LETTER

Ageing effects on the nanoindentation response of sub-micrometric 3Y-TZP ceramics

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Yttria-stabilized tetragonal zirconia (Y-TZP) ceramics are used as prosthesis material in hip replacement in virtue of their strength, fracture toughness and biological compatibility [1–3]. A critical issue of the zirconia ceramics is the martensitic transformation from tetragonal to monoclinic (t → m) phase, which can be triggered by mechanical stresses or humid environments [4]. This transformation leads to surface roughening [5], microcraking and grain pullout [6, 7]. Moreover, the presence of monoclinic zirconia changes the hardness of the prosthesis surface. In retrieved zirconia femoral heads, it was reported that the nanoindentation hardness decreased with the increase of the monoclinic phase content [8]. The t → m transformation is not an issue limited to bulk zirconia ceramics as it was also observed in alumina–zirconia composites [9]. Since one of the most important factors affecting the nucleation and growth of the t → m transformation is the grain size [4], in this work the surface mechanical response, specifically hardness and Young's modulus, of two thermally aged 3Y-TZP ceramics with different grain size is evaluated by depth-sensing indentation tests. Ageing treatments

have been shown to replicate the same t → m transformation effects observed in retrieved prostheses [10] and the assessment of the surface mechanical behaviour can give useful information about the wear and contact properties of these aged ceramics.

Two 3 mol% yttria-stabilized zirconia ceramics (3Y-TZP) were obtained starting from two different commercial powders (Kyocera, Japan). They were both mixed with 0.3 mol% of Al_2O_3, CIPed and HIPed. The final densities were almost 100% of the theoretical one and the mean grain sizes were 0.7 μm and 0.2 μm, respectively. In the following, these ceramics will be labelled as ZR07 and ZR02. Samples were cut, machined and polished. The ageing treatments were carried out in autoclave at 121 °C with a water vapour pressure of 0.235 MPa for different times: 12, 24, 36, 48 and 60 h. For each ageing time, one sample for each material was used. The depth-sensing indentation tests were carried out using a Berkovich diamond tip on a commercial nanoindenter (Nano Indenter XP™, MTS Systems Corporation, Oak Ridge, TN, USA). Four peak loads were used to investigate the indentation hardness and Young's modulus as a function of penetration depth: 10, 100, 200 and 400 mN. In each sample, at least 10 indentations were made at each peak load. Indentation hardness (H) and Young's modulus (E) were calculated by the data acquisition software of the nanoindenter (TestWorksTM ver. 4.06A) based on the model of Oliver and Pharr [11]. For the Young's modulus calculation, a Poisson ratio of 0.32 [12] was considered. The experimental data were statistically scrutinized by ANOVA [13].

As a deeper characterization of the nanoindentation response of these ceramics in un-aged state was

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reported in a previous paper [14], here we will focus mainly on the mechanical properties of the aged samples. In all the tested samples, the load–unloading curves were characterized by a substantial continuity, i.e. without any large pop-in or pop-out, independently of the ageing time and peak load. In Fig. 1, the contact depth is reported as a function of peak load and ageing time. When a same peak load was used, the contact depth was larger in ZR07 than in ZR02. If the contact depth in ZR02 was unaffected by the ageing time (Fig. 1a), the contact depth in ZT07 increased by increasing the ageing time (Fig. 1b). For both ceramics, the variation of the contact depth with the peak load gives an indication of the sampling depth of our nanoindentation tests so that it can be compared to the microstructural scale length of the tested ceramics, i.e. the mean grain size, and to the sampling depth of other investigation techniques such X-ray diffraction or

Raman piezospectroscopy. These techniques are commonly employed for the evaluation of the monoclinic phase content at the surface of zirconia ceramics but their sampling depth is at least 5 μm [5, 15].

