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Corrosion behavior of new titanium alloys for medical applications

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ABSTRACT

In this study, the ability of two titanium alloys to resist corrosion has been analyzed. This was accomplished by analyzing how the corrosion potential evolves with time as well as observing the Bode and Nyquist diagrams obtained with electrochemical impedance spectroscopy. The proportions of each alloy were A1 (94.4 % Ti, 4 % Mn, 0.6 % Al, 1 % Fe) and A2 (96.5 % Ti, 3 % Mn, 0.6 % Al, 0.2 % V). The two samples were covered in epoxy resin, cut in pieces, and polished using silicon carbide sheets of abrasive paper, the polishing was done progressively, using gradings from 280 to 1200 grit, ultimately using a 0.1 alpha alumina suspension for a last polish. Electrochemical tests were performed by immersing the polished samples in a Ringer Lactate solution. While the samples were immersed, they were connected to a saturated calomel electrode as reference electrode and to a platinum electrode acting as counter electrode. The two materials can resist to the effects of corrosion efficiently; initially it seemed that the alloy A1 improves its capacity to resist at corrosion when a positive potential is applied and loses it partially when a negative potential is applied. In alloy A2 the situation was similar but easier to observe, as when the supplied potential was too high or too low, the passivation of the material was not so good.

1. Introduction

Biomaterials have helped humans to replace and to repair organs and tissues, as well as to diagnose diseases. After the second half of the 20th century, the study of biomaterials has undergone a remarkable evolution that has led to major advances palpable by the public, which should encourage further study of these materials.

One of the elements whose use in biomaterials has been extensively studied is titanium [1]. The reason behind this is the fact that titanium possesses good mechanical properties [2] as well as an excellent resistance to the effects of corrosion. One of the mechanical properties of titanium that can be highlighted is its low specific weight, which is an important requirement for implants [2,3].

One of the most common alloys based on titanium is Ti-6Al-4V, composed of 6 % of aluminum and 4 % of vanadium, the rest being titanium. However, it has been shown that the use of this alloy in implants can cause health problems because aluminum or vanadium ions may be released in the human body [4]. Apart from this, this alloy has some undesirable mechanical properties such as a high modulus of elasticity [5]. Additionally, the mere presence of aluminum and vanadium can cause allergic reactions [6] and in the case of aluminum, it may also hinder bone mineralization [7].

As far as the structure of titanium is concerned there are two main possible structures. One is called α structure, which possesses a hexagonal close packed geometry, and the other is called β structure which possesses a body centered cubic geometry [8]. A change of temperature allows to vary between structure α and structure β [9], at approximately a temperature of 882.5 °C [6,7]. Titanium-based alloys possessing mainly titanium arranged in structure β tend to have a greater range of mechanical properties compared to alloys that mainly possess titanium in structure α [10]. It is possible with techniques that make use of microscopes to obtain images where the different phases can be seen [11].

There has been recent interest in studying the addition of manganese into titanium-based alloys, some of the reasons for this interest are the facts that it plays a role in the generation of bone collagen as well as cartilage [12] and because it participates in the quickening and activation of certain enzymatic systems. Also, adding manganese to alloys has the effect of reducing ductility proportionally to the amount of manganese added [11].

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Concerning the applicability of iron in titanium-based alloys, this element is needed by the human body for different purposes, being necessary its addition in some circumstances, such as low-weight newborns [13]. The iron that could be released into the body due to the corrosion of the implant does not carry risk because this element does not tend to accumulate and is easily metabolized by the organism [14].

One element that has been used multiple times in implants, especially dental ones, is aluminum [15], substituting obsolete materials with lower success rates such as stainless steel and gold. However, there are studies that argue there is a link between implants that have aluminum and the onset of Alzheimer's disease [16] as has been observed in mice [17]. Although there are other studies that deny this relationship [18], there is a tendency to look for biomaterials that lack aluminum. However, the abundance and low price of aluminum are the reasons alloys that make use of this element are still used.

This paper aims to study the ability to resist to the effects of corrosion of two alloys based on titanium with 4 % Mn and 1 % Fe (namely A1) and with 3 % Mn, and 0.2 % V (namely A2). The chemical composition of the experimental alloys was chosen based on the effect of β-eutectoid stabilizers, i.e., manganese and iron. Manganese can depress the transformation temperature from the α- to β-phase in Ti alloys. Mn is considered a β-phase stabilizer, being an essential element that is involved in the formation of bone cartilage and bone collagen. Iron can improve the mechanical properties, by reducing the growth rate of grains.

