Three-body abrasive wear behaviour of orthopaedic implant bearing surfaces from titanium debris

R. A. POGGIE, A. K. MISHRA, J. A. DAVIDSON
Orthopaedic Research Department, Smith & Nephew Richards Inc., 1450 E. Brooks Road, Memphis, TN 38116 USA

The abrasive wear behaviour of several orthopaedic bearing materials was characterized for fully conformal, reciprocating sliding contact against ultra-high molecular weight polyethylene (UHMWPE). The bearing surfaces investigated were nitrogen ion implanted Ti–6Al–4V, TiN coated Ti–6Al–4V, Ti–6Al–4V, F-799 Co–Cr–Mo, yttria-stabilized zirconia and a Zr–2.5Nb alloy with a zirconia ceramic surface. The third-body debris was introduced as either Ti–6Al–4V particles or oxidized titanium powder (black debris). The wear tests were performed in deionized water with the third-body debris entrapped between the UHMWPE and the hard bearing surface. Surface profilometry measurements, scanning electron microscopy (SEM) and optical microscopy showed the severity of damage to the hard bearing surfaces to increase with decreasing hardness. The abrasion damage to the UHMWPE increased as the roughness of the opposing, hard bearing surface increased. Surface profilometry and energy dispersive spectroscopy (EDS) also showed oxidized titanium (black debris) to form an adherent transfer layer on all of the hard bearing surfaces. Nitrogen ion implantation of Ti–6Al–4V was ineffective in reducing wear of both the Ti–6Al–4V substrate and the UHMWPE. Solid yttria-stabilized zirconia and zirconia-coated Zr–2.5Nb showed no evidence of abrasion damage and produced the least amount of UHMWPE wear. These results are attributed to the high hardness and excellent wear resistance of zirconia and the excellent wettability of ZrO_2 due to its relatively high ionic character in comparison to metals and covalently bonded compounds.

1. Introduction

Total joint replacement (TJR) procedures have been successful in providing pain relief and restoring mobility to arthritic patients for over 25 years. The very success of the procedure has increased the range of applications. For instance, TJR is being used to repair the hips and knees in younger, more athletic patients. This has increased the demand for bearing materials which possess higher strength, minimize friction and wear and endure for the life of the patient.

The bearing surfaces in TJR typically consist of a polished metal or ceramic material sliding against UHMWPE. The UHMWPE component is susceptible to abrasion from the harder counter bearing surface and both surfaces may be abraded by harder, third bodies. Wear debris (polyethylene, polymethylmethacrylate (PMMA), oxides, and metal) generated by the entire implant system has been associated with osteolysis and bone resorption [1–5]. Earlier investigations of the tissues surrounding retrieved and failed total joints suggested that metal debris (metallosis) was responsible for cell lysis. Recent investigations, however, indicate that UHMWPE debris is the leading cause of osteolysis and premature failure of implant systems [6–8]. Histological techniques developed in the mid 1980s have permitted the imaging of UHMWPE debris particles in the micrometre and sub-micrometre size range which had previously gone undetected. It is becoming increasingly evident that there are orders of magnitude more UHMWPE particles in the bone tissues surrounding an unstable TJR than any other type of debris. As such, reducing the total amount of wear debris generated by the TJR system, and especially from the UHMWPE articular surface, will increase the longevity and level of performance of total joint replacements.

Hard, third-body particles such as oxide and metal debris can become entrapped at the interface between the bearing surfaces. This can lead to abrasion and wear of both the UHMWPE and the hard, counter bearing surface. Abrasion is defined as a cutting mechanism in which material is removed and/or a plowing mechanism in which the surface is deformed in the form of grooves. Both act to increase the roughness of the abraded surface. The abrasion resistance of a material is most often directly proportional to its hardness [9–11]. The classical relationship for abrasive wear is [10].

$$V = (KPD)/(H)$$

where V is the volume of material removed (mm^3), K is an empirically determined wear coefficient related to both geometric and probability considerations, P is the normal load (newtons $\times 10^{-3}$), H is the hardness of the substrate ($kg\,mm^{-2}$) and D is the total sliding distance (mm). Metals such as Ti–6Al–4V and to a lesser extent, Co–Cr–Mo, are much more susceptible to abrasion than substantially harder ceramic materials such as zirconia and alumina. In addition, this relationship shows that UHMWPE (extremely soft in comparison to metals and oxides) is highly susceptible to abrasion by both hard third-body particles and the harder, counter bearing surface. Dowson [12] has shown that the volume of UHMWPE wear increases with the roughness (R_a) of the harder, counter bearing surface as $R_a^{1.2}$.

