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**STUDY OF THE BEHAVIOR AND ELECTROCHEMICAL PROPERTIES OF NOVEL
 β -METASTABLE TITANIUM ALLOY IN BIOMIMETIC ENVIRONMENT**

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 β -METASTABLE TITANIUM ALLOY IN BIOMIMETIC ENVIRONMENT**

Thesis presented as part of the Materials
Engineering Course of the Federal University of
Santa Catarina, as requisite to obtain the title of
Materials Engineer

Supervisors:
Prof. Dachamir Hotza
Dr.-Ing Benoît Ter-Ovanessian

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 β -METASTABLE TITANIUM ALLOY IN BIOMIMETIC ENVIRONMENT**

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RESUMO

Devido ao aumento da expectativa de vida e à consequente elevação no número de cirurgias ortopédicas, tem-se observado uma crescente demanda por materiais implantáveis com elevada biocompatibilidade e propriedades mecânicas otimizadas. As ligas de titânio tradicionais, como a Ti6Al4V, embora amplamente utilizadas, apresentam preocupações quanto à biocompatibilidade devido à liberação de elementos citotóxicos. Em resposta a essa limitação, este estudo teve como objetivo avaliar o comportamento eletroquímico e a biocompatibilidade da liga β -metastável de titânio Ti20Zr3Mo3Sn, em comparação ao titânio comercialmente puro (cpTi) e à liga Ti6Al4V. A caracterização eletroquímica foi realizada por meio de ensaios in vitro em solução tampão fosfatada (PBS) e em fluido sinovial biomimético (BSF), utilizando técnicas como potencial de circuito aberto (OCP), polarização potenciodinâmica (PP), espectroscopia de impedância eletroquímica (EIS) e análise de Mott-Schottky. Adicionalmente, foi empregada espectroscopia de fluorescência para avaliar a estabilidade lipídica no BSF antes e após os testes de corrosão. Os resultados demonstraram que a liga Ti20Zr3Mo3Sn apresentou desempenho eletroquímico comparável ao das ligas convencionais em PBS e BSF, com densidade de corrente passiva significativamente menor em BSF, indicando maior resistência à corrosão. Além disso, a análise por fluorescência indicou que a nova liga não promoveu desnaturação lipídica, sugerindo melhor biocompatibilidade. Concluiu-se que a liga Ti20Zr3Mo3Sn representa uma alternativa promissora às ligas de titânio convencionais, oferecendo menor citotoxicidade e estabilidade eletroquímica favorável em condições fisiologicamente representativas.

Palavras-chave: Titânio. Corrosão. Eletroquímica. Estudo in-vitro.

ABSTRACT

Due to increasing life expectancy and the corresponding rise in orthopedic surgeries, the demand for biocompatible and mechanically optimized implant materials has grown. Traditional titanium alloys, such as Ti6Al4V, while widely used, pose biocompatibility concerns due to the release of cytotoxic elements. In response, this study aimed to evaluate the electrochemical behavior and biocompatibility of the novel β -metastable titanium alloy Ti20Zr3Mo3Sn, in comparison to commercially pure titanium (cpTi) and Ti6Al4V. Electrochemical characterization was performed through in vitro assays in phosphate-buffered saline (PBS) and biomimetic synovial fluid (BSF), utilizing techniques such as open-circuit potential (OCP), potentiodynamic polarization (PP), electrochemical impedance spectroscopy (EIS), and Mott-Schottky analysis. Additionally, fluorescence spectroscopy was employed to assess the impact of corrosion processes on lipid stability within BSF. The results demonstrated that Ti20Zr3Mo3Sn exhibited electrochemical performance comparable to conventional alloys in both PBS and BSF, with notably lower passive current density in BSF, indicating enhanced corrosion resistance. Furthermore, fluorescence analysis revealed that the novel alloy did not induce lipid denaturation, suggesting superior biocompatibility. It was concluded that Ti20Zr3Mo3Sn presents a promising alternative to existing titanium alloys, offering reduced cytotoxicity and favorable electrochemical stability under physiologically relevant conditions.

Keywords: Titanium. Corrosion. Electrochemistry. In-vitro study.

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LIST OF ACRONYMS, SYMBOLS AND ABBREVIATIONS

BCC	– Body-centered cubic
BSF	– Biomimetic synovial fluid
CPE	– Constant phase element
CNRS	– Centre national de la recherche scientifique
cpTi	– Commercially pure titanium
Ecorr	– Corrosion potential
EIS	– Electrochemical impedance spectroscopy
GP	– Generalized polarization
HCP	– Hexagonal close-packed
I _{corr}	– Corrosion current density
I _{pass}	– Passive current density
MS	– Mott-Schottky
NHS	– National health service
OCP	– Open circuit Potential
OECD	– Organisation for Economic Co-operation and Development
PBS	– Phosphate-buffered saline
PDM	– Point-defect model
PP	– Potentiodynamic polarization
R _{sol}	– Resistance of the electrolyte
SF	– Synovial Fluid
THA	– Total hip arthroplasty
V	– Potential
XRD	– X-Ray Diffraction
Z'	– Real part of impedance
Z''	– Imaginary part of impedance
χ^2	– Chi-squared
ω	– Angular frequency of applied signal
ω'	– Integration variable over angular frequency

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1 INTRODUCTION

The increasing life expectancy has led to a rise in orthopedic surgeries, such as total hip arthroplasty (THA), necessitating biomedical implants with optimized durability, biocompatibility, and mechanical properties [1]. Titanium alloys have been the material of choice for such implants since 1950 due to their corrosion resistance and favorable strength-to-weight ratio [2]. However, widely used alloys like Ti6Al4V pose risks due to the release of cytotoxic vanadium and aluminum, which have been linked to neurodegenerative diseases [3], [4]. Consequently, there is a pressing need to develop novel β -metastable titanium alloys with improved biocompatibility and mechanical performance, particularly in biomimetic environments that simulate physiological conditions.

Despite advancements in alloy design, a critical gap remains in understanding the electrochemical behavior of these materials under conditions that mimic the synovial fluid of human joints. While studies have examined corrosion resistance in simplified electrolytes like phosphate-buffered saline (PBS), few have evaluated performance in complex biofluids that account for proteins, lipids, and hyaluronic acid [5][6]. This gap limits the translational potential of new alloys, as their long-term stability in vivo depends on interactions with biological media [7].

This study addresses this gap by investigating the electrochemical properties of the novel β -metastable alloy Ti₂₀Zr₃Mo₃Sn in comparison to commercially pure titanium (cpTi) and Ti6Al4V. The research is justified by its potential to advance the design of safer implant materials by replacing cytotoxic elements like Al and V with biocompatible alternatives and provide insights into corrosion mechanisms in biomimetic synovial fluid (BSF), a more clinically relevant environment than traditional electrolytes [8].

This work is structured as follows: reviews the literature on THA, stress shielding, and titanium alloy properties; details the materials and methods; presentation and discussion of the results; conclusions and implications for future research. By integrating materials science with electrochemical and biomimetic testing, this study aims to contribute to the development of next-generation orthopedic implants with enhanced longevity and patient safety.

2 OBJECTIVES

2.1 General objectives

The general objective of this work is to compare and analyze the electrochemical behavior of Ti₂₀Zr₃Mo₃Sn, a novel β -metastable alloy that has promising mechanical properties to combat stress shielding and less cytotoxic alloying elements, against cpTi, and Ti6Al4V in PBS and BSF.

The study of Ti₂₀Zr₃Mo₃Sn has the objective to obtain a new titanium alloy that has advantages to already established titanium alloy in the medical industry.

2.2 Specific objectives

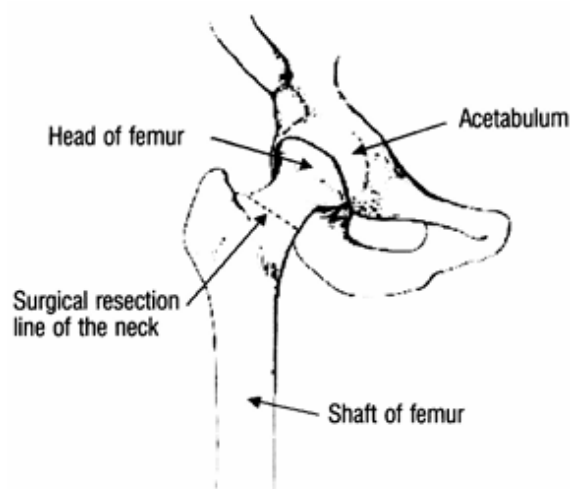
1. Evaluating open-circuit potential (OCP) and passive film stability over 24 hours.
2. Analyzing corrosion resistance via potentiodynamic polarization and electrochemical impedance spectroscopy (EIS).
3. Characterizing the semiconducting properties of passive films using Mott-Schottky analysis.
4. Assessing the interaction between alloys and BSF through fluorescence spectroscopy to detect lipid denaturation.

3 LITERATURE REVIEW

3.1 Total hip arthroplasty

At the end of the last century, we have seen a rise in their ageing population and long-term health problems associated with sedentary and low nutritional value lifestyles in Organisation for Economic Co-operation and Development (OECD) nations[1]. This in turn leads to health problems like obesity which puts more stress in the joints leading to higher cases of arthritis, arthrosis and osteoporosis[9]. The increase in the number of these pathologies has led to more total hip arthroplasty (THA) surgeries being performed in the OECD nations, with 75000 THAs being performed each year in the National health service (NHS) of the United Kingdom alone, as it is one of the most common orthopedic surgeries [9], [10]. THA involves the removal of the damaged femoral head and acetabular cartilage, which are then replaced with prosthetic components, with the intentions of restoring original biomechanical balance of the coxofemoral joint[11]. The main problem with the fixation and lifetime of the THA protheses is periprosthetic osteolysis which is the chronic bone resorption around the exogenous implant devices until the fixation is lost [12]. The following image shows the anatomy of a right hip with arrows indicating the names of each bone and where the bone is cut for THA.

Figure 1: Anatomy of right hip showing the site of surgical removal for total hip arthroplasty

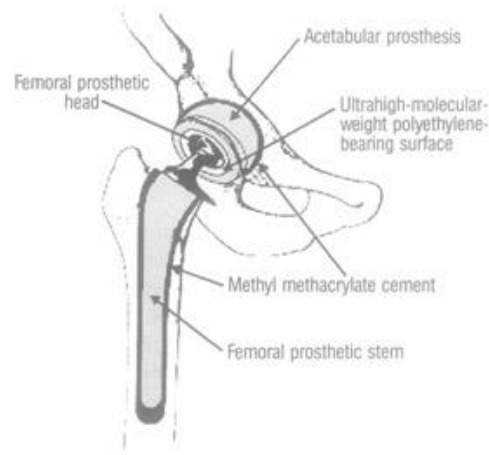


Source: (SIOPACK et al., 1995)

The prostheses utilized typically consist of a femoral stem with a ball component, often made from metal or ceramic, and an acetabular cup, usually composed of a metal shell with a plastic, ceramic, or metal liner [10], [13]. The materials used in the bearing of the prostheses greatly affect its longevity, currently there are three distinct types of bearing systems, metal on polyethylene, metal on metal and ceramic on ceramic. Metal on polyethylene bearings are widely used by their cost-effectiveness and their predictable lifespan, but their disadvantage is that the polyethylene debris generated by the wear of the bearing can cause periprosthetic osteolysis [14]. Metal on metal bearings can have a longer lifespan than metal on polyethylene bearings due to their reduced wear and they also have a lower dislocation rate, but the wear of the metal releases metallic ions, metallosis, and increasing the risk of cancer [15], [16]. Ceramic on ceramic bearings on the contrary of the other systems, release inert particles into the body and lower friction, but they are more expensive and can generate noise on movement [17].

