PIRAC Ti nitride coated Ti–6Al–4V head against UHMWPE acetabular cup–hip wear simulator study

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Wear behaviour of TiN(titanium nitride)-coated Ti and Ti–6Al–4V alloy against UHMW polyethylene was studied in hip simulation test. Ti alloys possess an excellent combination of mechanical properties and biocompatibility, however, they suffer from inadequate wear resistance. Thus, their use as articulating components of total joint replacements requires surface hardening, e.g. by TiN. Thirty-two millimetre diameter cp-Ti and Ti–6Al–4V femoral heads were coated with several micrometre thick TiN layers employing an original PIRAC nitriding method based on interaction of Ti alloy substrate with highly reactive monatomic nitrogen. The heads were tested against UHMWPE cups at 37 °C in Ringer's solution or in distilled water. Simulator tests were performed at peak pressures of 1.5 and 2.0 MPa in a constant rotation mode at the frequency of 1.5 Hz. The wear of UHMWPE was estimated by weight loss, and the worn metallic and polyethylene surfaces were examined in SEM.

The wear rate of UHMWPE cups articulating against PIRAC coated Ti and Ti–6Al–4V after up to 4×10^6 cycles was significantly lower than that of UHMWPE articulating against 316L stainless steel. No delamination of TiN coatings was observed after 4×10^6 cycles. These results suggest that TiN PIRAC coating on Ti–6Al–4V heads could minimise the wear of total hip replacements without compromising the mechanical properties of the femoral component.

1. Introduction

Wear damage and deposit of wear debris into body is an important issue in orthopaedics. Periprostetic osteolysis that has been linked to wear debris generated by UHMWPE components sliding against metal or ceramic parts is the most common cause of failure and lack of durability of total joint prostheses. Of all the surgical metals, Ti–6Al–4V alloy has the best combination of biocompatibility, stiffness and fatigue properties, however its wear resistance is inferior to that of 316L stainless steel and Co–Cr–Mo alloys. Coating Ti–6Al–4V with a hard layer of titanium nitride (TiN) is one of the promising strategies to improving the alloy wear behaviour. TiN-coating is biologically inert and has been approved by the Federal Food and Drug Administration for use with titanium and titanium alloy implant components. Earlier, physical vapour deposition (PVD) was used for depositing TiN on orthopaedic implants; these coatings, however, often suffered from lack of adhesion and tended to delaminate in *in vitro* wear simulation tests and clinical studies. To prevent the failure of TiN coating adhesion, surface modification methods capable of providing strong bonding at the TiN coating/substrate interface should be looked for. One such method is the recently developed PIRAC nitriding based on interaction of Ti alloy substrate with highly reactive monatomic nitrogen [1–4]. Conformable TiN PIRAC coatings grown on cp-Ti, Ti–6Al–4V, TiNi (Nitinol) and Ti–Nb alloys were reported to have strong adhesion to the substrate, excellent corrosion resistance and improved fretting behaviour [1–7]. In an on-going dog study, no signs of wear-related osteolysis were revealed around total hip prostheses with PIRAC nitrided Ti–6Al–4V femoral heads articulating against UHMWPE acetabular cups two years after implantation [7].

In the present work, wear of UHMW polyethylene sliding against TiN PIRAC coated Ti–6Al–4V alloy is evaluated in a hip simulator [8–12]. Simulation tests that can reproduce 1 million walking cycles (corresponding to $\sim$ 1 year clinical use) in a few weeks time provide a practical *in vitro* alternative to animal tests or clinical follow-up. Although not exactly reproducing the conditions encountered in clinical use, such simulation tests are useful in predicting tribological behaviour of new materials in comparison with those already in use.

2. Experimental

In a hip simulator, the repeated cyclic movement encountered in a human hip joint is reproduced. Four hip joint wear simulator units fabricated by Dematech Inc. (NJ, USA) (see Fig. 1) provide constant rotation around a vertical axis, or alternating rotation with $\pm 180^{\circ}$ amplitude. A constant load of up to 10 000 N can be applied during testing in a Dematech hip simulator.

