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Cyclic Polarization and Immersion Corrosion Test on HA/ZrO_2/316LSS for Application on Orthopedics Prosthesis

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Physiological corrosion is very dangerous; due to cab provoke methanosis, cancer or poisoning, caused by metallic orthopedic prosthesis degradation in the human body. By this, is necessary to realize electrochemical and immersion test. This work treats to test the Hydroxyapatite/Zirconia bilayer system on stainless steel 316L by extrapolation Taffel to obtain corrosion rate, cyclic polarization to obtain behavior anticorrosive and immersion to obtain behavior in physiological environment. To realize the electrochemical test was utilized Ringer solution as electrolyte and 37°C and 60 minutes in immersion. The immersion test was realized in Ringer solution and 37°C during 4, 8 and 12 weeks. The changes on samples were analyzed by Scanning Electron Microscopy (SEM). The bilayer system has behaved as core-shell system and improved the stainless steel, because the physiological solution was not contact with stainless steel 316L.

Keywords: Cyclic polarization, bioceramics, bilayer system, immersion test

1. INTRODUCTION

When the surgical options as physiotherapy did not quit the bone ache and inflammation, the prosthesis is an option to replacement a join. This is a possibility to return the mobility and improvement the life quality [1].

A metallic prosthesis option is the 316L stainless steel (316LSS), because present similar bone properties [2]. The 316LSS is resistant to industrial and marine atmospheres and saline, oxidant, reducing and no dynamics environments [3]. However, the 31l6LSS degrades into the human body and can provoke poisoning, necrosis or osteosarcoma at live tissue, due to that nickel and chromium ions release on the blood stream [4]. To avoid damages in the human body by 316LSS degradation products is necessary covering it with inert and reactive bioceramics [5].

The bioceramics are materials utilized to repair bone parts or cartilages [6]. The zirconia (ZrO_2) is an inert bioceramic, which shows compatibility and does not present reactivity in physiological media [7]. But zirconia needs be stabilized at the tetragonal phase by introducing yttrium oxide, chromite, calcium oxide or other oxides, because this is the indicated crystalline phase to resist the physiological attack [3].

Hydroxyapatite (HA) is other bioceramic mineral similar to the bone. This material has classified as a reactive bioceramic, because promotes the prosthesis osteointegration and it has low reject from the body [8]. The HA implantation in any biomedical application from four to eight weeks presents formation of lamellar structures [3].

Bioceramics coatings on 316LSS prosthesis are usually deposited by the sol-gel method, plasma spraying, laser ablation, and some biomimetics methods between others [9]. These techniques are used because good coatings on irregular shape prosthesis can be obtained, avoiding the direct metal - live tissue contact and protecting against the prosthesis corrosion [10].

The physiological corrosion appears in biomedical parts, especially in metallic parts as prosthesis [11]. This corrosion can be in vacuum, saline and chloride media at 37°C [5]. In order to perform physiological corrosion tests simulating the human body, it is necessary reproduce the conditions of the blood plasma with physiological solutions as Ringer or Hanks solutions between other and maintaining the temperature at 37°C [12].

This work is about the study of corrosion tests of the HA/ZrO_2/316LSS system by means of cyclic polarization, Taffel extrapolation and immersion test into physiological solutions.

2. EXPERIMENTAL PROCEDURE

A set of HA/ZrO2/360LSS samples was produced using the procedure described in a previous study [9]. The first layer was a zirconia film deposited by electrophoresis technique and the second layer was a hydroxyapatite coating deposited using the screen printing technique. After deposition, the HA/ZrO2/360LSS system was thermally annealed at 650°C for 5 min. The samples were labeled as follows (Table 1):

The physiological corrosion tests were achieved by cyclic polarization, extrapolation Taffel and immersion test. The conditions for cyclic polarization and Taffel extrapolation were using Ringer solution as electrolyte with pH = 7.4 ± 0.2, saturated calomel as reference electrode, and graphite as work electrode. Scanning rate of 5 mV/seg, open circuit stabilized for 60 minutes in immersion, starting at 0.15 mV versus saturated calomel electrode (SCE). These tests were performed using a potentiostat/galvanostato Princeton Applied Research, 273 model.

