Bioceramics

BIOTRIBOLOGICAL CHARACTERIZATION OF THE BILAYER SYSTEM: HA/ZRO$_2$ ON 316LSS

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ABSTRACT

Orthopedic prostheses have to be highly resistant to wear and physiological corrosion. The bilayer system HA/ZrO2/316LSS is proposed in this work as a coating that fulfills these requirements, because it a presents very good physiological corrosion resistance. The hydroxyapatite coating was deposited by screen printing on 316LSS previously covered by electrophoresis with a zirconia thin film and thermally treated at 650 °C for 5 min. The biotribological characterization was carried out on 316LSS hip heads and acetabular cups in Hip Simulator FIME II equipment, using bovine fetal serum (BFS) as a lubricant. Scanning electron microscopy images were obtained at the beginning and at the end of the test in order to observe the wear produced on the samples. EDS chemical analysis was also obtained. From the obtained results, the role of the hydroxyapatite as a solid lubricant was elucidated and it was concluded that the bilayer system actually works efficiently to protect the 316LSS prosthesis under extreme working conditions.

INTRODUCTION

New materials have been designed for specific implants and organs. In the last century, millions of people have had the need to use dental implants, bone substitutes (prostheses and refills) and hybrid organs (digestive apparatus parts) [1].

The human body is an engineering work; however, wear and degradation are part of the useful life, and, as with any machine, after failure some parts have to be substituted by implants or prostheses. Materials Science Scientifics have recently been trying to provide a solution to this specific requirement. In this application all the materials science areas are involved because the human body is formed of ceramics (hydroxyapatite, fluoroapatite), metals (Fe, Cr, Ca), polymers (keratin), composites (myosin and actin) and organic materials (albumin, glucose, cholesterol) [2]. Moreover, the human body transports substances and nutrients necessary for chemical stability using a fluid composed mainly of chlorides, called blood plasma. The blood plasma has a pH of 7.4, indicating that there is a lightly basic environment. However, it is highly corrosive and degrade

316LSS, Co-Cr and titanium alloys. Besides the problem of degradation by corrosion, the implants are also subject to wear, which can be attributed to three different causes: natural wear, chronic-degenerative diseases and lack of lubrication [3]. So the prosthesis must present mechanical stability, wear and corrosion resistance and biocompatible properties [4].

Biotribology is an area of tribology with applications in biomechanics, biomaterials, orthopedic and biologic systems [5]. Thus biotribology studies friction, wear and lubrication in diarthrosis systems like the hip joint [6].

The biotribological test has been designed to test whether materials reach the standard wear resistance in a physiological medium, simulating the movement conditions of the prosthesis in the body's service.

An osseous joint is a low friction complex mechanism that permits movement and transmission of load from bone to bone. The bones end in joints covered by articular cartilage tissue of about 2 mm thickness and lubricated by synovial liquid, in amounts of approximately 0.5–2 ml [7, 8].

The hip joint is the joint that demands the greatest wear resistance. For this reason, biotribological equipment is designed to simulate femoral heads. This joint presents simultaneous static and dynamic momentums composed of six movements in three sectional planes during the walk cycle. These movements are flexion-extension (FE), abduction-adduction (AA) and internal-external rotation (IE). All these movements are presented simultaneously within a period of approximately 1.1 seconds, with a charge-discharge cycle called Paul´s cycle that simulates the charge produced during the heel lean on the floor, the oscillation and the other heel lean [9]. The biomechanical simulators have been designed with these walk cycles and Paul´s cycles.

In the biotribological test, the physiological condition simulation as well as the biomechanical simulation must be controlled. This test presents extreme and accelerated conditions of load and movement. The results must confirm that the geometry and material design are adequate under these extreme operating conditions [10].

The biotribological behavior of the HA/ZrO_2/316LSS bilayer system proposed as a biomaterial is presented and analyzed in this work.

