Reduced Wear of Cross-linked UHMWPE Using Magnesia-stabilized Zirconia Femoral Heads in a Hip Simulator

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Abstract

Background To reduce wear, the ideal bearing surface in joint arthroplasty should be smooth and hydrophilic. Ceramics generally offer better wettability than metals and can be polished to a smoother finish. However, clinical studies have found no reduction in liner wear when using yttria-stabilized zirconia (Y-TZP) instead of cobalt chromium alloy (CoCr) femoral heads.

Question/purposes We (1) determined whether a hard, diamond-like carbon (DLC) coating would enhance the wettability of CoCr and magnesia-stabilized zirconia (Mg-PSZ) femoral heads without increasing roughness, and (2) compared their wear performance.

Methods In an observational study limited to CoCr and Mg-PSZ heads, we measured roughness and contact angle on as-received and DLC-coated heads. Eight heads then were subjected to 11 million cycles of wear in a hip simulator against cross-linked ultrahigh molecular weight polyethylene (XLPE) liners.

Results Mg-PSZ femoral heads were smoother and more hydrophilic than CoCr heads. Although DLC coatings did not reduce roughness, they reduced the contact angle of CoCr and Mg-PSZ substrates, which may provide enhanced lubrication in vivo. In hip simulator tests, liners bearing against CoCr heads wore at a greater rate compared with Mg-PSZ heads. The DLC coating on Mg-PSZ heads did not reduce wear further.

Conclusions The wear rate of XLPE versus Mg-PSZ was seven times less than CoCr heads, probably owing to lower roughness and greater wettability of Mg-PSZ heads.

Clinical relevance The use of Mg-PSZ femoral heads should lead to reduced wear in vivo compared with CoCr heads, but the clinical benefit of DLC-coated Mg-PSZ is unclear.

Introduction

CoCr alloys are widely used as bearing surfaces against UHMWPE for knee and hip arthroplasties [6–8]. CoCr is harder and more resistant to corrosion than previous metals used in joint replacement, such as stainless steel, but during normal wear releases embedded carbides; these carbides become third bodies that can scratch the surface and accelerate UHMWPE wear [1, 13, 46]. Additionally, CoCr surfaces exhibit low wettability, with reduced lubrication properties owing to the lower surface energy associated with metal oxide surfaces [13].

Ceramic materials generally offer a harder and more hydrophilic surface than CoCr and can be polished to a lower roughness [1, 12, 13, 46]. In hip wear simulator studies, Y-TZP [4] femoral heads induced less UHMWPE wear compared with CoCr heads [11, 39, 43], and a clinical study of patients having bilateral THAs comparing the two

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materials found zirconia heads exhibited less wear than CoCr heads [23]. However, recent clinical studies have reported no reduction in cross-linked UHMWPE (XLPE) wear when using Y-TZP, often generically referred to as “zirconia” [34], compared with CoCr femoral heads [17, 20, 21, 31, 45]. The failure to reduce wear might be explained by phase transformation and degradation of the metastable Y-TZP femoral heads [10, 15, 16, 26, 36, 37]. In contrast, Mg-PSZ [5] resists phase transformation and degradation in vivo and in artificial aging studies, maintaining its smooth surface finish and hardness [36, 37], but no clinical or simulator data are available to evaluate its potential to reduce wear.

DLC coatings are among several surface modification techniques proposed to enhance bearing surfaces in total joint arthroplasties by conferring the strength and stability of diamond, but at a lower cost [14, 25, 33]. The DLC deposition process can be tailored to produce a strong amorphous film with no grain boundaries and hardness values ranging from 10 to 80 GPa [33]. However, DLC-coated titanium alloy femoral heads failed in clinical use [47], and DLC-coated CoCr femoral heads reportedly do not reduce wear compared with uncoated CoCr heads in hip simulator tests [18], but the durability and wear performance of DLC-coated ceramic materials is unknown. DLC-coated Mg-PSZ reportedly forms a stronger construct than DLC-coated CoCr [35], suggesting an improved resistance to abrasive wear. The potential benefits of DLC-coated Mg-PSZ to reduce wear, however, are unknown.

In this observational study, we therefore determined whether (1) the addition of a hard DLC coating enhanced the wettability of CoCr and Mg-PSZ substrates without increasing surface roughness, (2) the use of Mg-PSZ resulted in less wear compared with CoCr femoral heads, and (3) the use of DLC-coated Mg-PSZ femoral heads further reduced wear. In addition, we qualitatively evaluated whether (4) the femoral head materials exhibited progressive roughening or other degradation of the bearing surface during the wear test.

