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Tribological behaviour of Ti6Al4V modified by surface treatments

F. BROSSA
Institute for Advanced Materials, JRC, Ispra (VA), Italy
A. CIGADA, S. FARÈ, R. CHIESA, L. PARACCHINI
Dip. Chimica - Fisica Applicata, Politecnico di Milano, Milano, Italy

At present, there are no good materials that can substitute ultra-high molecular weight polyethylene (UHMWPE), therefore the only way forward is to find a material for femoral heads with high wettability and hardness able to minimize the wear phenomena between metal and UHMWPE. In this work, the effects of surface treatments to improve the tribological behaviour of titanium alloy (Ti6Al4V) were studied. Ion implantation, CVD and PVD were the surface treatments investigated. Ti6Al4V modified and not modified samples were tested against γ-ray sterilized UHMWPE pins using a pin-on-flat wear test machine. The results have been compared with the wear behaviour of stainless steel (AISI 316L). Tests were carried out in accordance with ASTM F 732-82 practice, a specific wear test for materials used in total joint prostheses. Metal samples were characterized by SEM micrographs, roughness and hardness measurements, wettability and friction coefficient. UHMWPE wear rates were assessed by weighing the pins at intervals of 250 000 cycles and were expressed by linear regression analysis applied to the weight losses. Ion implantation of the titanium alloy results in lower wear of UHMWPE pins, in particular, chromium implantation is the most efficient among all surface treatments. A tentative explanation of the results is given.

1. Introduction

For the realization of hip prostheses, the coupling between the metallic femoral head and the polymeric acetabular cup is normally used. Many problems can occur on hip joint prostheses due to tribological phenomena, thus representing one of the most important cause of clinical failure. For metal/ultra high molecular weight polyethylene (UHMWPE) couplings, the cup decrease ranges between 0.1 and 0.3 mm/year. Wear particles can reduce the lifetime of an artificial joint due to granuloma tissue and resulting osteolysis [2, 3]. Therefore, the use of wear-resistant material combinations is imperative for the long-term success of articulating total joint replacements.

Titanium alloys are highly corrosion resistant and well tolerated by the human body due to a complex titanium-oxide film consisting mainly of TiO_2, TiO and Ti_2O_3 [1]. Nevertheless, an untreated polished titanium alloy under the mixed lubrication regime encountered in the human joint showed unstable articulation against UHMWPE. With modern surface engineering there are many possibilities to increase the wettability and stability of the titanium surface [4]. Using overlay coatings the bulk material is modified by deposition of layers very different in composition and structure from the base. In contrast, diffusion processes and in particular ion implantation [5] add special elements only at the surface of the existing substrate creating a gradual change in the chemical–physical properties.

The aim of the work is to study, using a pin-on-flat wear test machine, the tribological behaviour of Ti6Al4V treated in different ways.

2. Materials and methods

2.1. Pin-on-flat wear test machine

Tests were carried out on a pin-on-flat wear test machine (ASTM F732) schematically shown in Fig. 1. The pin-on-flat test is characterized by an oscillatory motion with a 25 mm stroke at a rate of 1 cycle/s, producing an average sliding speed of 50 mm/s.

The test load is 225 N and is applied along the longitudinal axis of the UHMWPE specimen, such that the average contact stress is 3.54 MPa. For each material, three sets of specimens were used as an indicator of the repeatability of the results. Each test is about 1 million cycles, stopped every 250 000 cycles to inspect the contact surface of the UHMWPE pin and counterface, and note the characteristics of wear progress.

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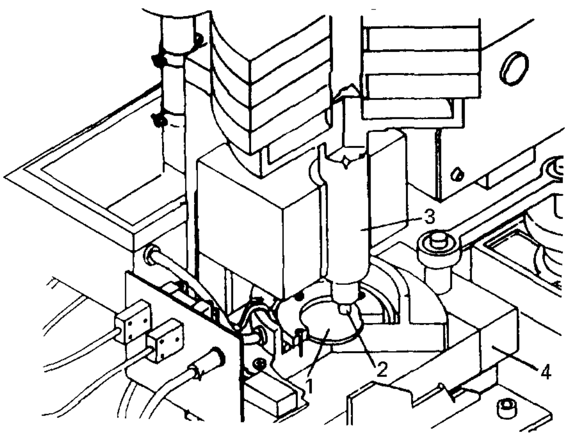

Figure 1 Pin-on-flat wear test facility: (1) metal specimen, (2) UHMWPE specimen, (3) load, (4) slide.

