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Tribological behaviour of Cl-implanted TiN coatings for biomedical applications

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Abstract

The tribological behaviour of the prosthetic pair TiN coated stainless steel/ultra high molecular weight polyethylene (UHMWPE) may be improved by chlorine-implantation of the TiN surface. Friction and wear were determined using a pin-on-disk apparatus and the wear mechanisms were investigated through scanning electron microscopy (SEM) and atomic force microscopy (AFM). Rutherford backscattering spectrometry (RBS) was used to determine the chlorine distribution profiles in the chlorine-implanted TiN coatings before and after the tribological experiments, while X-ray photoelectron spectroscopy (XPS) was used to characterize chemically the same samples. Chlorine-implantation led to a significant polymeric wear reduction when the lubricant was Hanks' balanced salt solution (HBSS). If bovine serum albumin (BSA) was added to HBSS, a strong decrease of both friction and polymeric wear was observed for implanted and non-implanted TiN coatings. The former case was explained by the formation of a titanium oxide layer on the TiN surface, while the latter derived from albumin adsorption.

Keywords: Chlorine ion-implantation; TiN coating; UHMWPE; Friction; Wear; Albumin

1. Introduction

Osteoarthritis and rheumatoid arthritis are rheumatic diseases which often require substitution of natural joints by prostheses, especially in what concerns hip and knee. The most common cause of failure and lack of durability of total hip prostheses is related with the generation of ultra high molecular weight polyethylene (UHMWPE) wear debris from the acetabular part, when sliding against the ceramic or the metallic ball which substitutes the femoral head. The debris can lead to the inflammation of surrounding tissues and give rise to a process of bone resorption (osteolyse), which often results in the loosening of fixation of the acetabular and/or femoral parts.

In order to improve the tribological performance of the UHMWPE components, several solutions have been proposed, such as the research of new formulations and processing methods for the polymer [1–3], changes in sterilization methods to avoid oxidative degradation [4,5] or surface treatments and coatings both on the polymeric and metallic parts [6–11]. Most of the studies focused on the effect of hard coatings or surface treatments as ion implantation found a significant reduction of the polymer wear and metallic surface abrasion [8,9,12,13].

Titanium nitride (TiN) is one of the most studied ceramic coatings due to its known biocompatibility [14,15]. This material leads to a significant increase in the metallic surface hardness, helps in the protection against corrosion [16,17] and reduces the bacterial colonization [18]. It is also responsible for

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a significant decrease of the metal ion release to the biological fluids [19].

Ion implantation is used to modify a large variety of surface properties, such as the surface hardness, the resistance to friction, wear, fatigue, corrosion and oxidation. The mechanical properties of the underlying material are preserved, since the depth of penetration of the ions is generally lower than 1 μm. There are several studies about the effect of the implantation of hydrogen, helium, nitrogen, argon, oxygen or carbon ions in biomaterials used in joint prostheses [9–11]. The role of chlorine ion in this type of applications was never investigated. However, it is known that when implanted on TiN coatings in cutting tools and forming dies, this ion gives rise to a significant decrease of friction and wear in dry conditions, which was attributed to a mechanism of self-lubrication [20,21].

The objective of the present work was to assess if chlorine-implanted TiN coating on the metallic components is a good solution to improve the tribological performance of prosthetic pairs. We investigate the tribological behaviour of these coatings deposited on stainless steel substrates rubbing against UHMWPE in lubricated conditions. As lubricants, the biological model fluid Hanks' balanced salt solution (HBSS) and solutions of albumin, the major protein present in the periprosthetic fluid, in HBSS were used. Friction and wear were determined using a pin-on-disk apparatus and the wear mechanisms were investigated through scanning electron microscopy (SEM) and atomic force microscopy (AFM) observations of both disks and pins. Rutherford backscattering spectrometry (RBS) was used to determine the chlorine distribution profiles in the chlorine-implanted TiN coatings before and after the tribological experiments while X-ray photoelectron spectroscopy (XPS) was used to characterize chemically the same samples. Comparison studies were made with Ar-implanted TiN coatings to elucidate the specificity of the chlorine ion. Argon ions were chosen due to the similarity in size with the chlorine ions. Since the surface wettability of the prosthetic materials is known to affect its tribological behaviour [22], the surface energy of the substrates was determined as well as the interfacial behaviour of the various combinations lubricant/prosthetic pair.

