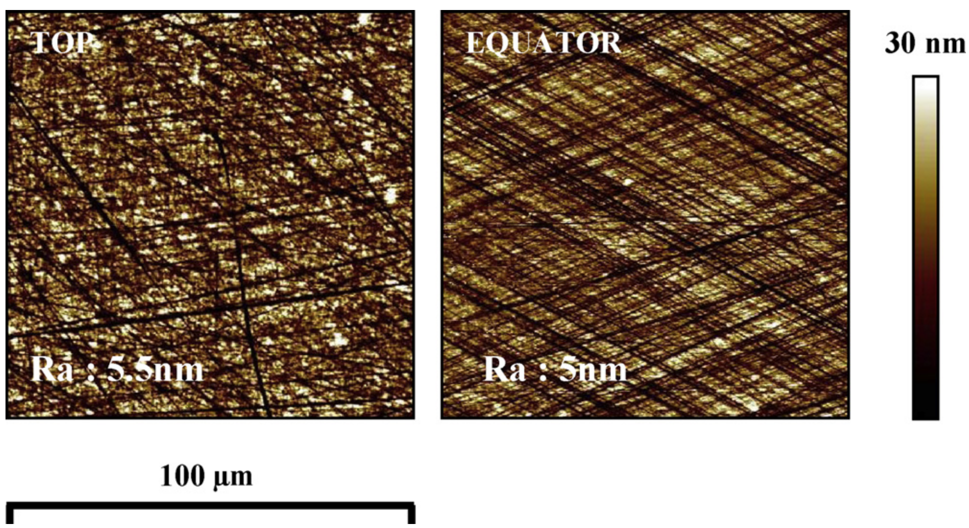


Fig. 10. AFM measurements of the topography at the top and at the equator of the worn 3Y-TZP femoral head. The dark straight lines are scratches (arithmetic averages of the roughness profile (Ra) are inlayed in the images). Note the probable presence of monoclinic spot at the top.

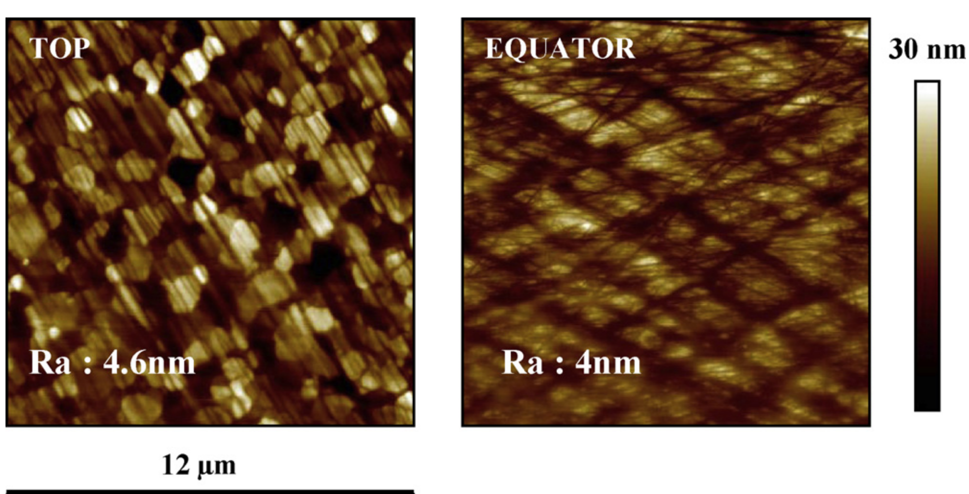


Fig. 11. AFM measurements of the topography at the top and at the equator of the as received worn ZTA femoral head (arithmetic averages of the roughness profile (Ra) are inlayed in the images).

3. Results and discussion

3.1. Ageing of unworn femoral heads

The LTD kinetics of the provided 3Y-TZP femoral head is shown in Fig. 2. For this implant, the initial monoclinic fraction was seen as null whereas after 20 h of autoclave treatment, this fraction has reached more than 40 vol.%. Top and equator locations exhibited a similar behaviour. XRD results were more heterogeneous at the bottom of the head. At this location, undesirable signal derived from the specific (ground) surface of the chamfer leads to a questionable reproducibility of the measurements. Reflected light DIC imaging displays the changes of aged 3Y-TZP surface structures (Fig. 3). As expected, the nucleation-growth mechanism of the monoclinic transformation occurred. Quantitative measurements of the topography before and during ageing were also done with AFM (Figs. 4 and 5). The initial state has a Ra of about 5 nm. As soon as the phase transformation has extended in surface, the roughness increased until reaching a threshold of Ra of about 30–35 nm (Fig. 5). This maximal roughness corresponds to a near totally t–m transformed surface. Further ageing will tend to lead to lower Ra (this trend has already been felt at the equator). From an ageing duration of 12.5 h, local coalescences of monoclinic spots have resulted in the formation of monoclinic stripes. Associated to wear, these areas could become a special place for grain pullout (Fig. 6).

