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Surface crystalline phases and nanoindentation hardness of explanted zirconia femoral heads

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One new and nine explanted zirconia femoral heads were studied using glancing angle X-ray diffraction, scanning electron microscopy, and nanoindentation hardness techniques. All starting zirconia implants consisted only of tetragonal zirconia polycrystals (TZP). For comparison, one explanted alumina femoral head was also studied. Evidence for a surface tetragonal-to-monoclinic zirconia phase transformation was observed in some implants, the extent of which was varied for different in-service conditions. A strong correlation was found between increasing transformation to the monoclinic phase and decreasing surface hardness. Microscopic investigations of some of the explanted femoral heads revealed ultra high molecular weight polyethylene and metallic transfer wear debris.

1. Introduction

The majority of zirconia ball heads [1] manufactured for use in total hip replacements are known as tetragonal zirconia polycrystal (TZP) ceramics. These ceramics exhibit a high fracture toughness that can be linked to the transformation from the metastable tetragonal phase (T) to a monoclinic phase (M) during crack propagation [2]. The T–M transformation is accompanied by a volume expansion whose stress field acts in opposition to the stress field that promotes the propagation of the crack. The toughness is improved because the energy associated with crack propagation is dissipated in the transformation process itself as well as in overcoming the compression stresses of volume expansion. Ironically, however, stability of the metastable tetragonal phase is crucial to successful wear performance of the joint. The surface tetragonal grains are not constrained by the matrix and can transform either spontaneously or due to abrasive wear, resulting in compressive layers just under the surface [3]. While this T–M transformation and the associated compressive stress in the ball head surface may in the short term improve the mechanical and wear performance of the joint, successive steps can originate in surface cracking, grain pullout, and a subsequent increase in wear of the surrounding ultra-high molecular weight polyethylene (UHMWPE) component [4]. As compared to zirconia, alumina is a harder material. However, in ultimate compressive load (UCL) tests of ball heads following the ISO 7206-5 standard [5], the UCL of zirconia heads can measure up to 2.5 times higher than that of alumina ball heads of the same diameter and neck length (for a comprehensive review see Piconi and Maccuaro [1]).

It should be noted that recent improvements in manufacturing of zirconia femoral heads involving hot isostatic pressing and sterilization steps have resulted in much higher quality zirconia with substantially less monoclinic phase. One report has shown that phase transformation of zirconia femoral heads causes deterioration of the surface roughness *in vivo* after total hip arthroplasty with a rise in monoclinic content from 1% to about 30% on the surface of the heads [6]. However, it has been established *in vitro* [7] that the presence of less than 40% monoclinic phase does not result in any measurable increase in polyethylene wear. In any case, wear tests involving zirconia against polyethylene cups have confirmed low wear rates comparable to those for alumina and substantially lower than those of metals [8].

In this paper, we discuss how surface hardness of explanted zirconia femoral heads that have undergone various degrees of phase transformation during service in the body is influenced by the corresponding surface crystalline phases. The surface hardness of an explanted alumina femoral head was measured for comparison. Electron microscopy was also used to examine the wear surfaces of the explanted femoral heads.

2. Experimental procedures

All femoral heads used in this study had a 28 mm diameter, standard neck and type I taper. The control in this study is a new head that has not been implanted. All

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TABLE I Summary of femoral head surface phase structure and hardness

Femoral head designation	Femoral head material	XRD surface phase identification	XRD integrated intensity ratio of monoclinic (− 111)/ tetragonal (101) peaks	Nanoindentation hardness (GPa)
A	Alumina	Rhombohedral	Not applicable	29.6
B	Zirconia	Tetragonal	0	18.4
C	Zirconia	Tetragonal	0	17.5
D (new)	Zirconia	Tetragonal	0	17.4
E	Zirconia	Monoclinic + tetragonal	0.0415	17.3
F	Zirconia	Monoclinic + tetragonal	0.2013	15.6
G	Zirconia	Monoclinic + tetragonal	0.394	15.2
H	Zirconia	Monoclinic + tetragonal	0.569	14.5
I	Zirconia	Monoclinic + tetragonal	1.240	13.1
J	Zirconia	Monoclinic + tetragonal	1.472	12.2
K	Zirconia	Monoclinic + tetragonal	3.077	10.6

heads were cleaned in an acetone bath for 15 min prior to measurements by X-ray diffraction (XRD), nanoindentation, and scanning electron microscopy (SEM). It was noted that the ultra high molecular weight polyethylene and metallic transfer wear debris was evident on some of the heads.