EXPERIMENTAL PROCEDURE

Substrate Preparation

The 316LSS femoral heads were schemed in a HAUS wheel; model HAA5, with ¾ of the sphere, 30 mm in diameter, joined to an offshoot 50 mm in length. The 316LSS acetabular cups were also machined in a Mazak wheel, model NEXUS250 II, with a 30 mm diameter and joined to an offshoot 30 mm in length. The substrate used was 316LSS because it is the material commonly used for prostheses in the Public Assistance Health System in Mexico. This alloy has a chromite thin film on the surface, and this oxide plays an important role in the anchorage of the bilayer coating as was described in a previous work [11]. The femoral heads and acetabular cups were polished with SiC sandpaper from 400 to 4000 mesh and with alumina of three different sizes: 1

μm, 0.3 μm and 0.05 μm. The samples were mirror polished; a final roughness of 0.06 μm was measured in both cases by a Taylor Hobson LTD profilometer.

ZrO_2 coating application

The 316LSS femoral heads and acetabular cups substrate was coated with a ZrO_2 film using the electrosynthesis deposition method (EDP). The deposition solution used in this process was 0.005M $ZrOCl_2$ (Aldrich)/water, and the electrodeposition was carried out by applying a bias potential of 9 mV with a deposition time of 90 sec. The deposited films were dried at 100 °C for 30 min in order to attain the complete elimination of the HCl formed during the $ZrOCl_2$ hydrolysis; the description of the electrodeposition conditions can be found in a previous work [11].

HA coating application

The hydroxyapatite (HA) coating was made by using a screen printing technique on the ZrO_2/316LSS. The HA paste was elaborated with HA (Alfa-Aesar) and propylenglycol (Baker) with a rate of 7:3. The paste was applied through a polymeric mesh with 120 threads/cm^2. The propylenglycol was evaporated by thermal treatment at 200 °C for 10 min. The complete bilayer HA/ZrO_2/316LSS system was thermally treated at 650 °C for 5 min. The deposition screen printing method and conditions were also described in a previous work [11]. The interface formed with the thermal treatment between HA and ZrO_2 coatings was analyzed by scratching the HA coating with a stainless steel spatula. Figure 1 shows photographs of the femoral heads and acetabular cups coated with the bilayer system and the interface. Hence the femoral heads and acetabular cups that were tested were 316LSS, ZrO_2/316LSS, HA/ZrO_2/316LSS and the HA/ZrO_2 interface.

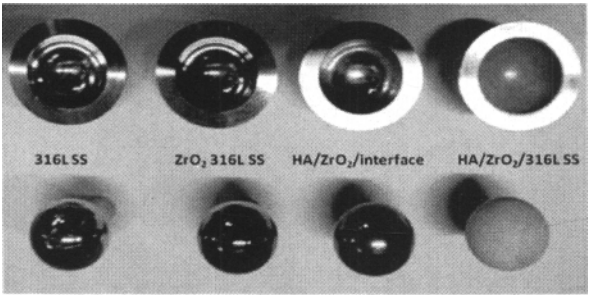


Figure 1.- Biotribological test joins.

All samples were tested in the FIME II biotribometer [12] in anatomical position and the AA, FE and IE movements were simulated. Every station was lubricated with 62.5 ml of fetal bovine serum diluted in 187.5 ml distilled water as recommended by Tiina Ahlroos [8]. After each step of 4 x 10^3 cycles the serum was changed, the articulations were washed and the weight of each femoral head and acetabular cup was registered. The tests continued until they reached 2 x 10^4

cycles, which is equivalent to 4 x 10^4 steps with a load of 3 KN, which is equivalent to the weight of a mass of 300 kg.

The joints morphology was analyzed before and after the test in two JEOL scanning electron microscopes, JSM-6490LV and 5910LV models, at low vacuum with backscattering electrons. Chemical analysis was carried out in a Phillips model XL30ESEM scanning electron microscope at high vacuum.

RESULTS AND DISCUSSION

In general, the expected service of an orthopedic prosthesis and in particular the most modern hip prosthesis is from 12 to 15 years. This is a long period; however, it can be reduced due to physiologic attack and wear on the prosthesis [13].

In figure 2, the movements and loads applied to the joints during the biotribological test are shown in accordance with the ISO 14242 norm [14].

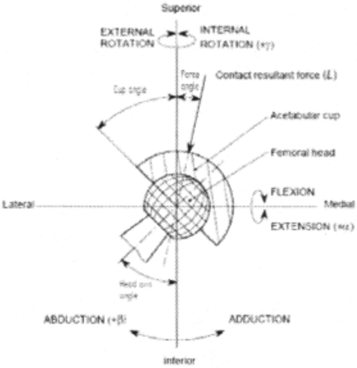


Figure 2.- Mobility and loads on hip join [14].

