Advances in Biomedical and Biomimetic Materials

Ceramic Transactions, Volume 206

A Collection of Papers Presented at the 2008 Materials Science and Technology Conference (MS&T08) October 5–9, 2008 Pittsburgh, Pennsylvania

Edited by

R. J. Narayan
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The American Ceramic Society

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Preface

This issue contains the proceedings of the "Advances in Biomedical and Biomimetic Materials" symposium, which was held on October 5–9, 2008 at the David L. Lawrence Convention Center in Pittsburgh, Pennsylvania, USA. The development of materials for dental and medical applications is a rapidly developing focus of activity in materials science and engineering. Novel processing, characterization, and modeling techniques continue to be developed that will provide enhanced diagnosis and treatment of medical conditions. Presentations were given on recent developments in biomedical and biomimetic materials, including scaffolds for tissue engineering; bioceramics; biomimetic materials; surface modification of biomaterials; metallic implant materials; nanoparticles for medical diagnosis and treatment; as well as novel materials for drug delivery and biosensing. This symposium enabled discussion among the many groups involved in the development and use of biomaterials, including materials researchers, medical device manufacturers, and clinicians.

We would like to thank the staff at The American Ceramic Society for making this proceedings volume possible. We also give thanks to the authors, participants, and reviewers of the proceedings issue. We hope that this issue becomes a significant resource in the areas of biomedical materials research and biomimetic materials research that not only contributes to the overall advancement of these fields but also signifies the growing roles of The American Ceramic Society, ASM International (The Materials Information Society), The Minerals, Metals & Materials Society, and the Association for Iron and Steel Technology in these rapidly developing areas.

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Bioceramics

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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.

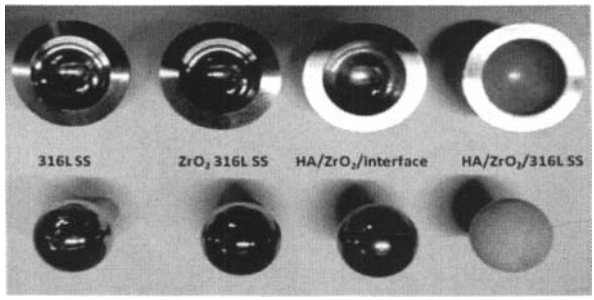

Figure 1.- Biotribological test joins.

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].

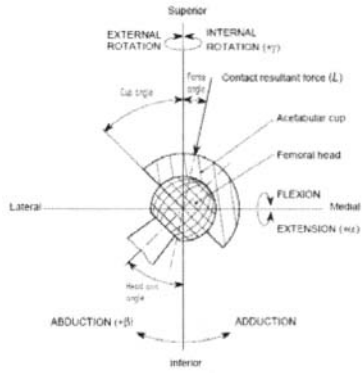

Figure 2.- Mobility and loads on hip join [14].

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.

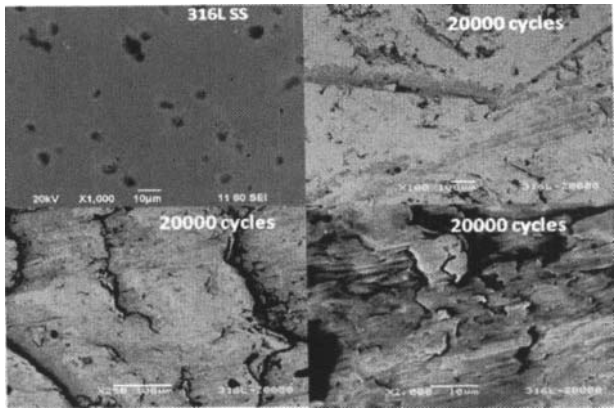

Figure 3. 316L SS SEM images a) before Biotribologycal test and after of 20000 cycles b) 100X, c) 250X and d) 2000X.

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].

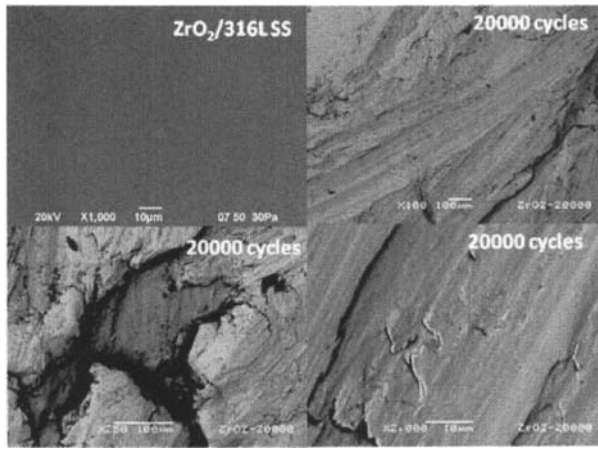

Figure 4. ZrO_2/ 316L SS SEM images a) before Biotribologycal test and after of 20000 cycles b) 100X, c) 250X and d) 2000X.

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.

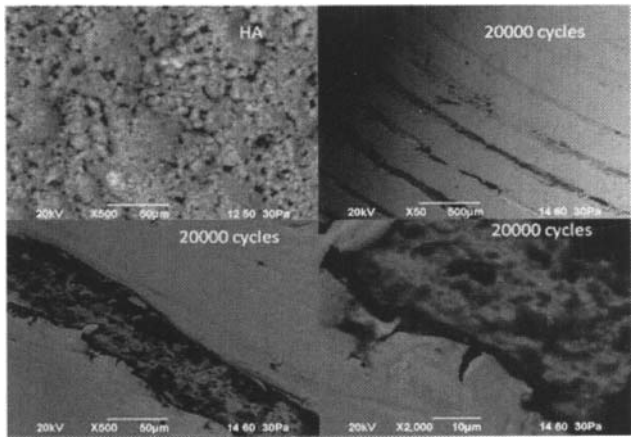

Figure 5. HA/ZrO_2/ 316L SS SEM images a) before biotribological test and after of 20000 cycles b) 50X, c) 500X and d) 2000X.

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).

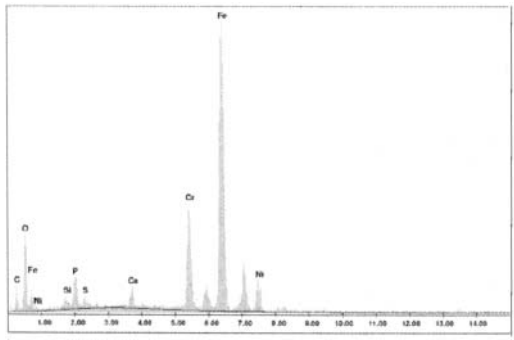

Figure 6. EDS microanalysis from furrows remain.

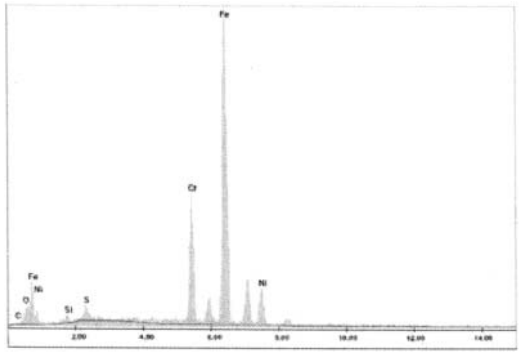

Figure 7. EDS microanalysis from out furrows.