THA is classified as a major orthopedic surgical intervention and is generally performed under regional or general anesthesia. It requires meticulous surgical technique to ensure proper alignment and fixation of the components, which can be cemented with polymethylmethacrylate or uncemented depending on the patient's bone quality and surgeon's preference. The following Figure shows how a prostheses with a metal on polyethylene is inserted into the femur and acetabulum, this prostheses is fixed in the region with polymethylmethacrylate.

Figure 2: A total hip arthroplasty with methyl-methacrylate used for fixation.



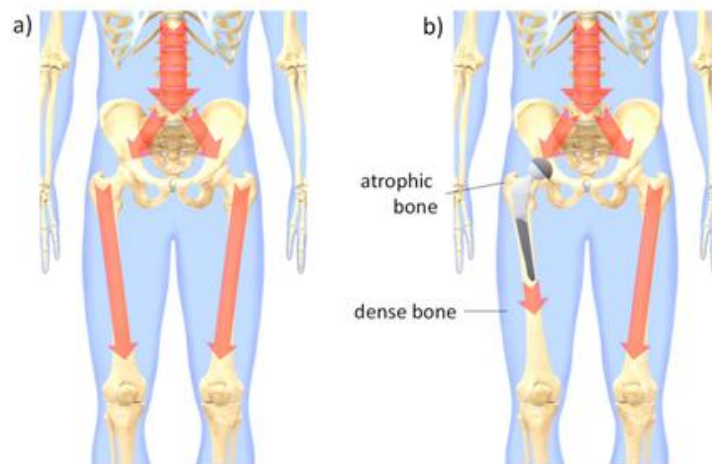
Source: (SIOPACK et al., 1995)

3.2 Stress shielding

The possible complications that a patient will acquire overtime after a THA surgery can be attributed to a diversity of factors involving the design of the implant utilized, surgical factors and patient factors[18]. One possible long term complication involving design factor is stress shielding, which is a biomechanical phenomenon that occurs when a prosthetic implant bears a significant portion of the load that would normally be transmitted through the surrounding bone[19]. This absorption of the load fragilizes the surrounding bone in accordance to Wolff's law which is a series of observations that the bones adapt their external shape and internal structure in response to the mechanical forces applied to it, this leads to reduced mechanical stimulation and subsequent bone resorption [20], [21]. When body weight is equally distributed around the lower limbs this phenomenon is regulated, but when a prothesis with different Young's modulus is introduced, the equilibrium is altered. Leading to a atrophic bone in the region of the femur that no longer receives mechanical stimulation because of the bone resorption, this subsequently causes the formation of a denser bone in the region exposed to higher mechanical stress than physiological[22]. This phenomenon can be modelled by utilizing composite beam theory that predicts that bone stress immediately after implantation is proportional to the relative structural

rigidity of the implant and bone. Therefore, a protheses with larger diameter will cause more significant bone loss, in comparison to one with smaller diameter[23].

Figure 3: Physiological distribution of the load (a) and altered distribution of the load due to the insertion of a hip prosthesis (b).



Source: (SAVIO; BAGNO, 2022)

In THA, this commonly affects the proximal femur, where stiff metallic implants, particularly those made of traditional cobalt-chromium or titanium alloys, alter the natural load distribution. That being that most of the load bypasses the proximal femur instead travelling through the protheses to the distal portion of the femur[22]. Over time, the lack of physiological stress on the peri-implant bone results in osteopenia and potential aseptic loosening of the prosthesis, compromising long-term implant stability [24], [25], [26].

Modification of the prosthesis design and material can reduce or aggravate the effect of the stress shielding. Conventional femoral stems, such as fully coated or stiff tapered stems, are associated with higher stress shielding due to their rigidity. In contrast, newer innovations like tapered, flexible stems aim to mimic natural load transfer, reducing bone loss[27]. Additionally, cementless implants with metaphyseal-loading designs promote proximal stress distribution, whereas diaphyseal-fitting stems may exacerbate distal stress transfer[28]. Understanding these dynamics is crucial for implant selection, as minimizing stress shielding improves bone preservation and long-term THA outcomes.

To increase the chances of success of a joint prosthesis and prolong its life in service, it is essential to manufacture it from metallic materials that have a low Young's modulus of elasticity, close to that of bone (around 10-30GPa) and a high ultimate strength, properties which are crucial to withstand the intense stress to which load-bearing implants are generally exposed [29]. Titanium (Ti) alloys and cobalt-chrome (Co-Cr) alloys are some of the most common materials utilized in THA implants, both are resistant to corrosion in the implantation area and possess suitable mechanical properties. But their Young's modulus is very distant from that of the bone, with Co-Cr having a Young's modulus of 200-230 GPa and Ti6Al4V having 110 GPa[30].

Table 1: Modulus of elasticity of some commercially used biomedical alloys and bone

Material	Microstructure	Young's modulus (GPa)	Yield Stress (MPa)	Ultimate tensile Strength (MPa)
Bone	Viscoelastic composite	10-30		90-140
Stainless steel 316L	Austenite	200	170	480
CoCrMo	Austenite	200-230	450	565
CpTi (grade 4)	α	105	480	550
Ti6Al4V	$\alpha+\beta$	110	680	780
Ti-11.5Mo-6Zr-4.5Sn (BIII)	β	79	620	690

Source: (GEPREEL; NIINOMI, 2013)

3.3 Titanium alloys

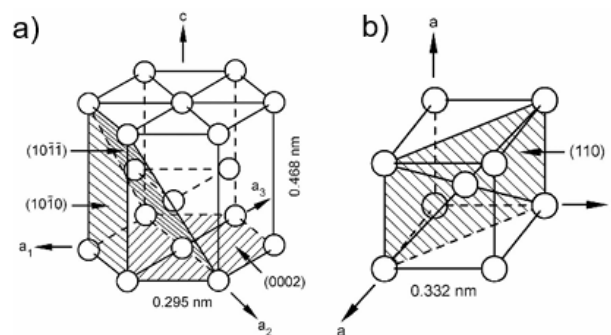
Titanium, first widely used in the 1950s for military and naval applications, has since become one of the world's most essential metals. Today, titanium alloys are applied in a broad range of fields, from aerospace engineering to medical prosthetics[2]. Several Key physical properties contribute to its popularity, one of them being its density that is approximately 60% that of steel, offering a lightweight yet strong alternative. Another key property is its strength, its tensile strength is comparable to that of martensitic stainless steel, making it suitable for high-stress applications[31]. One important aspect is its cost that is comparable to superalloys, balancing performance with economic viability. The manufacturability of titanium is advantageous since it is both castable and machinable, which enhances its versatility across various industries. Finally, its corrosion resistance is outstanding because of the passive oxide film of TiO_2 formed in its surface, particularly in the human body, making it ideal for biomedical uses[2], [32].

Currently Ti6Al4V alloy is one of the most widely used titanium alloys in biomedical devices, this is because they present good corrosion resistance and mechanical properties akin to bone structures. Although the TiO_2 film prevents the liberation of titanium metallic ions into the body, recent studies have shown that aluminum ions liberated from the passive film increase the chances of Alzheimer's disease and alloys containing vanadium have been associated with cytotoxicity and adverse reactions in the tissue[3], [4], [33]. These problems have incentivized the search for new titanium alloys that are less cytotoxic to be used in biomedical devices[8], [34].

New titanium alloys have been proposed over the years, one of the most promising groups of alloys are those containing beta stabilizer elements, which are also low cytotoxic, such as Zr, Nb, Mo and Ta. These alloying elements contribute to the stabilization of the β -phase of titanium alloys, which has a lower young modulus and better formability than near- α and α - β alloys, this causes a better load transfer from the implant to the bone tissue and decreases the likelihood of bone resorption and loosening[35]. Titanium alloys are constituted by two mains phases the α and β , the α -phase unit cell is hexagonal close-packed (HCP) while the β -phase has body-

centered cubic (BCC) unit cell, these two configurations possess different lattice parameters. Pura titanium is a near- α alloy while TAV is a α - β alloy, new alloys such as Ti-24Nb-4Zr-8Sn possess a β -metastable structure. This metastability of the β -phase allows the material to alter its lattice parameters when subjected to strain, conferring to it a super elasticity not achievable through the conventional alloys[36].

Figure 4: Unit cells of the crystal structures of titanium. a) Unit cell of α phase
b) Unit cell of β phase



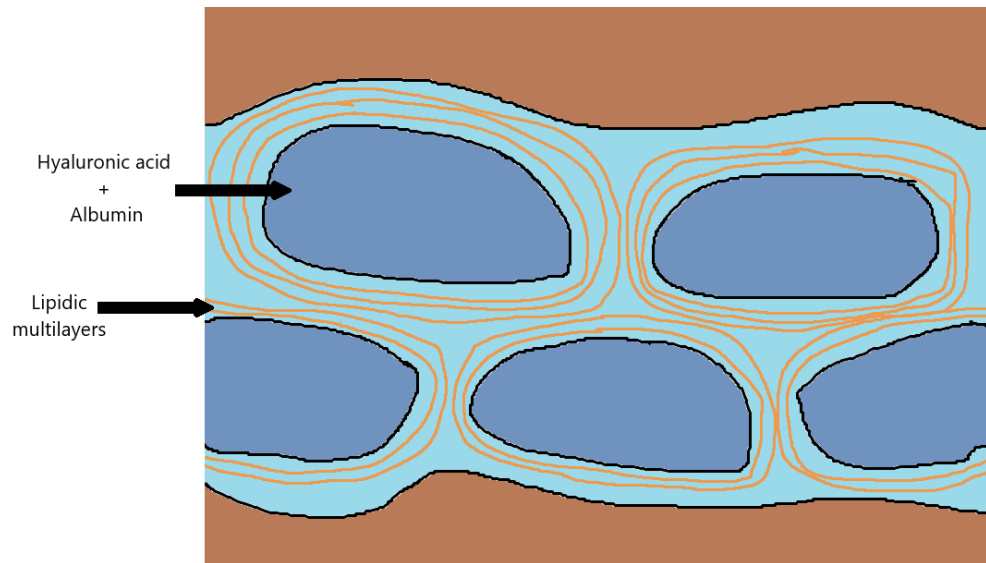
Source: (LÜTJERING; WILLIAMS, 2007)

3.4 Bio-mimetic environment

These advancements in new titanium alloys must be accompanied by studies of their electrochemical properties and as the new alloys are envisioned to be used as prostheses it's important to identify how they behave in bio-mimetic environments. Because of this there has been research done in different simulated body fluids including Ringer's solution, Hank's solution and phosphate buffered saline solution [37], [38], [39]. Ringer's solution is a commonly used physiological fluid in biomedical research, its composition does not include phosphates differently from Hank's solution and PBS [40]. Hank's solution is also a widely used physiological medium due to its similar ionic composition of human extracellular fluids, it has been used in corrosion analysis of Titanium alloys in previous studies and shown that they are passive in it [41], [42]. PBS is also a widely utilized physiological solution for corrosion analysis of titanium alloys, like Hank's solution it possesses a similar a ionic composition to human body fluids[43]. Titanium alloys have shown passive behavior in previous PBS studies[5], [44]. The lubricant present in the joints, known as Synovial Fluid (SF), is

primarily composed of proteins, phospholipids, and hyaluronic acid. Structurally, SF consists of multilayers of lipids surrounding the hyaluronic acid and proteins, forming a network of vesicles [6], [45]. This can be seen in the Figure below

Figure 5: Representation of healthy synovial fluid showcasing the lipidic multilayers and the enveloped hyaluronic acid mixed with proteins



Source: Author

Research has also been conducted under in-vitro conditions utilizing synovial fluid extracted from patients or through implantation in animals. However, with the development of bio-mimetic synovial fluid, it is now possible to simulate the properties of natural synovial fluid without the need for patient-derived samples[7], [46], [47]. This allows a more proximate simulation of the behavior of the material during application.