Figure 3 shows the SEM images of 316LSS substrates. Figure 3a shows the naked 316LSS substrate surface before the biotribological test: it presents some porosity. Figure 3b shows a low magnification (100×) SEM image of the 316LSS substrate after 20000 cycles of the biotribological test. The surface presents damage in several places, consisting of deep disordered furrows and deep holes. Images of different zones at different magnifications are presented in figures 3c (250×) and 3d (2000×), showing the damage produced by wear and fatigue of the substrate during the test. It is evident that the 316LSS substrate suffered loss of material during the test.

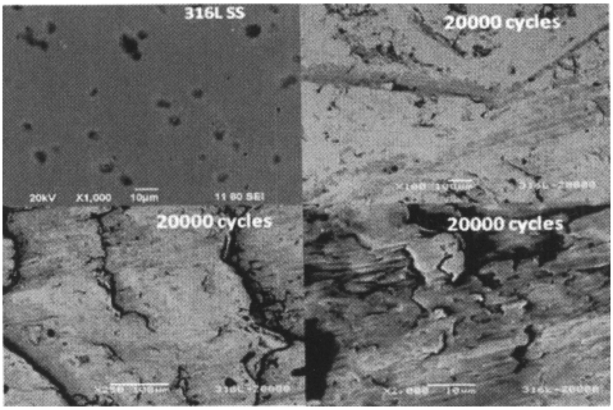


Figure 3. 316L SS SEM images a) before Biotribologycal test and after of 20000 cycles b) 100X, c) 250X and d) 2000X.

The different and darker gray zone observed and indicated in the backscattered electron-micrograph of figure 3b indicates the presence of a deposit of a different composition on the furrow, which may be a protein deposit in accordance with the reports by Chevalier et al. [19] and Caton [20]. The protein deposit originated from the bovine fetal serum used as lubricant in the biotribological test. Similar wear and fatigue damage was reported by Nakajima et al. on 304 SS in a fatigue test under physiological conditions; they detected loss of material and holes and marks, which were attributed to fatigue [15].

Figure 4 shows SEM images of the ZrO$_2$/316LSS system. The micrograph in figure 4a at 1000× presents a smooth and uniform zirconia film surface. The micrograph at 100×, after 20000 cycles of the biotribological test, is shown in figure 4b; it is evident that the damage to the sample caused by wear and fatigue provoked deep furrows. The micrograph at a higher magnification (250×) in figure 4c presents a zone with a big hole. At a higher magnification (2000×) the backscattered micrograph presents the damage to the sample with furrows that do not contain any deposits of a different composition. It is evident that there is no zirconia deposit on the surface. De Aza et al. reported that zirconia does not have the property of fixing proteins on the surface. Proteins are usually fixed on the surface due to the production of localized corrosion points; however, due to its high corrosion resistance, the tetragonal zirconia does not permit proteins to be fixed on it. The opposite case is presented by the monoclinic phase of zirconia, which is corrosion susceptible [18]. Patel and Spector obtained similar results in the analysis of ZrO$_2$/UHMWPE friction pairs; they found proteins adhered to the UHMWPE surface but not to the zirconia surface [19].

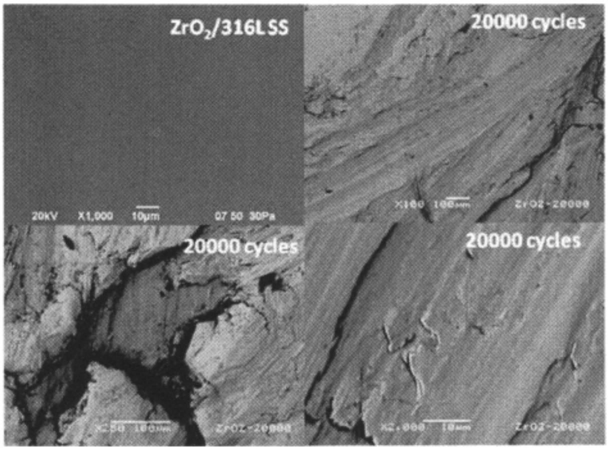


Figure 4. ZrO$_2$/ 316L SS SEM images a) before Biotribologycal test and after of 20000 cycles b) 100X, c) 250X and d) 2000X.

