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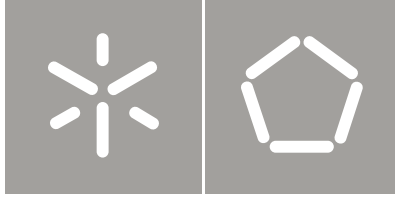
José Augusto Santos Sequeiros

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on the tribocorrosion of titanium

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UMinho | 2013

dezembro de 2013



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Tese de Mestrado
Ciclo de Estudos Integrados Conducentes ao
Grau de Mestre em Engenharia Biomédica
Ramo de Biomateriais, reabilitação e Biomecânica

Trabalho efetuado sob a orientação do
Professor Doutor Luís Rocha

e co-orientação do
Professor Jean-Pierre Celis

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Título da dissertação: "Influence of hydrogen peroxide on the tribocorrosion of titanium"

Ano de conclusão: 2013

Orientador: Professor Luís Rocha

Co-Orientador: Professor Jean-Pierre Celis

Designação do Mestrado: Biomateriais, reabilitação e Biomecânica

Ciclo de Estudos Integrados Conducentes ao Grau de Mestre em Engenharia Biomédica

Escola: Escola de Engenharia

Departamento: Departamento de Mecânica

É AUTORIZADA A REPRODUÇÃO INTEGRAL DESTA DISSERTAÇÃO APENAS PARA EFEITOS DE INVESTIGAÇÃO, MEDIANTE DECLARAÇÃO ESCRITA DO INTERESSADO, QUE A TAL SE COMPROMETE.

Guimarães, ___/___/_____

Assinatura: _____

Acknowledgements

First of all, I would like to acknowledge Professor Luís and Professor Celis, as my supervisors, for the possibility of working with them but also for all the advices, knowledge and trust on me.

My family for all the support, caring and patient during my five years of college, without them any of this was possible.

To all my friends, the ones that are part of my family now, the ones that had been there for me during all my years in college, on the bad times but mostly during the good ones.

Agradecimentos

Em primeiro lugar gostaria de agradecer ao Professor Luís e ao Professor Celis a oportunidade que me deram ao poder trabalhar com eles, por todo o seu apoio, conhecimento e confiança que depositaram em mim.

A toda a minha família, que esteve sempre presente e que sem ela, nada disto seria possível. Obrigado por todo o carinho e paciência ao longo destes anos.

À Judite que me ajudou e apoiou durante todos estes anos, e que esteve sempre presente, nos bons e nos maus momentos

A todos os meus amigos. Àqueles que a ida para a universidade forçou à distância e àqueles que criei com esta ida, agradeço estarem sempre presentes. Criei mais do que amigos, criei uma família. Espero poder contar com todos durante muitos e bons anos, já que sem vocês, a experiência académica não teria o mesmo impacto na minha vida.

A todos que me acompanharam na experiência de Erasmus, pelo apoio e conforto durante os seis meses em Leuven, pelo convívio diário e entreaajuda indispensável durante aquele tempo.

A toda a gente que conheci durante a minha permanência no laboratório, mas sobretudo à Alexandra e ao Fatih por todo o apoio e ajuda.

Resumo

O titânio é um material vastamente utilizado na medicina dentária graças à sua excepcional biocompatibilidade e óptima resistência à corrosão. Mesmo assim, alguns dos implantes são rejeitados. Embora resistente à corrosão, o titânio não é completamente inerte em condições *in vivo*, existindo a libertação de partículas de desgaste e iões resultantes da sua corrosão. A complexidade do ambiente da cavidade oral, quer pelas suas propriedades químicas, electroquímicas ou mecânicas, é um excelente campo de estudo, que necessita de um conhecimento mais aprofundado para evitar perdas médicas ou económicas.

O peróxido de hidrogénio é um composto químico comumente descrito como citotóxico para uma vasta gama de culturas animal, de plantas ou bacteriana. Este tem um papel preponderante na resposta imunitária dos seres vivos. Normalmente utilizado como agente de limpeza, em produtos de branqueamento de dentes ou para tratamento de feridas, o peróxido de hidrogénio está em constante contacto com tecidos, tornando-o um caso de estudo interessante na área biomédica.

O principal objectivo deste trabalho prende-se com o estudo, pela primeira vez, da influência do peróxido de hidrogénio na tribocorrosão do titânio. Alguns estudos foram conduzidos ao longo dos últimos anos relacionados com o efeito do H_2O_2 na corrosão do titânio, mas nenhum relacionado com tribocorrosão. Foram feitos ensaios de contacto recíproco em amostras imersas em saliva artificial, com diferentes concentrações de peróxido de hidrogénio, usando um contacto tribológico com a configuração de bola-em-plano, de modo a recriar o processo de mastigação num ambiente oral.