Table 1. Samples identification

Coating Sample	Label
316LSS	316LSS
ZrO_2 annealed 650 °C for 5 min	Z650
HA/ZrO_2 annealed 650 °C for 5 min	HZ650
HA/ZrO2 interface annealed 650 °C for 5 min	IHZ650

To perform the immersion test, Ringer solution at 37°C was used by means of an oil bath in order to maintain a constant and homogeneous temperature. A heat plate Ceramag Midi of Ika Works USA was utilized. The samples were immersed for twelve weeks and extracted for monitoring each four weeks, to analyze the morphological changes. When the samples were extracted, they were washed in ultrasonic acetone bath, to remove the salt excess. To analyze the morphological changes of samples immersed, analyzed at low vacuum in a scanning electron microscopy (SEM) JEOL 5910LV model.

2.1. Analysis and Discussion Results

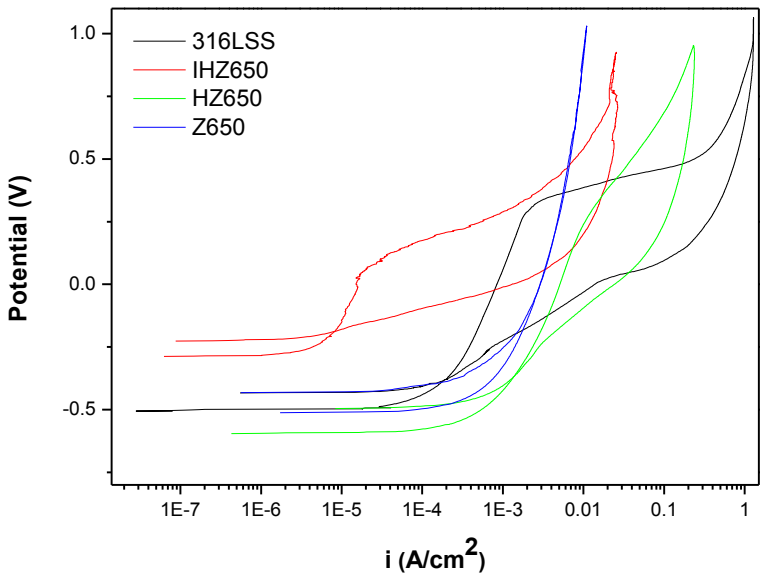

Figure 1. Cyclic polarization plots of 316L, Z650, HZ650 and IHZ650 samples.

Figure 1 shows a polarization cyclic graph of 316L, Z650, HZ650 and IHZ650 samples. The 316LSS polarization cyclic curve shows a starting potential at -440 mV (that is characteristic of austenitic stainless steel). The passive zone finished at +286 mV. The pitting nucleation and a right loop are obtained; the return potential at +1298 mV (that is characteristic of pitting propagation) and a positive hysteresis due to the irreversible damage by pitting are also observed. The cycle finished with a repassivation at -433 mV. The corrosion rate was 0.098 mm/year (Figure 2). Marxel Pourbaix [13]

described the biomaterial behavior, especially for 316LSS, by cyclic polarization in Ringer solution at 27°C.

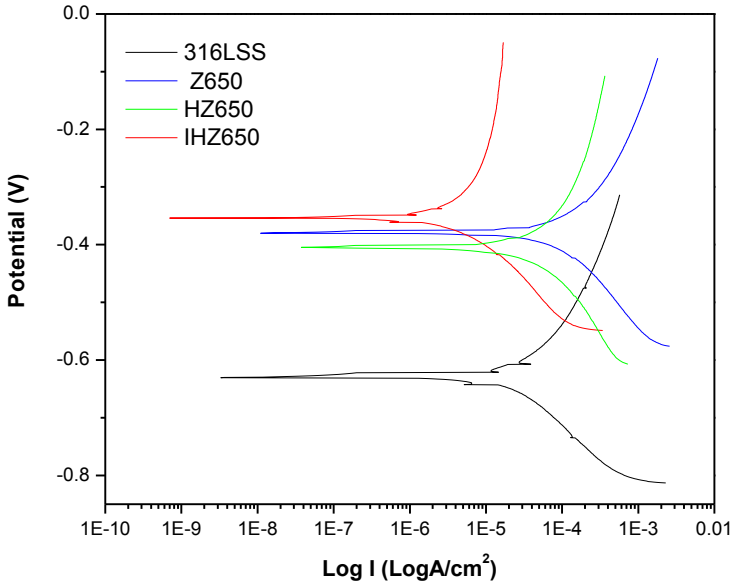

Figure 2. Taffel extrapolation plots of 316LSS, Z650, HZ650 and IHZ650 samples.

