Wear Behaviour of UHMWPE Against DC-Pulsed Plasma Nitrided and Duplex Treated AISI 316L Used in Hip Joint Replacements

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Wear behaviour of the artificial joint replacements plays a critical role in implant failure. The UHMWPE-AISI 316L tribological system, widely used on joint prostheses, was studied. Two surface modifications were applied to the stainless steel counterface: DC-pulsed plasma nitriding and duplex (DC-pulsed plasma nitriding + TiN coating by cathodic-arc evaporation) treatments. An Amsler Disc Machine Type A-135 was used as an approximation to real loading conditions. Worn surfaces, weight loss curves and wear debris were analysed. The results show that the nitriding and duplex treatments improve the wear resistance of the tribological system. Different types of damages were observed on the UHMWPE worn surfaces depending on the surface treatment of the stainless steel.

Introduction

Total hip replacements (THR) are exposed to a complex combination of mechanical, physical and chemical processes associated to hip biomechanics,[1,2] hip implant designs,[3,4] biological factors[5] and duration and frequency of daily activities, among others. The effect of these processes is related to wear behaviour, fatigue resistance, corrosion resistance and stress shielding of the orthopaedic implants.[6,7] The majority of THR implanted at the present time comprise a metal femoral head manufactured form either cobalt chrome or stainless steel, which articulates on an ultrahigh molecular weight polyethylene (UHMWPE) acetabular cup. Aseptic loosening of the implant is considered one of the most important limiting factors for a long implant life, which has been related to negative biological effects (tissues inflammation, osteolysis), due to the presence of wear particles of UHMWPE.[6,8]

The occurrence and severity of the adverse cellular responses depend on the number, size, material and morphology of the wear debris. Therefore, reducing the wear rate and the amount of generated particles should diminish the occurrence of long-term aseptic loosening.[8] Several surface treatments and structural modifications on UHMWPE have been developed and investigated to enhance tribological properties. However, being wear a system property and not a material property, the counterface material, to whom fewer studies are devoted, affects the final outcome.[9] Plasma-assisted surface treatments and coatings on the counterface are being studied in order to improve the wear behaviour of artificial joints.[10] Coating depositions assisted by plasma (e.g. TiN, DLC, etc.) have been applied in order to improve the wear behaviour of artificial joints.[11,12] The combination of plasma nitriding treatments as DC-pulsed plasma nitriding (DCPPN) and coatings by plasma-assisted physical vapour deposition (PAPVD) are extensively applied in other areas to improve the fatigue and wear resistance.[13] In some cases, applying this duplex surface treatment (DST), significant improvements on the surface and sub-surface properties, which were unobtainable through any individual

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DOI: 10.1002/ppap.200930306

technique, were achieved.[14,15] Hence, these kind of treatments are of potential use for biomedical applications.

Pre-clinic tests are adequate to study the effect of surface modifications and to predict the in vivo performance under normal conditions. In order to define test conditions, biomechanics information about loads, contact pressures, contact areas, temperatures, velocities and daily activities (duration and frequency) is required.[1,2,16,17] Among the post-operative daily patient activities, the normal walking is considered the most frequent one.[16,17]

Recent investigations indicate that the kinematics of normal hip and THR would differ due to surgical alterations in the soft-tissue supporting structure produced by total hip arthroplasty. These alterations would produce a microseparation between the femoral and acetabular components during normal walking conditions.[18,19]

A wear process of UHMWPE could be investigated using different complementary methodologies, (i) analysis of the weight loss curves, from which three periods can be described: running-in period, steady-state period and severe wear period,[20] and (ii) observation and analysis of worn surfaces and wear debris.[21,22] Wear mechanisms identified for UHMWPE are abrasive wear, adhesive wear and fatigue wear.[21]

The aim of the present work is to study the effect of plasma-assisted surface modifications of an AISI 316L counterface (DCPPN and DST) on the wear behaviour of the UHMWPE-AISI 316L tribosystem reproducing normal walking conditions including a microseparation to overcome the limitations in the performance of current joint replacements.