Materials and Methods

We examined five never-implanted Mg-PSZ [5] (Xylon Ceramic Materials, Inc, Alfred, NY, USA) and five wrought CoCr [6, 8] (DiSanto Technology, Inc, Shelton, CT, USA) 28-mm femoral heads. The surfaces of an additional five wrought CoCr and five Mg-PSZ 28-mm femoral heads were modified with an amorphous DLC coating by a proprietary radiofrequency plasma chemical vapor deposition (RF-CVD) process (Diamonex, Morgan Advanced Ceramics Inc, Allentown, PA, USA). The heads to be coated were fixed to a water-cooled electrode in a

vacuum chamber. After a negative bias was applied to the electrode, charged gases were injected into the chamber, forming plasma that bombarded the exposed surface with ions until a final coating thickness of approximately 3 μm was achieved. The resulting DLC coating was hydrogenated and generally amorphous, with no long-range crystal structures and approximately 20% to 30% sp^3 bonding, according to the coating vendor, exhibiting a nano-hardness of approximately 23 GPa [38]. For comparison purposes, pure diamond crystals consist of only carbon atoms arranged in a tetrahedral configuration with 100% sp^3 covalent bonds (and a hardness of approximately 100 GPa), whereas graphite contains no sp^3 bonding [33]. As the coating was applied near ambient temperature, the substrate did not expand during the deposition process, and dimensional tolerances were maintained.

We made surface topography measurements by three-dimensional, noncontact optical profilometry to determine whether the DLC coating improved roughness relative to the uncoated substrate. Optical profilometry phase-shifting scans (ZoomSurf 3D; Fogale Nanotech, Nîmes, France) were performed on each specimen at a magnification of $\times 10$ (633 $\mu\text{m} \times 476 \mu\text{m}$ scan area), using a monochromatic, red-light source (wavelength = 640 nm) and a CCD camera target (763 $\times$ 572 pixels), for a vertical resolution of approximately 0.2 nm and a lateral resolution similar to light microscopy (approximately 0.6 μm). Calibration of the profilometer was verified by scanning a NIST-traceable 9.1-nm step-height standard (VLSI Standards, Inc, San Jose, CA, USA). After subtracting the spherical form, average roughness (S_a) and root-mean-square roughness (S_q) [3] were calculated as the average of three scans per specimen (at the pole, equator, and midway between the pole and equator of the femoral head), using Mountains-Map® Topography ST 4.1 software (Digital Surf, Besançon, France).

Relative wettability was measured as the contact angle by the sessile drop method [41] using microfiltered, distilled water and a custom-designed micropipette-based platform. Femoral heads were cleaned ultrasonically in stages before testing, with 10 minutes in methanol, 20 minutes in acetone, and 5 minutes in isopropyl alcohol [41]. The femoral heads were mounted with the central axis horizontal, and consecutive 0.25- μL droplets of distilled water were imaged digitally as a silhouette against a bright background within 5 seconds of being deposited, using glue-free cotton swabs to dry the specimen surface between drops. Care was taken to avoid distorting the droplet from the kinetic energy of its delivery [30]. Because the femoral heads were never implanted or subjected to wear tests, their surfaces were assumed to be homogenous, thus, droplets were imaged in one location near the equator of each head, in approximately the same

location scanned for one of the roughness measurements, with the center axis horizontal. The contact angle of each specimen was calculated using the average of the last 10 of 20 total droplets, to minimize the influence of any residual organic material on the surface [2]. Contact angles were calculated using ImageJ software (National Institutes of Health, Bethesda, MD, USA) with the low-bond axisymmetric drop-shape analysis (LB-ADSA) plug-in [44].

Two CoCr, three Mg-PSZ, and three DLC-Mg-PSZ femoral heads were randomly selected for wear tests in an eight-station hip wear simulator. DLC-CoCr specimens were not considered for wear tests because DLC-coated CoCr specimens reportedly exhibit poor adhesion in scratch tests [35], and previous hip simulator studies suggest DLC-coated CoCr heads produce greater gravimetric wear compared with uncoated CoCr [18] and alumina femoral heads [40]. Eleven UHMWPE acetabular liners (eight wear specimens and three soak controls) were machined from GUR 1050 that had been cross-linked to 100 kGy by gamma irradiation and remelted at 150°C for 5 hours (MediTECH[®], Fort Wayne, IN, USA); however, they were not subsequently sterilized. The liners were presoaked at room temperature until weight gain stabilized at a low value. Specimens were tested in an EW series, eight-station hip wear simulator (Materials Technology Corporation, La Canada, CA, USA), an anatomically inverted design, at a frequency of 1.25 Hz using a Paul loading curve [32] with peak loads of 2.3 to 2.4 kN up to 3 million cycles, and peak loads of 2.4 to 2.5 kN up to 11 million cycles thereafter, following pressure transducer maintenance and recalibration. A solution of 25% bovine serum (6.6 gm% total protein before dilution; HyClone, Logan, UT, USA) with 20 mmol/L EDTA and 0.3% sodium azide was prepared and vacuum filtered through 0.2- μ m low-protein binding filters for use as a lubricant, and an eight-channel peristaltic pump (Rainin Instrument LLC, Oakland, CA, USA) dripped distilled water into each station to replace evaporated water during the tests. The experiment was paused intermittently to adjust serum levels and monitor bulk serum temperature to within 0.5°C. After each stage (every 375,000 cycles for the first 3 million cycles, and every 500,000 cycles for the final 8 million cycles), XLPE wear was measured gravimetrically [9], and roughness of the pole region of each femoral head was measured by optical profilometry at $\times 10$ magnification, as described earlier. Finally, each liner/head wear couple was rotated to a different station before resuming the test, so that each wear couple spent 1.375 million cycles at each of the eight simulator stations during the course of the 11-million-cycle wear test.