2. Materials and methods

The two Ti-rich alloys were obtained in a vacuum arc remelting MRF ABJ 900 equipment, from high purity granular raw materials in a controlled argon atmosphere. Before melting, a vacuum level of up to 10–5 mbar is obtained in the working chamber, using the diffusion pump and the molecular pump. When the oxygen level is low enough, the working chamber is filled with argon and the melting of the granular metallic material is started. The melting is done under electric arc formed between the metallic materials and a non-fusible Tungsten electrode with 2 wt% of Thorium. To obtain a good homogeneity of the alloy, the mini-ingots were six time remelted on each side, under high purity 5.2 Argon gas flow. Table 1 shows chemical composition of the studied alloys.

The two studied alloys were covered with epoxy resin and cut in pieces with parallelepiped geometry, obtaining the samples that were used to perform the analyses. Afterwards, the samples were polished using silicon carbide sheets of paper, taking advantage of its abrasive capabilities, in a Struers polishing machine model TegraPol 11. To prevent errors during the production of the samples, the polishing was done progressively, using the following gradings in this order: 280, 800 and 1200 granularity. Each process of polishing was repeated twice, under the following conditions: a speed of 150 (rpm), a duration of 120 (s) and a strength of 20 (N). Water was poured in small quantities during the polishing to prevent a high increase in temperature. After these steps, a last polish was applied to the samples using a 0.1 alpha alumina suspension.

After the samples were treated, the next step was submerging them in a Ringer Lactate solution (see Table 2) as has been previously done to characterize other materials, in this case trying to simulate the conditions of a liquid medium inside a living body. We have used the Lactated Ringer's solution because is an intravenous fluid that doctors use to treat dehydration and restore fluid balance in the body. The solution consists primarily of water and electrolytes and was added lactate, which was found that lowered the risk of acidosis (the abnormal buildup of acid in the blood). The lactate ions are transformed into bicarbonate ions allowing a regulation of the solution pH. Afterward, electrochemical studies were performed using a BioLogic potentiostat/galvanostat model SP-150 (BioLogic Science Instruments, Seyssinet-Pariset, France). Once the samples were conditioned, the electrochemical cell was prepared by incorporating three electrodes into the Ringer's solution a saturated calomel reference electrode (SCE), a working electrode which is the sample to be analyzed and a platinum wire as counter electrode). The resin tablet in which the sample is inserted must be partially submerged, so that the wire connected to it is not in contact with the solution.

After placing the alloys in the solution, the evolution of the corrosion potential with time was studied via BioLogic's EC-Lab software, using a saturated calomel electrode (SCE) as reference electrode and a platinum electrode as counter electrode. The other technique applied to the samples was an electrochemical impedance spectroscopy (EIS) [19,20], when impedance diagrams were obtained to characterize the materials [21,22]. The first measurement performed on the samples was the evolution of the corrosion potential versus time. This measures the potential of the working electrode against that of the SCE under open circuit conditions, so that no potential or current is applied to the cell. The measurement was carried out for 1 h for each sample. For the EIS technique, impedance measurements were made at a fixed value of potential versus to the final value obtained for each sample by the previous technique. EIS measurements were performed at various potentials in the range of −1.0 to +1.0 V vs SCE. A maximum time of 10 min was assigned to each measurement.

A metallographic study was done for the samples in order to characterize the properties of materials and the structural transformations that occur in them [23]. The samples were immersed in Kroll reactive for five seconds in order to obtain the metallographic structure via a microscope that used 100 magnifications. An inverted routine microscope for examining structural materials, model Axio Vert.A1 MAT was used to obtain metallographic images of the two studied samples studied after the samples were etched in Kroll reagent.

3. Results

As can be observed in Fig. 1, there is a tendency for the corrosion potential to increase its value as time evolves for the two samples in the established conditions. In the case of alloy A2, which possesses a quantity of 3 % of manganese, it can be seen that with less time the curve seems to reach a maximum.

By the second technique, electrochemical impedance spectroscopy, different values of potential were applied on each sample

Table 1
Composition of the studied alloys (% wt).