Experimental Part

Materials

The tribological system studied was UHMWPE-AISI 316L, in which three different surface conditions for the AISI 316L component were analysed. Surface conditions were:

– Surface obtained from the grinding process, untreated sample, as control (UT).
– DC-pulsed plasma nitriding treatments (DCPPN).
– Duplex surface treatment, DCPPN + TiN coating by cathodic-arc evaporation (DST).

The UHMWPE samples were identified by adding a '-PE' after the treatment identification. The AISI 316L samples were identified by adding a '-SS' after the treatment identification.

DCPPN was carried out in an industrial equipment described elsewhere.[23] Before plasma nitriding, the samples were sputter cleaned in the plasma reactor with a gas mixture composed of 50% Ar + 50% H_2 during 3 h to remove the passive film characteristic of stainless steels. Main parameters of the DCPPN process were: time, 20 h; temperature, 673 K; pressure, 650 Pa; atmosphere, 75% H_2 + 25% N_2; tension, 700 V; pulse$_{on/off}$, 70–200 μs; current density, ~1 mA · cm^{-2}.

Table 1. Surface roughness (R_a) and microhardness of the samples before the wear tests.

Samples	$R_a \pm \Delta R_a$ [μm]	$HV_{0.03N}$
UT-SS	0.68 ± 0.07	170
DCPPN-SS	0.83 ± 0.07	1 260
DST-SS	0.50 ± 0.07	2 500

The pre-nitrided samples were afterwards coated with a Ti/TiN layer by cathodic-arc evaporation industrial equipment described elsewhere,[14] to obtain the desired DST. A sputter cleaning had been performed before the coating process. The conditions of coating deposition were as follows: arc current, 60 A; bias voltage, 150 V; argon pressure, 6.7×10^{-2} Pa; substrate temperature, 673 K; cathode-substrate distance, 135 mm; deposition time, 2 h; nitrogen pressure, 2.7 Pa.

The surface roughness (R_a) of the samples before the wear tests was measured utilizing a Taylor Hobson model Surtronic 3+ profilometer. These measurements were done perpendicular to the principal sliding direction of the bearing surfaces. The reported values for each surface condition were the average of five measurements. Microhardness measurements of the UT-SS, DCPPN-SS and DST-SS samples were performed in a Frank Prüfen + Messen microhardness tester; three measurements were taken to determine the average value. The roughness and microhardness values before the tribological tests are shown in Table 1.

Microstructures of the formed phases of the DST and DCPPN samples were studied in the previous works.[14,24]

Wear Test

Wear tests were carried out with an Amsler Disc Machine Type A-135. Normal load, sample movements and geometry were selected and combined in order to simulate the loading cycle for THR during normal walking condition. Details of the set-up configuration are given in Figure 1a. The top and bottom components correspond to the UHMWPE and AISI 316L samples, respectively. The movements of the samples and the flow of the lubricant are indicated. The rotational velocity of the bottom sample (AISI 316L) was constant ($\omega = 50$ rpm) and the UHMWPE component carried out two displacements (horizontal and vertical). Thus, two sliding directions were obtained. The movement of the bottom sample was associated to the principal sliding direction, while the horizontal displacement of the top sample was associated to a secondary sliding direction. The horizontal movement reduces the contact area, producing consequently an increase in the contact pressure (Figure 1b, point 2). Modifying the amplitude of this movement, the maximum and minimum values of contact pressure can be regulated. The vertical movement controls the separation period of the loading cycle (Figure 1b, point 3). Figure 1c shows the contact pressure cycle. The abrupt decrease in

DOI: 10.1002/ppap.200930306

the contact pressure is related to the beginning of the microseparation stage.

The mean and peak values of pressure were 3 and 4.5 MPa, respectively. The microseparation was adjusted to 1 mm. Loading and motion were synchronized at 1.2 Hz, following data taken from the literature.[1,16,18] Deionized water was used as a lubricant in a closed circuit at $37 \pm 1\,^{\circ}$C.

It is important to highlight that only a half of the contact area of the UHMWPE was exposed to the loading cycle previously described. For this reason, the wear study was carried out only in this half-area.