For the ZTA femoral head, none of the used techniques identified any effect of ageing. To illustrate that, Fig. 7 compares the XRD pattern for the initial state to that obtained for an ageing of 50 h at 134 °C, 2 bar. For both, no monoclinic peak is observed. Neither reflected light DIC microscopy, nor AFM suggested any sign of degradation (Figs. 8 and 9).

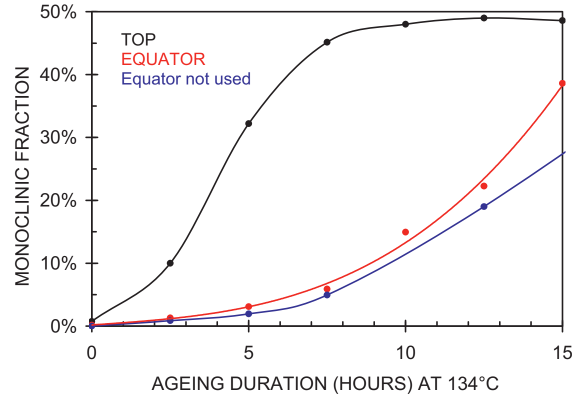


Fig. 12. Evolution of the monoclinic fraction versus ageing time in autoclave measured by X-ray diffraction for the worn 3Y-TZP femoral head.

3.2. Ageing of worn femoral heads

For implants worn by a walking hip simulator (and before ageing), it appeared that only the top of the heads presented a surface modification. Indeed, whatever the material, the surface at the equator is identical to that found on the unworn femoral heads, i.e. hip simulation did not alter the surface at the equator. At the top of the monolithic zirconia femoral head, it seems that the wear produced monoclinic spots (Fig. 10), even if XRD monoclinic still lies below the detection limit (below 1%). Concerning the worn ZTA femoral heads, the top presents a specific topography: the finer grinding stripes seem to have been erased (polished) (see Fig. 11) and selective phase dissolution by a tribo-chemical process seems to have occurred, in agreement with previous works.[13]

Fig. 12 shows the XRD monoclinic content versus time measured at the top (worn area) and the equator (almost un-worn