Glancing angle XRD (Cu-K_α anode) was used with a 1-degree incident beam directed at the topmost surface of the ball, opposite to the bore entrance. This topmost surface corresponds to the area where most of the cyclic loading is expected. Surface hardness of the femoral heads was measured (also at the topmost surface of the ball) to a depth of 700 nm using a Nanoindenter XP system with continuous stiffness attachment. The indenter was a diamond Berkovich tip with nominal 50 nm radius. A total of 15 indents were made on each head at different locations with remarkably consistent results.

3. Results and discussion

Table I shows a summary of the femoral heads tested in this study along with their measured surface phase structure and hardness after patient retrieval. The hardness values shown here are taken from a surface depth of 450 nm. The sample labeled ''D (new)'' is the un-implanted TZP head and served as a control in this study. Sample A is the explanted alumina head that was determined to have a rhombohedral crystal structure and had the highest measured hardness of 29.6 GPa. This value is consistent with the nanoindentation hardness of 29.8 GPa for alumina abrasive particles [9]. Two of the explanted zirconia heads (B and C) did not show transformation into a monoclinic phase, possibly due to a shorter duration of service while in the patient and therefore less strain on the femoral head. In fact, clinical data obtained for sample C shows that it was implanted for only 10 months. This should be compared with sample J and K which were implanted for 60 and 62 months, respectively, and had a much higher degree of T–M transformation with correspondingly lower hardness values. The average measured hardness with standard deviation of the three tetragonal heads (B, C, and D) is 17.8 $\pm$ 0.6 GPa. By comparison, the measured hardness for samples J and K were 12.2 $\pm$ 1.0 GPa and 10.6 $\pm$ 0.3 GPa, respectively.

Fig. 1 shows XRD patterns from the rhombohedral alumina (sample A), tetragonal zirconia (sample D), and the tetragonal + monoclinic zirconia (sample G) femoral heads. The filled triangles indicate peaks indexed to the tetragonal zirconia phase while the open circles refer to the monoclinic phase. The ratio of integrated intensity of the monoclinic (− 1 1 1) and tetragonal (1 0 1) peaks is given in Table I and is meant to provide a measure of the relative amount of these phases in the surface region probed by XRD as well as by nanoindentation. This assumes that no preferred grain texture is present from one ball to the next. This is believed to be a reasonable assumption considering the powder sintering process used in their fabrication. From Table I and as plotted in Fig. 2, it can be seen that with increasing monoclinic content, the measured hardness drops steadily for a ratio up to about 1.5. Although the data is limited above this ratio, the trend suggests that the rate of change in hardness is dropping, with a possible steady-state value