Figure 5 shows SEM images of the HA/ZrO$_2$/316LSS system. In figure 5a, the porosity and roughness of the surface before the biotribological test are shown. In figure 5b, after 20 x 10^3 cycles, it is observed that the bilayer coating has disappeared and that circular furrows containing material of different composition are now present. At an amplification of 2000×, protein deposits (figures 5c and 5d) can be observed in these furrows. The proteins deposits are remains of the fetal bovine serum used as lubricant throughout the test.

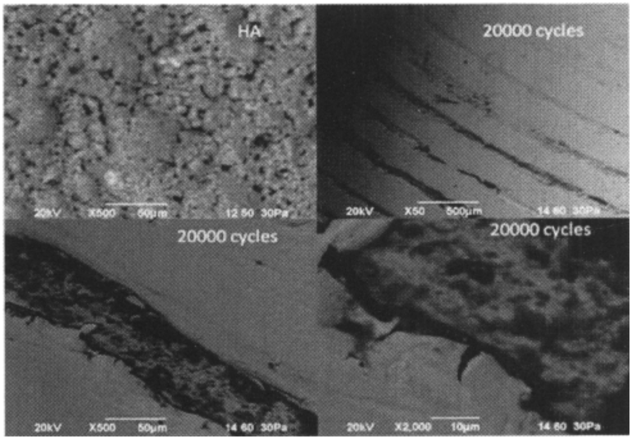


Figure 5. HA/ZrO$_2$/ 316L SS SEM images a) before biotribological test and after of 20000 cycles b) 50X, c) 500X and d) 2000X.

To determine that the remains in the furrows are proteins, EDS microanalyses were performed. These measurements confirmed that the remains in the furrows predominantly contained phosphorous, which corresponds to phosphorus based proteins from the fetal bovine serum. Also, Ca and O were detected, which may possibly be the remains of the HA coating, and some elements (Fe, Ni and Cr) of 316LSS were detected too (figure 6). To verify the loss of the HA and ZrO_2 coatings, EDS was also carried out outside the furrows, and only the 316LSS elements were detected (figure 7).

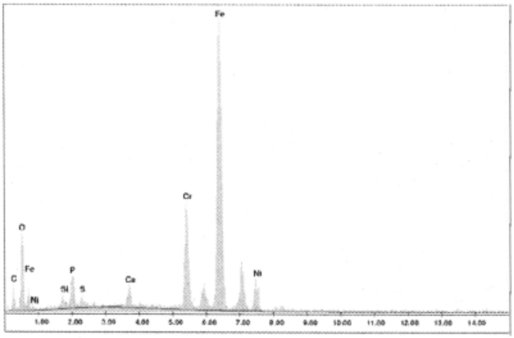


Figure 6. EDS microanalysis from furrows remain.

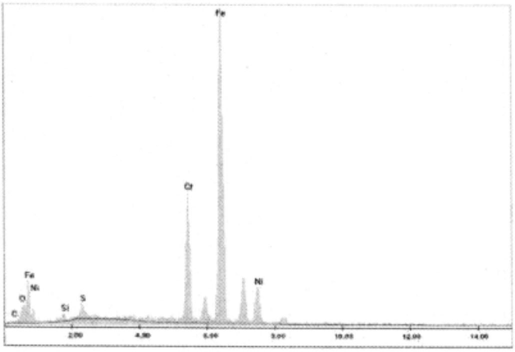


Figure 7. EDS microanalysis from out furrows.

Hermanson and Söremark detected that in HA-ZrO$_2$ bifunctional composites, the mechanical properties were found to be good after evaluation of their properties using NaCl solution as a lubricant at 37°C. They observed an important effect of slip due to HA. However, the HA remains are not toxic, because the HA is important to the general mineral organism stability during the bone's natural wear [16].

On the other hand, Wang et al. determined that a HA/ZrO$_2$ partially stabilized system has the property of attracting and fixing proteins, due to which the system presents an efficient marginal lubrication, and this lubricating property was noticeable during the wear test [17].

It should be pointed out that in this work; the hip joint lubrication is of the marginal type. This means that the tested hip joint has with the minimum lubricant necessary between the femoral head and the acetabular cup.