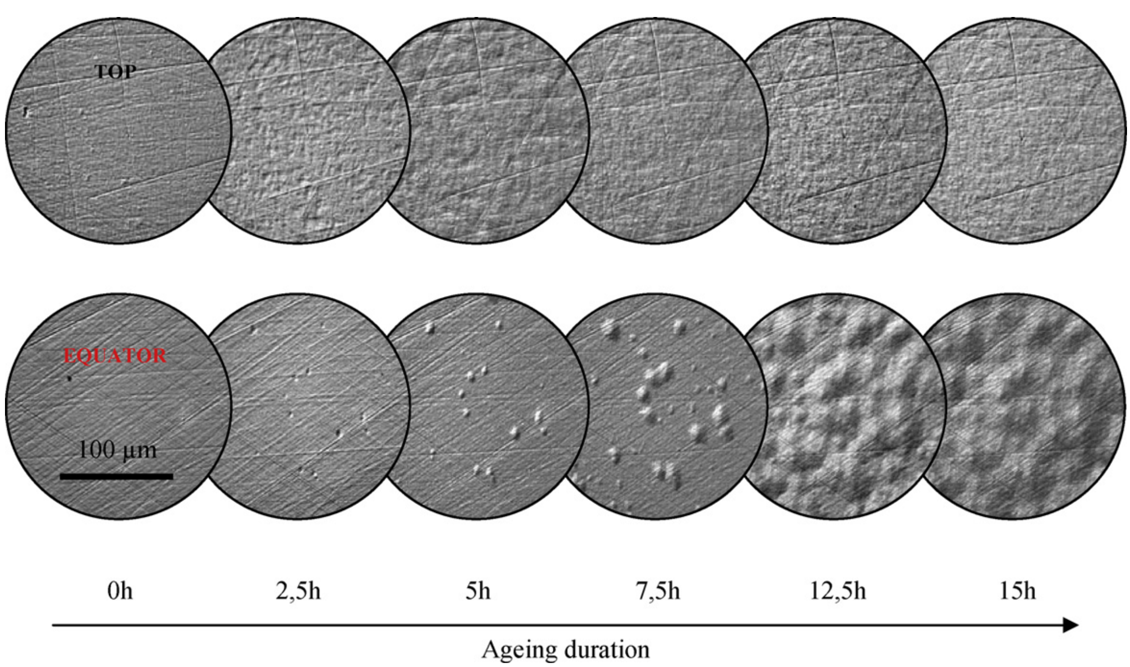


Fig. 13. Nucleation and-growth process of the monoclinic spot periodically observed by reflected light DIC microscopy for two locations of the worn 3Y-TZP femoral head.

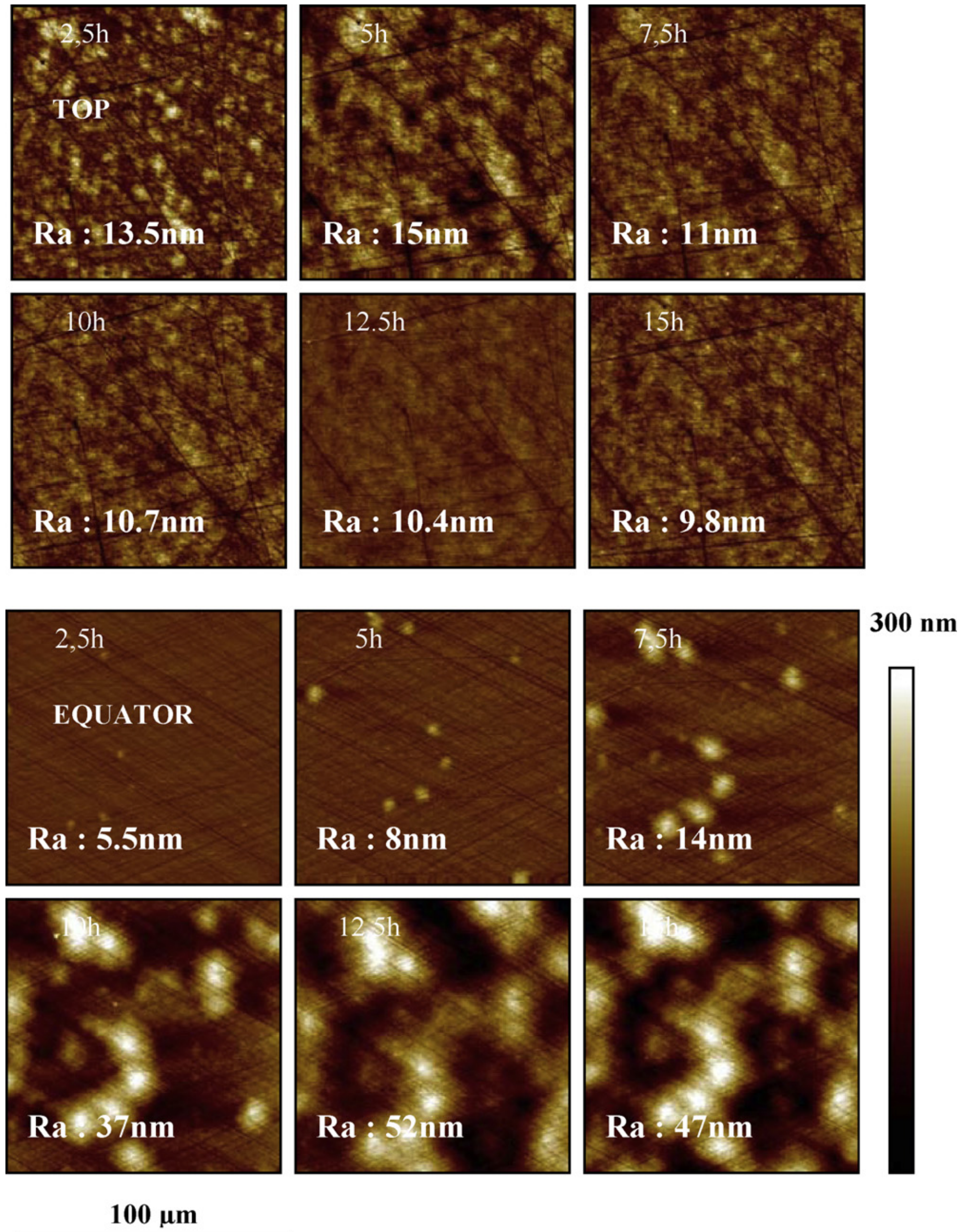


Fig. 14. AFM micrographs (height image) of the progressive nucleation and growth of monoclinic phase as function of the exposure time in hydrothermal environment (ageing duration and Ra are inlayed in the images) for the worn 3Y-TZP femoral. Note the different behaviour at the top and the equator.