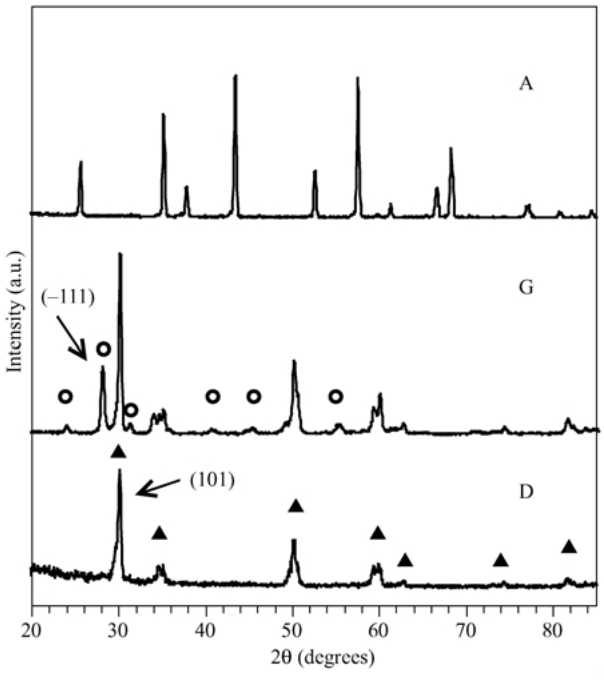

Figure 1 Glancing angle XRD patterns of explanted femoral heads for samples A, G, and D taken with Cu-K_α radiation. The diffraction peaks belonging to the tetragonal zirconia phase are labeled by (▲) and peaks belonging to the monoclinic phase are labeled by (○). All diffraction peaks for sample A can be indexed to the rhombohedral alumina.

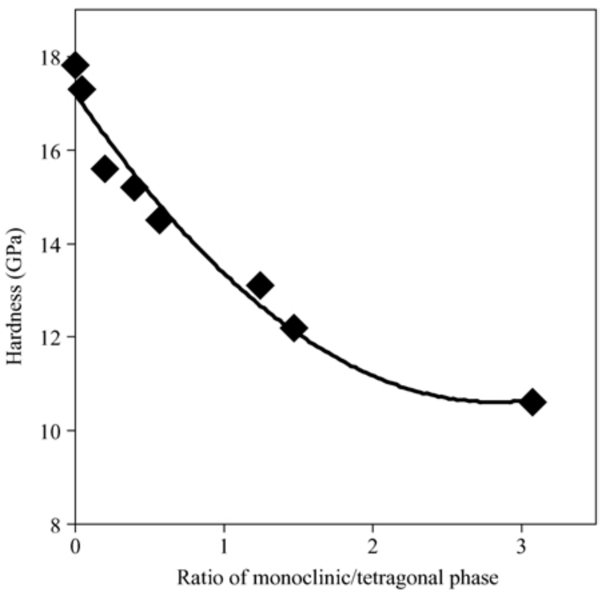

Figure 2 Dependence of femoral head nanoindentation surface hardness on the XRD integrated intensity ratio of the monoclinic zirconia (− 1 1 1) peak to tetragonal zirconia (1 0 1) peak. The solid curve is a quadratic fit to the data and drawn as a guide to the eye.

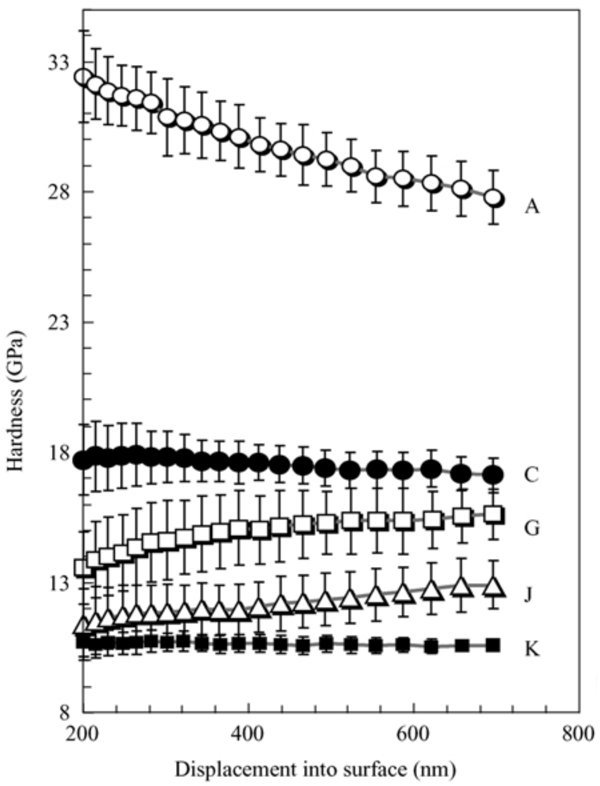

Figure 3 Nanoindentation surface hardness of femoral heads (A, C, G, J, and K) as a function of indentation depth. Sample A is for alumina while the remaining samples are zirconia femoral heads. The data shown with representative error bars are an average over the fifteen independent measurements on the same sample.