Figure 8 shows SEM images of the HA/ZrO$_2$ interface. Figure 8a shows a smooth and uniform surface of the HA/ZrO$_2$ interface before the biotribological test. After 20000 cycles, a protein layer adhered to the surface is observed in figure 8b. Figures 8c and 8d, with more amplification, show the morphology inside and around furrows of other zones, with a lot of damage and protein deposits. It is observed that the sample was damaged by severe friction (figure 8c). Figure 8d shows the interior of furrows and there are observed remains of proteins. This is confirmed by EDS analysis, which detected phosphorus, calcium and the 316LSS components (figure 9).

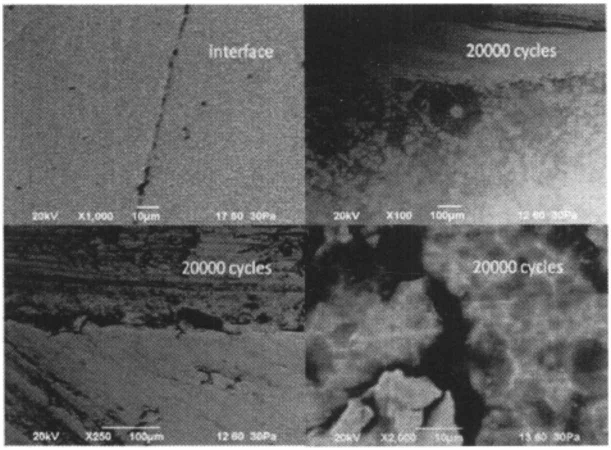


Figure 8.- HA/ZrO$_2$ interface SEM images a) before biotribological test and after of 20000 cycles b) 100X, c) 250X and d) 2000X.

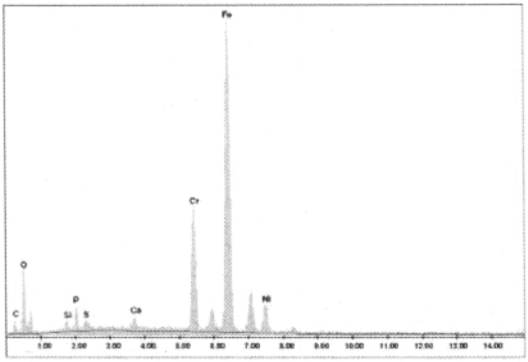


Figure 9.- EDS microanalysis from surface interface

The proteins adherence, according to Chevalier et al., is due to the martensitic tetragonal to monoclinic zirconia transformation due to friction. They observed this transformation during tests using water and fetal bovine serum as lubricant [20]. Caton also detected the martensitic tetragonal to monoclinic transformation and the proteins' adherence on a zirconia surface. He determined that the adherence of proteins on the surface generates incipient corrosion points [21]. On the other hand, Paff and Willmann determined that zirconia hydrothermal decomposition *in vivo* is delayed by approximately 10 years. However, when monoclinic zirconia appears and is heterogeneously distributed, it produces stress points that generate decrements in the mechanical properties, hence the pure zirconia prosthesis presents imminent failure *in vivo* [22]. Moreover, Piconni et al. detected fractures in the femoral heads, originated by the zirconia hydrothermal transformation. They also observed a proteins cumulus near the fractures and pitting corrosion on the zirconia surface [23].

The surface evolution of the sample throughout the biotribological test and the analysis of the loss of weight of the wearing pieces give important information about the detached material that could go into the bloodstream from the prosthesis inside a human body.

The initial weights of the samples before the biotribological test are reported in Table 1. Following the test, the weight lost by each tested sample is reported in Table 2. From this data, figure 10 shows the graphs of weight loss versus number of cycles of the 316LSS, ZrO_2/316LSS, HA/ZrO_2/ 316LSS and HA/ZrO_2 interface femoral heads and acetabular cups. The complete system lost more weight than the HA/ZrO_2 interface, but the interface presents more damage than the complete system. This is due to the HA coating thickness, which apparently has lower wear resistance than the HA/ZrO_2 interface, so the HA is detached from the deposit in the first cycles and then behaves like solid lubricant. The ZrO_2/316LSS system presented a very similar weight loss to the total system until 12000 cycles, after which an abrupt fall in the weight of the acetabular cups was observed. For the femoral heads, the system presented an initial weight loss from the first cycles, but this loss is less than the loss of the naked 316LSS, which indicates that the zirconia film is actually protecting the 316LSS surface. Then the weight loss stabilized from 8000 to 12000 cycles, after which the weight loss accelerated. This different behavior between the case of the acetabular cups and that of the femoral heads could be due to the fact that in the test the acetabular cup is fixed to the upper offshoot and the femoral head is in constant movement. It can be concluded that the zirconia film protects the 316LSS until 12000 cycles, after which the zirconia film was destroyed in the test.