In Fig. 2, the hardness of the two zirconia ceramics is shown as a function of ageing time and peak load. As can be seen, the hardness in ZR02 was constant without any influence of the ageing time or peak load (Fig. 2a). This is in agreement with the results of Tsukuma et al. [16] according to which if the mean grain size is smaller than 0.4 μm no t → m transformation occurs in 3Y-TZP ceramics. In particular, the results of the 10 mN tests are worthy to be noted. Even after an ageing time of 60 h, no indication of significative modification was observed at this low contact depth (Fig. 1a). On the contrary, the hardness in ZR07
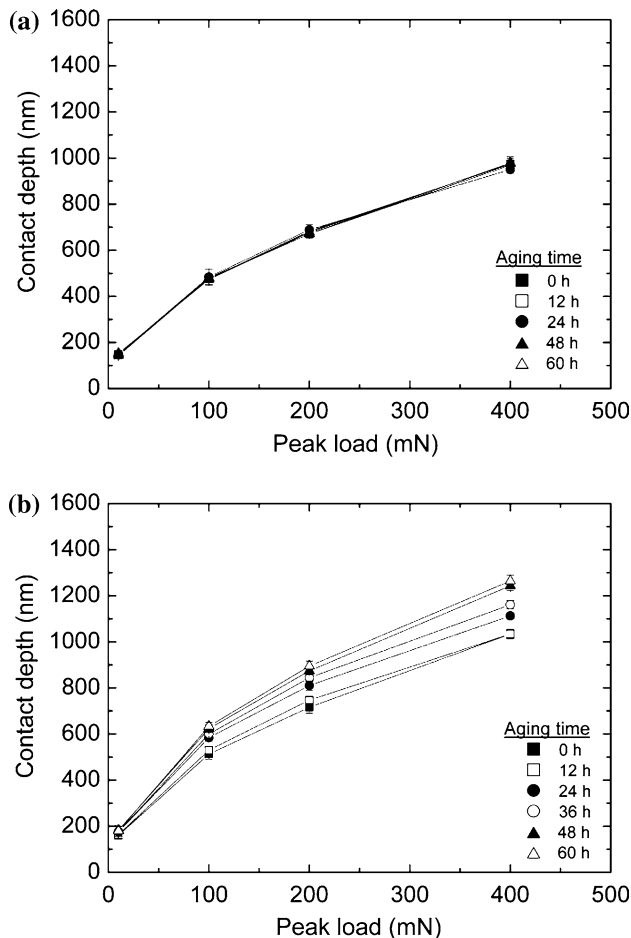
Fig. 1 Contact depth as a function of peak load and ageing time. Each point is the mean of at least 10 indents and errors bars are ±1 standard deviation. (a) 3Y-TZP with a mean grain size of 0.2 μm (ZR02); (b) 3Y-TZP with a mean grain size of 0.7 μm (ZR07)
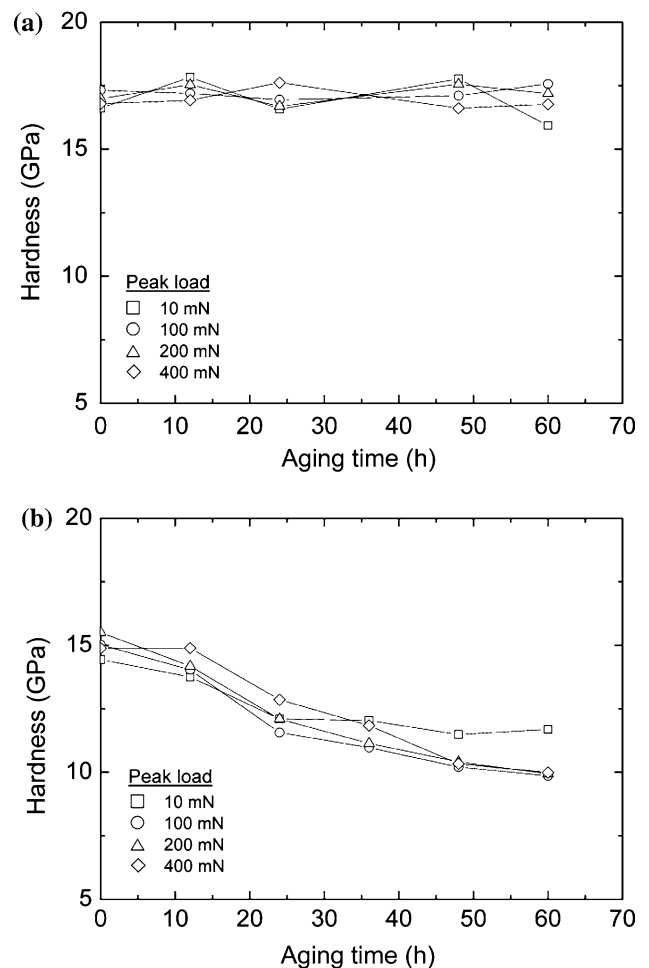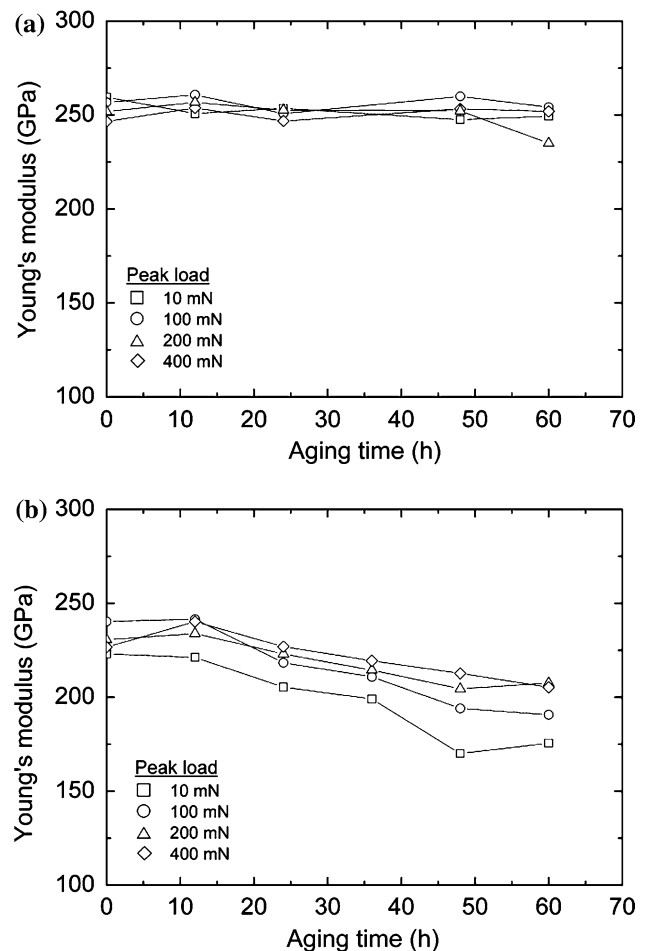