3.5 Electrochemistry

Electrochemistry plays a important role in many areas of material engineering, nowadays being a fundamental cornerstone of understanding chemistry and physics in relation to materials. This knowledge is utilized in many for uses such as: Electrochemical deposition, formation of oxide layers and semiconductors, new polymer materials and nanotechnologies[48], [49].

Corrosion is one electrochemical phenomenon that affects most metallic materials and represents an increased cost of maintenance in a wide array of areas; therefore, the study of this phenomenon is essential to produce longer lasting materials.

Corrosion is an attack by a chemical or an electrochemical reaction with the environment, for corrosion to occur the presence of four elements, an anode, cathode, electrolyte and a metallic path for the flow of electrons.

In a corrosion cell, the anode functions as the negative terminal. As the more reactive metal, it releases electrons that travel through a metallic pathway toward the cathode. The cathode, which acts as the positive terminal, is the site of reduction reactions that consume the electrons generated by the anode. The process also requires the presence of an electrolyte, which is an electrically conductive solution encompassing both electrodes and enabling corrosion to occur. For potential measurements, a system involving three electrodes is employed. The working electrode is where the reaction of interest takes place, and measurements are recorded. The reference electrode provides a stable and known reference potential against which the working electrode's potential is compared. Finally, the counter electrode, also known as the control electrode, completes the electrical circuit, ensuring the flow of current between it and the working electrode[49].

The oxidation of the surface layer of a metal is called passivation which is a process that creates a passive stable film as barrier between the environment and the metal. These passive films are very thin, in the scale on nm, and behave like semi-conductors with metallic properties, allowing a limited amount of conductivity of cations between the metallic matrix and the environment. This causes the corrosion rate to dramatically slow down because of the reduction of current density for cathodic reduction and the increase of current density for anodic polarization.

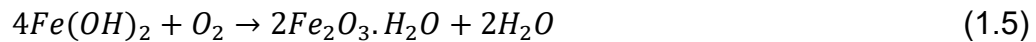
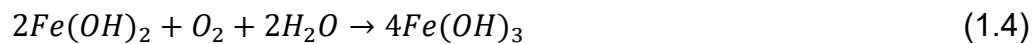
Some transition metals like Fe and Ti possess what is called an active-passive behavior where they exhibit a S-shaped polarization curve. This curve is representation of the relationship between potential (V) and current density is very important as it delineates three reaction zones: active, passive and transpassive. In the cathodic zone the metal is actively corroding and as the potential increases the current density rises sharply as it corresponds to the metal undergoing anodic dissolution, this is the expected behavior of a metal in an aggressive environment. In the passive zone the metal is protected by a stable oxide film that is adhered to its surface, as previously stated this severely reduces the corrosion rate[49]. Lastly there is the transpassive

zone that occurs at very high potentials, in this zone the oxide layer breaks down leading to a rise in current density, which provokes an accelerated corrosion and compromises the integrity of the material.

3.5.1 Corrosion types

Corrosion comes in many forms and types and although it can be not detrimental initially over time it starts to affect the strength, mechanical properties and appearance of the material. Which if not considered can cause catastrophic failure during operation such as the failure of cable bolts in mining operations. As commented before the environment affects drastically how the corrosion will occur in the material, these environments can be saline, dry, wet or acidic for example[50].

One of the most common corrosion types is uniform corrosion, it occurs when a small amount of electrolyte is present on the surface of a metal, such as seawater on steel. It occurs by the exchange of electrons between the anodic and cathodic areas where the oxidation of the metal and the reduction of the oxygen occurs respectively[51]. An example reaction of steel in aqueous environment can be seen in the equations below.



In the equation (1.1) the oxidation of iron generates electrons that react with the oxygen and water in equation (1.2) to generate a hydroxyl ion. This ion then reacts with the ferrous ion, in equation (1.3), to generate Iron(II) hydroxide than can then either react with water and oxygen to generate iron(III) oxide-hydroxide as in equation (1.4) or just with oxygen to generate hydrated iron oxide as in equation (1.5).

Another important corrosion type is galvanic corrosion that occurs when two metals with different electrochemical potentials are joined together while in contact with a corrosive electrolyte[52], [53], [54]. This can be a problem, or it can be used to prolong the life of a piece, as one of the metals can be used as a metal sacrifice. This

occurs because, as the name implies, a galvanic cell is formed between the two metals, during the process the main driving force of corrosion is the difference in potential between the two metals. The difference in potential of two metal can be surmised with the help of a galvanic table which classifies metals from more anodic to more cathodic, the farther apart the metals are the more rapidly the anodic metal will corrode[55]. The mechanism through which this occurs is the same as previously discussed in corrosion cells, since a galvanic cell is a corrosion cell.

Different factors affect the magnitude of galvanic corrosion, the first one being how far apart the two metal are from each other in the galvanic table which indicates how rapidly the corrosion will occur as previously stated. Secondly the nature of the environment will affect corrosion as it affects the pathways of ions and electrons in galvanic cell. Lastly, the area, distance, and geometry of the metal significantly influence corrosion reactions[49]. Specifically, an unfavorable ratio of cathodic to anodic metal surface areas can accelerate the corrosion rate, this occurs because the metal with the smaller surface area experiences a higher current density. If this smaller area corresponds to a more anodic metal, it will corrode more rapidly as it reacts with its environment, thereby accelerating the overall corrosion process. As for the distance it is widely known the conductivity is inversely proportional to distance, therefore the shorter the path between the two metals the more galvanic damage will be found. Lastly the geometry of the components also affect galvanic corrosion since continuity of the pieces affects its polarization.

Crevice corrosion is a type of corrosion common in bio-medical devices used in joints, since there are discontinuities between the bio-medical devices and the bone it is connected to. This type of corrosion occurs when there are small spaces between metal to metal or metal to non-metal, the presence of cracks or fissures and deposition detritus on the surface of the materials[56]. Several factors can contribute to the intensity of crevice corrosion, some then are the type and geometry of the crevice, the composition of the alloy, the characteristics of the passive film and the mass transfer in and out of the crevice[57]. There are many different mechanisms that explain crevice corrosion, one of them is metal ion concentration, according to it there is a difference between the metal ion concentration in and out of the crevice, because of that a

corrosion cell is formed. As the area with low metal concentration becomes the anode and the area with high metal concentration becomes the cathode[58].

One of the most serious corrosion types is pitting, since it damages the materials, but it is quite difficult to identify it. Pitting is a localized corrosion that creates cavities or pits in the metal while large part of the surface remains unaffected, while the damage is localized it necessitates the changing of the whole piece when identified since it can cause catastrophic failure[59]. Generally pitting occurs in marine environments where there is a higher concentration of ions, but it can also occur in pipes when transporting hard or soft water. For pitting to occur it is necessary for a passive film to be present on the surface of the metal, that could be the oxide of a passive-active metal or a coating. Since uniform corrosion is unlikely to occur in active-passive metals, pitting works by destroying the passive film on certain spots in the surface causing the formation of a small anode area which subsequently starts acting as a corrosion cell[60]. Nowadays it is possible to analyze the pitting potential of a metal through electrochemical techniques, one of them being the polarization hysteresis where we observe the anodic polarization behavior of a metal. In this technique, a open circuit potential is started and subsequently the anodic polarization scan is conducted in the noble direction at a slow rate and upon reaching a predetermined value it reverses and move towards an active potential closing the loop. This analysis divides the plot in 3 regions, the first one representing a resistance to pitting, followed by a region where the pits already initiated growth but there is no formation of new ones. Lastly in the final region where the potential has reached critical pitting potential it generates new pits and deepens the ones already formed[49], [61].

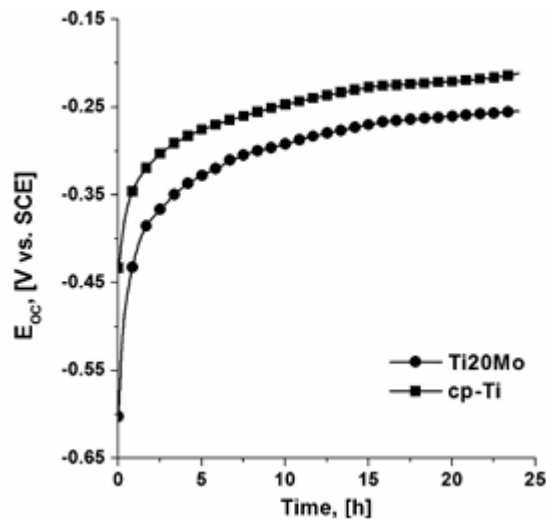
Intergranular corrosion occurs between the grain boundaries, it is a form of localized corrosion in a metal in a corrosive environment[62]. It can cause the dislodgment of the grain causing peeling of the surface of the metal. This form of corrosion is more common in stainless steel, aluminum and nickel alloys with different mechanisms of corrosion for each alloy.

3.5.2 Open-circuit potential

Open-circuit potential is conducted with the utilization of three electrodes and a potentiostat to find the steady-state conditions of the material tested, it is expected

that the potential (V) will rise over time until reaching stability indicating the growth of a passive film in the sample[63]. As can be seen in Figure 6.

Figure 6: OCP graph of potential versus time of cp-ti and Ti20Mo in artificial saliva solution along 24 hours.



Source: (MARECI et al., 2010)

OCP is a weak indicator of the corrosion resistance of a material, so although useful its results alone cannot be used to prove with certainty the effectiveness of a material over another when it comes to corrosion resistance.