The level of statistical significance associated with differences between the mean roughness measurements and between mean contact angle measurements of noncoated

and coated groups was calculated by a heteroscedastic, two-sided unpaired t-test (Excel, Microsoft Corp, Redmond, WA, USA). Soak control-corrected mass lost or gained during wear tests was plotted for each femoral head type as a function of the number of wear cycles completed, and linear and nonlinear regression were performed to determine the most appropriate curve fit after the liners stopped gaining weight. Regression curves for each type of femoral head were calculated and compared by Prism software (GraphPad Software, Inc, La Jolla, CA, USA). The slopes of the final portion of the regression curves were assumed to represent steady-state wear, allowing us to compare the wear rate of CoCr and Mg-PSZ femoral heads, and compare the wear rate of uncoated and DLC-coated Mg-PSZ femoral heads. Post hoc power analyses were performed assuming normally distributed data, known nonequal variances, and $\alpha = 0.05$ (Power on X, MMI-Software, Newcastle upon Tyne, UK). Briefly, the effect size was based on the difference between the means divided by the pooled variance, while the statistical power and the value of delta (δ) were based on the effect size and the number of specimens in each group. A threefold reduction in wear or wear rate compared with CoCr was considered to be clinically important. Statistical power greater than 0.80 was required to avoid Type II errors (low power means the null hypothesis cannot be rejected).

Results

The surface topography of CoCr heads was dominated by carbide inclusions on the order of 300 to 500 nm deep, whereas Mg-PSZ heads were characterized by small linear features, typically 100 μ m long and 50 to 150 nm deep, created during the final polishing process (Fig. 1). The DLC coating appeared to help fill in low points on the surface, reducing the depth of carbide inclusions found in CoCr surfaces, but the topographies of DLC-coated CoCr and Mg-PSZ specimens were similar to their respective uncoated substrates (Fig. 1). The DLC coating had little effect on surface roughness measurements of Mg-PSZ substrates (Table 1), whereas the DLC coating reduced S_a ($p = 0.06$; power = 0.55) and reduced S_q ($p = 0.03$) on CoCr substrates. Wettability (Fig. 2) was enhanced by the DLC coating, transforming CoCr from a hydrophobic surface ($\theta_c = 93.0^\circ$) to a hydrophilic surface ($\theta_c = 72.3^\circ$; $p < 0.001$) and reducing the contact angle of Mg-PSZ specimens (from $\theta_c = 78.6^\circ$ to 70.5° ; $p = 0.004$). The average contact angles of DLC-CoCr and DLC-Mg-PSZ were similar ($p = 0.15$; power = 0.29).

In hip wear simulator tests, all XLPE test liners initially gained weight relative to the soak controls, possibly owing to protein adsorption. Liners bearing against CoCr heads

Fig. 1A–D Representative surface plots of femoral heads from each group examined in this study are shown: (A) CoCr, (B) DLC-CoCr, (C) Mg-PSZ, and (D) DLC-Mg-PSZ. DLC coatings appeared to fill in small imperfections, especially for CoCr substrates, but did not change the overall topography. For all images, the spherical form has been removed. Lateral axes are $633 \mu\text{m} \times 475 \mu\text{m}$; the vertical axes of all images are fixed at 680 nm for comparison purposes (Magnification, $\times 10$).

Fig. 2A–D Representative droplets and contact angle (θ_c , average $\pm$ S.D.) for each specimen type are shown: (A) CoCr, $\theta_c = 93.0^\circ \pm 1.0^\circ$, (B) DLC-CoCr, $\theta_c = 72.3^\circ \pm 2.1^\circ$, (C) Mg-PSZ, $\theta_c = 78.6^\circ \pm 3.2^\circ$, and (D) DLC-Mg-PSZ, $\theta_c = 70.5^\circ \pm 1.4^\circ$. DLC coatings reduced contact angle relative to uncoated CoCr and Mg-PSZ substrates ($p < 0.0001$ and $p = 0.004$, respectively).