Testing lasted 4×10^5 cycles and was interrupted at regular intervals of approximately 1×10^5 cycles, in order to monitor the weight loss and to collect lubricant for ulterior isolation of the wear debris. The metallic and polymeric samples were ultrasonically cleaned in ethanol for 5 min and dried before weighing. The solution used to clean the polymeric samples and the lubricant was filtered using a low vacuum system with a 0.2 μm pore size membrane.

Two sample sets were tested for each surface condition. The weight loss of UHMWPE samples was determined using a Mettler Toledo AB204 (accuracy of ±0.0001 g). Weight loss was then plotted as a function of the number of cycles in order to evaluate the wear resistance of UHMWPE in the testing conditions.

In order to assess the water absorption of the polymer samples, a control sample was immersed in deionized water at $37 \pm 1^{\circ}$C to monitor the rate of water absorption during the same test period. The weight of the control sample of UHMWPE did not evidence water absorption, so the influence of this effect on the weight loss results was negligible.

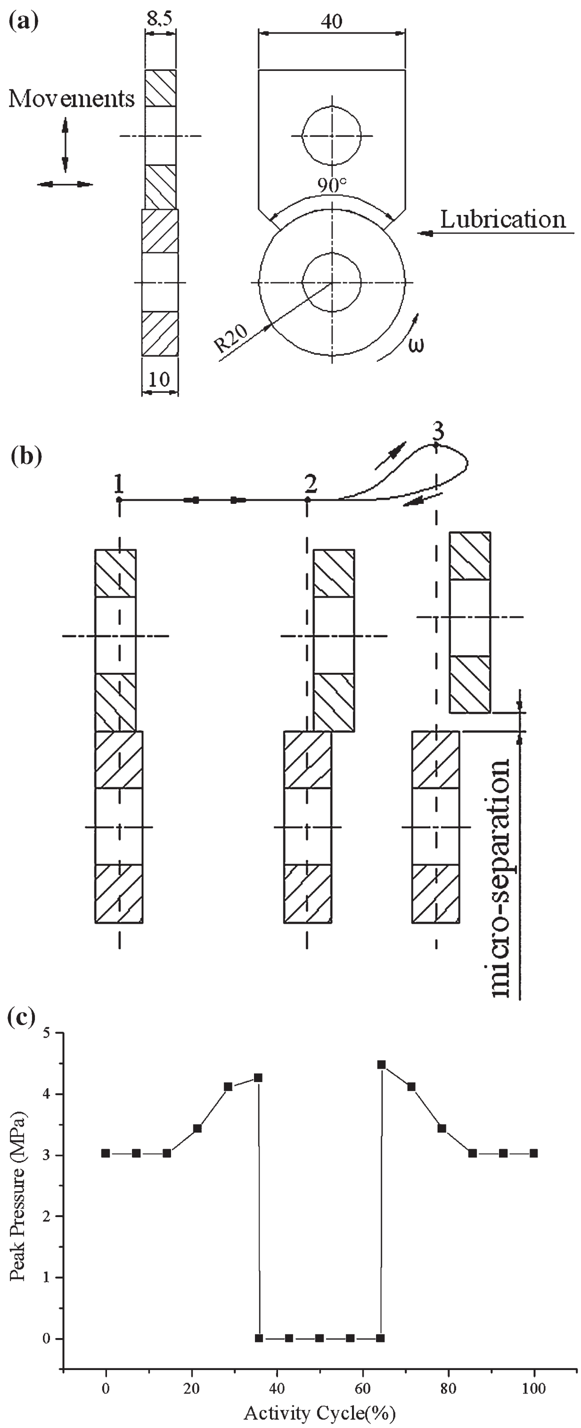

Figure 1. (a) Set-up configuration (dimension in mm), (b) description of the relative position of the samples during wear test: point 1, initial position; point 2, reduction of contact area (increase of contact pressure); point 3, microseparation, (c) contact pressure cycle.