3.5.3 Electrochemical impedance spectroscopy

EIS is a versatile technique used to investigate the electrochemical properties of a material through applying a potential in various frequencies and measuring its response[64], [65]. The data acquired through the measurements can then be used to ascertain properties such as corrosion resistance, passive film growth and rate of ion transport. It is also possible to then simulate the equivalent electrical circuit of the electrochemical system with the response acquired. An important prerequisite for the analysis of EIS data is the utilization of the Kramer-Kronig test, as it allows to ascertain the validity of data obtained and to verify if the data was influenced by bias[66]. The Kramer-Kronig test works by verifying the linearity of the time-invariant with the causal system between the real (Z') and imaginary (Z'') part, this is done by

calculating the theoretical Z'' with Kramer-Kronig relation and Z' data to then compare it to experimental data[67], [68]. The equation utilized can be seen below:

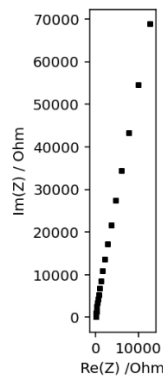
$$Z'(\omega) = \frac{2}{\pi} \cdot \int_0^{\infty} \frac{\omega' \cdot Z''(\omega')}{\omega^2 - \omega'^2} d\omega' \quad (2.1)$$

$$Z''(\omega) = \frac{2}{\pi} \cdot \int_0^{\infty} \frac{\omega' \cdot Z'(\omega')}{\omega^2 - \omega'^2} d\omega' \quad (2.2)$$

In equation 2.1 we calculate the theoretical value of Z' with Z'' where ω is the angular frequency of the applied signal of the EIS and ω' is the variable for integration representing the frequency domain over which the data is evaluated. For equation 2.2 the same applies but utilizing Z' to obtain the theoretical value of Z'' . This then allows us to find the error between the theoretical value and the experimental data, identifying if a data set presents instrumental noise, non-linear behavior or instability of the system[66].

With the validated data the equivalent electrical circuit of the system can then be found by analyzing the Nyquist and bode plots. The Nyquist plot is composed of Z' in the X-axis and Z'' in the Y-axis, where each point corresponds to a specific frequency, where the high-frequency is generally found on the left side of the plot. This type of graph correlates the real and imaginary parts while frequency varies[69]. An example of Nyquist plot can be seen below.

Figure 7: Nyquist curve of Ti₂₀Zr₃Mo₃Sn in PBS

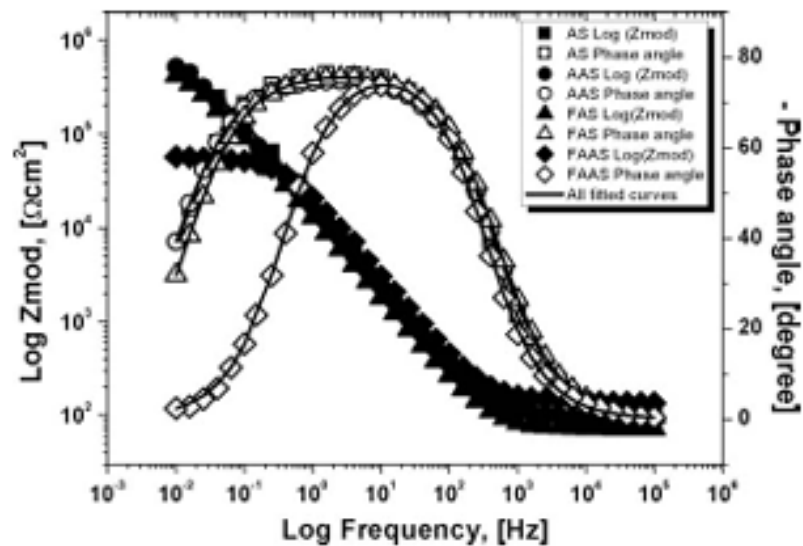


Source: author

There are two types of bode plots magnitude plots and phase plots both then are necessary to be able to analyze the nature of an electrochemical system, they

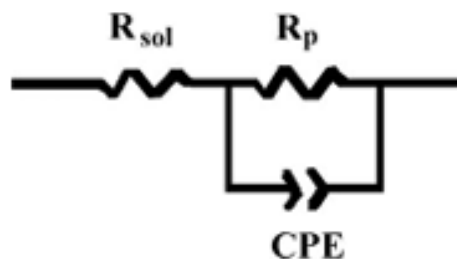
respectively correlate magnitude and phase angle of the impedance as a function of the frequency[69]. The magnitude plot consists of the magnitude of the impedance ($|Z|$) in the Y-axis in a logarithmic scale and the frequency of the applied signal in the X-axis also in the logarithmic scale. In the phase angle plot the Y-axis the phase angle, which indicates the phase difference between the applied voltage and the resulting current, the X-axis is the same as the magnitude bode plot. Since both graphs have the same X-axis they can be represented together, a bode plot obtained by Mareci et al[70]. can be seen below with the equivalent circuit he used to fit the data obtained.

Figure 8: Bode plots for a Ti50Ta alloy in different media.



Source: (MARECI et al., 2009)

Figure 9: Equivalent circuit of fitted impedance data



Source: (MARECI et al., 2009)

The fitting of the data to an equivalent electrical circuit is generally done with specialized software such as ZView and ECLab, in the equivalent circuit obtained by

Mareci et al. it is possible to see the main elements of a equivalent circuit. That being the resistance of the electrolyte (R_{sol}), the capacitor of the system, the constant phase element (CPE), and the resistance of the passive film. The validity of this fitting is evaluated through the χ^2 (chi-squared) test that is the sum of the error-squared of Z' and Z'' , the equation for χ^2 used for evaluating the validity of the fitting can be seen below.

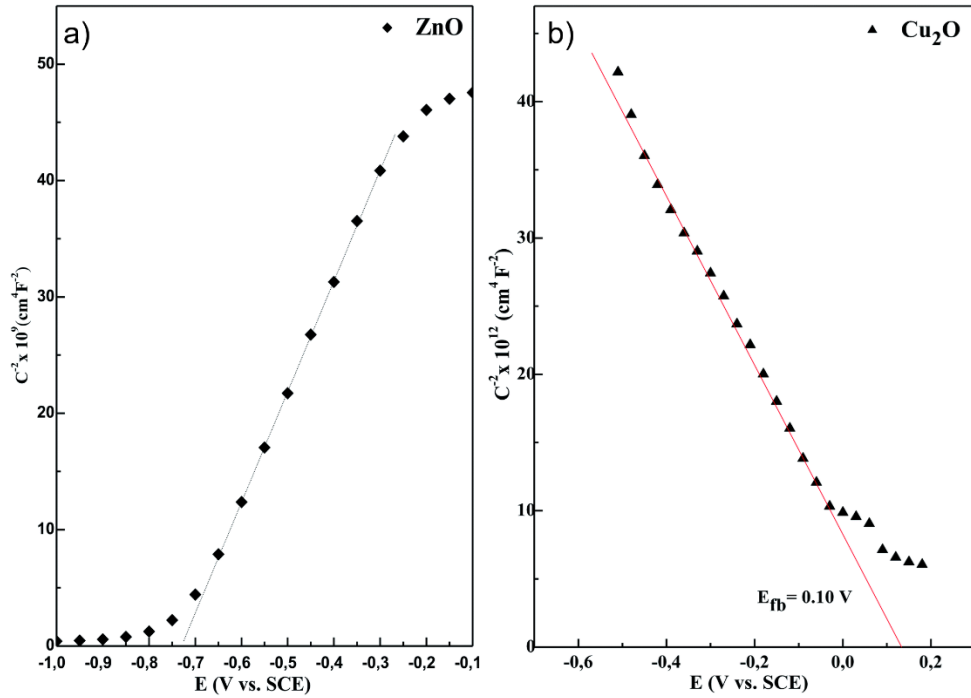
$$\chi^2 = \sum_i \left(\frac{(Z'_{exp,i} - Z'_{model,i})^2}{\sigma_{Z'}^2} + \frac{(Z''_{exp,i} - Z''_{model,i})^2}{\sigma_{Z''}^2} \right) \quad (3.1)$$

Where the $Z'_{exp,i}$ and $Z''_{exp,i}$ are the real and imaginary parts of the experimental impedance data at a i frequency, $Z'_{model,i}$ and $Z''_{model,i}$ are the real and imaginary parts of modeled impedance data and lastly the $\sigma_{Z'}$ and $\sigma_{Z''}$ are the standard deviations of the real and imaginary parts respectively.

3.5.4 Mott-Schottky

The Mott-Schottky (MS) analysis is used to study the electronic properties of the passive film, particularly their semiconducting behavior such as if they're n-type or a p-type. A N-type semi-conductor presents a abundance of electrons as the majority carriers of charge while vacancies are the minority carriers. For a P-type semiconductor the opposite is true, the vacancies where electrons should be the majority charge carriers while the electrons are the minority charge carriers[71]. This behavior can be identified through the appearance of the graph, below are two Mott-Schottky obtained by Bengas et al, where the graph a) shows a plot of ZnO that posses a n-type behavior and graph b) that shows the p-type behavior of Cu₂O.

Figure 10: Mott–Schottky plots of a) ZnO showing n-type behavior and b) Cu₂O showing p-type behavior



Source: (BENGAS et al., 2019)

Titanium oxide is expected to present an n-type behavior that is due to the presence of oxygen vacancies where free electrons are the majority carriers. Another important property that can be identified with Mott-Schottky is the charge carrier density (N_d) which represents the number of charge carriers, electrons or vacancies, present in a volume unit. The value of the charge carrier density can be found through the following equation.

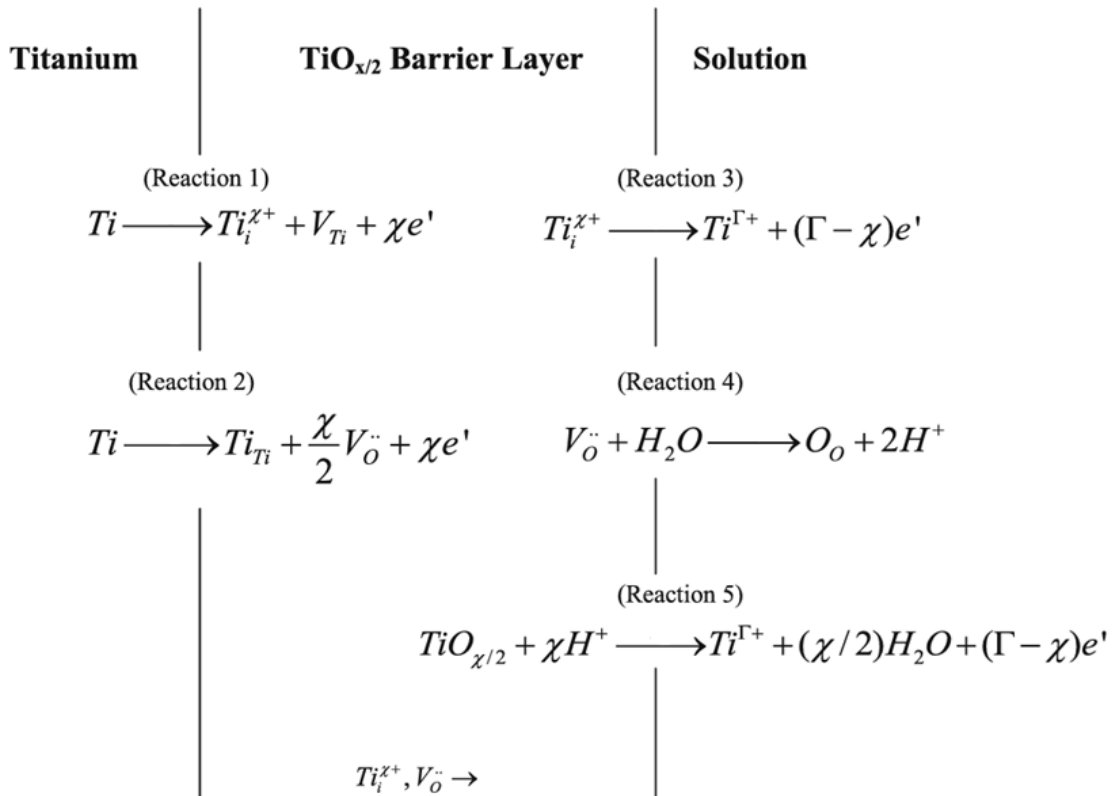
$$N_d = \frac{2}{\epsilon \epsilon_0 e \cdot \text{slope}} \quad (4.1)$$

In (4.1) the ϵ is the dielectric constant of the material, ϵ_0 is the permittivity of free space and e the elementary charge. It is important to denote that in the Mott-Schottky there are two slopes in n-type and p-type behaviors, so the N_d changes after reaching an inflection point.