Table 1. Pretest average roughness and root-mean-square roughness data for each specimen type

Specimen	Sa (nm)*	Sq (nm)*
CoCr	24.8 ± 5.2	34.3 ± 5.6
DLC-CoCr	18.7 ± 2.4	26.1 ± 0.91
Mg-PSZ	8.49 ± 0.95	10.7 ± 1.1
DLC-Mg-PSZ	8.20 ± 0.39	10.6 ± 0.34

Sa = pretest average roughness; Sq = root-mean-square roughness; *average $\pm$ SD.

began to lose weight after 1.125 million cycles. Liners interacting with Mg-PSZ and DLC-Mg-PSZ heads began to lose weight after 3.5 million cycles, but overall exhibited a

net mass gain up to 8.5 million cycles (Fig. 3). Protein precipitation from the bovine serum was observed in all stations within the first 5000 cycles of each stage, but bulk serum temperature was similar among CoCr, Mg-PSZ, and DLC-Mg-PSZ stations (mean values of 34°C , 32°C , and 33°C , respectively). After 11 million total wear cycles, the original machining marks were obliterated completely, with liners bearing against CoCr heads exhibiting somewhat larger scratches than those bearing against Mg-PSZ or DLC-Mg-PSZ (Fig. 4). Wear mass lost from liners bearing against CoCr femoral heads (average of 68.6 mg) was more than an order of magnitude greater ($p = 0.11$; power = 0.99 , $\delta = 7.6$) than those bearing against Mg-PSZ heads (average of 4.0 mg), whereas liners bearing against DLC-Mg-PSZ

Fig. 3 The plot shows the average gravimetric XLPE liner bearing wear against CoCr, Mg-PSZ, and DLC-Mg-PSZ femoral heads. All liners initially gained weight (“negative” wear) compared with the soak controls. Liners bearing against CoCr heads exhibited an overall regression curve (dotted line) best represented as a second-order polynomial. Liners bearing against Mg-PSZ and DLC-Mg-PSZ heads exhibited linear wear rates and lower steady-state wear rates compared with CoCr.

Fig. 4A–D These photographs of typical XLPE liner surfaces show the articular surface of a (A) soak control with machining marks, and test liners after 11 million cycles bearing against (B) CoCr alloy, (C) Mg-PSZ, and (D) DLC-coated Mg-PSZ femoral heads (Magnification: $\times 300$).

exhibited similar wear compared with uncoated Mg-PSZ (Table 2). Regression analyses revealed that a second-order polynomial provided the best overall fit ($p < 0.001$) for liners bearing against CoCr heads, whereas linear regression was better for the Mg-PSZ and DLC-Mg-PSZ

data ($p < 0.001$) (Fig. 3; Table 2). Comparing data from the last 2 million cycles (Table 2) revealed CoCr femoral heads induced a wear rate seven times greater ($p = 0.016$) than Mg-PSZ femoral heads (11.7 versus 1.7 mg/million cycles), whereas DLC-Mg-PSZ femoral heads exhibited a

Table 2. Summary of hip wear simulator data

Parameter	CoCr	Mg-PSZ	DLC-Mg-PSZ
*Mass lost after 11 million cycles			
Sample 1 (mg)	57.3	4.5	5.0
Sample 2 (mg)	79.8	3.0	5.4
Sample 3 (mg)	N/A	4.4	7.2
Average $\pm$ SD (mg)	68.6 $\pm$ 16	4.0 $\pm$ 0.8	5.9 $\pm$ 1
Is average mass lost different from Mg-PSZ?	No, $p = 0.11$; power = 0.99, $\delta = 7.6$	N/A	No, $p = 0.09$; power = 0.45, $\delta = 2.6$
†Overall regression model (after liners stopped gaining weight)			
Best fit	2 nd -order polynomial	Linear	Linear
Equation	$0.805x^2 - 2.59x + 0.979$	$1.57x - 13.5$	$2.28x - 19.7$
r^2	0.948	0.976	0.889
p Value	< 0.0001	< 0.0001	< 0.0001
‡Steady-state wear (final 2 million cycles only)			
Mean wear rate (mg/million cycles)	11.7	1.7	2.6
95% confidence interval	0.934 to 22.6	1.2 to 2.1	1.7 to 3.6
r^2	0.440	0.821	0.745
p Value	0.037	< 0.0001	0.0002
Is wear rate different from Mg-PSZ?	Yes, $p = 0.016$	N/A	No, $p = 0.06$; power = 0.75, $\delta = 3.4$

* Net wear (mass lost after correcting for soak controls) of XLPE liners for each femoral head type after 11 million cycles; †after liners stopped gaining weight, the CoCr wear data were best described by a second-order polynomial, whereas the Mg-PSZ and DLC-Mg-PSZ data were best described by linear regressions; ‡steady-state wear rate data revealed that CoCr wore at a significantly greater rate than Mg-PSZ, but DLC-coated Mg-PSZ femoral heads did not further reduce wear.

greater ($p = 0.06$; power = 0.75, $\delta = 3.4$) wear rate compared with uncoated Mg-PSZ (2.6 mg/million cycles).

