Wear 303 (2013) 211–215

Contents lists available at SciVerse ScienceDirect

Wear

journal homepage: www.elsevier.com/locate/wear

# Tribological behavior of a novel alumina/nano-zirconia/niobium biocomposite against ultra high molecular weight polyethylene

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ARTICLE INFO

*Article history:*
Received 23 November 2012
Received in revised form
6 March 2013
Accepted 7 March 2013
Available online 22 March 2013

*Keywords:*
Sliding wear
Cermets
Bio-tribology
Joint prostheses
Solid lubricants

ABSTRACT

The present work has studied the dry sliding behavior of $Al_2O_3$–$nZrO_2$–Nb micro–nanobiocomposites against ultrahigh molecular weight polyethylene (UHMWPE) in air. The tests were carried out with a reciprocating wear tester with an applied load of 30 N, a sliding speed of 0.06 m/s and sliding distance up to 10 km. Under the adopted testing conditions, the ceramic–metal composite against UHMWPE shows one and a half order of magnitude lower wear rate than the monolithic alumina; and friction coefficient as low as half of that for pure alumina–UHMWPE system. This behavior is related with: (a) the improvement in mechanical properties (toughness and strength) that will lead to the corresponding improvement in wear properties, and (b) the formation of a self-lubricating layer that will provide sufficient lubrication in order to considerably reduce the friction, as compared to monolithic alumina against UHMWPE combination.

## 1. Introduction

Despite the brittleness, ceramic materials are among the most wear resistant materials because of their hardness, elastic modulus and fracture strength [1]. However, the coefficient of friction between ceramics is generally high under unlubricated sliding conditions [2,3]. On the other hand, their low intrinsic toughness can promote the intergranular fracture mechanisms leading to grain pull-out process. In this case, the material removal is the dominant wear mechanism, and the wear rate increases dramatically. One of the most common biomaterials combinations used for heavy load bearing applications, particularly in traditional hip replacement, is the ultrahigh molecular weight polyethylene (UHMWPE) against alumina ceramics. Nevertheless, it has been reported that fine UHMWPE wear debris, generated primarily at the interface between the femoral head and the acetabular cup, promotes osteolysis [4,5]. This wear particle induced bone loss is one of the main problems affecting the long-term stability of UHMWPE in load bearing implants [6,7]. Many researchers have tried to minimize the wear induced osteolysis by modificating the design or the properties of the UHMWPE [8,9]. However these approaches do not seem to be a real solution [10]. An alternative and more effective solution is to introduce a self-lubricating ceramic composite material as counterface, consisting of a hard ceramic matrix and a supply of a solid lubricant which is embedded into the ceramic matrix. In this situation it is likely that stresses associated with the sliding movement and temperature contribute to the deformation of the ductile phase that transfers to the contact surface, promoting the formation of a lubrication layer. This layer can be worn away during further sliding but it is regenerated by the composite material in the sliding contact. The formation of this lubrication layer is expected to reduce the friction coefficient as well as the wear rate. It has also been found that the experimental conditions such as load, sliding speed and temperature have an important effect on the layer formation [11–14]. The use of self-lubricating composite materials has been studied previously with different monolithic ceramic matrices such as zirconia [15], alumina [16,17], SiC [18] or $Si_3N_4$ [13].

In a previous work [19], we have developed a new generation of $Al_2O_3$–$nZrO_2$–Nb micro–nanobiocomposites that open the possibility to tailor new materials with toughening mechanisms operating at different scales. For a scale below the one of the matrix microstructure, this enhances the “intrinsic” fracture properties of the material. This intrinsic increase of resistance to crack initiation and propagation due to a structural synergism between the matrix phase and dispersoid, should lead to an increase in the catastrophic failure strength. On the other hand, the extrinsic mechanism like bridging of the ductile metallic elongated particles can enhance the crack growth resistance [20–22]. These results

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http://dx.doi.org/10.1016/j.wear.2013.03.015

have demonstrated that nanocomposite and ductile phase toughening concepts can be successfully used together to enhance the intrinsic fracture toughness and crack growth resistance of ceramic materials.

In this work niobium was chosen because of two main reasons. First, its ductility is a convenient advantage in order to improve the resistance to crack propagation mentioned above. On the other hand its proven biocompatibility [23,24], makes this metal an excellent candidate to be used as biomaterial. Therefore, this particular cermet combination may be considered to be used in the field of biomaterials [25].

The aim of this work was to evaluate the wear behavior of UHMWPE against $Al_2O_3$–$nZrO_2$–Nb micro–nanobiocomposites in dry conditions. These preliminary tests were not designed to provide long-term wear characteristics, but rather to differentiate the polymer/ceramic as well as polymeric/biocomposite combinations at short time intervals.