Mott-Schottky is a technique that is used to identify the nature of the reactions occurring in the passive film through the point-defect model (PDM). The PDM is a theoretical framework that is used to explain the growth and breakdown of passive oxide films on metals and alloys, it describes the processes from film formation, steady-

state growth, film breakdown and the role of the environment. It focuses on atomic-scale imperfections within the oxide layer such as vacancies and interstitials. Vacancies are missing atoms in the oxide lattice, these can be either metal or oxygen vacancies, while interstitials are extra atoms located in positions between the regular lattice points. These imperfections facilitate the transport of ions through the oxide layer, which causes the growth and repair of the passive layer. Another important aspect of the PDM is being able to discern the nature of passive oxide film, since p-type films generally contain a deficiency of metal ions or an excess of cation vacancies, while n-type films generally contain an excess of cations in interstitial sites or anion vacancies[72]. Roh and Macdonald studied the growth behavior of titanium oxide in a 0.5 M H₂SO₄ solution. The following Figure presents a simplified overview of the reactions they identified using the PDM framework, offering valuable insights into the defect mechanisms governing the oxide's stability and growth.

Figure 11: Schematic of physico-electrochemical processes that are postulated to occur within the point-defective anodic oxide barrier layer



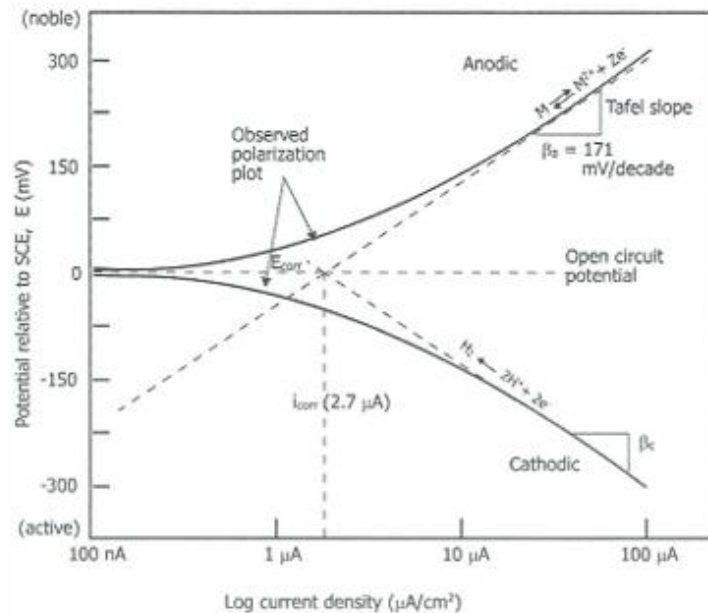
Source: (ROH et al., 2019)

Reaction 1 shows the injection of the interstitial titanium cation (Ti_i^{x+}) and a titanium vacancy (V_{Ti}) into the barrier layer from titanium atom (Ti), these interstitials are then ejected into the solution ($Ti_i^{\Gamma+}$) after migrating from the barrier layer as can be seen in reaction 3. In reaction 2 the oxygen vacancies (V_o) and titanium cations in their expected lattice site (Ti_{Ti}) are generated at the innermost part barrier layer during its rua freiformation, in reaction 4 these defects then migrate to the interface of the barrier and solution where they interact with water injecting the oxide ion (O_o) in the barrier layer. Γ and χ represent the oxidation state of the ions and vacancies respectively[73].

3.6 Potentiodynamic polarization

Potentiodynamic polarization (PP) is a technique used to analyze the current response of the material as the potential increases over time, this provides insights such as the kinetics of anodic and cathodic reactions and the susceptibility of corrosion of the material. As with previously discussed techniques, the experimental setup for Potentiodynamic polarization involves the utilization of a corrosion cell, that consists of the working, reference and control electrodes, the data obtained in this test plots a graph of potential (V) versus the current density (A/cm^2). Through this plot it is possible to obtain the key information such as the corrosion potential (E_{corr}), corrosion current density (I_{corr}) and passive current density (I_{pass}). E_{corr} indicates the potential where the anodic and cathodic reactions are equal. I_{corr} is obtained through Tafel extrapolation where the cathodic and anodic branches of the curve are extrapolated linearly, the point of intersection between the two of them at corrosion potential is the corrosion current density. The I_{corr} gives the corrosion rate of the material, a higher I_{corr} indicates a higher rate of corrosion and thus lower corrosion resistance. This extrapolation can be seen in the following hypothetical Tafel plot.

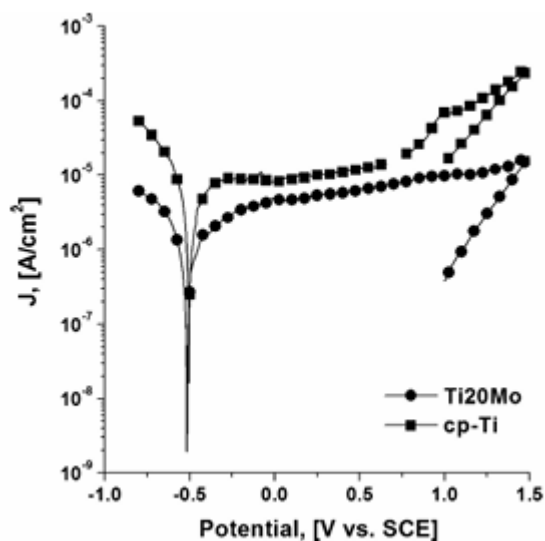
Figure 12: Hypothetical Tafel plot of log current density versus potential relative to SCE



Source: (AHMAD, Zaki, 2006)

In this polarization curve the log of the current density is plotted in the x-axis and the potential in the y-axis, in it we can see the Tafel extrapolation and that OCP aligns with the corrosion potential of the material. i_{pass} is the minimum current density necessary for the metal to remain in its passive state, a lower i_{pass} indicates better corrosion resistance. Mareci et al. studied the electrochemical properties of cpTi and Ti20Mo alloy in artificial saliva, the polarization curve he obtained shows that Ti20Mo presented a superior corrosion resistance to cpTi[63].

Figure 13: Polarization curve of cpTi and Ti20Mo in artificial saliva



Source: (MARECI et al., 2010)

In the polarization plot we can see that the E_{corr} is approximately -0.5 V for both materials and that the I_{pass} is lower for Ti20Mo alloy in comparison to cpTi, indicating its superior corrosion resistance. According to previous studies the passive current density for cpTi and Ti6Al4V are similar, which may indicate a similar mechanism for the formation of the passive film when tested in the same medium[74].

4 MATERIALS AND METHODOLOGY

4.1 Materials:

4.2 Alloys:

Three distinct alloys samples were utilized: cpTi, Ti6Al4V and Ti20Zr3Mo3Sn. The latter was manufactured at (Metallurgical Chemistry Laboratory, INSA Rennes, France). The metals used were purchased in massive form from Goodfellow Company with commercial purity and introduced into the crucible of the furnace cut into very small pieces to facilitate the uniformity of the chemical composition. To obtain the samples of Ti20Zr3Mo3Sn a Cold crucible levitation melting (CCLM) high frequency induction furnace under argon atmosphere was used to control de grain size the alloy ingots were homogenized in a tubular furnace under high-vacuum (10^{-7} mbar) with a heating rate of 20°C/min. After synthesis, the alloy ingot underwent a rolling operation with a degree of reduction of approximately 90% to obtain a metal strip from which specimens for tensile testing and samples for biocompatibility and corrosion testing were cut. All the specimens and samples were solution treated at 900°C for 30 min in the beta-phase field and water quenched to maintain the characteristic high-temperature beta microstructure at room temperature.

The evaluation of the composition of the produced samples of Ti20Zr3Mo3Sn were done with the technique of X-Ray diffraction, the obtained results were then checked for characteristic peaks of the β -phase and the alloying elements. The samples of cpTi an Ti6Al4V were square shaped with 15mm sides and 5 mm thickness, while Ti20Zr3Mo3Sn samples were circular with a radius of 1,3 mm and a thickness of 0,7mm.

4.3 Electrolyte:

Two distinct electrolytes were used, phosphate buffered saline solution and biomimetic synovial fluid manufactured at (Laboratoire de Mécanique des Contacts et des Structures, INSA Lyon, France). PBS solution was made using PBS tablets (delivered by EMD Millipore Corp., Burligton, USA) composed of 140 mM NaCl, 10 mM phosphate buffer, and 3 mM KCl and deionized. The solution has a pH value of 7.4 approximately. BSF was made using 0.3mg/ml EggPC, (delivered by Avanti Polar

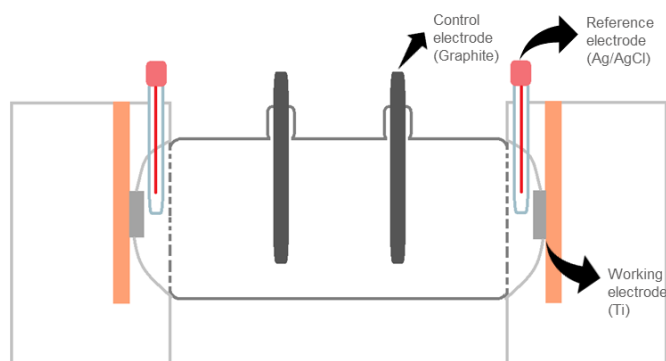
Lipids, Inc., Alabaster, USA) 3mg/ml hyaluronic acid (delivered by SIGMA ALDRICH, co., St. Louis, USA) and 20mg/ml bovine serum albumin. Where first a solution of 9-parts chloroform to 1-part ethanol was used to dissolve the EggPC in a glass balloon, where the solution is evaporated in a roto evaporator leaving lipid vesicles on the walls of the glass balloon. After the complete evaporation of the solution bovine serum and hyaluronic acid are added to the container and agitated until they become well incorporated with the lipid vesicles, afterwards the solution is filtered.