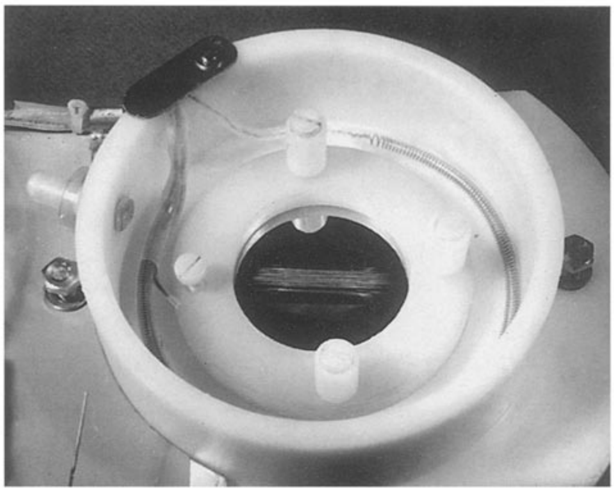

Figure 2 Test chamber; the metal disc and the three control pins are easily seen.

2.2. Materials

Tests were effected by using metal discs with diameters of 40 mm and height of 3 mm and the UHMWPE specimen was a flat ended circular cylinder with a diameter of 9 mm and a height of 13 mm.

Metal materials tested were AISI 316L, untreated Ti6Al4V and Ti6Al4V treated using ion implantation, PVD and CVD surface treatments. The elements implanted were nitrogen, oxygen and chromium, PVD coating is ZrN and CVD film is TiO_2 with two different thicknesses. The ion implantation was chosen because the gradual modification of the surface chemical composition by the introduction of interstitial elements showed an increase in wettability and hardness. The ion implantation was carried out by a high current implanter, model 1090 (DANFYSIC), using a gradual energy technique. The ZrN PVD coating was commercially performed by TTN. TiO_2 CVD film was deposited in laboratories at the Institute for Advanced Materials (CCR, Ispra – Va). UHMWPE pins were subjected to 2.5 MRad γ-ray sterilization and were pre-soaked in serum for 8 weeks before wear test to minimize the absorption during the test.

2.3. Method

Tests were carried out placing the metal disc in a teflon test chamber in bovine serum (pH 7) at 37 ± 1 °C, treated with NaN_3 to minimize bacterial degradation during the wear test (Fig. 2). Three UHMWPE specimens were placed in the chamber as controller of serum soaking during the wear test.

The UHMWPE specimens were examined every 250 000 cycles in order to measure the weight loss and at the end of the test, the UHMWPE wear rates were calculated.

Optical microscopy and SEM were used to analyse metal counterfaces. The surface roughness was measured with a laser facility (RM600, Rodenstock) in accordance with DIN 4762 standard. Nanoindenter measurements were checked on treated and untreated Ti6Al4V to determine hardness (Nano Indenter II, Nano Instruments Inc.). Thus, in order to verify the wettability of metal specimens, the dynamic contact

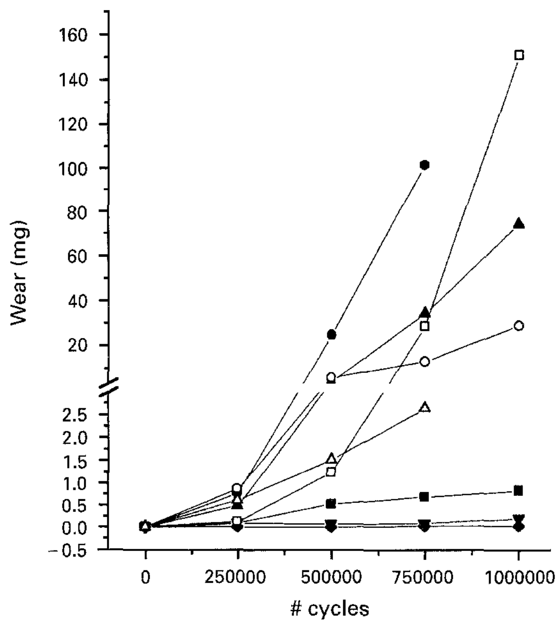

Figure 3 Pin-on-flat weight loss results.
–■– AISI 316L
–●– Ti6Al4V
–▲– Ti6Al4V nitrogen impl.
–▼– Ti6Al4V oxygen impl.
–◆– Ti6Al4V chromium impl.
–□– Ti6Al4V + TiO_2 (0.5 μm) CVD coating
–○– Ti6Al4V + TiO_2 (1.5 μm) CVD coating
–△– Ti6Al4V + ZrN PVD coating

angle was calculated using the CAHN DCA 322 apparatus. Pin-on-disc tests (Tribometer Pin on Disc, CSEM) were carried out to evaluate the friction coefficient of the couplings. Test conditions for the pin-on-flat wear test were: load 10 N with a contact stress of 3.54 MPa, the metal disc was fixed in a teflon test chamber with serum bovine at 37 °C and test length was 1000 m.