Abrasive damage to the hard bearing surface can be minimized or eliminated by increasing its hardness above that of the hardness of debris which could potentially become entrapped at the contact interface [9–11]. Richardson [13] and Mishra and Finnie [14] showed that severe abrasion can be expected if the substrate hardness is less than 0.8 that of the third bodies. These studies and tribological theory suggest that a transition region from mild abrasion to virtually no abrasion occurs when the hardness of the substrate is increased from 0.8 to 1.2 times that of the third bodies. Therefore, an orthopaedic bearing surface can be considered immune to abrasive wear if its hardness is approximately 1.2 times that of, or greater than, the hardness of the hardest third-body debris present in the joint space. Consequently, eliminating abrasive wear of the hard substrate reduces the rate of UHMWPE wear since the roughness of the hard bearing surface remains unchanged as a function of time.

Alumina (Al_2O_3) and yttria-stabilized zirconia (ZrO_2) are becoming the bearing surfaces of choice for total hip arthroplasty. Their relatively high cost, however, has limited their use in an increasingly cost-conscious environment. Clinical studies and laboratory tests have consistently shown that Al_2O_3 and ZrO_2 are virtually immune to abrasive wear, and that the wear of UHMWPE is significantly less than their metal counterparts (Ti–6Al–4V, F-75 and F-799 Co–Cr–Mo, and 316L stainless steel) [6–8, 15, 16]. In addition to their excellent abrasion resistance, alumina and zirconia oxide ceramics possess a high level of ionic character (atomic bonding) and are therefore highly wettable by polar compounds such as H_2O contained in synovial fluid. A highly wettable surface contributes to lower wear by providing a more tenacious fluid barrier at the interface between the opposing bearing surfaces. This decreases the physical interaction between the surfaces which in turn lowers frictional interaction and wear of the bearing system.

2. Experimental materials and methods

The bearing materials tested in this investigation are listed in Table I. Table I also shows the Vickers hardness values and the thickness of the surface coatings, where applicable.

TABLE I Vickers hardness values H_v and coating thickness for the metal and ceramic bearing surfaces tested in this investigation

Material	H_v	Coating thickness (μm)
Ti–6Al–4V	330	Uncoated
N + Ti–6Al–4V	700	0.1–0.2
F-799 Co–Cr–Mo	420	Uncoated
TiN-coated Ti–6Al–4V	1630	3.0
Yttria-stabilized zirconia	1430	Uncoated
Zirconia-coated zirconium	1430	4.0

The polymeric bearing surfaces were GUR 415 UHMWPE with a Shore hardness of approximately 65 "D". Two types of third body debris were introduced to the interface between the hard bearing surfaces and the UHMWPE pins. The first type of debris was Ti–6Al–4V particles with an average size of 150–250 μm and the second type of debris was oxidized titanium powder (black debris) with a mean particle diameter of 1.48 μm. The latter is more representative of debris which may be produced from fretting wear at interfaces between mated metal components.

The hard bearing surfaces were in the form of 12–16 mm thick, 25–35 mm diameter discs with one surface polished to an R_a of 0.05 μm or less. The TiN surface was an overlay coating approximately 3 μm in thickness with an abrupt interface between the TiN coating and the Ti–6Al–4V substrate. The ZrO_2 surface on Zr–2.5Nb was produced via a high temperature diffusion process which results in a gradual transition in chemical and physical properties between the ZrO_2 surface and the Zr–2.5Nb substrate. Nitrogen ion implantation of Ti–6Al–4V was performed with 3×10^{17} ions cm^{-2} and an energy of 60 keV. The maximum penetration depth of nitrogen was approximately 0.15–0.20 μm.

The UHMWPE pins were 18 mm long and 12.7 mm in diameter with an as-machined (turned) surface finish. The as-machined surface finish aided in the microscopic and visual assessment of wear damage to the UHMWPE. The pins were flat-ended to provide for fully conformal contact against the opposing, hard bearing surfaces.