4.4 Corrosion tests:

The samples were prepared by polishing then with silicon carbide grit paper from 800 to 4000, followed up by using 3 μ m and 1 μ m diamond paste until mirror-polish was achieved. The electrochemical measurements were conducted using a standard three electrode system, connected to a potentiostat (SP-300, BioLogic) with a computer running the EC-Lab® Software (BioLogic) to control and register the measurements. The electrodes were; the samples being the working electrode with a 1cm² of contact area with solution, graphite as counter electrode and a Ag/AgCl reference electrode. The working electrodes were fixed with a copper plate connected to the potentiostat by a copper cable when using the PBS solution. For the BSF tests the samples were put into resin while connected to a copper cable, the sample was then submerged into BSF solution, and the electrolyte solution was kept as 38°C during the measurements. The experimental system can be seen in Figures 14 and 15. Figure shows the system for PBS and Figure shows the system for BSF.

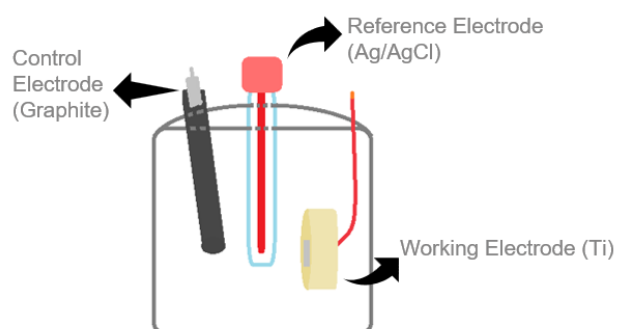
The experimental protocol flowchart in image 16 shows the order of analysis conducted, where first they are polished until mirror polish is achieved, followed by submerging the samples in either PBS or BSF. Then two different procedures are conducted, both start with OCP followed by EIS, procedure one finishes with PP and procedure two finishes with MS. From the experiments conducted in BSF a vial of the electrolyte was taken for later analysis of its properties through fluorescence. All data presented in this paper consists of the average and standard deviation of the most representative results for each experiment and sample.

Figure 14: Experimental system utilized for PBS samples



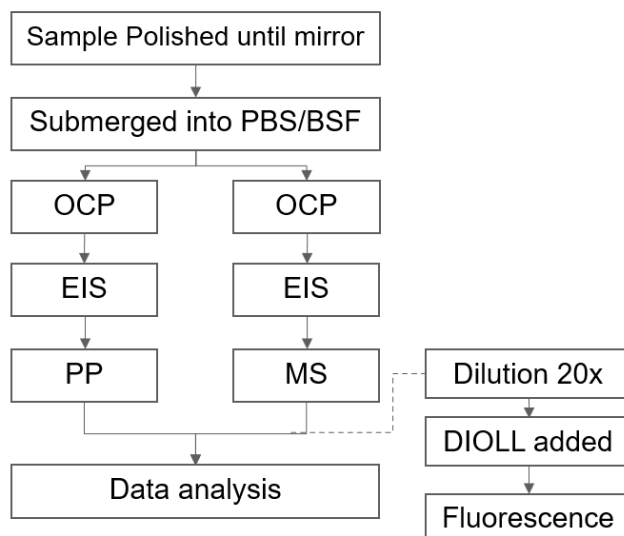
Source: Author

Figure 15: Experimental system utilized for BSF samples



Source: Author

Figure 16: Experimental protocol flowchart of the order of analysis



Source: Author

4.5 Open-circuit potential

Open-circuit potential was the first analysis to be conducted, it lasted the period of 24 hours taking measurement every 5 seconds until achieving the steady-state of the working electrode. The OCP was done before each corrosion test and the settings utilized in EC-Lab® Software (BioLogic) can be seen in table.

Table 2: Settings parameters utilized for OCP

Setting	Setting value
Recording time (h)	24
Record every (s)	5
Potential range (V)	-2.5 to 2.5

Source: Author

4.6 Potentiodynamic polarization

Potentiodynamic polarization was conducted from -0.2 to 1.5 vs OCP with a scanning rate of 1 mV/s, EC-Lab® Software (BioLogic) was used to plot the polarization curves that were then used to estimate the current corrosion density of the samples.

Table 3: Setting parameters utilized for potentiodynamic polarization

Parameter		Value
Scan	Ewe with dE/dt (mV/s)	1
	From Initial potential (V vs OCP)	-0.200
	From Final potential (V vs ref)	1.500
Record	average current over potential step	<I>
	over the last	70%
	Average N	8
Potential range (V)		-2.5 to 2.5

Source: Author

4.7 Electrochemical impedance spectroscopy

EIS was performed at OCP with results being record from the range of 10^5 to 10^{-2} Hz, with a sinus amplitude of 15 mV. The data obtained is used to construct an spectra bode plot of magnitude / phase angle versus frequency. Based on the data obtained, an equivalent circuit is used to model the experimental spectra and with the equivalent circuit built, it is possible to obtain the resistance and capacitance of parts of the system. SIMAD software developed by Centre national de la recherche scientifique (CNRS) was utilized to simulate and acquire the fitting parameters. Measurement model developed by Watson, Et al, was utilized to find the general capacitance (C_{∞}), polarization resistance (R_p).

Table 4: Setting parameters utilized for Electrochemical impedance spectroscopy

Parameter	Value
Initial frequency (Hz)	10^5
Final frequency (Hz)	10^{-2}
Points per decade in logarithmic spacing	9
Sinus amplitude (mV)	15.0
Wait period before each frequency	0.10
Average number of measures per frequency	3

Potential range (V)	-2.5 to 2.5
Current range	Auto
Bandwidth	8

Source: Author

4.8 Mott-Schottky analysis

Mott-Schotcky analysis was executed from the range of -0.6 V vs OCP to 1,2 V vs OCP, with measurements taken in increments of 0.5 V. The spectras were recorded from the range of 10^5 to 10^{-2} Hz with a sinus amplitude of 15 mV. The SPEIS results are a collection of spectras collected at different potential, they are analyzed collectively through the use of the Mott-Schotcky technique. This technique involves the construction of the Mott-Schotcky curve of the reciprocal of square capacitance ($1/C^2$) by the potential (V). The EIS and SPEIS experimental results were interpreted through the graphical approach to obtain the resistivity of the solution, CPE, alpha and generalized polarization. Measurement model was used to find the resistivity of the solution, general capacitance and general polarization. SIMAD software developed by CNRS was utilized to simulate and acquire the fitting parameters.

4.9 Experimental Data Validation

The validity of the obtained EIS data was confirmed trough the linear Kramer Kroning methodology with the use of the program Lin-KK developed by M. Schönleber, D. Klotz and E. Ivers-Tiffée in the Karlsruhe Institute of Technology. The frequency, real and imaginary data are inputted into the program where the residual, the according deviation, indicates the reproducibility of the measured impedance spectrum.

4.10 Fluorescence analysis

Fluorescence was executed to identify the presence of lipids in the BSF prepared and how they behave before and after the corrosion experiments. A parcel of BSF was collected before and after the corrosion tests for each sample. For the identification of lipids, the BSF was diluted 20 times and was excited at the frequencies of 270 and 290 nm as to identify the peaks of tyrosine and tryptophan respectively. For the behavior analysis a DIOLL probe was added to the BSF sample

and the peaks at 450 and 500 nm were excited at 21°C and 37°C. With the two peaks the generalized polarization (Gp) can be calculated through the following equation (5)

$$Gp = \frac{(I_{em}(450nm) - I_{em}(500nm))}{(I_{em}(450nm) + I_{em}(500nm))} \quad (5)$$

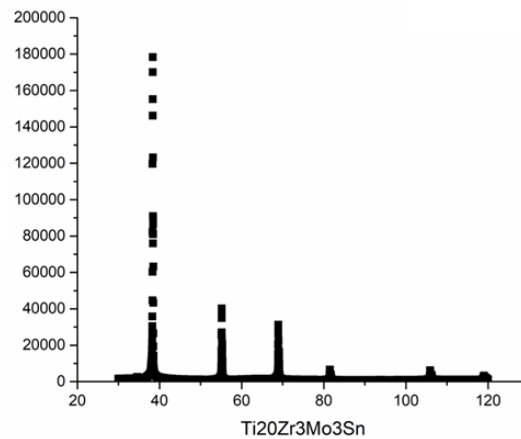
The results are then compared between the two temperatures to identify the behavior of the samples.

5 RESULTS AND DISCUSSION

5.1 Alloys

In Figure 16 we can see in the XRD analysis conducted on one of the samples allowing us to obtain the diffractogram of the sample, analysing the peaks we are able to ascertain that the sample was indeed beta-titanium even though the peaks were slightly dislocated to the right.

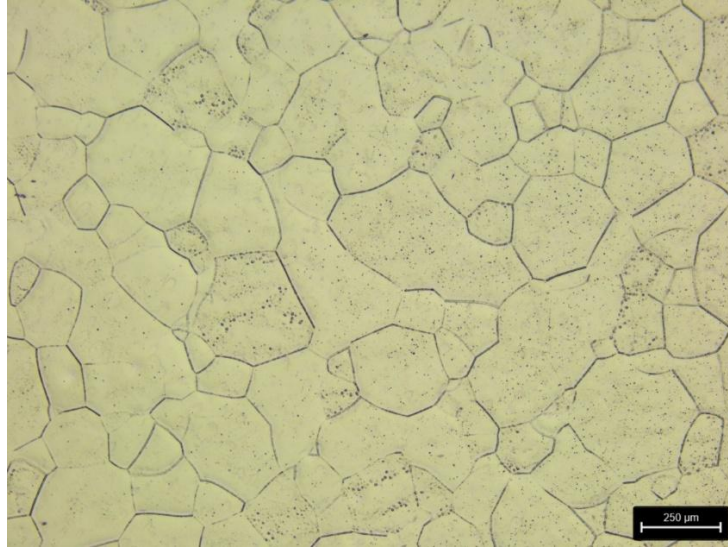
Figure 16: XRD graph of Ti₂₀Zr₃Mo₃Sn



Source: Author

In Figure 17 the solution treatment was effective as the obtained microstructure does not show elongated grains characterized by the rolling process.

Figure 17: Microstructure of Ti₂₀Zr₃Mo₃Sn sample through optical microscope



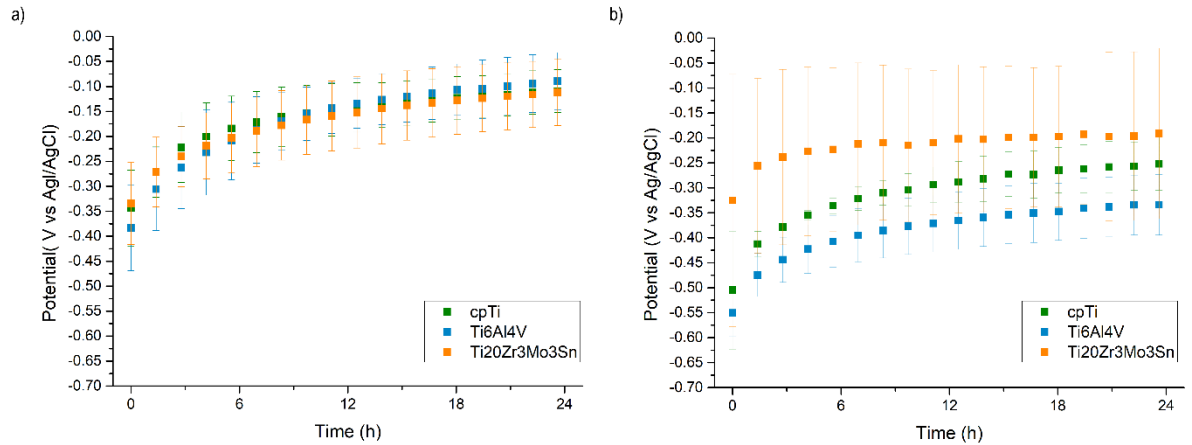
Source: Author

5.2 OCP

The open circuit potential is dependent on the nature of the interface between metal and solution; therefore, it's not a property specific to the alloy since it varies with temperature, surface condition, oxygen concentration on the electrolyte and its composition.