Progressive roughening at the pole region of the femoral heads was not observed for any materials used in the hip wear simulator tests, although optical profilometry became increasingly difficult to perform for all femoral head types owing to decreased surface reflectivity, possibly attributable to protein deposition. The CoCr heads became scratched and qualitatively rougher in appearance, with evidence of carbide pullout, but the remaining carbide inclusions were deeper than the scratches and dominated the surface topography, whereas the scratches were gradually polished out during the test (Fig. 5). Mg-PSZ and DLC-Mg-PSZ heads did not roughen or become smoother, and DLC-Mg-PSZ heads did not exhibit pitting or other coating damage.

Discussion

Ceramic materials induced less wear than CoCr femoral heads in simulator studies [11, 39, 43], but recent clinical studies reported no difference in wear of XLPE liners bearing against Y-TZP and CoCr femoral heads [17, 20, 21, 31, 45]. The use of DLC coatings [14, 25, 33] has been proposed as a method to enhance bearing surfaces in joint

replacement, but DLC-coated metal femoral heads failed in clinical use [47] and did not reduce wear in simulator tests [18]. However, the wear performance and durability of uncoated and DLC-coated Mg-PSZ femoral heads is not known. The purpose of this observational study was to determine whether (1) the addition of a hard DLC coating would enhance the wettability of CoCr and Mg-PSZ substrates without increasing surface roughness, (2) the use of Mg-PSZ would result in less wear compared with CoCr femoral heads, and (3) the use of DLC-coated Mg-PSZ femoral heads would further reduce its wear potential. In addition, we qualitatively evaluated whether (4) the femoral head materials exhibited progressive roughening or other degradation during the wear test.

The primary limitation of our observational study was that only eight wear stations (two CoCr, three Mg-PSZ, and three DLC-Mg-PSZ heads) were available in our hip simulator, which reduced the power and made it difficult to discern why liners bearing against CoCr began to wear at a nonlinear rate. Given the time and other resources required to perform any wear simulator test, and the fact that only liners bearing against CoCr heads exhibited a net mass loss after 5 million cycles, we believe it was better to run one longer test as an observational study instead of two shorter but identical tests, although two identical tests would have doubled the number of specimens. Second, we lacked

Fig. 5A–C Typical surface topography is shown before wear testing (top row) and after 4 million cycles (bottom row) for (A) CoCr, (B) Mg-PSZ, and (C) DLC-Mg-PSZ femoral heads (Magnification, $\times 10$). Lateral axes are $554\ \mu\text{m} \times 418\ \mu\text{m}$.

load/soak controls (only soak controls were available). Because the soak controls were not cyclically loaded, they might have absorbed less fluid than the wear test specimens, leading to an apparent “negative” mass loss, even after soak correction. The initial net mass gain of the XLPE liners relative to the soak controls probably is attributable to protein deposition. Protein films have been directly observed on the bearing surfaces of retrieved implants, and initially may have enhanced wear resistance [49]. Third, femoral head temperature could not be controlled. Protein precipitation from the bovine serum used as a lubricant was observed in all stations, regardless of material type. This suggests that despite average bulk serum temperatures of 34°C or less, the head/liner interface temperature may have exceeded 60°C [27] in all stations. Fourth, the use of only distilled water to measure contact angle prevented the calculation of surface-free energy, but the contact angle data clearly illustrated the enhanced wettability of DLC-coated heads relative to noncoated heads. Finally, this study was limited by the lack of specific information regarding the deposition conditions or the DLC coating. Based on the contact angle data, along with previously published nano-indentation [38] and scratch test data [35], we are satisfied that the DLC coatings on the Mg-PSZ and CoCr specimens in this study are substantially similar, allowing a valid comparison, regardless of the exact coating composition.

Mg-PSZ femoral heads were smoother and more wettable than CoCr heads, whereas DLC coatings improved wettability but did not affect the average surface roughness when compared with uncoated CoCr and Mg-PSZ substrates. Smooth counterface surfaces and hydrophilic surfaces promote a lower coefficient of friction and

enhanced lubrication [1, 12, 13, 46]. The lower roughness of uncoated Mg-PSZ and the absence of large substrate discontinuities, such as carbide inclusions found in CoCr surfaces, imply that DLC coatings may be more durable on Mg-PSZ than on CoCr substrates [42, 48].