Wear testing was performed using a reciprocating, linear wear tester [17]. The nominal contact stress was 10 MPa, the cycling rate was approximately 3 Hz and the sliding distance for one half-cycle was 3.2 mm. The short sliding distance was chosen to ensure the entrapment of debris for the duration of each wear test. The tests were performed for 500 000 uninterrupted cycles in a deionized water bath. The third-body particles were introduced to the contact interface prior to the start of each wear test. Nine Ti–6Al–4V particles or, for the finer debris, approximately 0.002 g of black debris were used for each 500 000-cycle test. Three wear tests were performed for each of the materials listed in Table I and for each of the two debris types.

The abrasive damage to the hard substrates was evaluated using surface profilometry, SEM and EDS. Abrasive wear for the tests with nine Ti–6Al–4V particles was quantified by calculating the area between the original, unworn surface and the abraded surface (the area between the damage profile and the original surface). Three profilometer traces were recorded for each wear track. Abrasion of the hard substrates for the tests with black debris was more difficult to quantify and, thus, qualitatively ranked on a scale of 0 to 5 with 0 representing no abrasive wear, 3 representing abrasion (scratching) barely observable with the unaided eye, and 5 representing significant abrasion and severe scratching. A more quantitative measure of the wear track area was prohibited by the adherence of the black debris to the metal/ceramic surfaces. The abrasive wear to all of the UHMWPE surfaces was determined qualitatively using optical stereomicroscopy and SEM. Weight loss measurements were not possible due to the embedding of metal and oxidized debris within the UHMWPE. As such, the majority of worn UHMWPE samples showed a weight gain, when in reality, wear of the UHMWPE was clearly evident with the unaided eye, optical stereomicroscopy and scanning electron microscopy. Although qualitative in nature, the measurement of wear via visual description provided the means to accurately rank the wear of the UHMWPE with respect to counterface material.

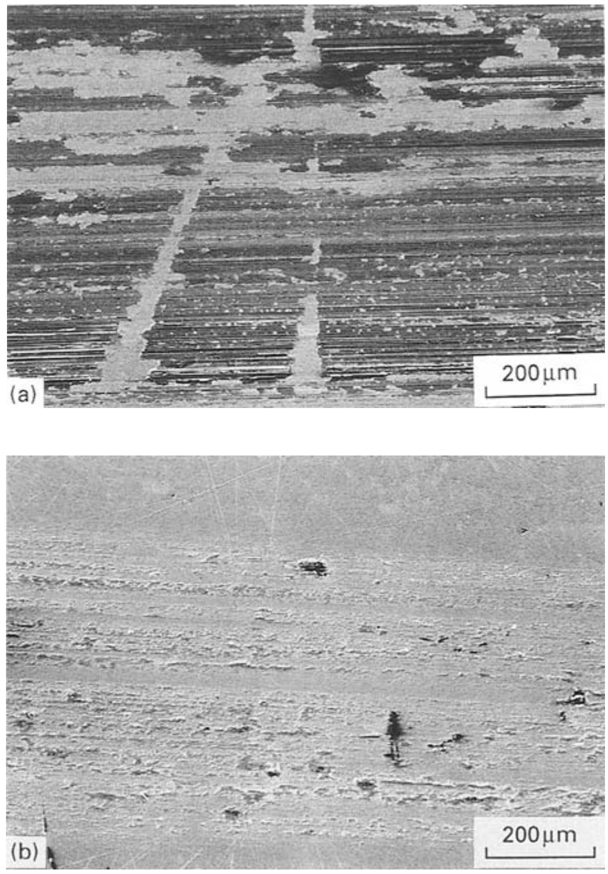

Figure 1 Scanning electron micrographs of the worn surfaces of (a) F-799 Co–Cr–Mo and (b) yttria-stabilized zirconia. Both materials were worn against UHMWPE for 500 000 cycles with nine entrapped Ti–6Al–4V particles. (a) shows minor abrasion of the Co–Cr–Mo and a transfer layer primarily composed of oxidized titanium. (b) shows only transferred material and *no* evidence of abrasion of the zirconia.

3. Results

Table II is a summary of the abrasive wear damage to the hard substrates as measured by profilometry for the larger Ti–6Al–4V debris and the qualitative ranking method for the fine, TiO_2, black debris. Table II and the hardness values in Table I clearly show that abrasive wear decreases with increasing hardness.

Fig. 1a and 1b are scanning electron micrographs of the worn surfaces of F-799 Co–Cr–Mo and solid yttria-stabilized zirconia, respectively. Fig. 1a shows minor abrasive damage to the Co–Cr–Mo and patches of transferred titanium oxide (darker contrast regions). Fig. 1b shows patches of transferred titanium oxide and no abrasive damage. SEM and optical microscopy showed the severity of abrasion to increase with decreasing hardness which is in agreement with the profilometry data listed in Table II.