Foi observado que o peróxido de hidrogénio tem uma importante influência no comportamento corrosivo do titânio. Quão maior a concentração de H_2O_2 , menor a tendência para a corrosão deste, mas por outro lado apresenta uma velocidade de corrosão maior. Também a resistência à corrosão do sistema é fortemente afectada, diminuindo com o aumento da concentração de H_2O_2 . A maior conclusão do trabalho prende-se com o facto de a presença do peróxido de hidrogénio diminuiu o volume de desgaste e diminuiu o tempo de estabilização electroquímica do sistema quando em contacto recíproco.

Abstract

Titanium is widely used in dentistry due to its exceptional biocompatibility and high corrosion resistance. Even though, some dental implants are lost. Titanium is not completely inert when in vivo conditions, leading to the release of wear debris and corrosion ions which have a hostile effect on the surrounding tissues. The complexity of the oral cavity conditions, either by its chemical, electrochemical and even physical properties is an important subject to study and to try to understand, to avoid the medical and economical losses.

Hydrogen peroxide is a compound commonly described as cytotoxic to a wide range of animal, plant and bacterial culture. It is usually used as bleach, teeth whitening product or wound treatment. It is also the most important intermediate in an inflammatory response. The constant presence of hydrogen peroxide on the human body increases its scientific importance in a biomedical point of view.

The main objective of this work is to understand, for the very first time, the influence of hydrogen peroxide on the tribocorrosion of titanium. Several studies had been conducted over the last years regarding the influence of H_2O_2 on the corrosion of titanium, but its influence had never been associated with tribocorrosive mechanisms. Reciprocating sliding tests were performed on samples immersed on artificial saliva with different concentrations of hydrogen peroxide using a reciprocating ball-on-plane tribometer in order to mimic the mastication process in an oral environment.

As the main conclusions of this work, it was observed that the presence of hydrogen peroxide has an important influence on the corrosive behavior of CP-Ti. The higher the concentration of H_2O_2 , the lower tendency to corrosion on the samples, although they showed an higher corrosion rate. The corrosion resistance of the system is strongly affected by the presence of H_2O_2 , decreasing it as the higher the concentration. And the most important conclusion is that the presence of H_2O_2 influences how titanium it behaves when in reciprocating sliding contact. Its presence decreases the wear volume loss and decreases the needed time to achieve a stabilized state in a tribological contact.

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List of Abbreviations

| | |
|--------------------------------|--|
| AS | Artificial Saliva |
| Al | Aluminium |
| Al ₂ O ₃ | Alumina |
| C | Carbon |
| CP-Ti | Commercially Pure Titanium |
| C _p | Polarization Capacitance |
| COF | Coefficient of Friction |
| e ⁻ | Electron |
| EIS | Electrochemical Impedance Spectroscopy |
| F ⁻ | Fluoride |
| Fe | Iron |
| H | Hydrogen |
| H ₂ O | Water |
| H ₂ O ₂ | Hydrogen peroxide |
| Hf | Hafnium |
| HF | Hydrogen fluoride |
| HNO ₃ | Nitric acid |
| Mo | Molybdenum |
| N | Nitrogen |
| Nb | Niobium |

| | |
|------------------|------------------------------|
| O | Oxygen |
| O ₂ | Molecular Oxygen |
| OCP | Open circuit potential |
| OM | Optical Microscope |
| Pd | Palladium |
| Ra | Average Roughness |
| R _p | Polarization Resistance |
| R _e | Electrolyte Resistance |
| SEM | Scanning Electron Microscopy |
| SCE | Saturated Calomel Electrode |
| SiC | Silicon Carbide |
| Sn | Tin |
| Ta | Tantalum |
| TiO ₂ | Titanium Dioxide |
| UK | United Kingdom |
| UM | Universidade do Minho |
| USA | United States of America |
| V | Vanadium |
| Zr | Zirconium |

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Chapter 1

Introduction

1. Introduction

1.1. Motivation and Objectives

Dentistry is a medicine branch which main goal is to prevent or repair any related problem with oral cavity or stomatognathic system. The use of dental implants to restore a function is a common practice among dentists. These implants are normally made of biocompatible metals, placed in the jaw bone. Commercially-pure titanium is the most common metal used due to its outstanding corrosion resistance. Although some implants might be lost.