in hardness of about 10–10.5 GPa eventually being reached for samples with high content of the monoclinic phase. The data trend for Fig. 2 was plotted using a quadratic fit simply to provide a visual guide to the eye, and convey the general trend in the data. The quadratic fit to the hardness data is shown below.

$$\mathrm{H\ (GPa)} = 17.205 - 4.6715x + 0.8276x^2$$

where H is the hardness in GPa and x is the ratio of integrated intensity of the monoclinic (− 1 1 1) and tetragonal (1 0 1) diffraction peaks and is listed in Table I.

The general trend in the hardness data may be explained as follows: As more monoclinic phase is formed the associated volume expansion lowers the local atomic density, and therefore hardness, of the material. The volume expansion initially improves toughness by placing cracks in compression and stops them from propagating. Continued transformation to monoclinic phase, however, may result in the inability of the material to support this expansion without subsequent crack nucleation, propagation, and/or grain pullout [4]. This is especially true near the surface where compressive stresses tend to accumulate. The onset of these defects is more likely to initiate on the surface of the femoral head. The transition point marking the onset of accelerated grain boundary degradation and crack formation may be associated with the change in the observed rate of hardness decrease shown in Fig. 2. Beyond a certain monoclinic content the surface stresses more rapidly accelerate the formation of mechanical defects. The surface hardness eventually approaches a more constant value since the resulting plastic deformation releases localized compressive stress near the surface that would otherwise aid in maintaining hardness [10]. Experimental measurements of fracture toughness as a function of monoclinic phase content will be needed to further confirm this explanation.

Fig. 3 shows the nanoindentation hardness as a function of indentation depth for femoral heads A, C, G, J, and K. Each data point represents the average of 15 indents and is plotted with a standard deviation error bar. Again, sample A is the alumina head and exhibits the highest hardness as expected. In comparison to zirconia, it shows a slight decrease in hardness with increasing indentation depth. This could be due to an indentation size effect (ISE) whereby the measured hardness increases with decreasing indentation load and which is especially pronounced for ceramics. The ISE has been attributed to a variety of contributions including the elastic recovery of the indentation [11], surface dislocation pinning [12], dislocation nucleation [13], deformation band spacing [14], surface energy of the test specimen [15], and statistical measurement errors [16]. Residual stress may also influence measured hardness values. Both conventional and nanoindentation hardness tests reveal an apparent decrease in hardness with increasing stress from compression to tension. Pharr *et al.* [17] have shown through finite element simulations that this effect is not a real change in hardness but occurs because the procedure for determining contact area from the nanoindentation load-displacement data does not account for pileup around the indentation. Whether the observed trend of decreasing hardness with increasing indentation depth for the alumina head is due to an ISE or to the effect of compressive stresses would require further investigation.

For samples C, G, J, and K, characterized by increasing monoclinic content, respectively, the average hardness values over the range of depth are as expected.

With increasing monoclinic content, the average hardness of the zirconia femoral heads decreases and this holds throughout the range of indentation depth. One might expect that since the T–M transformation is probably on the order of many microns in surface depth, the measured hardness for each head would, for large bulk depth measurements, reach the value characteristic of tetragonal zirconia (i.e. about 17.5 GPa).

Fig. 4(a) and (b) shows low magnification SEM images taken from an explanted alumina head and an explanted zirconia head on regions were no visible metallic transfer wear was observed. Compared to the zirconia head, the alumina head showed more evidence of surface defects and pitting. Studies of wear of the UHMWPE component against alumina or zirconia show that surface roughness has a large influence on wear rates [18, 19]. The manufacturing and/or finishing process of the alumina head may result in higher porosity and surface roughness than the zirconia head. Fig. 4(c) shows the metallic and UHMWPE transfer wear debris sometimes observed on the zirconia heads. The surface becomes much more roughened in these localized areas and therefore the potential for accelerated wear is evident.