Wear Characterization

The surfaces of the UHMWPE and AISI 316L samples were examined before and after the wear tests by scanning electron microscopy (SEM) in a Philips SEM 505 equipment. Worn surfaces were analysed to identify wear mechanisms. The wear debris obtained was also characterized. Energy dispersive spectroscopy microanalyses (EDS) were done to detect metallic particles embedded in the worn surfaces or in the wear debris.

Polymer degradation was studied by means of Fourier transformed infrared spectroscopy (FTIR). A Nicolet Magna 550 Series II spectrometer was employed. The results were compared to an untested UHMWPE spectrum.

Results and Discussion

The weight loss curves of the UHMWPE samples are plotted in Figure 2 for each surface condition. In all the cases, the weight loss of UHMWPE increased with increase in the number of cycles. The largest weight loss of UHMWPE corresponds to the untreated (UT-PE) condition. On the other hand, the duplex (DST-PE) condition evidenced the best wear behaviour. From the weight loss curves, it was possible to identify different tendencies that can be associated to different periods of the wear process of UHMWPE.[20] In fact, every curve showed a running-in and a steady-state periods, although the severe wear period was not clearly defined. Regarding the metallic

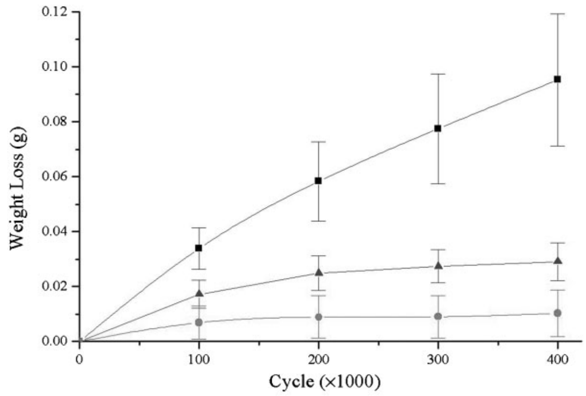

Figure 2. Weight loss curves of UHMWPE tested against AISI 316L; untreated (UT ■), DC-pulsed plasma nitriding treatment (DCPPN ▲) and duplex surface treatment (DST ●).

samples, they did not present appreciable weight loss for all the surface conditions studied.

After the wear tests, all the UHMWPE sample surfaces presented a smooth and well polished macroscopic appearance. SEM observation of these worn surfaces evidenced different damage types, defined by Mc Kellop[25] as changes in the appearance of the bearing surfaces. Figure 3 shows images of worn surfaces of the UHMWPE samples. The UT-PE samples showed a surface with numerous ripples perpendicular to the principal sliding direction and localized foldings (Figure 3a). Similar ripples were found on worn UHMWPE surfaces and were associated to fatigue wear,[21] while the wear mechanisms that control the formation of foldings are not well understood yet.[25] The presence of polymeric particles adhered to the surface (Figure 3b) would also indicate that an adhesion wear mechanism participated. The microscopic appearance of the DCPPN-PE surfaces was smooth and with small sites, where ripples could hardly be distinguished (Figure 3c). As shown in Figure 3d, the DST-PE samples presented a surface not as smooth as for the DCPPN condition, but without a defined wear damage. Embedded metallic particles were not found on any of the polymeric worn surfaces. In addition, after SEM observation, no polymeric adhesion and traces of corrosion were detected on the metallic surfaces.

In Figure 4, SEM images of different wear debris are shown. In all the tests, the wear debris presented plate-like particles and, in several cases, they were accompanied by smaller particles with irregular shape (Figure 4a). The plate-like particles presented in some cases irregular and, in others, smooth surfaces (Figure 4b). There were also rolled plate-like particles, which evidenced different morphologies in each side, as observed by other authors.[21] In the experiments, metallic particles were not found in the wear debris. This result is consistent with