Spherical 32 mm diameter heads were fabricated from Ti–6Al–4V alloy, cp-Ti and 316L stainless steel by machining followed by polishing and lapping. The 316L heads were further used as a reference. Acetabular cups/liners with the inner diameter of 32 mm and outer diameter of 50 mm were machined from UHMWPE. To obtain a smoother working surface of UHMWPE, a 32 mm diameter tool steel ball (mirror finish) was pressed against the socket at 100 °C under pressure of 10 MPa.

Ti–6Al-4V and cp-Ti heads were coated with 2–2.5 μm thick TiN–Ti_2N layers by PIRAC nitriding at 900 °C for 4 h. The detailed procedure of PIRAC nitriding is described elsewhere [2]. PIRAC coated surfaces were polished to a mirror finish with surface roughness less than 0.2 μm.

Simulation tests were performed in the constant rotation mode at the frequency 1.5 Hz roughly corresponding to the frequency of human gait. A few tests were also performed with alternating rotation at the frequency of 3 Hz. Two sets of tests with two different loads were conducted: 2350 and 3250 N, corresponding to the static pressure on a hemisphere of 1.5 and 2 MPa, respectively. Ringer's solution and distilled water were chosen as liquid media, since both create tougher conditions for wear as compared to serum acting as a good lubricant. The nominal test temperature was 37 °C. However, when the operating pressure was 2 MPa, the temperature of the liquid increased to 40–42 °C, most probably as a result of friction heat. According to Eddidin and Kurtz [10], a slight increase of temperature during hip simulator test of UHMWPE against different femoral heads does not have a significant effect on the wear rate. UHMWPE sockets were presoaked in the test solution for one week to minimise moisture absorption during testing. During testing, an acetabular cup was placed in a UHMWPE vessel with a taper (conical) fit. After 0.5×10^6 cycles, the cup was removed from the simulator, cleaned, dried by absorbing paper and weighed using an analytical balance of 0.01 mg. The wear of UHMWPE sockets was estimated by their weight loss.

Polyethylene cups and metallic heads were examined before and after wear tests by optical microscopy, scanning electron microscopy (SEM) with chemical microanalysis (EDS) and X-ray diffraction (XRD).

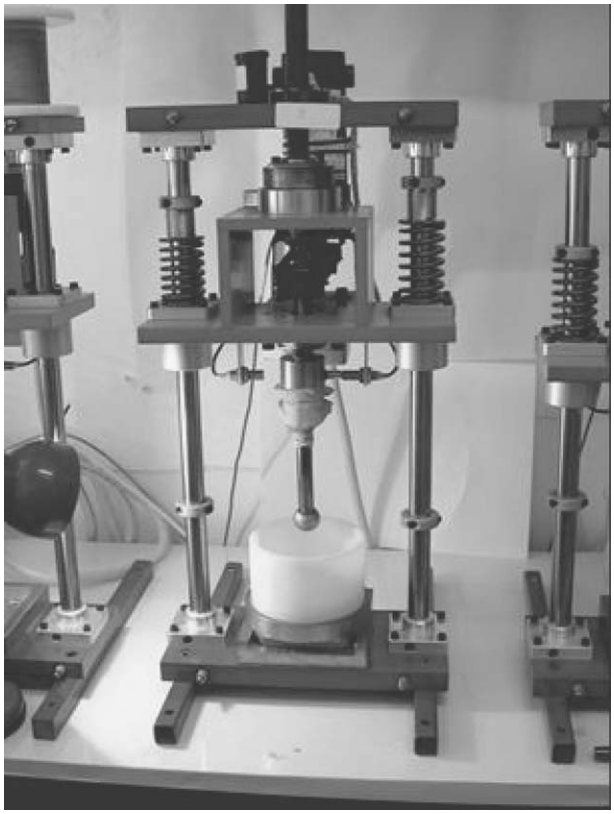

Figure 1 Wear simulator fabricated by Dematech Inc. (NJ, USA).