He concluded that on the 316LSS surface an irreversible pitting was produced. In other work, cyclic polarization experiments at 316LSS were performed and pitting nucleation and propagation were observed [14]. Shieu et al determinated that 316LSS pitting nucleated and propagated on and under surface, leaving the 316LSS sample useless [15].

The polarization cyclic curve for Z650 sample shows a starting potential at -509 mV, but the breaking potential was not observed. The loop is on the right, indicating pitting susceptibility of Z650 sample. The return potential has observed at +1026 mV and the cathodic curve is on anodic curve. This indicates that the ZrO_2 coating presented chloride attack resistance (figure 1). The corrosion rate was 0.037 mm/year (Figure 2). A similar behavior reported Gaertner et al [16], for a ZrO_2 coating on 316LSS. They accomplished a cyclic polarization test in a saline electrolyte and observed that the ZrO_2 coating was very resistant to the chloride attack.

The cyclic polarization curve for the HZ650 sample shows a start potential at -594 mV, the breaking potential was observed at +198 mV and later was detected hydrogen released characteristic curve, this occur when the hydroxyapatite has dissolved. The loop is on the right, the returning potential is at 996 mV and pitting nucleation was detected. The cycle finished with a repassivation at -497 mV (figure 1). The corrosion rate was 0.391 mm/year (Figure 2). Kannan et al [17] described the HA/316LSS during the cyclic polarization in HNO_3 solution. They determinated that HA was dissolved and released hydrogen and this is an essential remineralization process part.

The cyclic polarization curve of IHZ650 sample shows a start potential at -287 mV. The breaking potential was obtained at +0.019 mV. The loop was on the right and the returning potential was at +865mV, pitting nucleation and propagation were observed. The cycle finished at -222 mV

(figure 1). The corrosion rate was 0.071mm/year (Figure 2). This interface fulfills the F2129-06 norm, because the suitable behavior under cyclic polarization and satisfies the biomaterial requirements [18].

In the figure 2 shows the Taffel extrapolation plots of the substrate and all samples. The behavior of the Z650 and IHZ650 systems shows an improvement respect to the corrosion rate of the 316LSS substrate. However, for HZ650 sample apparently there is not an improvement. However, the attack was directed to the HA layer and this process is similar to biomineralization [19].

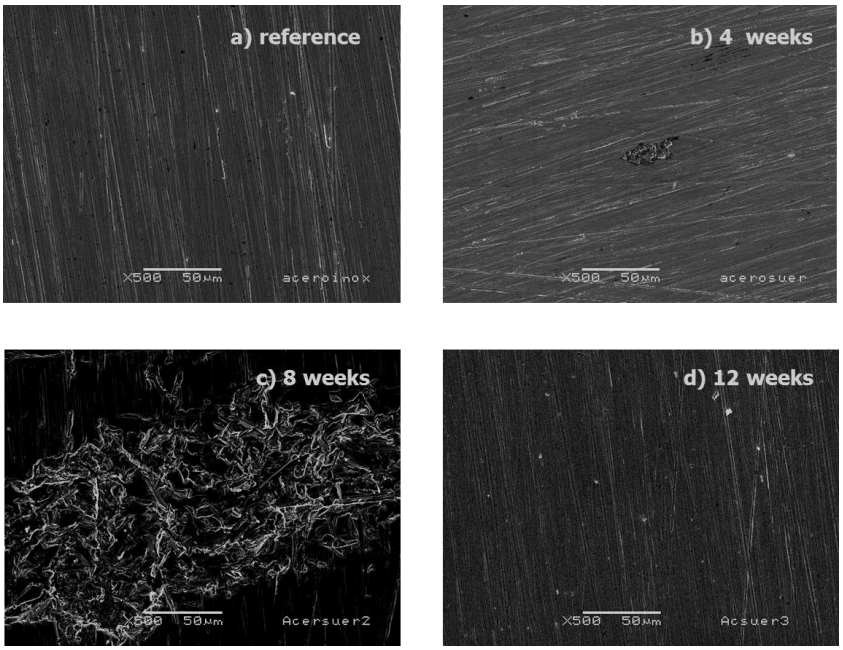

Figure 3. SEM images of 316LSS substrates tested in Ringer solution during a) zero weeks as a reference, b) 4 weeks, c) 8 weeks and d) 12 weeks.