Fig. 2 Hardness as a function of ageing time and peak load. Each point is the mean of at least 10 indents. (a) ZR02. Typical data dispersion as follows: 13, 7, 4 and 4% for peak load of 10, 100, 200 and 400 mN, respectively. (b) ZR07. Typical data dispersion as follows: 15, 6, 5 and 3% for peak load of 10, 100, 200 and 400 mN, respectively

significantly decreased with the increase of the ageing time. For peak loads of 100 mN and 200 mN, the decrease was observed just after the 12-h treatment. For all the peak loads, the decrease rate was the highest for an ageing time between 12 h and 24 h. After the 24-h treatment, there was a steady hardness decrease for the high-load indentations (100, 200 and 400 mN) which seems to slow down for the longer ageing times, 48 h and 60 h, when the hardness reached a common value of about 10 GPa. For the 10-mN indentations, the hardness reached a steady value of about 12 GPa after an ageing time of only 24 h.

The general hardness decrease with the ageing time must be ascribed to the increase of monoclinic phase content as already reported by Catledge et al. [8]. Even if their un-implanted zirconia was harder than the un-aged zirconia of this study, the decreasing trend of the hardness with the monoclinic phase content reported by those authors looks very similar to that reported here as a function of ageing time. Curiously, even if the hardness of monoclinic zirconia phase is in the range 6–7 GPa [17, 18], neither in the work of Catledge et al. [8] nor in our experiments values close to that range were found. In literature, no content profile of the monoclinic phase is reported for depths comparable to those shown in Fig. 1. Notwithstanding this, from the hardness values plotted in Fig. 2, we can infer some simple hypotheses about the t → m transformation at these depths. Considering the 10-mN indentations, we see that the hardness did not change by increasing the ageing time over 24 h. This implies that, after the 24-h treatment, there was no further increase of monoclinic phase content in a surface thickness comparable to that sampled by the 10-mN indents. This thickness can be quantified considering the analogy of testing a film on a substrate. To avoid the influence of the mechanical properties of the substrate, the penetration depth in the film should be less than one tenth of the film thickness [19]. From the contact depth values shown in Fig. 1, we see that the thickness of the saturated surface layer after 24 h should be at least 1.6 μm, i.e. about two grain layers. One possible explanation for the monoclinic content saturation is that the t → m transformation was hindered by the microcracks introduced by the previously transformed grains which left a good fraction of tetragonal grains in an unconstrained state and hence less prone to transformation [20]. At larger scales, such a saturation was already observed in aged Y-TZP ceramics [21, 22]. The decreasing trend of the hardness with the ageing time for the higher peak loads (100, 200 and 400 mN) points out that the thickness of the