3. Results and discussion

After 4×10^6 cycles of hip simulation tests in either Ringer's solution or distilled water, the surface of PIRAC nitrided heads retained its golden colour typical of TiN (Fig. 2). No cracking or delamination of the TiN coating was observed. The absence of delamination is especially important indicating strong adhesion of the coating to the substrate. The surface morphology of PIRAC nitrided head after 2×10^6 cycles in Ringer's solution as observed in SEM (Fig. 3) is similar to that of the unworn head. XRD pattern taken from the surface of the head after 4×10^6 cycles under pressure of 2 MPa in distilled water (Fig. 4) is not different from that of the untested head suggesting that no significant thinning of the TiN coating occurred during testing. A few scratches appeared on the surfaces of some heads in the course of testing, most probably caused by hard particles coming from the air. These scratches, however, did not seem to affect the wear rate of polyethylene, since the weight loss results were similar in the case of the scratched and unscratched heads. As can be seen in Fig. 5, the surface

Figure 2 A 32 mm diameter TiN-coated Ti–6Al–4V femoral head (PIRAC, 900 °C, 4 h) after 4×10^6 cycles of hip simulation tests in distilled water, at 2 MPa.

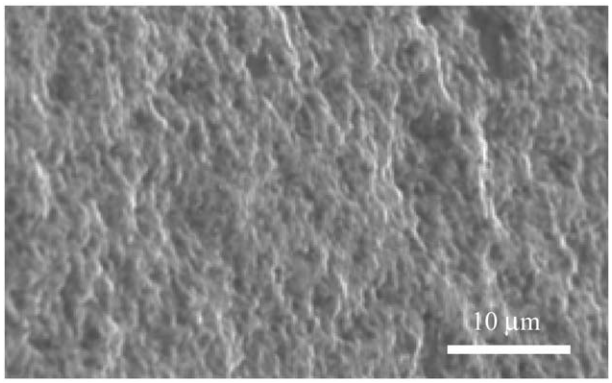

Figure 3 SEM micrograph of TiN-coated Ti–6Al–4V femoral head (PIRAC, 900 °C, 4 h) after 2×10^6 cycles of hip simulation tests in Ringer's solution, at 2 MPa.

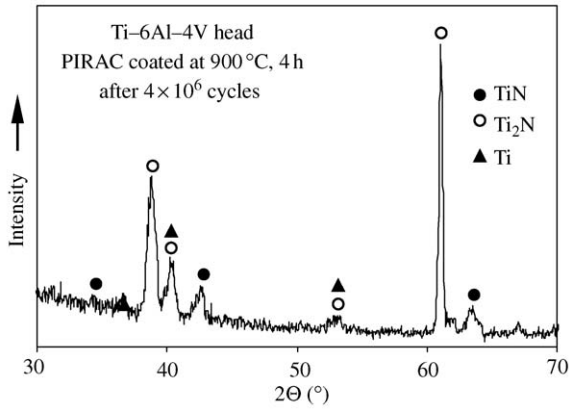

Figure 4 XRD pattern of TiN-coated Ti–6Al–4V femoral head (PIRAC, 900 °C, 4 h) after 4×10^6 cycles of hip simulation tests in distilled water, at 2 MPa. The intensity of TiN peaks has not changed compared to the as-PIRAC-coated head.