The figure 3 shows SEM images of 316LSS at different magnifications after and before the immersion corrosion test. The image 3a, that corresponds to control sample, shows inclusions and the surface roughness. The 3b image shows the 316LSS tested for 4 weeks and depicts pitting formation. The 3c image shows the results after 8 weeks of test and allows observing a bigger pitting for a selected region of the sample. For 12 weeks of testing, 3d image shows the 316LSS sample with a several small pitting distributed on the sample surface. This corrosion occurs because 316LSS is susceptible to chloride, which provokes an important grade of pitting corrosion on the 316LSS surface [20], occasioning its degradation and the realizing of nickel and chromium ions to the stream blood, provoking allergies, cancer or poisoning [21]. This type of degradation has been studied by means of in vivo corrosion [22], and in these studies have determinated that the 316LSS causes histological changes. Considering this degradation of steel, it is necessary to perform a thermal annealing or to protect the piece with a coating in order to avoid a direct contact with live tissue [23].

Figure 4 shows SEM images at 1500X of the Z650 sample. For all images (4a, b, c, d), it is observed that ZrO_2 coating has not dissolved and they show uniform and stable appearance. A similar

behavior was reported by Survilliene [24], who carried out studies on ZrO_2 coatings on chromium substrates and determinated that the coating was resistant to chloride, Na_2SO_4 and H_2SO_4 attack.

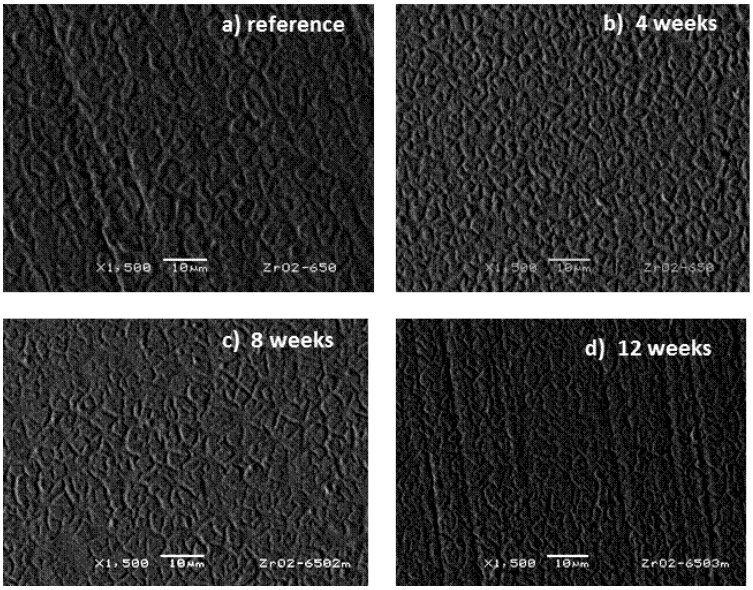

Figure 4. SEM images of Z650 sample tested in Ringer solution during a) zero weeks as a reference, b) 4 weeks, c) 8 weeks and d) 12 weeks.