Table 1. 316LSS and Coatings total weight before the biotribological test

Material	Femoral ball weight	Acetabular cup weight
316L SS	128.960 g	161.385 g
ZrO_2/316L SS	129.433 g	161.617 g
HA/ZrO_2/316LSS	129.208 g	161.657 g
HA/ZrO_2 Interface	128.200 g	161.656 g

Table 2. Total weight lost after the test.

Material	Total weight lost of the femoral ball	Total weight lost of the acetabular cup
316L SS	2.201 g	1.014 g
ZrO_2/316L SS	2.697 g	1.163 g
HA/ZrO_2/316LSS	0.074 g	0.046 g
HA/ZrO_2 Interface	0.021 g	0.013 g

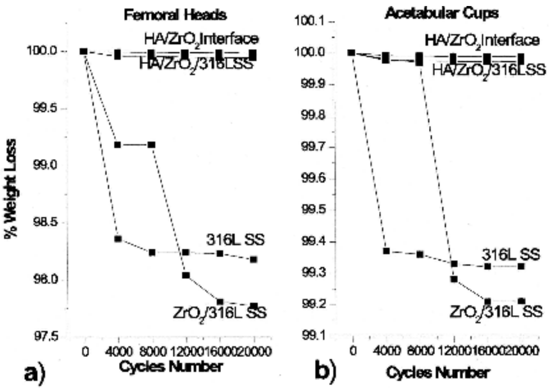
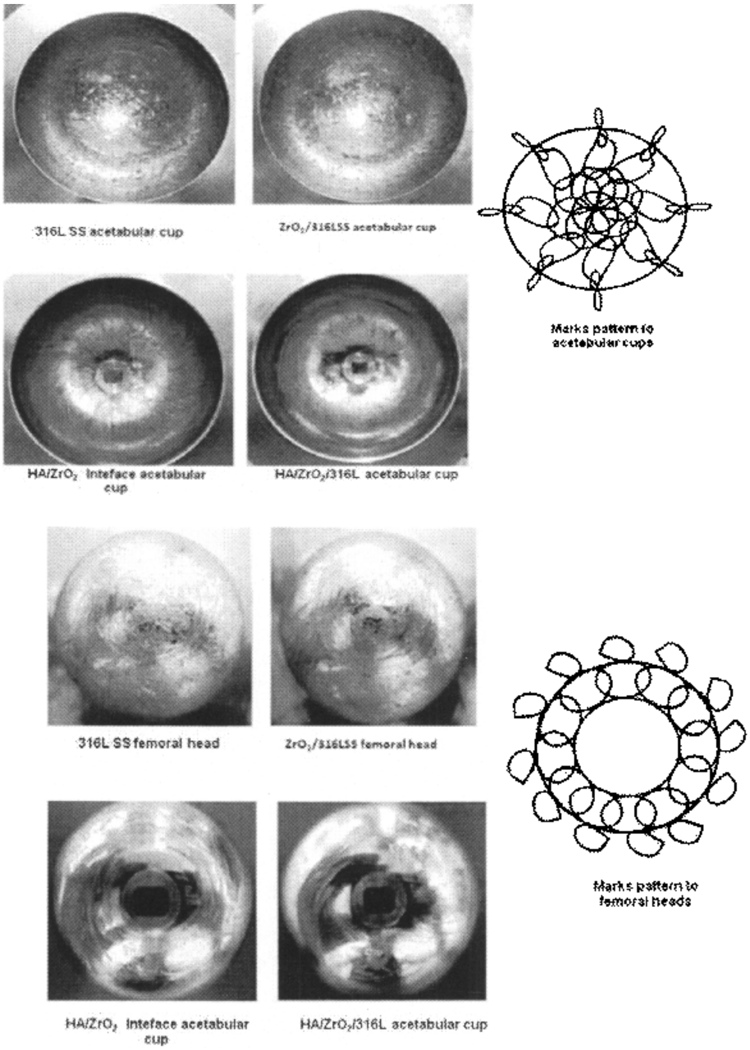


Figure 10.- Plots of percentage of weight lost versus number of cycles for a) femoral heads and b) acetabular cups.