Some studies related to the corrosion mechanisms on titanium on the presence of hydrogen peroxide had already been carried out, although, the novelty of this work is to understand, for the first time, the role of hydrogen peroxide on the tribocorrosion mechanisms of CP-Titanium. The investigation of the corrosion mechanisms was carried out in order to supplement data for the interpretation of the tribocorrosion mechanisms. The chosen electrolyte to perform this study was Fusayama's artificial saliva, which mimics the oral environment electrochemical properties. Hydrogen peroxide was added to the artificial saliva mimicking the concentrations found in bleaching products. The main objectives for this work are:

- to evaluate the corrosive behavior under these conditions and compare them with previous works;

- to assess the tribocorrosive behavior of titanium samples immersed in artificial saliva, with and without hydrogen peroxide;

- to achieve an understanding on the effect of the hydrogen peroxide on the surfaces and how it influences its composition.

- evaluate how the concentration of H_2O_2 influences the wear volume loss when in a reciprocating contact.

1.2. Dissertation Organization

The dissertation is divided in six chapters. The first, “Chapter One - Introduction” has the objective to introduce the work and to define the its main objectivest. State of the Art chapter has the goal of give an overview of the field of the study, how it had been studied and what had been done during the years.

“Chapter 3 – Materials and Methods” explain how experimental work had been performed, which materials and equipment had been used and which techniques were chosen to achieve the objectives. The next chapters are related with the presentation and discussion of results, being divided in “Chapter 4 - Corrosion” and “Chapter 5 - Tribocorrosion”.

The conclusions and proposals for future work are in “Chapter 6 – Conclusions and Future Work”.

Chapter 2

State of the Art

2. State of the Art

2.1. Introduction

Dental implants are used in dentistry with high rate of success, although some of them might be lost [1]. Several reasons for these failures had been pointed out, including, for example, surgical trauma, bone weakness, condition of the patient, and inappropriate implantation of the implant or the wear of the prosthesis [2]–[4]. In dentistry, commercially pure titanium (CP-Ti) and titanium alloys are the first choice for oral prosthesis [5]. This fact is supported by, mainly, their biocompatibility and excellent corrosion resistance [6]. Nevertheless, as a metal, titanium follows the general patterns of degradation in environmental situations. Metals undergo electrochemical reactions with the environment, leading to the formation of chemical compounds, corrosion products [7].

2.2. Titanium

Commercially pure titanium (CP-Ti) and titanium alloys are the most used and attractive material for biomedical applications [6], [8], [9]. The characteristics that make titanium so well suited for this kind of application are the biocompatibility [10], excellent corrosion resistance [11] and mechanical properties closer to the ones present on bone than the rest of materials [12], [13]. CP-Ti has four different grades for biomedical applications, which are dependent of the quantities of Fe, C, O, N and H [3], [14]. On Table 1, the difference between the grades in terms of composition can be seen. In dental replacement, the CP-Ti grade 2 is the most used. The differences observed in oxygen concentration provide different mechanical properties for example ductility and strength while differences in hydrogen and nitrogen may cause an embrittlement effect on titanium [15].

Table 1 – Composition of Commercially pure Titanium, Grades 1, 2, 3 and 4 [15]

| Grade | Fe | O | C | N | H | Ti |
|-----------------------|------|------|-----|------|-------|-----------|
| CP – Titanium Grade 1 | 0.20 | 0.18 | 0.1 | 0.03 | 0.015 | Remaining |
| CP – Titanium Grade 2 | 0.30 | 0.25 | 0.1 | 0.03 | 0.015 | Remaining |
| CP – Titanium Grade 3 | 0.30 | 0.35 | 0.1 | 0.05 | 0.015 | Remaining |
| CP – Titanium Grade 4 | 0.50 | 0.40 | 0.1 | 0.05 | 0.015 | Remaining |

Different alloys are developed due to the necessity of getting properties well suited for the application in cause, even though these are used mainly for hard tissues replacement. One of the most important aspects of titanium is its biocompatibility. Even though, it can be improved by the use of non-toxic elements in the composition of its alloys [16]. It is important to notice that the changing of the chemical composition will also affect, as example, the corrosion resistance of the material. A large number of different titanium based alloys are used for biomedical applications. In Table 2, it is possible to see the wide range of titanium alloys.