3. Results and discussion

The results, expressed in terms of weight loss of the UHMWPE specimens, are summarized in Fig. 3. Through these results, it can be observed that the

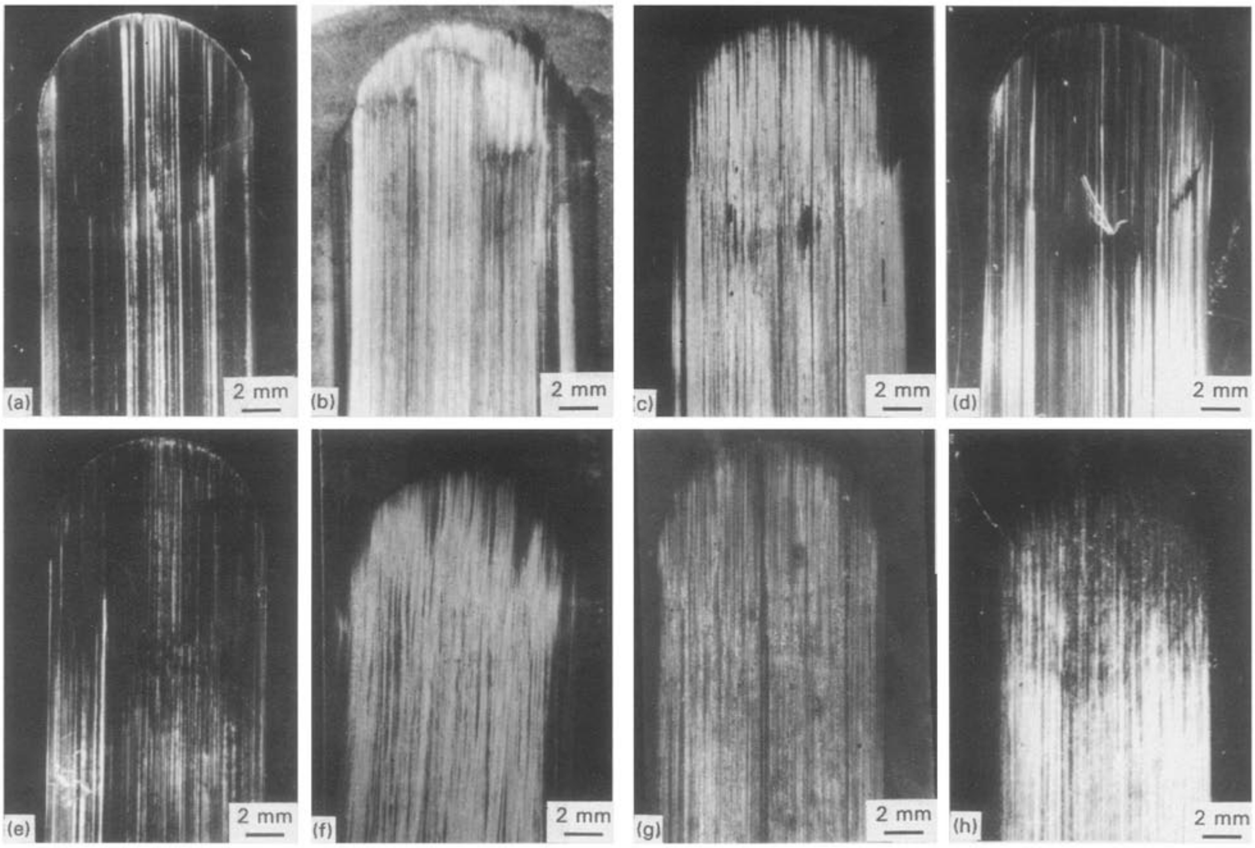

Figure 4 Metal discs after 1 million cycles of pin-on-flat test: (a) AISI 316L; (b) Ti6Al4V; (c) Ti6Al4V nitrogen implanted; (d) Ti6Al4V oxygen implanted; (e) Ti6Al4V chromium implanted; (f) Ti6Al4V + TiO_2 (0.5 μm) CVD coating; (g) Ti6Al4V + TiO_2 (1.5 μm) CVD coating; (h) Ti6Al4V + ZrN PVD coating.

weight loss measurements decrease from untreated Ti6Al4V to Ti6Al4V chromium implanted. The untreated titanium alloy tests were interrupted at 750 000 cycles due to the very high UHMWPE wear rate achieved in comparison to the other tests. Titanium with a ZrN PVD coating shows good behaviour, probably due to the hardness of the coating. The TiO_2 CVD film has a different behaviour depending on the thickness of the coating: TiO_2, 0.5 μm thick shows a high wear rate due to coating debonding, while with a thickness of 1.5 μm, UHMWPE wear decreases.

After the test, the UHMWPE pins were glossy to the eye and metallic discs showed dense patterns of looping scratches on both Ti6Al4V and nitrogen implanted Ti6Al4V. In contrast, a uniform pattern of fine surface scratches was visible on treated Ti6Al4V that caused low UHMWPE wear (Fig. 4).