As can be seen in table 5 the OCP value after 24H was -0.09 V for cpTi, -0.10 for Ti6Al4V and -0.13 V for Ti₂₀Zr₃Mo₃Sn in PBS. The curves demonstrate a rapid increase during the first hour which demonstrates the growth of the passive film on the surface of the material overtime, following the initial hour the growth of the passive film slows down indicating a closer equilibrium between the alloy and the environment. The samples submerged in BSF presented the same behavior during the 24 hours period, where there was a rapid increase in the passive film followed by a gradual increase in thickness. Table 5 shows the OCP values for the samples in BSF, the OCP value for cpTi was -0.25 V, for Ti6Al4V it was -0.34 V and for Ti₂₀Zr₃Mo₃Sn it was -0.23 V. Figure 18 shows the gradual increase in potential over the 24 hours immersion period

Figure 18: OCP graph of potential over time of tested alloys in a) PBS and b) BSF



Source: Author

Table 5: OCP for titanium alloys in bio-mimetic environment after 24 hours of immersion

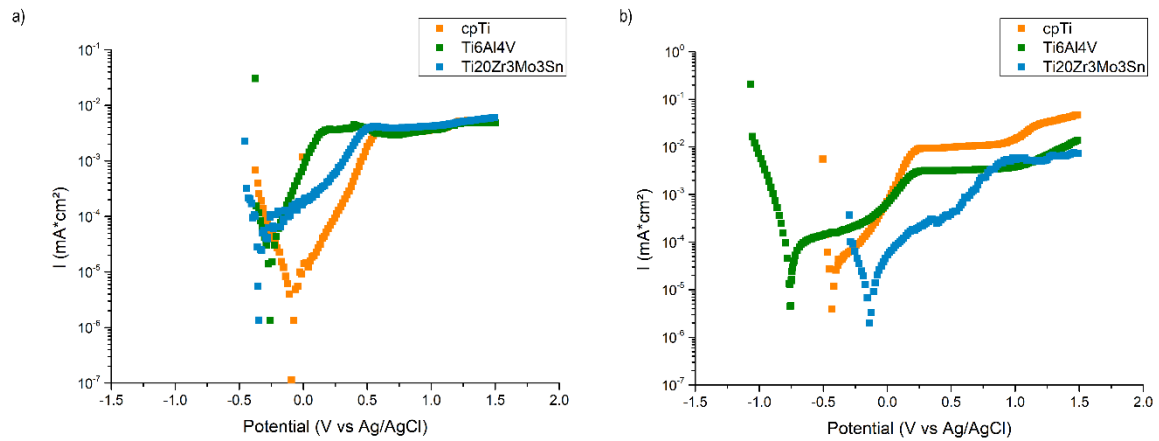
Electrolyte	PBS (V)	BSF (V)
cpTi	-0.108 ± 0.04	0.251 ± 0.05
Ti6Al4V	-0.101 ± 0.06	-0.340 ± 0.06
Ti20Zr3Mo3Sn	-0.111 ± 0.06	-0.191 ± 0.21

Source: Author

5.3 Potentiodynamic Polarization

Figure 19 displays the plotted graphs of the current density corrosion of the alloys tested in PBS and BSF after 24 hours. As can be seen all sampled materials present a typical passive behavior in both environments, it is observed that after the corrosion potential is reached there is a logarithmic increase in the current until reaching the passive potential where it stabilizes into the passive current density. The passive current densities at different voltages are shown in table 1, alloys tested in PBS presented similar values of passive current density as can be seen in table 1. In BSF it is observed that there is a more significant difference in the passive current density between alloys, Ti20Zr3Mo3Sn presented a comparable passive current density between the tested samples in PBS, while in BSF it presented the lowest passive current density.

Figure 19: Polarization curves for sampled alloys in (a) PBS and (b) BSF.



Source: Author

Table 6: Passive current density of sampled alloys in PBS and BSF along an increase of potential.

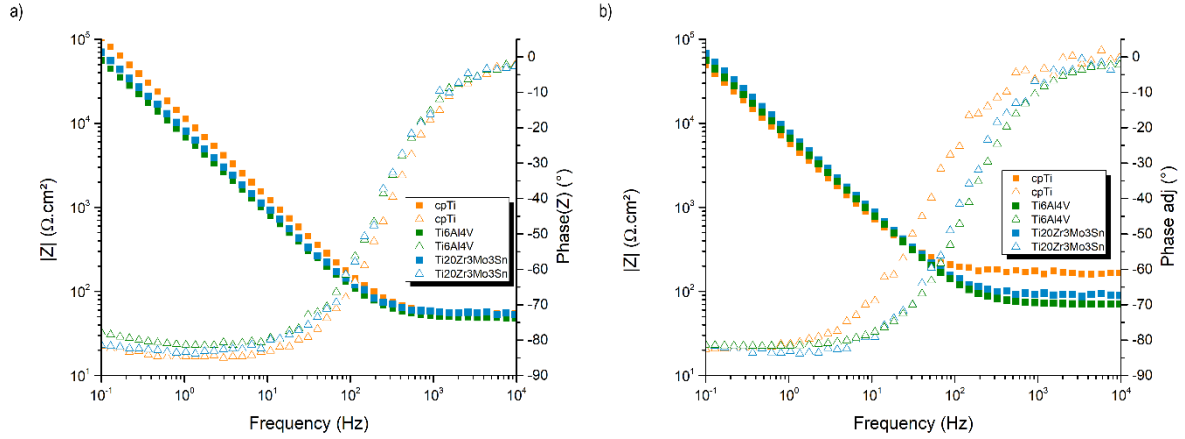
Electrolyte	PBS			BSF		
	Passive current density (mA/cm²) *10 ⁴			Passive current density (mA/cm²) *10 ⁴		
	0 V	0.5 V	1 V	0 V	0.5 V	1 V
cpTi	8.31 ± 8.19	17.1 ± 3.64	35.7 ± 0.711	-8.38 ± 3.34	87.9 ± 14	118.5 ± 17.3
Ti6Al4V	2.77 ± 2.60	29.3 ± 5.45	32.9 ± 2.25	7.82 ± 4.66	69.5 ± 2.47	84.6 ± 1.91
Ti20Zr3Mo3Sn	1.75 ± 1.08	39.6 ± 4.21	41.6 ± 3.63	1.42 ± 1.43	23.1 ± 12.9	43.7 ± 8,84

Source: Author

5.4 Electrochemical impedance spectroscopy

The results shows that the impedance values for the alloys in PBS were all similar with a low dispersion between each experiment, this can be seen in Figure 20 (a). For BSF the values were similar to each other but with a higher dispersion of results between each sample, the shape of its Bode representation and the values acquired as it can be overserved in Figure 20 (b).

Figure 20: Z bode and phase bode spectra for sampled alloys in (a) PBS at 38° C and (b) BSF at 38 °C.



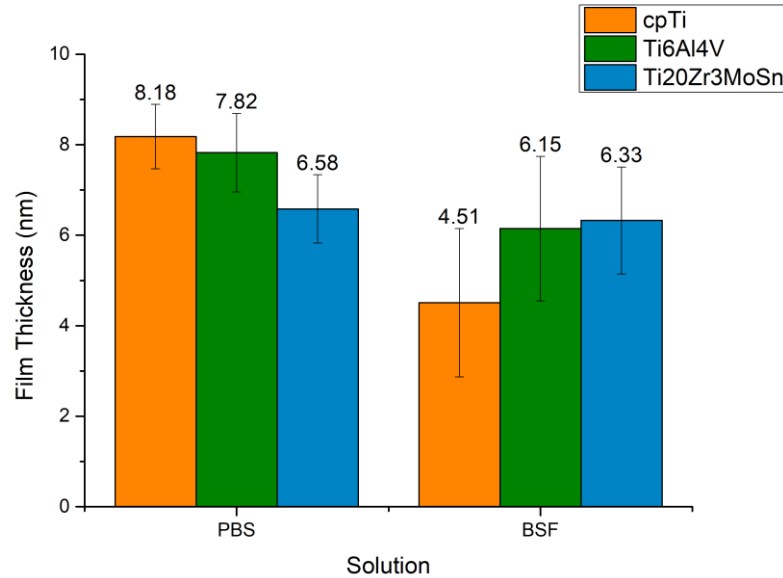
Source: Author

A pronounced level of noise was identified at higher frequencies making reliable analysis difficult, therefore for all following analysis the frequencies used were in the range of 10^{-1} to 10^4 Hz. For the EIS the principal property analyzed was the film thickness of the samples, which can be obtained using equation (6).

$$\delta = \frac{\varepsilon \varepsilon_0}{C_{\infty}} \quad (6)$$

Where ε is the dielectric constant of the material (89.9), ε_0 is the vacuum permittivity (8.8542×10^{-14} F cm⁻¹), C_{∞} is the limiting capacitance at high frequency and δ is the film thickness in cm which is then converted to nm for easier comprehension. The results can be seen in Figure 21.

Figure 21: Average film size of sampled alloys in PBS and BSF.

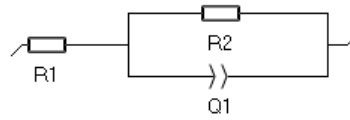


Source: Author

The results show a similar film size in all studied materials were similar between each other and between different bio-mimetic environments. The results show that under representative conditions Ti20Zr3Mo3Sn has a similar film thickness to commercial alloys.

The phase angle bode plot of the samples shown in Figures 20 (a) and (b) all sampled alloys presented a single peak. This indicates that a simple equivalent circuit can be used to model their behavior, the utilized equivalent circuit can be seen in Figure 22. The fitting parameters utilized were the resistance of the electrolyte solution (R1), the resistance of the passive film (R2), constant phase element of the passive film (Q1), alpha is the indicator to how close the film resembles a pure capacitor. All fitting parameters were similar between each alloy in PBS, while in BSF it was found a larger variance between each alloy. Because all sampled materials could be represented by a simple equivalent circuit in both electrolyte solutions, the results indicate that the effect of the lipids is not high enough to generate another film over the alloys impeding the passage of electric charges. The results of the fitting are seen in table 3 and 4.

Figure 22: Simple equivalent circuit.



Source: Author

Table 7: Fitted values for the parameters of sampled titanium alloys in PBS.