Table 2 – Different Titanium alloys used on biomedical applications [17]

| | |
|---------------------------|-----------------------|
| CP-Ti Grade 1, 2, 3 and 4 | Ti-12Mo-6Zr-2Fe |
| Ti-6Al-4V | Ti-15Mo |
| Ti-6Al-7Nb | Ti-16Nb-10Hf |
| Ti-5Al-2.5Fe | Ti-15Mo-5Zr-3Al |
| Ti-5Al-3Mo-4Zr | Ti-15Mo-3Nb |
| Ti-15Sn-4Nb-2Ta-0.2Pd | Ti-35.3Nb-5.1Ta-7.1Zr |
| Ti-15Zr-4Nb-2Ta-0.2Pd | Ti-29Nb-13Ta-4.6Zr |
| Ti-13Nb-13Zr | |

These different alloys were designed for different applications, and its variation is in the mechanical properties, as tensile strength, fracture toughness or fatigue resistance [17].

2.3. Titanium characteristics

Titanium forms a stable, strongly adherent and protective film [18]. This film is spontaneously formed when the surface is exposed to a fluid. This very thin (2-6 nm) oxide film [19] is capable of an instant regeneration due to its high affinity to oxygen [20]. This layer offers an effective barrier against electron and ion transport [18]. In a comparative study of different metals and alloys, it was shown that titanium exhibited the lowest corrosion tendency in a representative environment of the human mouth [19]. The contact with several compounds that might be harmful for the implant is a constant in the oral environment. Some with external influence as the use of toothpastes, food, drinks, mouth rinses or whitening products [21]–[23] or even some others with biological influence as the presence of bacteria colonies or an inflammatory response [3], [4], [24]. Some bacteria strains and leukocytes are responsible for the production of lactic acid or hydrogen peroxide which attack Ti surfaces [19]. It had been studied the influence of bacterial colonies on the surface of titanium and how the surface characteristics, as roughness, influence the growth of these colonies [25]. The results show a positive feedback, if surface topography is rougher, it is more susceptible to colonies growth and when they are present the surface roughness tends to increase also [26], [27]. Some retrieved implants were found with a thicker oxide layer comparing to the ones tested in vitro. Despite the

excellent titanium corrosion resistance when tested in vitro, the in vivo ones display different results. Metal ions are sometimes found on the tissues surrounding implant [11], [25].

On Table 3, some mechanical properties as tensile and yield strength, roughness, young modulus and type of alloy are shown.

Table 3 – CP-Ti different grades and some mechanical properties comparing with bone [15], [17]

| Alloy | Tensile strength (MPa) | Yield strength (MPa) | Ra (%) | Young Modulus (GPa) | Type of alloy |
|---------------|------------------------|----------------------|--------|---------------------|------------------------|
| CP-Ti Grade 1 | 240 | 170 | 30 | 102.7 | α |
| CP-Ti Grade 2 | 345 | 275 | 30 | 102.7 | α |
| CP-Ti Grade 3 | 450 | 380 | 30 | 103.4 | α |
| CP-Ti Grade 4 | 550 | 485 | 25 | 104.1 | α |
| Bone | 90-140 | - | - | 10-40 | Viscoelastic composite |

Several studies reference the importance of these properties as a factor of extreme importance on the failure rate of the implant [28]–[31]. The osseointegration process can suffer different paths depending on the characteristics of the surrounding material. As example, *Bearing et al* [29] stated that the type of alloy of the material plays an important role in the solubility of hydrogen and oxygen. The solubility of oxygen plays an important role on the formation of the oxide film, which will act as an effective barrier to penetration of several compounds. The destruction of it, by some mechanism, will easily allow the diffusion of the compounds [32]. For instance, the diffusion of hydrogen on titanium affects its structure [29]. When the solubility limit of hydrogen in titanium is exceeded, the precipitation of hydrides begins. The absorption of hydrogen results in embrittlement and increases the possibility of cracking under stress conditions [33].

2.4. Dental Implants

The improvement of healthcare leads to a consequent longer life for humans. This aging process can explain the increasing use and importance of biomaterials [34], [35]. A general use of biomaterials can be pointed out, as a replacement implant, a knee joint implant or a dental implant, as also a localized drug delivery or a support for tissue regeneration [7].

The usage of a material as a replacement for a determined missing part of the human body is a practice used ever since. Different metallic, ceramic and polymeric materials are used for their compatibility with body tissues [36]. Metals are used due their high strength, durability and resistance to fracture while ceramics and polymers are used for their chemical resistance [28]. Titanium is widely used as the main choice for dental implants. Although, the use of titanium as a material for dental replacement is a “recent” common practice in dentistry, rising only on early 1970’s, twenty years after *Branemark* [2][12] began his research.