These results are confirmed by laser roughness analyses, that show higher roughness in metal discs with high wear rates (Table I). A statistic analysis (one-way ANOVA test) shows that, at the 0.05 significance level, the means of roughness measurements on different metal-treated specimens after 1 million cycles are significantly different.

Wettability results show good correlation with weight loss measurements (Fig. 4). Dynamic contact angles of metal specimens are low for couplings with a low UHMWPE wear rate (Fig. 5). In contrast, Ti6Al4V and nitrogen–implanted Ti6Al4V are hydrophobic: less wettability agrees with a high wear rate. It is possible to observe how ion implantation is

TABLE I Roughness measurements

Material	Roughness before tests (R_a)	Roughness after tests (R_a)
AISI 316L	0.020 ± 0.01	0.064 ± 0.00
Ti6Al4V	0.044 ± 0.03	1.804 ± 0.87
Ti6Al4V N impl.	0.033 ± 0.02	0.904 ± 0.02
Ti6Al4V O impl.	0.045 ± 0.02	0.131 ± 0.01
Ti6Al4V Cr impl.	0.058 ± 0.00	0.116 ± 0.00
Ti6Al4V + TiO_2 (0.5 μm)	0.060 ± 0.05	0.732 ± 0.01
Ti6Al4V + TiO_2 (1.5 μm)	0.054 ± 0.04	0.712 ± 0.00
Ti6Al4V + ZrN	0.068 ± 0.03	0.323 ± 0.01

able to change a hydrophobic surface (Ti6Al4V) in a hydrophile surface.

Also friction coefficient results can be correlated with UHMWPE weight loss. Nanoindenter measurements show that there is no good correlation with the wear rate (Fig. 6).

Ion implantation on titanium alloy is a technique for reducing the friction coefficient in the Ti6Al4V/UHMWPE coupling. This treatment induces changes in the chemical structure of the surface by creating hard phase carbide, nitride and oxide precipitates, and thus a highly disordered structure in the surface layers of the lattice. The increased surface activity produces more adherent oxide layers increasing wear resistance of ion-implanted titanium alloy. Pin-on-flat wear tests

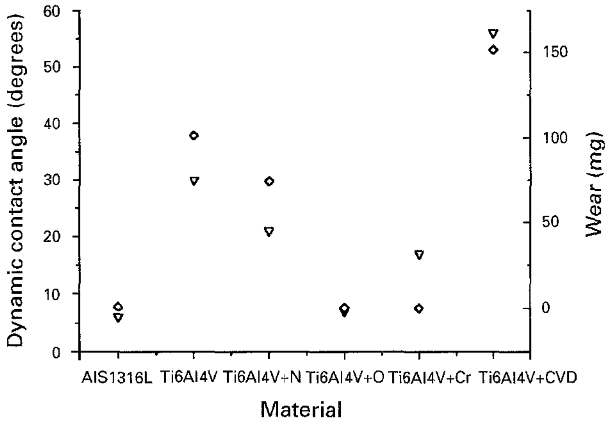

Figure 5 Dynamic contact angles (∇) and UHMWPE wear rate (◇).

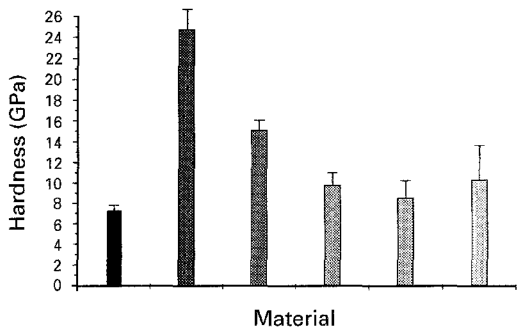

Figure 6 Nanoindenter measurements
■ Ti6Al4V
■ Ti6Al4V nitrogen impl.
■ Ti6Al4V oxygen impl.
■ Ti6Al4V chromium impl.
■ Ti6Al4V helium impl.
□ Ti6Al4V $+TiO_2$ (0.5 μm) CVD coating

carried out on Ti6Al4V implanted with helium and xenon have shown a reduced effect compared to samples implanted with oxygen or chromium. These results confirm that the effects of ion implantation depend on the element implanted.

4. Conclusions

Tests show the good wear resistance of UHMWPE against Ti6Al4V bearing surface ion implanted with oxygen and chromium or coated with ZrN by PVD. With these surface treatments it is possible to decrease the wear rate to significantly lower values than those of untreated Ti6Al4V.

In particular, ion implantation on Ti6Al4V reduces friction between the titanium alloy and the UHMWPE. This effect is not totally justified by the surface hardening caused by lattice disorder, interstitial elements or dispersed compounds. Probably, the chemical composition of the surface is responsible for the improvements obtained.

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