TABLE II Abrasion damage of the hard bearing surfaces as measured from two-dimensional profilometry traces of the worn regions

	Ti–6Al–4V particles	TiO_2 black debris
Material	abrasion damage (μm^2)	ranking[a]
Ti–6Al–4V	1426	Severe (5)
N + Ti–6Al–4V	1485	Severe (5)
F-799 Co–Cr–Mo	226	Light (2)
TiN-coated Ti–6Al–4V	5	None (0)
Yttria-stabilized zirconia	0	None (0)
Zirconia-coated Zr–2.5Nb	0	None (0)

[a] Ranking: 5 represents the most severe wear observed and 0 represents *no* observable abrasive wear.

UHMWPE wear was qualitatively measured and ranked by comparing the removal of the grooves (SEM analysis of the degree of wear of the as-machined surface) on the surfaces of the UHMWPE pins. The zirconia surfaces wore the UHMWPE the least, the Ti–6Al–4V and N^+ ion implanted Ti–6Al–4V surfaces wore the UHMWPE the most and the TiN and F-799 Co–Cr–Mo surfaces wore the UHMWPE an intermediate amount. Fig. 2a and 2b show the surfaces of UHMWPE pins worn against N^+ ion implanted Ti–6Al–4V and yttria-stabilized zirconia, respectively. The UHMWPE pin worn against zirconia clearly shows the abrasion of the UHMWPE to be confined to those regions in which the third-body debris was entrapped. In addition, the grooves in the as-machined surfaces of the UHMWPE pins were clearly evident over a majority of the original, unworn surface area. In comparison, the UHMWPE pin worn against N^+ ion implanted Ti–6Al–4V shows abrasion of the UHMWPE to be prevalent over a majority of the contact area and little or no evidence of the original, unworn, as-machined surface.

The transfer of TiO_2 (black debris) to the hard bearing surfaces was observed for all of the materials tested in this investigation. Examples of this (darker in contrast in the micrographs) are shown in fig. 1a and

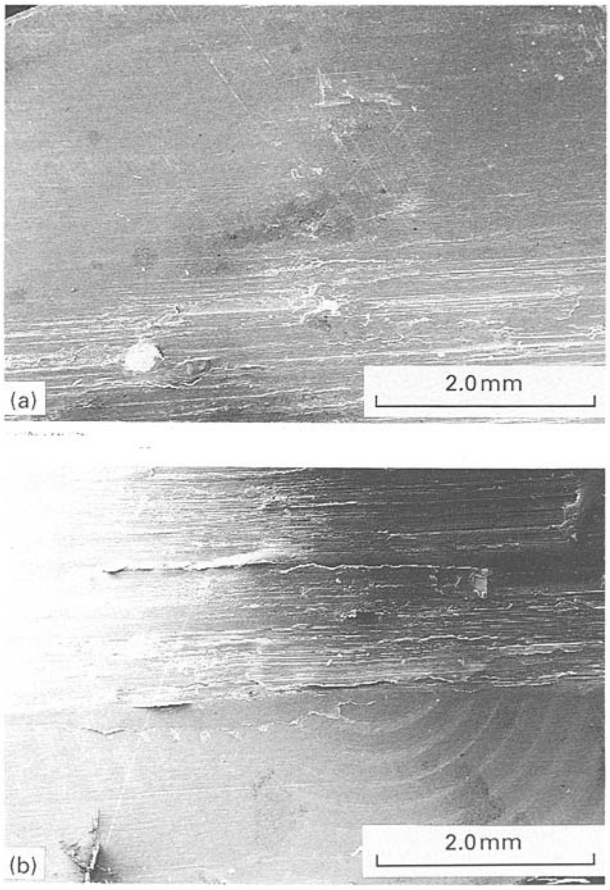

Figure 2 Scanning electron micrographs of the worn surfaces of UHMWPE pins worn against (a) nitrogen ion implanted Ti–6Al–4V and (b) yttria-stabilized zirconia. (a) shows severe abrasion and minor abrasion over the entire UHMWPE surface with *no* evidence of the original, as-machined surface while (b) shows abrasion of the UHMWPE confined to those areas which correspond to the entrapped Ti–6Al–4V debris with clear evidence that the as-machined surface remained in tact.