Dentistry plays an important role nowadays. Whether related to the oral cavity or digestive system track, it can restore normal function of the system or aesthetics [5], [21], [38]. Dentistry deals with diagnosis, prevention and treatment of diseases or injuries of the stomatognathic system [3][5]. With an estimated market of over 2 million implants placed per year[28], it is easy to say that is an increasing market with a lot of eyes on it. This way, the failure rates can play an important role. The implant survival rate of dental implants goes around 90% [1], [3], [39], depending on if it is a short or long term implant, the place of implantation (maxilla, mandibular bone or anterior mandibular bone) [1] and a specific condition of the patient, as example, age, smoking condition, hypertension, cardiac condition, pulmonary disease, diabetes, the use of steroids, chemotherapy or radiation therapy [1], [10], [28].

The most frequently used implants are the endosseous ones (between 300 and 400 thousand just in the USA) and it has an expected growth of 7% to 9% annually [3], [10], [26], [28], which are hold on the bone, and they will be the support for all the rest of the implant parts. Figure 1 shows a schematic representation of the dental system and how it will look as a replacement. Dental implants consist in a three part construction, fixed on the bone by a screw which will support the abutment and the crown. These parts are normally made of different materials, normally a metal-ceramic combination [40]. The use of zirconia as the crown is

common due its teeth appearance while the screws are made of metallic materials, namely titanium.

After the installation of endosseous implants, there are three possible responses that may occur in host tissues: acute or chronic inflammatory process, causing early implant failure; the formation of connective tissue surrounding implant, leading to osseointegration failure; and living and functional bone tissue formation around the implants, resulting in osseointegration [5], [41], [42]. Beyond the implant loss, early marginal bone loss around endosseous implants is also considered as a failure [39]. It can be said that all biomaterials induce infection [28], [42], since they are in contact with cells and fluids in body, acting as receptors to microbial attachment [43]. This process may lead to an inflammatory reaction [10] with consequent loss of bone in the place of the implant and rejection of it [2].

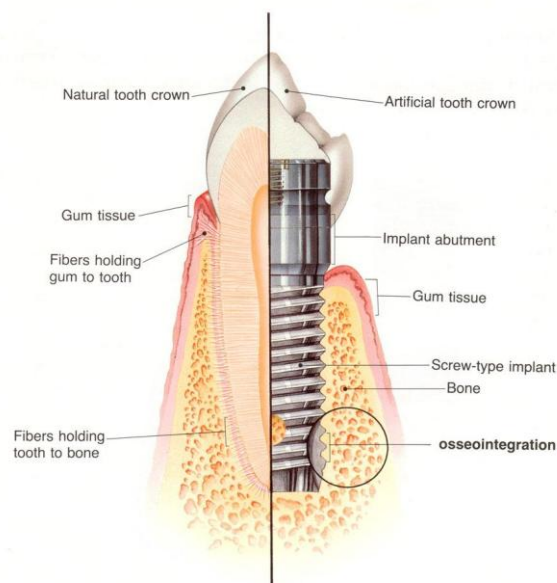


Figure 1 – Schematic illustration of a normal tooth and an endosseous implant, left and right respectively [3]

Another cause for dental implant failure is the stress applied in abutment. The act of chewing or mastication can cause an occlusal force which can lead to an overload on implant structure [40], [43], [44]. This condition can lead to a release of wear debris to the adjunct

tissue. The releasing of metal ions represents a health risk, existing the possibility of dissemination in all body [45].

The importance of surface properties in implant osseointegration as morphology, topography, roughness, chemical composition, surface energy, surface energy, surface composition, chemical potential, residual stress, the existence of impurities, thickness of titanium oxide film and the presence of metallic and nonmetallic compounds on the surface is described in several papers [5], [26], [29], [46], [47], reporting how these different properties interact and determine the activity of the attached cells that are close to the dental implant surface.

The oral cavity provides an ideal environment for the study of biological processes, a clear advantage over other areas of the body is the ease of accessibility. Furthermore, the materials within the mouth interact continually with physiological fluids, containing biologically important ionic species [41], [47], [48]. The mouth is also home to bacteria, single cell species whose adhesion and proliferation on surfaces is governed by processes that are similar to those of tissue cells, but whose spread and behavior might be harmful [43], [45].