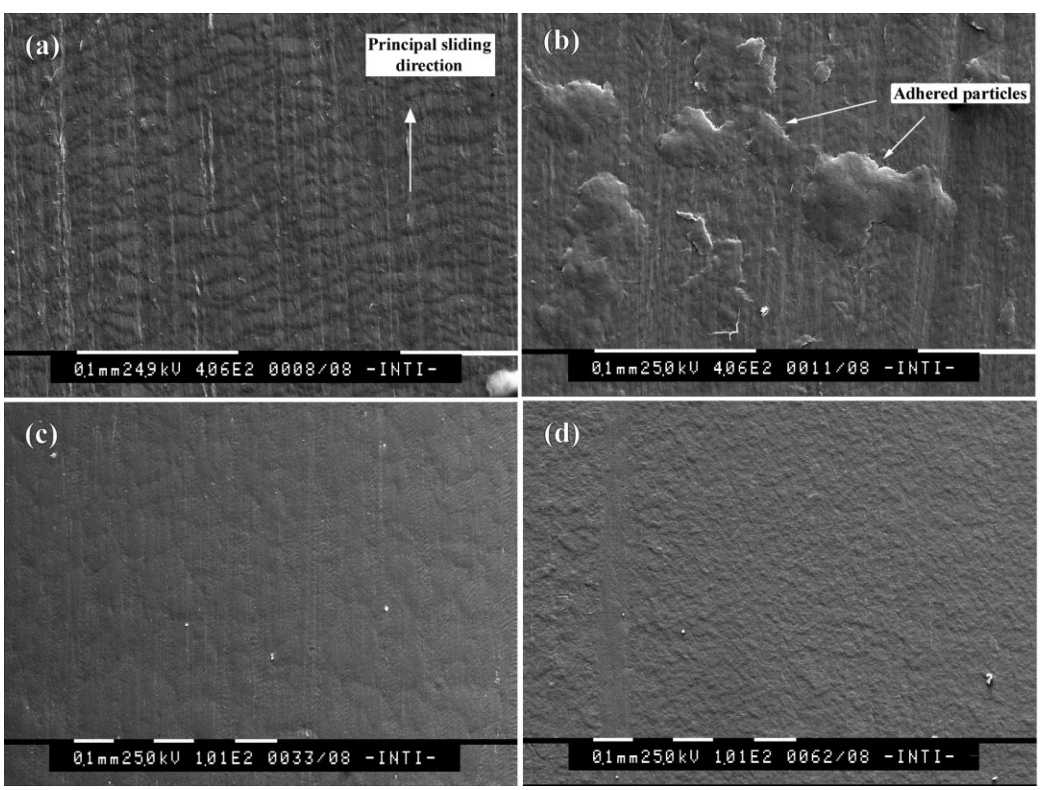

Figure 3. SEM images of different worn surfaces of UHMWPE; (a,b) UT-PE (×400), (c) DCPPN-PE (×100), (d) DST-PE (×100).

Plasma Process. Polym. **2009**, *6*, S75–S80

DOI: 10.1002/ppap.200930306

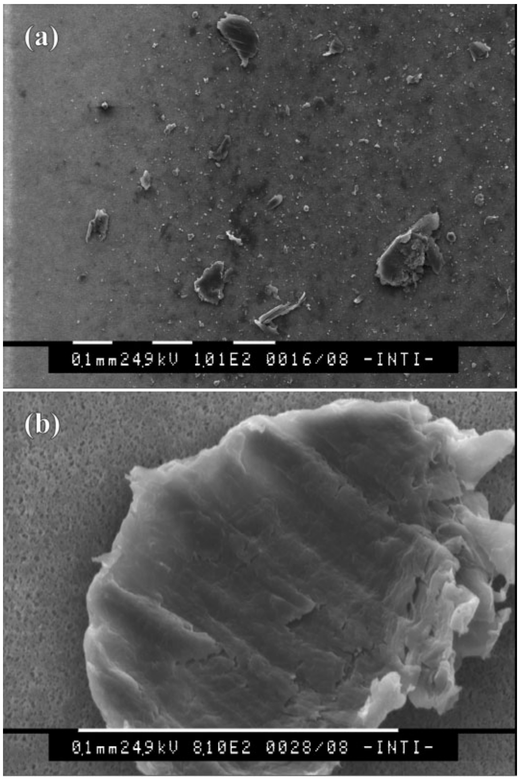

Figure 4. SEM images of wear debris particles; (a) plate-like particles accompanied by smaller particles with irregular shape (×100), (b) irregular side of a plate-like particle (×800).

the absence of embedded metallic particles on the polymeric worn surfaces.