Element	Alloy A1	Alloy A2
Ti	94.4	96.2
Mn	4	3
V	–	0.2
Fe	1	–
Al	0.6	0.6

Table 2
Composition of the Ringer Lactate solution.

Element	Concentration (mg/mL)
NaCl	3000
KCl	150
$CaCl_2$	100
$NaC_3H_5O_3Al$	1550

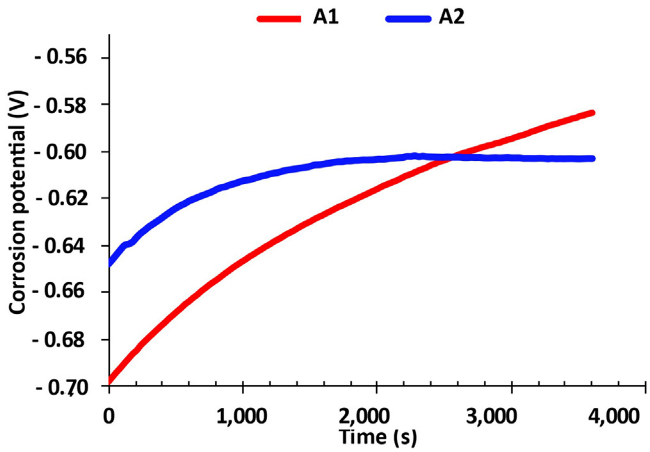

Fig. 1. Evolution of corrosion potential with time for each alloy.

as can be appreciated in Figs. 2 and 3 while a frequency sweep was performed; the values of potential that were considered are between −1.0 to 1.0 V vs SCE. The spectra shown in the Figures represent the Bode diagrams and the potential values that offer the best and worst results were chosen, as well as an intermediate value in each case.

In the Bode diagram for alloy A1 (see Fig. 2) it can be seen that as the potential of the sample increases, a layer develops on its surface which resists corrosion better and thus increases the corrosion resistance of the material. As the potential increases, the phase angle increases due to the increase in the thickness of the passive film that grows on the metal surface.

In the case of alloy A2, as the value of potential is increasing, the formed passive layer that resulted most efficient result 0.2 V and using a higher or a lower value of potential caused the material to not resist to corrosion with the same effectivity. In Fig. 3 it can be observed that when a potential of 1 V vs SCE or −1 V vs SCE was applied through the electrode, the alloy did not reach a very high impedance, meaning that the generated protective layer is not so good.

After the Bode diagrams for each alloy were obtained, Nyquist diagrams were done for both of them. For alloy A1 the Nyquist diagram obtained in Fig. 4 would lead to believe that the value of applied potential that favors polarization resistance (and therefore corrosion resistance) is −0.2 V due to the fact that with this potential a curve of higher radius is appreciated.

In the case of alloy A2, as can be observed in Fig. 5, the resulting curves are not in conflict with the information present in Fig. 3, confirming that a potential of 0.8 gives the best results. For both alloys, as the potential increases, the growth of the passive film is nucleated, the thickness increases and the resistance to corrosion is also increased.

The results of the metallographic study can be observed in Figs. 6 and 7. The image obtained through the microscope for the

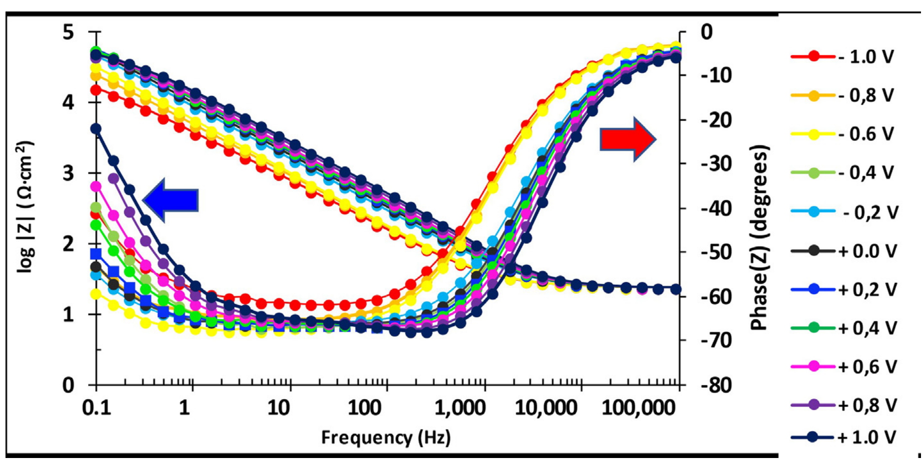

Fig. 2. Results of EIS for alloy A1 in a Bode diagram.