Liners bearing against Mg-PSZ femoral heads exhibited a wear rate that was seven times less than that of CoCr heads, possibly attributable to enhanced lubrication from the lower roughness and greater hydrophilicity of Mg-PSZ. Liners bearing against CoCr femoral heads exhibited consistent XLPE mass loss similar to reported hip simulator data up to 5 million cycles [19]. However, the rapid increase in wear of the XLPE liners bearing against CoCr after approximately 8 million cycles cannot be explained easily with just two CoCr femoral heads, and may be attributable to increased macroscopic roughness of the head, such as a raised edge that was worn down gradually with subsequent wear [1, 13, 46]. A similar increase in wear was not observed for Mg-PSZ femoral heads, which exhibited linear wear rates up to 11 million cycles, suggesting that the use of Mg-PSZ femoral heads instead of CoCr heads in THA will lead to reduced wear in vivo.

Additional reduction of wear was not achieved by using DLC-coated Mg-PSZ femoral heads instead of uncoated Mg-PSZ heads. Galvin et al. [18] likewise reported a small increase in wear of liners bearing against DLC-coated CoCr femoral heads, relative to noncoated femoral heads. The true advantage of a DLC-Mg-PSZ femoral head might be in its resistance to abrasive wear [35]. Debris from a fractured alumina ceramic component can lead to severe damage of metal components [22, 24, 29]. Owing to the difficulty in removing 100% of all debris after alumina

component fracture, the use of a DLC-Mg-PSZ femoral head may be indicated at revision to reduce the likelihood of additional damage. Future hip wear simulator tests may include bovine serum loaded with third-body alumina particles to examine the durability of each femoral head type in an abrasive environment.

Although the CoCr femoral heads in the current test were easily scratched, likely owing to third-body wear from carbides excavated during the test [13], the roughening of CoCr heads reported by others after 7 million cycles [28] was not observed. However, the roughness scans were limited to a small area near the pole and were dependent on the reflectivity of the surface, which decreased for all material types during the tests. Compared with Y-TZP, Mg-PSZ is much more stable and resistant to phase transformation [36, 37], and as expected, no degradation of the surface of Mg-PSZ was observed. In contrast to the poor clinical performance of DLC-coated titanium alloy heads [47], DLC-Mg-PSZ heads did not roughen or exhibit pitting during the wear tests.

Cross-linked UHMWPE liners bearing against Mg-PSZ femoral heads exhibited a lower wear rate than those bearing against CoCr femoral heads, likely owing to the lower roughness and better wettability of the ceramic material. If a similar reduction in wear also occurs in clinical use, the use of Mg-PSZ femoral heads could constitute an important improvement in the long-term performance of total hip replacements. However, the low wear rate offered by Mg-PSZ was not further reduced by the addition of a DLC coating, despite a reduction in contact angle. Although DLC coatings may be advantageous to better resist abrasive third-body wear, its wear performance as tested does not justify the added cost.