Similar behavior was reported by Affatato et al., who analyzed ZrO_2–ZrO_2, ZrO_2–Al_2O_3 and HA/ZrO_2–HA/ZrO_2 hip joints in physiological conditions with fetal bovine serum as a lubricant. In this work, they determined that ZrO_2–ZrO_2 pairs presented good wear resistance but they also detected zirconia hydrothermal transformation. In ZrO_2–Al_2O_3 pairs, they detected a reduction of the fracture incidence, and in the HA/ZrO_2 –HA/ZrO_2 pairs they found significant improvements in the wear resistance and the material did not lose biocompatibility properties [24]. Baroud and Willmann also determined that HA coatings tend to become detached, but the debris produced by the wear are not toxic, and for this reason the coating did not loose the biocompatibility property [25].

Lawn determined that trilayer structures (ceramic/ceramic/substrate) show good acceptance in the biomechanics area, especially in dental devices and in orthopedic prostheses. This is because these structures perform like core-armor. The ceramic/ceramic part acts like armor and this is the system's functional part. The ceramic/substrate part acts like a nucleus, protecting the substrate from physiologic attack, and for these reasons the materials design should be very meticulous [26]. The HA/ZrO_2/316LSS system studied in this work actually acts in the way described by Brian R. Lawn.

It is worthwhile to depict the marks detected on the femoral heads and the acetabular cups surfaces, which are due to the walk and Paul's cycles. These marks coincide well with mark patterns described by Colonius and Saikko in 2002 [29, 30]. Figure 11 shows the patterns formed during the biotribological test and the comparison of them with the Paul's cycles (figure 11).



316L SS acetabular cup

ZrO$_2$/316LSS acetabular cup

Marks pattern to acetabular cups

HA/ZrO$_2$ Inteface acetabular cup

HA/ZrO$_2$/316L acetabular cup

316L SS femoral head

ZrO$_2$/316LSS femoral head

Marks pattern to femoral heads

HA/ZrO$_2$ Inteface acetabular cup

HA/ZrO$_2$/316L acetabular cup

Figure 11 marks produced during biotribological test in 316L SS, ZrO$_2$/316L SS, HA/ZrO$_2$/316L SS and HA/ZrO$_2$ interface femoral balls and acetabular cups, compared with the marks patterns

Reinisch, Judmann and Pausschitz, based on the ISO 14242, determined that 5,000,000 cycles are equivalent to 5 years *in vivo* service [27]. With this data, it was determined that 20000 cycles of the system are equivalent to 7.3 days in service. Bergman determined that a person walks at 6 km/hr on average [28]. Hence, it is possible to determine that in 7.3 days a person with a hip prosthesis would walk 1051.2 km. This paper analyzes the behavior of the HA/ZrO$_2$/316LSS system during 20000 cycles of the biotribological test under extreme wear conditions in order to elucidate expectations of the proposed system in its application as a coating for hip joints.

CONCLUSIONS

A biocompatible HA/ZrO_2 bilayer on 316LSS substrates was tested in a biotribometer machine. It was determined that this bilayer coating on steel substrates has low wear resistance when working at the extreme conditions of the hip biotribological tests. These results evidence the convenience of developing new, softer biotribological tests for evaluating this kind of biocompatible coating.

The biotribological tests of the hip-joint samples reported in this work were performed under similar conditions described in the test of ISO 14242. However, the number of cycles was limited at 2 x 10^4, which is significantly lower than the 3 or 5 x 10^6 cycles commonly used for this ISO test. It indicates that the proposed HA/ZrO_2/316LSS system does not show good behavior under the extreme conditions tested for hip prosthesis applications. However, this work made it possible to evaluate the behavior of the HA/ZrO_2 bilayer on 316LSS substrates under very demanding conditions in physiological media. According to the results obtained, the HA/ZrO_2 bilayer on 316LSS substrates could be adequate as a biocompatible and wear protective coating on prostheses with low tribological demands, such as the buccal prosthesis, and can also be recommended for scaffold applications.

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