1b for Co–Cr–Mo and zirconia. EDS analysis showed the transferred material to be primarily comprised of oxidized titanium debris. The transferred material was typically confined to those areas immediately adjacent to the debris particles entrapped within the UHMWPE which were also sliding against the hard substrates.

4. Discussion

The fluid environment of artificial hip and knee joints can contain third-body debris of varying composition, size, quantity and hardness. The most likely sources of debris are the articulating surfaces, the PMMA cement mantle, cortical bone from the implant–bone interface, the surgical procedure and the implant device itself. The implant, if not well fixed, may be abraded by bone or bone cement and yield oxide and metal wear debris. In addition, although not common, spherical beads or wire from the bone ingrowth surfaces have been found in the UHMWPE bearing surfaces in retrieved components [18]. The third-body debris used in this investigation was selected to be reasonably representative of debris which could potentially originate from interfaces between modular components, abrasion of the implant and metal debris from bone ingrowth surfaces.

Clinical and laboratory studies have shown the vast majority of debris found in the total joint environment to be UHMWPE debris originating from the UHMWPE articulating surfaces. The two primary wear mechanisms for UHMWPE are abrasive wear and fatigue/delamination wear. The contribution that each of these wear mechanisms makes to total UHMWPE wear largely depends on the COF, adhesive interaction between the opposing surfaces, contact stress and roughness of the hard, counter bearing surface. As discussed earlier, UHMWPE wear is extremely sensitive to the roughness, R_a, of the opposing surface and was found by Dowson to be proportional to $R_a^{1.2}$ [12]. Therefore, it is extremely desirable for the hard counter bearing surface to remain as smooth as possible for the expected service life of the implant system. If the surface roughness remains unchanged, the abrasive component of UHMWPE wear will remain characteristic of the initial R_a of the hard bearing surface. The surface roughness of metallic and ceramic orthopaedic bearing surfaces in the unworn condition is typically 0.015–0.050 μm for both total hip and total knee replacements.

A comparison of Figs 1 and 2 and the data in Table II suggests that abrasion of the Ti–6Al–4V surfaces contributed to increased wear of the UHMWPE, as observed using SEM. In contrast, the zirconia bearing surfaces showed no evidence of abrasion and also produced the least amount of UHMWPE wear. The low hardness associated with Ti–6Al–4V, and to a lesser extent, for Co–Cr–Mo, increased their susceptibilities to abrasion by third-body particles with similar hardness. Abrasion is severe if the debris/substrate hardness ratio is greater than approximately 1.2. As the debris/substrate hardness ratio changes from 1.2 to 0.8 (the transition region discussed in the Introduction), the severity of abrasion decreases markedly and is extremely low or non-existent for hardness ratios less than 0.8. The Vickers hardness ratios for the Ti–6Al–4V and TiO_2 third bodies to the hard substrates is shown in Table III. Inspection of Table III shows that abrasion is predicted for Ti–6Al–4V, Co–Cr–Mo and N^+ ion implanted Ti–6Al–4V (hardness ratio greater than 0.8) and should not occur for TiN and zirconia (hardness ratio less than 0.8). Evaluation of the abrasive damage incurred by the hard substrates showed that abrasion did indeed occur for the softer materials and did not occur for TiN and the zirconia surfaces.

There are two primary components of UHMWPE wear; the first is abrasion by an opposing, hard counterface and the second is fatigue/delamination type wear caused by adhesive interaction between the opposing, articulating surfaces. As discussed previously, softer materials such as the Ti–6Al–4V, and to a lesser extent, Co–Cr–Mo, were abraded. This was also reflected by the obvious differences in wear of the UHMWPE caused, in large part, by the roughened metallic surfaces. In contrast to the metals, the zirconia and TiN surfaces were not abraded. Profilome-

TABLE III The ratio of hardness for the third-body debris and the hard bearing surfaces

Debris type	Ti–6Al–4V	Co–Cr–Mo	N ± Ti–6Al–4V	TiN	Zirconia surfaces
Ti–6Al–4V particles	1 0	0.8	0.47–1 0[a]	0.2	0.2
TiO_2 black debris[b]	2 1	1.7	1.00–2.1[a]	0.4	0.5

[a] The hardness of the ion implanted layer decreases rapidly from the free surface due to the shallow depth of effective hardening (only 0.1–0 2 μm). The maximum hardness of the layer is approximately 700 DPH at a depth of 0.05 μm, the hardness at approximately 0.2 μm is 500 DPH and the hardness at 1.0 μm is that of untreated Ti–6Al–4V (330 DPH).