area), compared to results obtained on an un-worn head. At the top, the kinetics of the transformation appear much faster compared to an unworn area. This behaviour is in agreement with a previous work conducted on flat samples,[14] which showed that the variation of ageing sensitivity is related indirectly to the surface roughness via the induced surface stress state. Wear induces scratches and stresses acting as nucleation sites for the transformation. This is particularly important, since most (if not all) of the ageing kinetics obtained so far are given for as-processed surfaces without the effect of applied realistic loading and wear conditions. Such ageing kinetics is therefore certainly underestimated.

Reflected light DIC and AFM imaging shows the nucleation and growth process of monoclinic spots on the worn 3Y-TZP

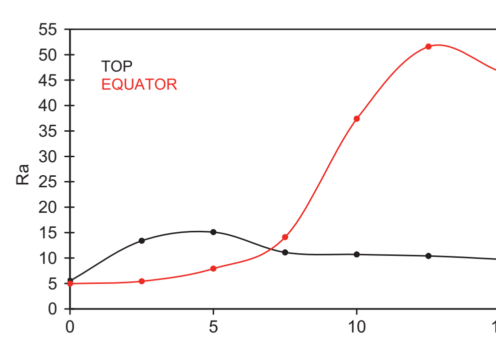


Fig. 15. Evolution of the arithmetic average of the roughness profile (Ra) versus ageing time in autoclave measured by AFM for the worn 3Y-TZP femoral head.