## 2. Experimental

### 2.1. Materials processing

Alumina nanopowders with 1.7 vol% (2.5 wt%) of $ZrO_2$ were prepared from powder-alkoxide mixtures using $\alpha$-$Al_2O_3$ (99.99%) (TM-DAR, Taimei Chemicals Co. Ltd.), with an average particle size of $d_{50}$=0.15 μm, a BET specific surface area of 14.5 $m^2/g$ and the following chemical analysis (ppm): Si (10), Fe (8), Na (8), K (3), Ca (3), Mg (2), Cu (1), Cr ( < 1), Mn ( < 1), U ( < 0.004), Th ( < 0.005) and zirconium IV-propoxide (70% solution in 1-propanol) (Sigma-Aldrich, Spain). In order to eliminate the humidity, alumina powder was first heated to 250 °C for 10 h. Stable slurry was prepared by dispersing alumina powder in anhydrous 99.97% ethanol. The sol was diluted in anhydrous 99.97% ethanol (66.7 vol% sol; 33.3 vol% anhydrous ethanol) and then added drop wise to the alumina slurry. After drying under magnetic stirring at 70 °C, the powders were thermally treated at 850 °C for 2 h in order to remove organic residuals and were subsequently attrition milled with alumina balls for 1 h. Further details on the powders preparation procedure are shown in Schell et al. [26].

Niobium powder (Goodfellow) of 99.85% purity and with an average particle size of $d_{50}$=35 μm was attrition milled with zirconia balls in a Teflon container for 4 h using isopropyl alcohol as liquid media. Due to this process, niobium particles with a lamellar shape, high-aspect ratio and a $d_{50}$=41 μm were obtained. In previous works, we have demonstrated that the ability of the metallic particles to deform plastically is higher when reducing their thickness. This provides the composite material with improved mechanical properties that are not achievable without milling the niobium particles [20].

Alumina–$nZrO_2$ and alumina–$nZrO_2$ with 20 vol% milled niobium suspensions of 80 wt% solid content were prepared using distilled water as liquid media and a 3 wt% addition of an alkali-free organic polyelectrolyte as surfactant. The mixtures were homogenized by milling with zirconia balls in polyethylene containers at 150 rpm for 24 h and then dried at 90 °C for 12 h. The resulting powders were ground in an agate mortar and subsequently passed through a 75 μm sieve. The powders were hot pressed at 1500 °C for 1 h with heating and cooling rates of 600 °C/h in an inert 100% Ar atmosphere. As a result, discs with 50 mm diameter and 5 mm thickness were obtained.

For comparison purposes, an alumina pure sample was also prepared. Finally, in order to make the pins for the tests, the produced materials were machined carefully to obtain prismatic bars with 15 mm × 3 mm × 4 mm dimensions.

### 2.2. Wear experiments

Wear experiments were carried out in a tribometer (Model MT/60/NI; Microtest, Madrid, Spain) with a reciprocating motion, in which the stationary pin, is loaded with a dead weight on the horizontal UHMWPE reciprocating plate. The rectangular pin contact surface (3 mm × 4 mm) was polished with diamond paste down to 1 μm and then with a colloidal silica suspension to avoid geometrical discontinuities in the contact region, providing a relatively constant contact pressure between the pin and the UHMWPE plate (40 mm × 30 mm) during the test. Previous to the wear test, the samples were washed ultrasonically in an acetone bath for 5 min and then dried at 90 °C for 30 min.

The tangential friction force between the pin and the plate was measured by the strain gauges fixed on leaf springs attached to the transverse bar holding the wear pin. The strain-gauge output voltage was passed through an amplifier and plotted on a chart recorder. Subsequently, by converting this voltage to friction force, friction coefficient data were collected. A constant force of 30 N was applied, resulting in an apparent contact pressure of about 2.5 MPa, a value similar to those borne by the femoral heads [27].

A sliding velocity of 0.06 m/s was applied. The test duration was associated with a traveling distance of 10 km. After each sliding test, the worn surfaces were cleared by blowing pressurized air before post-mortem observations. All tests were performed under the same conditions. The specific wear rate $W$, was measured using Eq. (1):

$$W = \frac{\Delta m}{\rho F_N S} \tag{1}$$

where $\Delta m$ is the weight wear loss of the components (pin and UHMWPE plate) after the wearing test, $\rho$ is the specimen density, $F_N$ the applied load and $S$ the sliding distance. The wear mass loss and the density of each specimen was measured with an electronic balance (Sartorius, LA120S, Goettingen, Germany), resolution 0.1 mg. The microstructure of sintered specimens surfaces was polished down to 1 μm and the pin surface after wear test was studied by scanning electron microscopy (SEM, Hitachi, model S3000 N).

## 3. Results and discussion

Fig. 1 shows SEM images of a thermally etched, polished section of, (a) monolithic $Al_2O_3$, (b) $Al_2O_3$–$nZrO_2$ composite and (c) $Al_2O_3$–$nZrO_2$–Nb micro–nanobiocomposite. In Fig. 1b the $ZrO_2$ and $Al_2O_3$ grains are the brighter and darker phase, respectively. In Fig. 1c the brighter phase are the niobium grains. In this particular case, the thermal etching was carried out in Ar atmosphere, to avoid the Nb oxidation.

Fig. 2 represents the friction coefficient as a function of the sliding distance registered during the wear test for the different materials when worn against UHMWPE. As it can be observed the friction coefficient increases throughout the first meters of sliding and then stabilizes in all cases. This behavior can be attributed to a wear process of the UHMWPE during the first 4000 m in the case of the ceramic materials and 1000 m for the reinforced composite. This wear process establishes a smooth wear track surface, by plowing away the surface asperities or roughness peaks. As the wear proceeds further, the wear track becomes smoother and the coefficient of friction fixes on a steady level. It is important to notice that in the case of the reinforced composite, the difference between the first friction coefficient value and that for the steady level is lower than in the other materials. This may be attributed to the role that niobium plays in the tribological system. It is also important to point out that the final friction coefficient value is