[b] The hardness of rutile TiO_2 is approximately 700 DPH.

try measurements and SEM analysis showed that TiN and zirconia were completely resistant to abrasive wear. There were, however, clear differences in UHMWPE wear for sliding against TiN and zirconia which were not related to changes in roughness of the hard bearing surface.

Microscopic (SEM) characterization, comparison and ranking of the worn UHMWPE surfaces showed that UHMWPE worn against zirconia produced the least amount of UHMWPE wear and that TiN wore the UHMWPE more than zirconia. The difference in UHMWPE wear between the zirconia surfaces and TiN is attributed to zirconia being more wettable than TiN. Wettability is related to the bonding character of the surface (ionic, covalent, metallic or "mixed" character) [19, 20] which is also related to the difference in electronegativity of the elements [21] which make up the surface (Zr and O for zirconia and Ti and N for the TiN coating). ZrO_2 possesses an ionic character (scale of 0.0 to 1.0) of approximately 0.58 while TiN is approximately 0.38 [21].

Polar compounds, such as H_2O, bond readily to zirconia (high surface energy and good wettability) which provides for more effective lubrication of the zirconia and less solid–solid interaction between the articulating surfaces as compared to TiN. This in turn results in a lower coefficient of friction (COF) for zirconia in contact with UHMWPE as compared to TiN. A previous study showed the COF for zirconia-coated Zr–2.5Nb, TiN and Ti–6Al–4V sliding against UHMWPE in DI water to be 0.040 ± 0.008, 0.082 ± 0.002, and 0.112 ± 0.007, respectively [17]. The COF and contact stress at the bearing interface determine the magnitude of shear stress within the near surface of the UHMWPE. This, in turn, determines the degree of fatigue/delamination type wear; as the COF increases so does the potential for increased UHMWPE wear.

The higher UHMWPE wear observed for Co–Cr–Mo, and especially Ti–6Al–4V, in comparison to zirconia is in part due to differences in wettability. Several studies have shown lubricating compounds, such as water, to readily chemisorb to ceramics and not to metals [19, 22, 23]. The passive oxide film which overlays Ti–6Al–4V is comprised of TiO_2, TiO, and Al_2O_3 and is highly susceptible to mechanical disruption and, therefore, oxidative wear. It has been reported that a shear stress as low as 0.15 MPa will cause mechanical disruption of the passive oxide film on titanium alloy surfaces [24]. Therefore, the wettability of Ti–6Al–4V, under articulating conditions typical of TJR, is dependent on the wettability of both the surface oxide film and the underlying metal. Metals are not very wettable and the overall wettability of Ti–6Al–4V under sliding wear conditions is also relatively low in comparison to oxide ceramics such as Al_2O_3 and ZrO_2.

The transfer of oxidized titanium debris was observed for all of the bearing surfaces tested in this investigation. This phenomena occurs when there is a complete breakdown of lubrication at the interface between the UHMWPE (which contains entrapped third-body particles) and the opposing, hard bearing surface. The absence of a lubricating film permits the physical interaction (solid–solid, Van der Waals bonding and/or direct chemical interaction such as metal–metal) between both entrapped third bodies and the opposing UHMWPE and the hard substrate. This creates a finite probability that the third-body debris and/or UHMWPE will adhere and transfer to the opposing, hard surface. The tendency for material transfer will decrease as the wettability and lubricious character of the hard substrate increases. Therefore, in the presence of lubricating media such as synovial fluid contained in the joint space, ceramics show a lower tendency for adhesive wear and a lower coefficient of friction for sliding against UHMWPE.

The high hardness and excellent wettability inherent to zirconia minimizes the wear of UHMWPE caused by both the abrasive and fatigue/delamination mechanisms of wear. Those surfaces with low hardness, namely Ti–6Al–4V and N^+ implanted Ti–6Al–4V, were abraded by the third-body debris which in turn increased UHMWPE wear.

5. Conclusions

1. The abrasion resistance of the materials tested in this investigation was directly proportional to their respective near-surface hardness. A bearing surface specifically targeted for total joint replacement should possess a hardness greater than approximately 1000–1200 Vickers DPH. Zirconia and TiN were found to be abrasion resistant while the Ti–6Al–4V, and to a lesser extent Co–Cr–Mo, were abraded by both Ti–6Al–4V and TiO_2 third-body debris.