Parameters	Fitting with SIMAD			Fitting with measurement model			
	R1 ($\Omega \cdot \text{cm}^2$)	Q1 ($\text{F} \cdot \text{cm}^{-2} \cdot \text{sn}^{-1}$) $\cdot 10^{-5}$	Alpha	R2 ($\Omega \cdot \text{cm}^2$) $\cdot 10^5$	Rp ($\Omega \cdot \text{cm}^2$) $\cdot 10^{-5}$	C $_{\infty}$ ($\text{F} \cdot \text{cm}^{-2} \cdot \text{sn}^{-1}$) $\cdot 10^{-5}$	Film Thickness* (nm)
<i>cpTi</i>	55.98 ± 7.8	1.59 ± 0.2	0.94 ± 0.01	9.66 ± 4.3	9.92 ± 3.3	1.34 ± 0.1	8.17 ± 0.7
<i>Ti6Al4V</i>	56.15 ± 4.2	2.20 ± 0.2	0.92 ± 0.01	10.14 ± 5.2	5.78 ± 1.6	1.68 ± 0.1	7.82 ± 0.9
<i>Ti20Zr3Mo3Sn</i>	50.56 ± 2.4	2.29 ± 0.3	0.93 ± 0.02	8.65 ± 6.6	4.55 ± 3.8	1.89 ± 0.2	6.5 ± 0.1

Source: Author

* Calculated with equation (6)

Table 8: Fitted values for the parameters of sampled titanium alloys in BSF.

Parameters	Fitting with SIMAD			Fitting with measurement model			
	R1 ($\Omega \cdot \text{cm}^2$)	Q1 ($\text{F} \cdot \text{cm}^{-2} \cdot \text{sn}^{-1}$) $\cdot 10^{-5}$	Alpha	R2 ($\Omega \cdot \text{cm}^2$) $\cdot 10^5$	Rp ($\Omega \cdot \text{cm}^2$) $\cdot 10^{-5}$	C $_{\infty}$ ($\text{F} \cdot \text{cm}^{-2} \cdot \text{sn}^{-1}$) $\cdot 10^{-5}$	Film Thickness* (nm)
<i>cpTi</i>	100.97 ± 14.2	4.84 ± 2.9	0.92 ± 0.04	77.18 ± 22.2	6.73 ± 5.5	1.97 ± 0.76	4.51 ± 1.6
<i>Ti6Al4V</i>	69.95 ± 3.5	2.48 ± 0.3	0.92 ± 0.01	14.31 ± 2.9	5.14 ± 1.6	1.39 ± 0.47	6.15 ± 1.6
<i>Ti20Zr3Mo3Sn</i>	82.83 ± 2.2	2.84 ± 1.2	0.93 ± 0.002	46.03 ± 18.6	6.74 ± 1.9	1.30 ± 0.30	6.33 ± 1.2

Source: Author

* Calculated with equation (6)

5.5 Mott-Schotck analysis

Typical Mott-schotck plots are shown in Figure 23 demonstrate the behavior of the tested alloys in PBS. Through the graph, N-type semi-conductive behavior is seen as expected in all the alloys analyzed, it was also identified two distinct slopes in the depletion phase of the materials[75]. The presence of these slopes indicates two distinct charge carrier densities at different potential, in this manner we utilize the following equation (7) and (8)[76].

$$N'_d = \frac{2}{\varepsilon\varepsilon_0 e S1} - N_d \quad (7)$$

$$N_d = \frac{2}{\varepsilon\varepsilon_0 e S2} \quad (8)$$

Where N'_d is the charge carrier density of the first slope, N_d is the charge carrier density of the second slope, e is the electron charge (1.6×10^{-19} C) and $S1$ and $S2$ are the first and second slope respectively. The electrochemical properties of the three alloys can be seen in table 9.

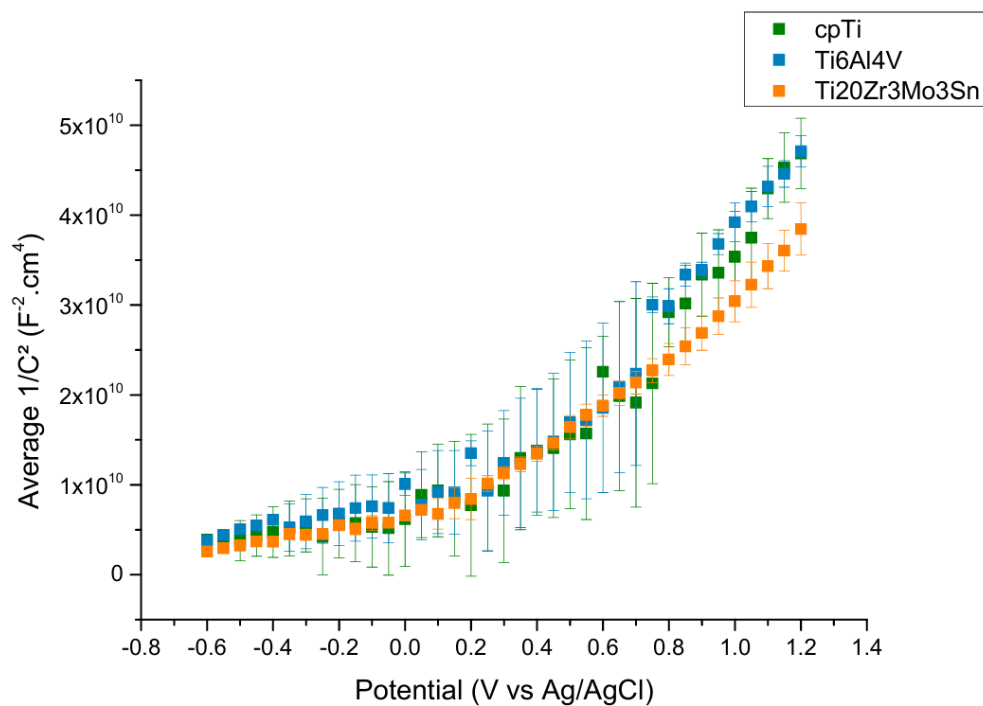
Table 9: Charge carrier density of sampled titanium alloys in PBS after 24 hours of immersion.

Sample \ Properties	$N'_d \text{ (cm}^{-3}) * 10^{17}$	$N_d \text{ (cm}^{-3}) * 10^{17}$
cpTi	1.96 ± 1.5	0.501 ± 0.063
Ti6Al4V	1.89 ± 0.9	0.482 ± 0.047
Ti20Zr3Mo3Sn	1.62 ± 0.37	0.552 ± 0.079

Source: Author

It is observed that all samples exhibit a difference of at least one order of magnitude between the initial and subsequent charge carrier densities. Additionally, there is no significant variation in charge carrier density among the different alloys.

Figure 23: Average Mott-Shottky plot of sampled alloys in PBS.

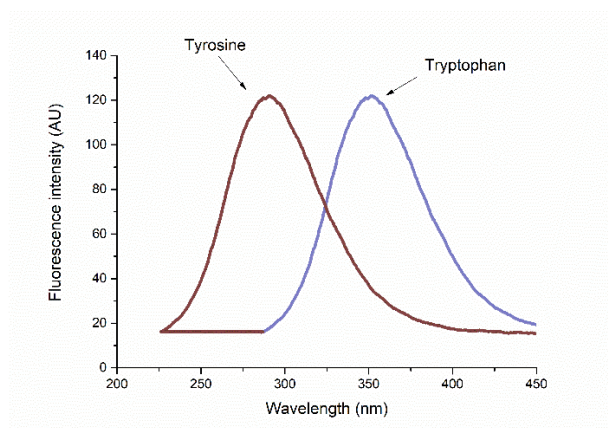


Source: Author

5.6 Fluorescence analysis

The presence of tyrosine and tryptophan peaks in BSF samples, both before and after corrosion experiments, confirmed the successful preparation of BSF. The peaks for tyrosine and tryptophan can be seen in Figure 24:

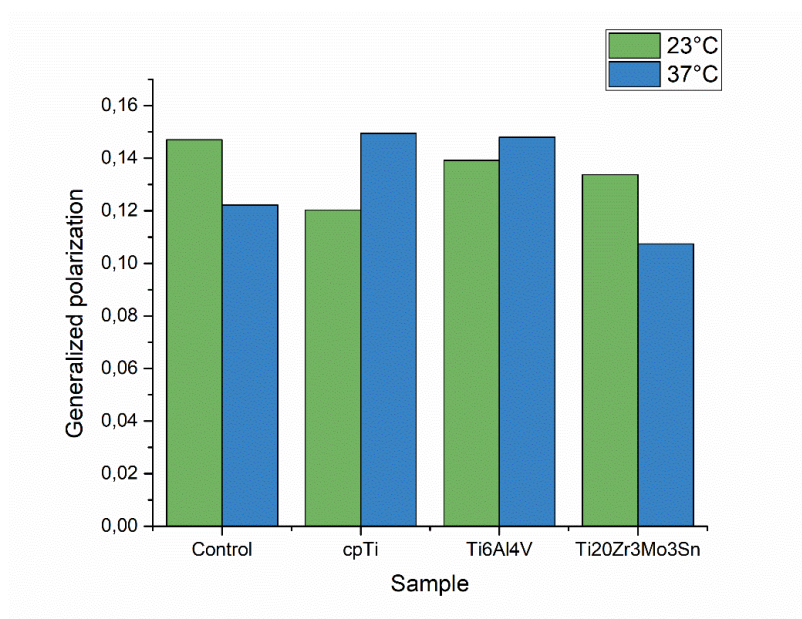
Figure 24: Example of tyrosine and tryptophan peaks in fluorescence analysis



Source: Author

Additionally, these results indicate lipid denaturation in the BSF used for the cpTi and Ti6Al4V corrosion tests. The Figure 25 presents the calculated generalized polarization values for the control sample (untreated BSF) alongside those subjected to corrosion testing.

Figure 25: Generalized polarization of sampled alloys in BSF.



Source: Author

In synovial fluid, the expected behavior of lipid vesicle membranes is fluidization upon temperature increase, as observed in the control sample. However, in the presence of cpTi and Ti6Al4V, the BSF underwent detrimental changes during

corrosion testing, manifesting as increased membrane rigidity—evidenced by a rise in Gp. In contrast, the BSF exposed to the novel alloy Ti₂₀Zr₃Mo₃Sn did not exhibit membrane stiffening. Instead, it retained the anticipated fluidization response, aligning with the behavior of healthy synovial fluid as demonstrated by the control group.

6 CONCLUSION

The results obtained from OCP, EIS and PP have shown similar electrochemical properties of Ti₂₀Zr₃Mo₃Sn when compared to the traditional alloys of cpTi and Ti6Al4V, indicating that the novel alloy could be used in place of the commercially used alloys with the advantage of the absence of cytotoxic alloying elements and more desirable mechanical properties. The fluorescence analysis has also shown that Ti₂₀Zr₃Mo₃Sn did not affect negatively lipid vesicles after the corrosion experiments, indicating favorable biocompatibility in contrast to traditional alloys.

During the analysis of the data some questions were raised, but due to time constraints during the internship it was not possible to delve further into the topics. Further X-ray photoelectron spectroscopy to analyze the surface is important to better understand how the oxide surface is interacting with both electrolyte solutions. Further biological analysis, such as osseointegration studies, to study the behavior of Ti₂₀Zr₃Mo₃Sn when in contact with live cells.

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