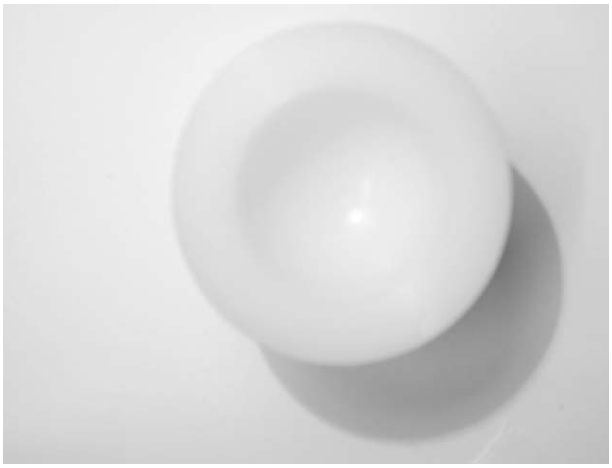

Figure 5 An UHMWPE cup after 4×10^6 cycles of hip simulation tests in distilled water, at 2 MPa.

of UHMWPE cup remained smooth after 4×10^6 cycles in distilled water under pressure of 2 MPa.

The wear of UHMWPE cups in the simulation tests conducted in the constant rotation mode is shown in Fig. 6. Each point on the plot is an average of six separate simulation tests. The weight loss of UHMWPE in distilled water under the pressure of 1.5 MPa is comparable to the data reported for UHMWPE wearing

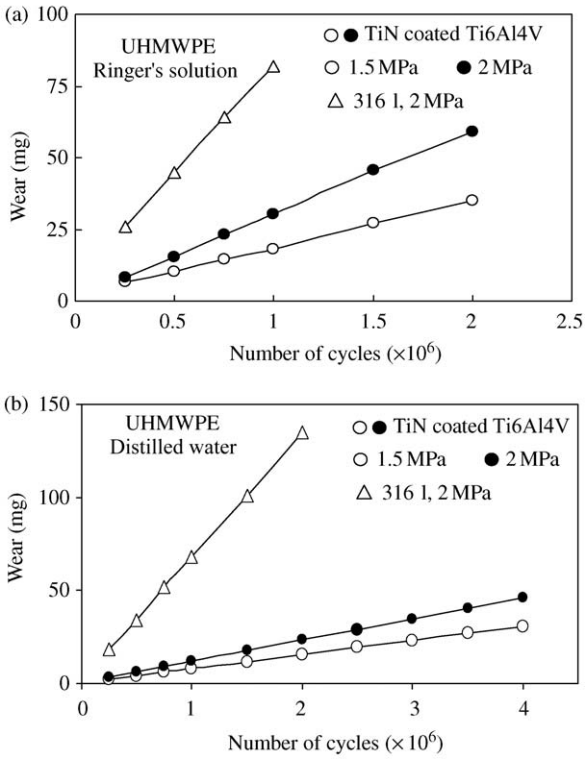

Figure 6 Wear loss of UHMWPE cups against 316L stainless steel and TiN-coated Ti–6Al–4V femoral heads: (a) in Ringer's solution; (b) in distilled water.

against Ti–6Al–4V heads of the same diameter PVD coated with TiN, under a similar load [9]. It can be seen that that in our test, the wear loss of UHMWPE cups against TiN PIRAC coated Ti–6Al–4V heads is significantly lower than that of UHMWPE against 316L stainless steel heads, both in Ringer's solution and in distilled water. Similar results were obtained in the tests with alternating $\pm 180°$ rotation up to 1×10^6 cycles.

4. Summary

An original PIRAC nitriding method was employed for the coating of Ti–6Al–4V alloy with several micrometer thick TiN coatings. PIRAC nitrided femoral head were tested against UHMWPE cups in a hip simulation test for up to 4×10^6 cycles. Both in distilled water and Ringer's solution, the wear rates of UHMWPE against PIRAC nitrided Ti alloy heads was significantly lower than the corresponding wear rates against 316L heads used as a reference. No delamination of the TiN layer was observed after testing indicating strong coating adhesion. These results suggest that TiN PIRAC coating on Ti–6Al–4V heads could minimise the wear of total hip replacements without compromising the mechanical properties of the femoral component.

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