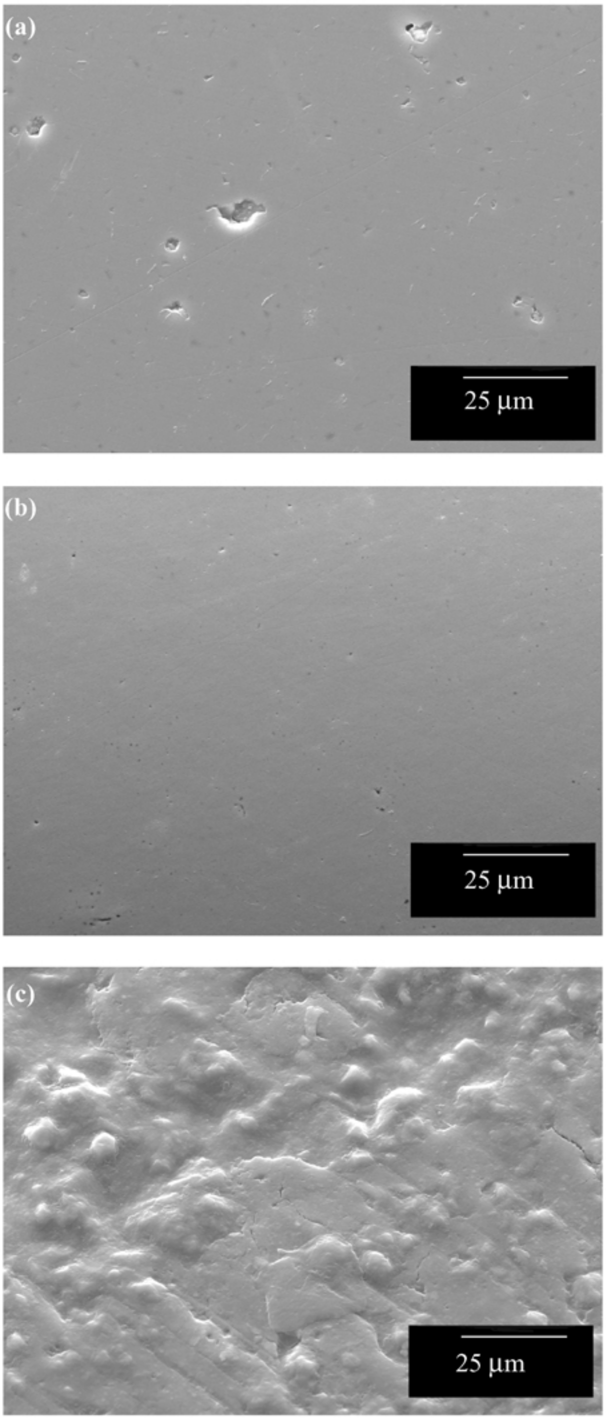

Figure 4 Low magnification SEM images from explanted (a) alumina and (b) zirconia femoral heads. The alumina head (a) showed more pitting and higher surface roughness than the zirconia head (b). The micrograph in (c) shows an area from the zirconia femoral head with metallic and polyethylene wear debris on the surface.

4. Summary

The increasing surface transformation from tetragonal to monoclinic phase observed for explanted zirconia femoral heads is strongly correlated to a decrease in measured surface hardness. This can be explained by the volume expansion associated with this transformation and the associated decrease in local atomic density. The rate of hardness decrease is lowered beyond a certain monoclinic content and appears to reach a constant value of about 10.5 GPa. Above this monoclinic content, the zirconia may undergo accelerated mechanical degradation due to the inability of the material to support the volume expansion without subsequent crack nucleation, propagation, and/or grain pullout. This transition point marking the onset of accelerated grain boundary degradation and crack formation may be associated with the change in the observed rate of hardness decrease. Metallic and UHWMPE transfer wear with subsequent roughening typically observed on the explanted femoral heads could lead to accelerated degradation and wear of the implant.

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