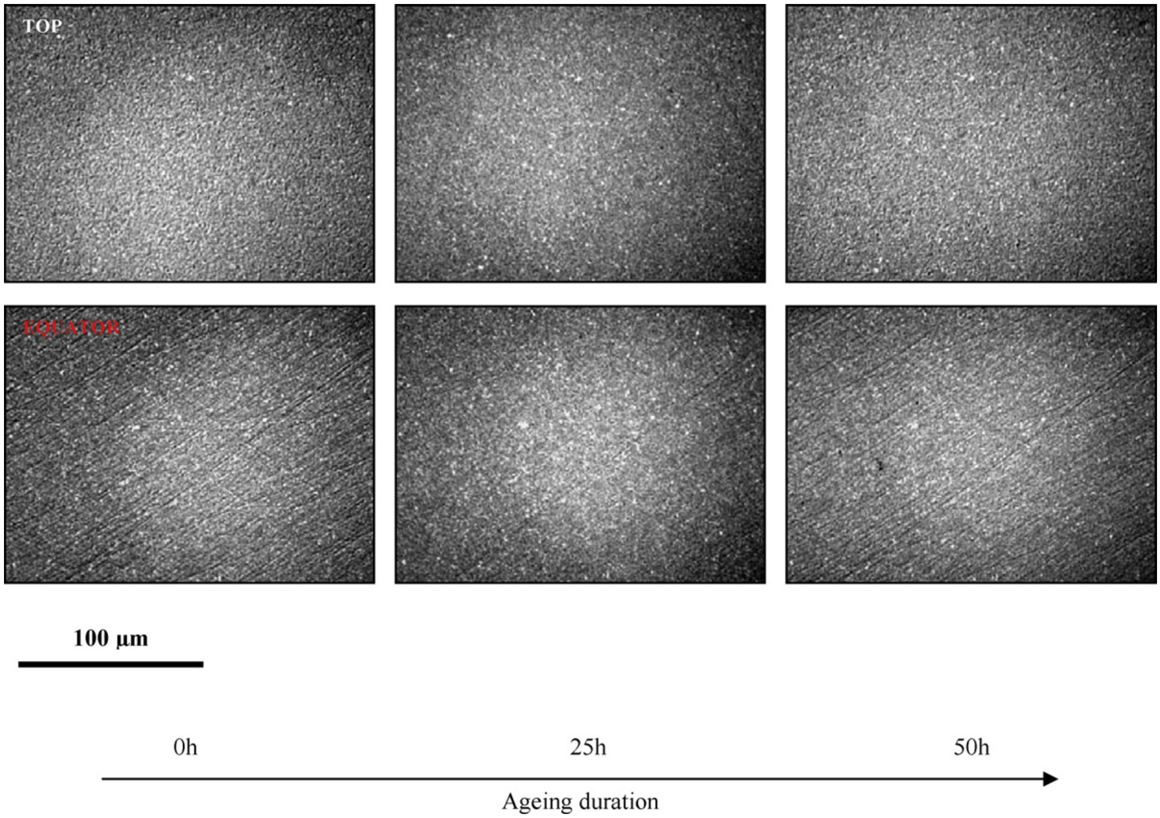


Fig. 16. Reflected light DIC observation of the surface of a worn ZTA femoral head, for two locations, before and after 25 h and 50 h autoclaving at 134 °C, 2 bars. No evidence of surface change due to t–m transformation is detected.

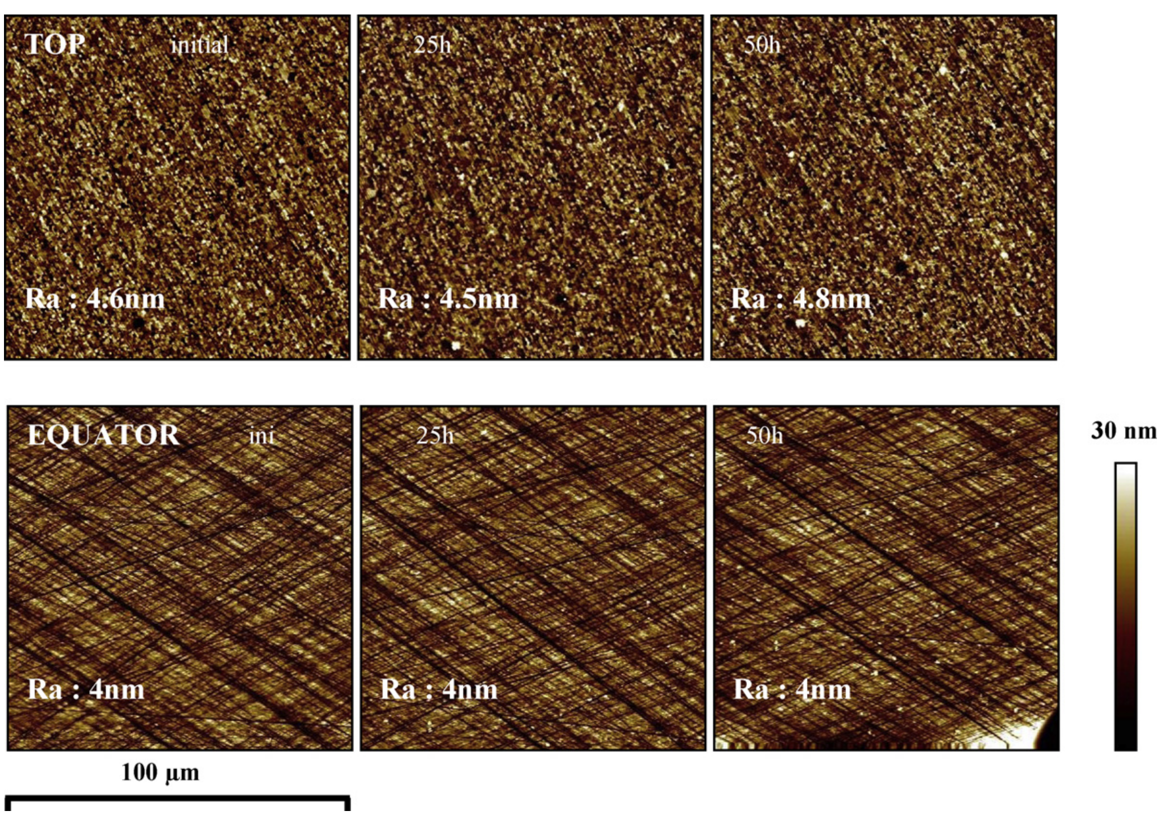


Fig. 17. Atomic force microscopy observations of the same large areas before and after ageing of 25 h and of 50 h at 134 °C, 2 bar of a worn ZTA femoral head. No transformation of the surface is observed.