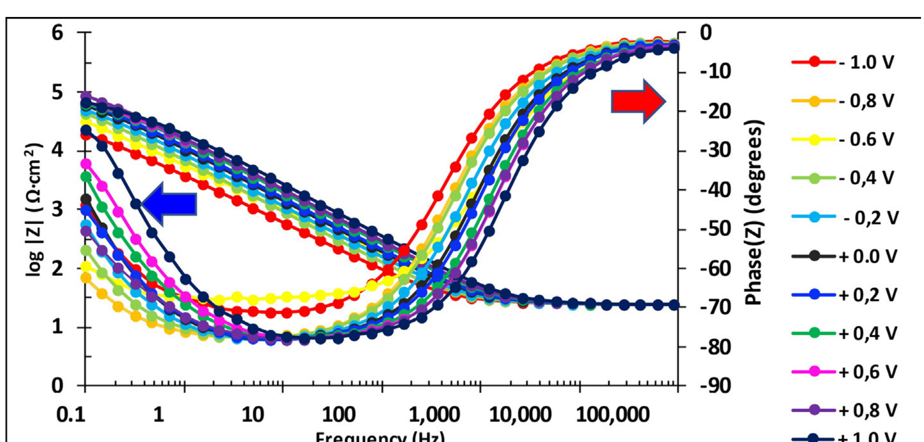

Fig. 3. Results of EIS for the sample A2 in a Bode diagram.

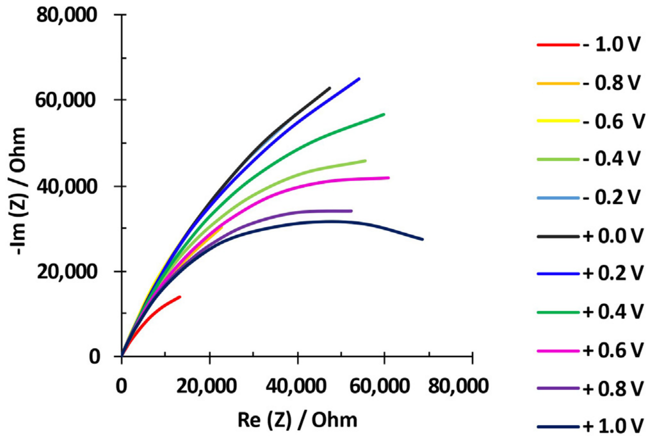

Fig. 4. Results of EIS for the sample A1 in a Nyquist diagram.

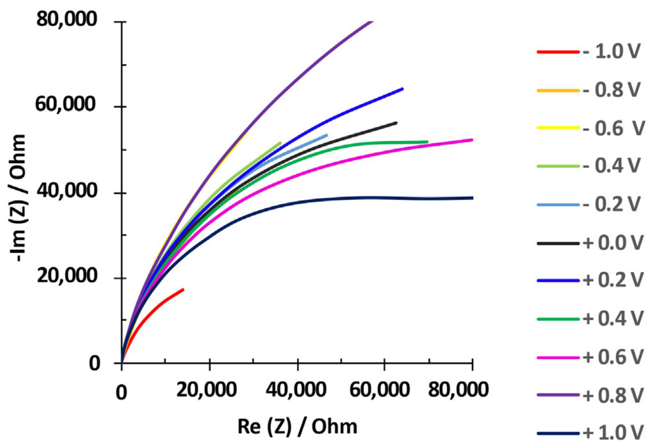

Fig. 5. Result of EIS for sample A2 in a Nyquist diagram.