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References

1. Affatato S, Bergaglia G, Junqiang Y, Traina F, Toni A, Viceconti M. The predictive power of surface profile parameters on the amount of wear measured in vitro on metal-on-polyethylene artificial hip joints. *Proc Inst Mech Eng H*. 2006;220:457–464.
2. Agathopoulos S, Nikolopoulos N. Wettability and interfacial interactions in bioceramic-body-liquid systems. *J Biomed Mater Res*. 1995;29:421–429.
3. American Society of Mechanical Engineers. ASME B46.1-2002: *Surface Texture (surface roughness, waviness, and lay)*. New York, NY: American Society of Mechanical Engineers; 2002.
4. American Society for Testing and Materials. *ASTM F1873-98: Standard Specification for High-Purity Dense Yttria Tetragonal Zirconium Oxide Polycrystal (Y-TZP) for Surgical Implant Applications*. West Conshohocken, PA: American Society for Testing and Materials; 1998 (Withdrawn 2007).
5. American Society for Testing and Materials. *ASTM F2393-04: Standard Specification for High-Purity Dense Magnesia Partially Stabilized Zirconia (Mg-PSZ) for Surgical Implant Applications*. West Conshohocken, PA: American Society for Testing and Materials; 2004.
6. American Society for Testing and Materials. *ASTM F799-06: Standard Specification for Cobalt-28Chromium-6Molybdenum Alloy Forgings for Surgical Implants*. West Conshohocken, PA: American Society for Testing and Materials; 2006.
7. American Society for Testing and Materials. *ASTM F75-07: Standard Specifications for Cobalt-28 Chromium-6 Molybdenum Alloy Castings and Casting Alloy for Surgical Implants*. ASTM International: West Conshohocken, PA; 2007.
8. American Society for Testing and Materials. *ASTM F1537-08: Standard Specification for Wrought Cobalt-28Chromium-6Molybdenum Alloys for Surgical Implants*. West Conshohocken, PA: American Society for Testing and Materials; 2008.
9. American Society for Testing and Materials. *ASTM F1714-96: Standard Guide for Gravimetric Wear Assessment of Prosthetic Hip Designs in Simulator Devices*. West Conshohocken, PA: American Society for Testing and Materials; 2008.
10. Chevalier J, Calès B, Drouin JM. Low-temperature aging of Y-TZP ceramics. *J Am Ceram Soc*. 1999;82:2150–2154.
11. Clarke IC, Gustafson A. Clinical and hip simulator comparisons of ceramic-on-polyethylene and metal-on-polyethylene wear. *Clin Orthop Relat Res*. 2000;379:34–40.
12. Cuckler JM, Bearcroft J, Asgian CM. Femoral head technologies to reduce polyethylene wear in total hip arthroplasty. *Clin Orthop Relat Res*. 1995;317:57–63.
13. Davidson JA. Characteristics of metal and ceramic total hip bearing surfaces and their effect on long-term ultra high molecular weight polyethylene wear. *Clin Orthop Relat Res*. 1993;294:361–378.
14. Dearnley PA. A review of metallic, ceramic and surface-treated metals used for bearing surfaces in human joint replacements. *Proc Inst Mech Eng H*. 1999;213:107–135.
15. Deville S, Gremillard L, Chevalier J, Fantozzi G. A critical comparison of methods for the determination of aging sensitivity in biomedical grade yttria-stabilized zirconia. *J Biomed Mater Res B Appl Biomater*. 2005;72:239–245.
16. Fukatsu K, Pezzotti G, Hayaishi Y, Sugano N. Evaluation of phase stability in zirconia femoral heads from different manufacturers after in vitro testing or in vivo retrieval. *J Arthroplasty*. 2009;24:1225–1230.
17. Fukui K, Kaneuji A, Sugimori T, Ichiseki T, Kitamura K, Matsumoto T. Wear comparison between a highly cross-linked polyethylene and conventional polyethylene against a zirconia femoral head minimum: 5-year follow-up. *J Arthroplasty*. 2011;26:45–49.
18. Galvin A, Brockett C, Williams S, Hatto P, Burton A, Isaac G, Ingham E, Fisher J. Comparison of wear of ultra-high molecular weight polyethylene acetabular cups against surface-engineered femoral heads. *Proc Inst Mech Eng H*. 2008;222:1073–1080.
19. Hermida JC, Bergula A, Chen P, Colwell CW Jr, D'Lima DD. Comparison of the wear rates of twenty-eight and thirty-two-millimeter femoral heads on cross-linked polyethylene acetabular cups in a wear simulator. *J Bone Joint Surg Am*. 2003;85:2325–2331.
20. Ise K, Kawanabe K, Tamura J, Akiyama H, Goto K, Nakamura T. Clinical results of the wear performance of cross-linked polyethylene in total hip arthroplasty: prospective randomized trial. *J Arthroplasty*. 2009;24:1216–1220.
21. Kawate K, Ohmura T, Kawahara I, Tamai K, Ueha T, Takemura K. Differences in highly cross-linked polyethylene wear between zirconia and cobalt-chromium femoral heads in Japanese