transformed (or saturated) surface layer increases with the ageing time, as expected. Since for peak load of 100, 200 and 400 mN the hardness after the 60-h treatment does not significantly change with respect to the 48-h treatment, it can be argued that the thickness of the saturated surface layer after the 48-h treatment reached a value of about 12 μm, as inferred from the film-on-substrate analogy and Fig. 1. Another indication, which can be inferred from the data of Fig. 2b is that the saturation level of the monoclinic phase content can be lower at the surface, say the first two micrometers, than at the interior of the material as, after the 36-h treatment, the hardness at 10 mN was statistically higher than at 100 mN and 200 mN. The higher hardness at the very first surface layer (tests at 10 mN) is even more evident after the 60-h treatment.

The Young's modulus of the two zirconia ceramics is shown in Fig. 3 as a function of ageing time and peak

Fig. 3 Young's modulus as a function of ageing time and peak load. Each point is the mean of at least 10 indents. (a) ZR02. Typical data dispersion as follows: 14, 9, 5 and 4% for peak load of 10, 100, 200 and 400 mN, respectively. (b) ZR07. Typical data dispersion as follows: 10, 6, 5 and 3% for peak load of 10, 100, 200 and 400 mN, respectively

load. As for the hardness, in case of ZR02 we did not observe any influence of the ageing time or peak load confirming the very good stability of this ceramic (Fig. 3a). On the other hand, after a treatment of at least 24 h, the Young's modulus of ZR07 steadily decreases with the increasing of the ageing time independently of the peak load (Fig. 3b). This steady decrease continued up to a treatment of 60 h only for the 400-mN indentations. For the other peak loads, the Young's modulus of the 60-h aged samples was not statistically different from the 48-h aged samples. After an ageing time of 60 h, the initial values of Young's modulus decreased of about 10–20%, depending on the peak load (Fig. 3b).

The general decrease of the Young's modulus with the increase of the ageing time was again due to the increase of monoclinic phase content. However, differently from the hardness, the change of the Young's modulus cannot be due to the intrinsic properties of the monoclinic phase, as its Young's modulus is about 240 GPa [23] comparable to that of the tetragonal phase. The only plausible explanation for the Young's modulus decrease is the presence of microcracks associated to the volume expansion of the t → m transformation. The observation that after a 12-h treatment the hardness was already affected by the presence of monoclinic zirconia but the Young's modulus was not, compare Figs. 2b and 3b, seems to suggest that microcracking is not a concomitant process with the t → m transformation, at least in the initial stage. As indicated by the decreasing trend of the Young's modulus, the depth of the microcracked region increased with the increase of the ageing time. Due to the longer range of the elastic field with respect to the plastic field [24], the Young's modulus was influenced by the peak load in a different way than the hardness. The Young's modulus measured at the higher peak load was in fact slightly or significantly higher than that measured at lower peak loads (Fig. 3b). If the 10 mN Young's modulus became lower than that measured at the other peak loads already after an ageing time of 12 h, the 100 mN Young's modulus became significantly lower than that measured at 200 mN and 400 mN only after an ageing time of 36 h. This behaviour reflects the ratio between the depth of the microcracked region and the range of the elastic field associated to each peak load. If the elastic field extended beyond the microckracked region, the elastic response received a contribution also from the crack-free region. The larger is the crack-free region sampled by the elastic indentation field, the higher is the resulting Young's modulus.

As a final comment, it is fair to make present that our conclusions regarding the thickness of the saturated layer and the presence of microcracking in the transformed layer have been formulated only on the basis of the nanoindentation outcomes. Of course, more work is needed, especially with other characterization techniques, in order to give a more clear picture of the microstructural evolution of the first surface layer in these ceramics after thermal ageing. However, even considering very cautiously our speculative inferences, the present experimental investigation clearly shows how the surface mechanical behaviour of aged zirconia ceramics is influenced, at different sampling depths, by ageing time and mean grain size. In this respect, the very good mechanical stability shown in all the situations by the 200-nm grained zirconia has to be emphasized.

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