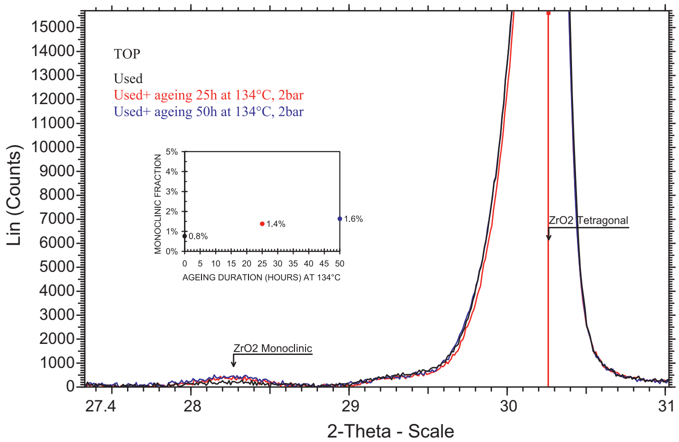


Fig. 18. Superposed X-ray diffractograms before ageing and after an 25 h and 50 h at 134 °C, 2 bar of a worn top ZTA femoral head. Contrary to the equator, a little presence of the monoclinic structure is detected with a slight increase with time.

surface (Figs. 13 and 14). The AFM quantitative measurements of the topography are shown in Fig. 15, for the top (worn area) or the equator (un-worn area) of the heads. This is interesting to see that, as nucleation rate of the transformation is faster for a worn surface, the roughness is in fact lower for the worn area, for which the monoclinic content is the highest. Therefore, only complementary XRD, AFM and DIC can provide an accurate description of the transformation of the surface towards the monoclinic state and its impact on surface topography. Having a roughness still lying under acceptable values after ageing in the worn area is not sufficient, since we have to keep in mind that transformation to such high ratios after 10 h of ageing (roughly 10–20 years in vivo) would mean that a micro-cracked zone of several microns depth is present.[4–6]

For the worn ZTA femoral head reflected light DIC microscopy showed no sign of degradation (Fig. 16). AFM measurement and XRD results appeared to show the presence of a very slight surface transformation at the top of the head. At this location, respectively, the Ra switch from 4.6 nm to 4.8 nm (Fig. 17) and the monoclinic fraction goes from 0.8% to 1.6%

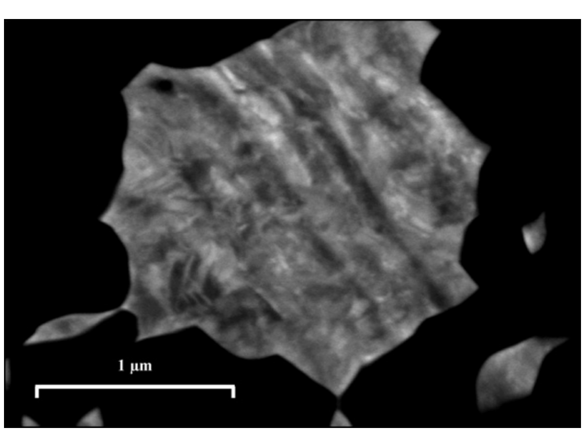


Fig. 19. SEM image (BSE mode) of a large zirconia grains at the top of worn ZTA femoral head showing twinning associated to t–m transformation.

after 50 h autoclaving (Fig. 18). It seems obvious that a superficial phase transformation was initiated by the wear test as evidenced by the contrast obtained in SEM in the largest zirconia grains, due to twinning during the t–m transformation (Fig. 19).

However, the very small changes in roughness and the XRD results indicate the minimal influence of wear and ageing on the structural integrity of the ZTA heads. Especially, considering that 50 h of ageing corresponds roughly to 50–200 years in vivo, this insures an almost full stability and integrity during the life expectancy of patients.

4. Conclusion

Kinetics of transformation was evaluated for as received or worn ZTA and 3Y-TZP femoral heads. Despite the presence of 3Y-TZP in the composite, no evidence of ageing was shown for the unworn ZTA implants even with an accelerated test of 50 h at 134 °C, 2 bars unlike previous studies on some ZTA where LTD was observed.[12,13] As expected, the monolithic 3Y-TZP exhibited significant degradation.

The area of the 3Y-TZP femoral head worn on a hip simulator is prone to a rapid ageing compared to a head straight from manufacture. This shows clearly for the first time that the prediction of resistance to ageing cannot be conducted without taking into account the process of wear related to the bearing surfaces of a hip joint.

For the ZTA implants tested in this work, the wear, however, seems less critical in the ageing behaviour.

Work is in progress to complete the global picture of ageing and its effect on the integrity of 3Y-TZP and ZTA heads by performing wear tests after accelerated ageing in autoclave and fatigue testing of as-received or aged femoral heads.

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