- patients: a prospective, randomized study. *J Arthroplasty*. 2009; 24:1221–1224.
22. Kempf I, Semlitsch M. Massive wear of a steel ball head by ceramic fragments in the polyethylene acetabular cup after revision of a total hip prosthesis with fractured ceramic ball. *Arch Orthop Trauma Surg*. 1990;109:284–287.
 23. Kim YH. Comparison of polyethylene wear associated with cobalt-chromium and zirconia heads after total hip replacement: a prospective, randomized study. *J Bone Joint Surg Am*. 2005;87: 1769–1776.
 24. Koo KH, Ha YC, Jung WH, Kim SR, Yoo JJ, Kim HJ. Isolated fracture of the ceramic head after third-generation alumina-on-alumina total hip arthroplasty. *J Bone Joint Surg Am*. 2008;90: 329–336.
 25. Lappalainen R, Anttila A, Heinonen H. Diamond coated total hip replacements. *Clin Orthop Relat Res*. 1998;352:118–127.
 26. Lawson S. Environmental degradation of zirconia ceramics. *J Eur Ceram Soc*. 1995;15:485–502.
 27. Liao YS, Benya PD, McKellop HA. Effect of protein lubrication on the wear properties of materials for prosthetic joints. *J Biomed Mater Res*. 1999;48:465–473.
 28. Liao Y-S, Hames M, Fryman JC, DiSilvestro M. Phase stability of zirconia and alumina/zirconia composite heads against UHMWPE liners in a temperature-controlled hip simulation study. *Key Eng Mater*. 2005;284–286:991–994.
 29. Miki H, Sugano N, Yamamura M, Nakamura N, Nishii T, Yoshikawa H. Serious metallosis of a metal head due to fragmented ceramic screws in a cemented THA. *Arch Orthop Trauma Surg*. 2006;126:192–196.
 30. Murray MD, Darvell BW. A protocol for contact angle measurement. *J Phys D: Appl Phys*. 1990;23:1150–1155.
 31. Nakahara I, Nakamura N, Nishii T, Miki H, Sakai T, Sugano N. Minimum five-year follow-up wear measurement of longevity highly cross-linked polyethylene cup against cobalt-chromium or zirconia heads. *J Arthroplasty*. 2010;25:1182–1187.
 32. Paul JP. Force actions transmitted by joints in the human body. *Proc R Soc Lond B Biol Sci*. 1976;192:163–172.
 33. Robertson J. Diamond-like amorphous carbon. *Mater Sci Eng R*. 2002;37:129–281.
 34. Roy ME, Whiteside LA. Letter to the Editor: Clinical comparison of polyethylene wear with zirconia or cobalt-chromium femoral heads. *Clin Orthop Relat Res*. 2010;468:624–625; author reply 626–627.
 35. Roy ME, Whiteside LA, Katerberg BJ. Diamond-like carbon coatings enhance scratch resistance of bearing surfaces for use in joint arthroplasty: hard substrates outperform soft. *J Biomed Mater Res B Appl Biomater*. 2009;89B:527–535.
 36. Roy ME, Whiteside LA, Katerberg BJ, Steiger JA. Phase transformation, roughness, and microhardness of artificially aged yttria- and magnesia-stabilized zirconia femoral heads. *J Biomed Mater Res*. 2007;83A:1096–1102.
 37. Roy ME, Whiteside LA, Katerberg BJ, Steiger JA, Nayfeh TA. Not all zirconia femoral heads degrade in vivo. *Clin Orthop Relat Res*. 2007;465:220–226.
 38. Roy ME, Whiteside LA, Xu J, Katerberg BJ. Diamond-like carbon coatings enhance the hardness and resilience of bearing surfaces for use in joint arthroplasty. *Acta Biomater*. 2010;6: 1619–1624.
 39. Saikko VO. Wear of the polyethylene acetabular cup: the effect of head material, head diameter, and cup thickness studied with a hip simulator. *Acta Orthop Scand*. 1995;66:501–506.
 40. Saikko V, Ahlroos T, Calonius O, Keränen J. Wear simulation of total hip prostheses with polyethylene against CoCr, alumina and diamond-like carbon. *Biomaterials*. 2001;22:1507–1514.
 41. Salehi A, Tsai S, Pawar V, Sprague J, Hunter G, Varma S, Namavar F. Wettability analysis of orthopaedic materials using optical contact angle methods. *Key Eng Mater*. 2006;309–311: 1199–1202.
 42. Sheeja D, Tay BK, Lau SP, Nung LN. Tribological characterization of diamond-like carbon coatings on CoCr-Mo alloy for orthopaedic applications. *Surf Coat Tech*. 2001;146–147:410–416.
 43. Smith SL, Unsworth A. Simplified motion and loading compared to physiological motion and loading in a hip joint simulator. *Proc Inst Mech Eng H*. 2000;214:233–238.
 44. Stalder AF, Kulik G, Sage D, Barbieri L, Hoffmann P. A snake-based approach to accurate determination of both contact points and contact angles. *Coll Surf A*. 2006;286:92–103.
 45. Stilling M, Nielsen KA, Søballe K, Rahbek O. Clinical comparison of polyethylene wear with zirconia or cobalt-chromium femoral heads. *Clin Orthop Relat Res*. 2009;467:2644–2650.
 46. Sychterz CJ, Engh CA Jr, Swope SW, McNulty DE, Engh CA. Analysis of prosthetic femoral heads retrieved at autopsy. *Clin Orthop Relat Res*. 1999;358:223–234.
 47. Taeger G, Podleska LE, Schmidt B, Ziegler M, Nast-Kolb D. Comparison of diamond-like carbon and alumina-oxide articulating with polyethylene in total hip arthroplasty. *Materi- alwissenschaft und Werkstofftechnik*. 2003;34:1094–1100.
 48. Wang R, Mercer C, Evans AG, Cooper CV, Yoon HK. Delamination and spalling of diamond-like-carbon tribological surfaces. *Diamond and Related Materials*. 2002;11:1797–1803.
 49. Wimmer MA, Sprecher C, Hauert R, Täger G, Fischer A. Tribochemical reaction on metal-on-metal hip joint bearings: a comparison between in-vivo and in-vitro results. *Wear*. 2003; 255:1007–1014.