The FTIR spectra of the UHMWPE tested samples did not evidence the presence of oxidation products, for every surface condition. This result suggests that wear and debris formation were faster than oxidation.[26] Thus, polymeric wear oxidation would not have affected the wear behaviour of the tribosystem studied.

According to the literature, the wear process of UHMWPE is extremely sensitive to the roughness of the counterface; a decrease in the initial roughness of the counterface can enhance the wear behaviour of UHMWPE.[10,27–29] In this work, the DST condition evidenced the lowest initial roughness, while the DCPPN condition presented the larger value. On the other hand, despite the lack of consensus on the role of hardness of the counterface on the tribological properties of polymers,[30] it has been reported that a harder and more scratch-resistant surface would reduce the wear rate of UHMWPE.[29,31,32] In this work, the DST condition presented the hardest surface, while the untreated condition was the softest one. Thus, relating the weight loss results with the surface characteristic described above, the DST condition generated the hardest surface and the lowest initial roughness of the counterface, so this would explain the best wear behaviour achieved. Moreover, although the DCPPN condition presented the largest initial surface roughness value, the wear behaviour was better than the UT condition; therefore, the benefits of the surface hardness of the counterface in the DCPPN condition outweigh the effect of a rougher surface.

Furthermore, the weight loss curves obtained and the observed worn surfaces showed correlated features. The UT condition showed the greatest weight loss and it also evidenced damages (foldings and traces of adhesion) that the DCPPN and DST condition did not. The DCPPN condition presented a weight loss lower than that obtained for the UT condition but, as in the UT-PE samples, ripples were found. However, on the DCPPN-PE samples ripples were hardly distinguishable. Moreover, on the DST-PE surfaces no defined damages were observed in accordance with the best wear behaviour. Therefore, these observations suggest that the surface treatments would delay the appearance of damage on the worn surface in agreement with the improvement of the wear behaviour. In this sense, as the ripples are related to a fatigue wear mechanism, it would be expected that they appear on the DST-PE sample surfaces by increasing the number of wear cycles.

Further studies with longer wear test and analysis of size and shape distribution of the wear debris are planned in order to provide a deeper understanding on the wear behaviour of the UHMWPE-AISI 316L tribologycal system.

Conclusion

The results obtained show that plasma-assisted surface modification of the counterface improves the wear behaviour of UHMWPE in a simulated normal walking condition. The best wear behaviour was achieved for the DST condition followed by the DCPPN condition. All the weight loss curves evidenced a running-in period and a steady-state period. A severe wear period was not clearly defined. A higher counterface hardness value improved the wear behaviour of UHMWPE-AISI 316L tribosystem and could outweigh the effect of a rougher surface as it was shown for the DCPPN condition. The DCPPN and DST surface conditions would delay the appearance of damage on the worn surface in agreement with the improvement of the wear behaviour. For the UT-PE samples ripples, foldings and polymeric adhesion were observed on the worn surfaces of UHMWPE. Ripples were also found on the DCPPN-PE samples but they were hardly distinguishable. No defined wear damage was found on the DST-PE surfaces.

In conclusion, plasma-based surface treatment of the counterface has been demonstrated to reduce the wear of UHMWPE on simulated walking conditions.

Acknowledgements: The authors would like to thank *INTI-Mecánica*, *INTI-Plásticos*, for the technical support, *IONAR S.A.* for the nitriding treatments, *Implantes FICO*® for providing the UHMWPE samples, Dr. *G. Ybarra* from INTI-Procesos Superficiales for discussions and FTIR spectra and Dr. *G. López* from the University of the Basque Country for discussions.

Received: September 30, 2008; Accepted: January 23, 2009; DOI: 10.1002/ppap.200930306

Keywords: austenitic stainless steel; joint replacement; plasma treatment; UHMWPE; wear

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