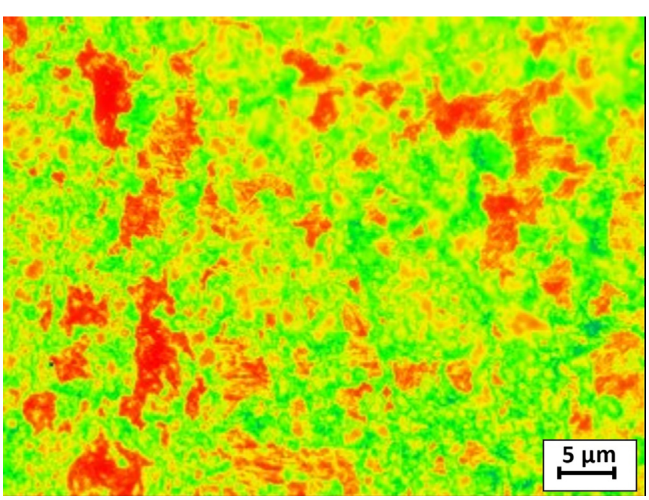

Fig. 6. Metallographic image obtained of alloy A1.

alloy A1 allow to clearly distinguish two different phases, the phase that possesses titanium with β structure or a mixture of α and β structure in color green/yellow and the regions that present only titanium with α structure, present in color red.

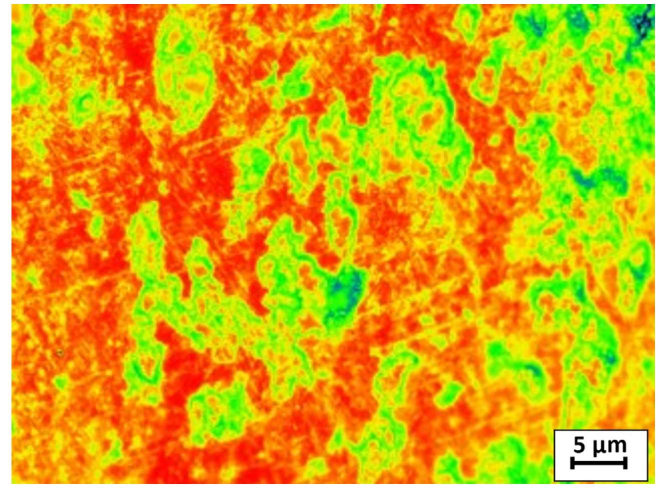

Fig. 7. Metallographic image obtained for alloy A2.

In alloy A2 two regions were observed as well, with small surfaces presenting a dark blue color result of the Kroll reactive chemically burning these regions. It can be observed that there is a tendency in this material to present more zones that solely present titanium with α structure.

4. Conclusions

The obtained results seem to indicate that the two samples can resist the effects of corrosion in environments similar to the Ringer Lactate solution.

From open circuit potential it can be deduced that both alloys tend to passivate as the potential increases. In the case of sample A2 this increase occurs up to a certain time and then the value of potential remains constant over a wide range of time. In other words, the two materials do not tend to corrode for the time spans used in the study, instead they tend to form a passive layer that protects them from the effects of corrosion. This statement should be verified in further studies by performing more tests in the future to observe the evolution of the behavior of the samples for longer periods of time.

Having confirmed that the alloys tend to passivate, with the use of electrochemical impedance spectroscopy it was possible to compare the different materials. The main information that was obtained with this technique was how the passive layers that protect against the effects of corrosion vary between the different materials and when different values of potential are applied. The two materials can resist to the effects of corrosion efficiently; initially it seemed that the alloy A1 improves its capacity to resist at corrosion when a positive potential is applied and loses it partially when a negative potential is applied. In alloy A2 the situation was similar but easier to observe, as when the supplied potential was too high or too low, the passivation of the material was not so good.

From the metallographic study, a tendency was observed for the alloy A1 to possess more regions where the material presents titanium with β structure than alloy A2, which mainly presented regions with α structure.

CRediT authorship contribution statement

Héctor Guerra-Yánez: Conceptualization, Methodology, Investigation, Writing – original draft. **Néstor Rubén Florido-Suárez:** Formal analysis, Software, Validation. **Ionelia Voiculescu:** Software, Validation, Investigation, Writing – review & editing. **Julia Claudia Mirza-Rosca:** Conceptualization, Validation, Investigation, Writing – review & editing.

Data availability

Data will be made available on request.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Julia Claudia Mirza-Rosca reports financial support was provided by University of Las Palmas de Gran Canaria. Ionelia Voiculescu reports a relationship with Polytechnic University of Bucharest that includes: employment, funding grants, and non-financial support.

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