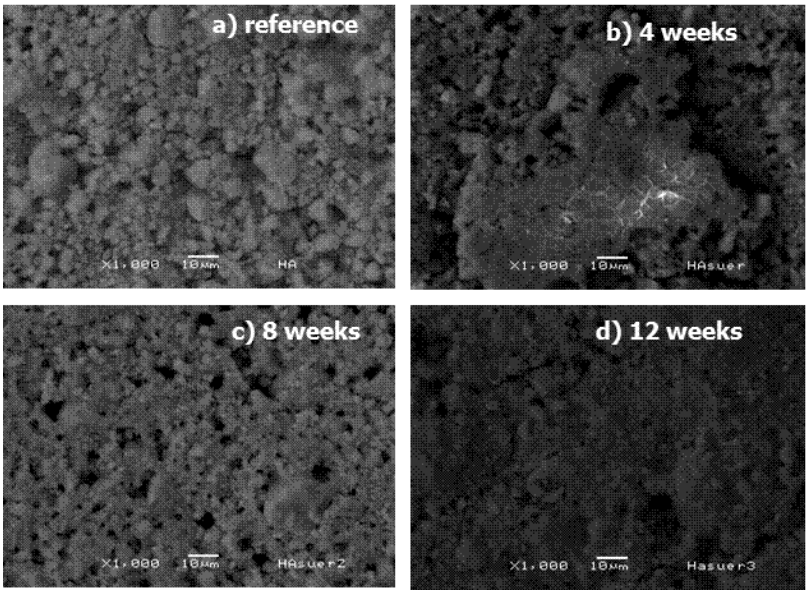

Figure 5. SEM images of HZ650 sample tested in Ringer solution during a) zero weeks as a reference, b) 4 weeks, c) 8 weeks and d) 12 weeks.

Figure 5 shows SEM images at 1000X of the HZ650 sample. All these images show the sample surface evolution from zero to 12 weeks of the immersion test. Figure 5a shows a rough, porous and irregular surface due to the HA/ZiO_2 bilayer. Figure 5 b, c and d shows the system tested for 4 and 8

weeks with surfaces with uniform roughness and porous surfaces. After 12 weeks of testing, the test of the HZ650 sample shows a less porous surface, so that porosity tends to disappear [26], as is the case of HA biomimetic deposition [27]. This process is similar to the process occurring inside the human body when the physiologic liquids react with the HA layer and increases a resorption between osseous tissue and HA coating prosthesis [25].

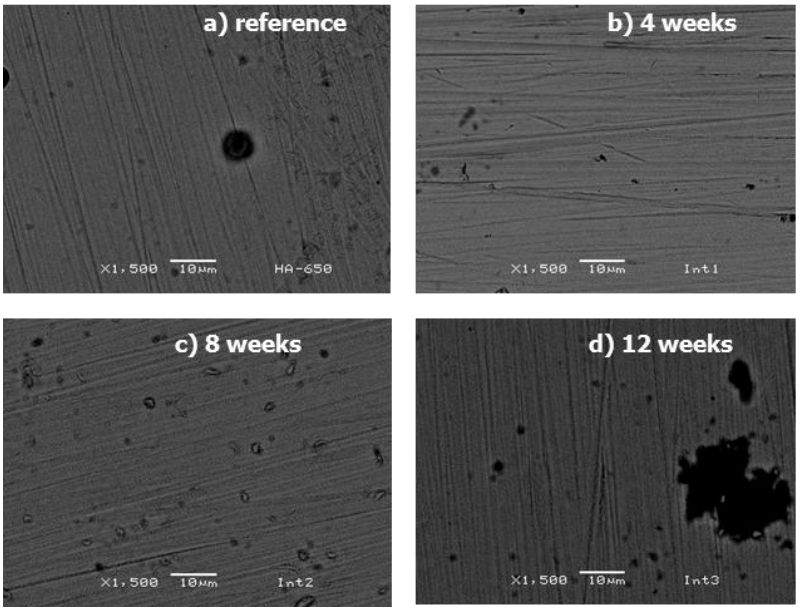

Figure 6. SEM images of IHZ650 sample tested in Ringer solution during a) zero weeks as a reference, b) 4 weeks, c) 8 weeks and d) 12 weeks.

Figure 6 shows SEM images at 1500X of IHZ650 samples. Figure 6a shows the samples before the immersion test and illustrates uniform surface and some HA coating residues. The images 4b,c and d correspond to the samples tested for 4, 8 and 12 weeks and for these surfaces any damages by pitting or salt clusters are not observed. Hae wom-Kim et al [28] reported a similar behavior on HA/ZrO_2 interface. Also they performed experiments into chloride medium observing uniform and flat surfaces, but without damages on the surface.

3. CONCLUSION

The bilayer system HA/ZrO_2/316LSS, is a good candidate to be used as biomaterial for protecting 316LSS pieces of prosthesis. Polarization cyclic behavior and corrosion rate tests showed an improvement of 316LSS substrates. The ZrO_2 interlayer acts as a protective coating against corrosion. The HA coating offered the characteristic bone resorption process during the immersion test. All the studied samples can be considered as core-shell system due to their biofunctional and anticorrosive properties.

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