2. The dependence of UHMWPE wear on the wear resistance of the hard bearing surfaces was demonstrated by this study. Wear of the UHMWPE decreased as the abrasion resistance of the opposing

bearing surfaces increased. Abrasion of the Ti–6Al–4V and Co–Cr–Mo surfaces increased their respective surface roughness values which, in turn, increased the abrasion component of wear of the UHMWPE. Wear of the UHMWPE was least for sliding against the zirconia bearing surfaces.

3. The hard bearing surfaces which were not abraded by the third-body debris, namely TiN and zirconia, wore UHMWPE at differing rates. A qualitative ranking of UHMWPE wear (SEM micrographs of worn surfaces) showed less UHMWPE wear for zirconia than for TiN. This is attributed to the higher ionic character, higher wettability and more lubricious nature of zirconia as compared to TiN.

References

1. P BULLOUGH "*The hip*" The Hip Society, Program Chair, Augusto Sarmiento (C. V. Mosby, St Louis, USA, 1973) p. 80.
2. I. CLARKE, P. CAMPBELL and N KOSSOVSKY, ASTM Symposium on Biocompatibility of Particulate Implant Materials, October 1990, San Antonio, TX.
3. P. CAMPBELL, S. NASSER, N KOSSOVSKY and H. AMSTUTZ, ASTM Symposium on Biocompatibility of Particulate Implant Materials, October 1990, San Antonio, TX.
4. W LANZER, G. CRANE, G. HOWARD and J. DAVIDSON, Proceedings of Sixteenth Meeting, Society of Biomaterials, Charleston, SC, 1990.
5. A LOMBARDI, T. MALLORY, B VAUGHN and P. DROUILIARD, *J. Bone Joint Surgery* **71-A** (1989) 1337.
6. G GUALTIERO, I. GUALTIERI, M. HENDRIKS and S. GAGLIARDI, *Clin. Orthop. Related Res.* **282** (1992) 81.
7. H. OONISHI, Y. TAKAYAKA and I CLARKE, *J. Long-Term Effects of Medical Implants* **2** (1992) 37.
8. P. ZINCHNER and H -G WILLERT, *Clin. Orthop. Related Res.* **282** (1992) 86.
9. E. RABINOWICZ,"*Friction and wear of materials*" (John Wiley, New York, Chichester, Brisbane, Toronto, 1965).
10. J ARCHARD, in "The *wear control handbook*" edited by M. B. Peterson and W. O. Winer (American Society of Mechanical Engineers, 1980).
11. F BOWDEN and D TABOR, "*The friction and lubrication of solids-Part II* (Oxford University Press, London, 1964).
12. D. DOWSON, M. DIAB, B. GILLIS and J ATKINSON, in "*Polymer wear and its control*" (American Chemical Society, 1985).
13. R. RICHARDSON, *Wear* **11** (1968) 245.
14. A. MISHRA and I. FINNIE, *Wear* **85** (1983) 57.
15. T TATEISHI, K. KONDO and K MIURA, Proceedings of 33rd Japanese Congress of Materials Research (Society of Materials Science, Kyoto, Japan, 1990) p. 141.
16. H OONISHI, H. IGAKI and Y TAKAYAMA, *Bioceramics* **1** (1989) 272.
17. R. POGGIE, J. WERT, A MISHRA and J. DAVIDSON in "*Wear and friction of elastomers*" (American Society for Testing and Materials, STP 1145, 1992).
18. A GUSTAFSON, I. CLARK, P CAMPBELL, *J. Long Term Effects of Medical Implants*, **3** (1993) 91.
19. S. MORI, *Jpn. J. Tribol.* **36** (1991) 161.
20. L. PAULING, "*The nature of the chemical bond*" (Cornell University Press, Ithaca, NY, 1940).
21. L. DARKIN and R. GURRY, "*Physical chemistry of metals*", Ch. 4 (McGraw-Hill, NY, 1953) p. 79.
22. R GATES, S. HSU and E KLAUS, *STLE Trib. Trans.* **32** (1989) 357.
23. M SEMLITSCH, M TEHMANN, H. WEBER, E. DORRE and H. WILLERT, *J. Biomed. Mater. Res.* **11** (1977) 537.
24. R. BUCHANAN, E. RIGNEY and J. WILLIAMS, **21** (1987) 367.