We should point out that the citotoxicity studies which are necessary to qualify Cl-implanted TiN coating as a biomaterial, are presently under way.

2. Experimental

2.1. Materials

Disks of UHMWPE (CHIRULEN®, Poly Hi Solidur, Germany) with 7 cm of diameter were cut from sheet with 1 mm of thickness. The counterfaces were pins of AISI 316L austenitic, stainless steel with 1 cm of diameter coated with TiN. The TiN coating was deposited by PVD—arc evaporation with a METAPLAS coating machine, at 300 °C, using a Ti cathode. The samples were etched with titanium ions at 900 V bias voltage to remove any possible oxide on the surface. In the deposition process the following parameters were used: 200 A cathode deposition current; 100 V bias voltage and 1.4×10^{-2} mbar for the nitrogen pressure. The thickness of TiN coating, measured with a profilometer, varied between 1.2 and 1.6 μm and the average roughness (R_a), measured by AFM for an analysed surface area of 225 μm^2, did not exceed 30 nm.

TiN coated substrates were implanted with chlorine ions, with a nominal fluence of 1×10^{17} cm^{-2} and energy 150 keV, at room temperature. For comparison purposes, some substrates were implanted with argon ions in the same conditions. In these conditions the total energy density deposited in the TiN coating was 2.4 kJ/cm^2 at a rate of 0.43 W/cm^2. The base pressure in the implantation chamber was in the range of 10^{-5} Pa, and the pressure during implantation was in the range of 10^{-3} Pa.

All substrates were cleaned in an ultrasonic bath with Extran® diluted solution for 10 min and with distilled and deionised water for 2 × 10 min and dried overnight at room temperature in a vacuum oven. To test the possibility of water absorption by polymeric substrates, a few were immersed in water for 2 h, but no increase in weight was detected.

Hank's balanced salt solution (Sigma, ref. H8264) and solutions of bovine serum albumin (BSA; Serva ref.11930) in HBSS with a concentration of 4 mg/mL were used as lubricants.

The standard liquids used for measuring static contact angles were water (distilled and deionized) and diiodomethane (Merck ref. 6053, doubly distilled under vacuum).

2.2. Methods

2.2.1. Tribological tests

The tribological experiments were carried out at room temperature on a rotating pin-on-disk tribometer Wazau TRM1000. A normal load of 67.5 N was applied which corresponds to a pressure in the contact zone of 0.88 MPa. The tangential sliding velocity was 46 mm/s and the sliding distances were 1000 m. The wear rate of UHMWPE, whose density is 935 kg m^{-3}, was calculated following a weight loss measurement technique. The results are the average of, at least, three experiments for each system.

2.2.2. RBS

Chlorine distribution profiles were measured by Rutherford backscattering spectrometry (RBS). All the RBS analyses were performed using 2 MeV He^+ beams from a 2.5 MV Van de Graaff accelerator. The backscattered ions were detected by means of two silicon surface barrier detectors, placed at angles of 140° and close to 180° to the incoming beam direction, and having energy resolutions of 13 and 18 keV, respectively.

2.2.3. SEM and AFM

Analysis of the surfaces by scanning electron microscopy was performed on Hitachi S2400 equipment. For SEM observations, the polymeric surfaces were previously covered with gold.

A Dimension D3100 with a Nanoscope IIIa controller from Digital Instruments was used for AFM measurements. The imaging was performed in TappingMode using commercial tapping mode etched silicon probes. The measurements were performed under ambient conditions.