2.5. Tribocorrosion

2.5.1. Definition

Tribocorrosion can be defined as a term that integrates two of the major areas in material studies, tribology and corrosion. In one hand, tribology is the science and technology of friction, lubrication and wear of two interacting surfaces in relative motion [49], [50]. This term was used for the first time in 1966, in a British Department of Education and Science report [49][51]. This field of science applies an operational analysis to problems of great economic significance such reliability, maintenance and wear of technical equipment [52]. Wear results in loss of material, being responsible for a decrease in mechanical performance [53]. On the other hand, corrosion is the reaction of a material with the surrounding environment. This reaction can result in a deterioration of the material properties [48]. With this, tribocorrosion can be defined as the study of the influence of environmental factors on the tribological behavior of surfaces [54]. It can be said that the mechanical process of degradation combined with a corrosive action of the

surrounding environment lead to the degradation of the material [3], [54], as can be seen in Figure 2.

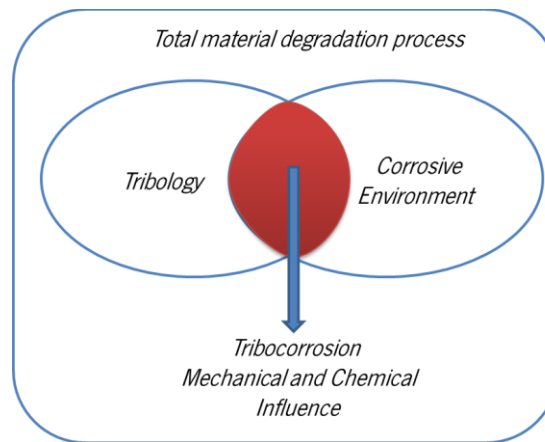


Figure 2 – Tribocorrosion basic concept (adapted from [54])

This research area has an important role in materials science, since tribocorrosion can be identified as a major cause of material wastage and mechanical performance decrease [55]. Several biomedical and industrial fields can be acknowledged when this term comes upon. Dental implants, contact lenses, stents, heart valves, any artificial replacement and its lubrication [51]. In industrial area some examples can be pointed out as marine and off-shore equipment, hot strip mills, cutting tools, chemical pumps, food processing and mining equipment [55]. With the medical and economic importance of this research area, the challenge consists on finding out all the characteristics of the process and how to decrease its influence in material wastage.

2.5.2. Tribology

As already said, tribology can be defined as the science of wear, friction and lubrication. The main focus of this chapter is going to be the wear. This term can define the progressive loss of substance resulting from mechanical interaction between two contacting surfaces [50]. The interaction of the surfaces can take different forms and characteristics, and different configurations can be used to study each interaction. The most common tribological contacts are sliding, rolling, fretting, impact and flow, Figure 3 gives an illustrative view of the phenomenon.

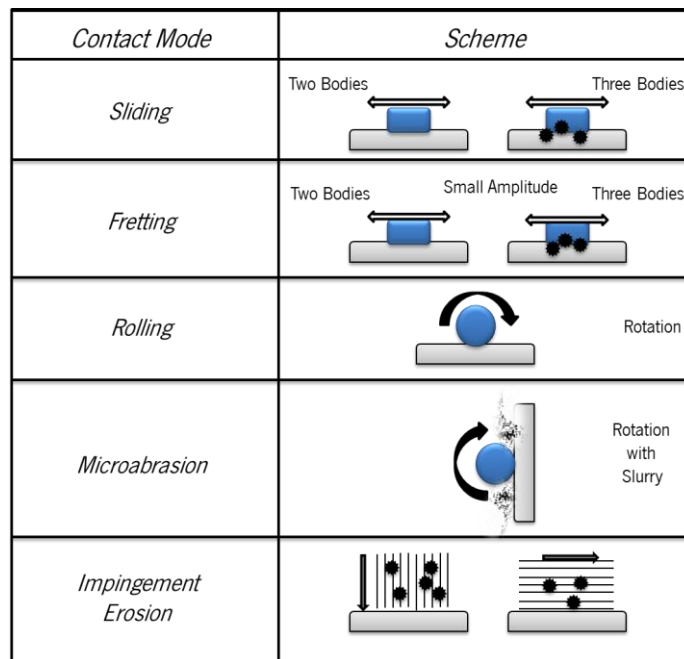


Figure 3 – Wear contact [54]

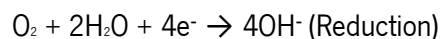
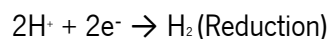
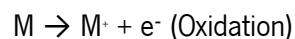
In the sliding contact mode, the relative motion between the surfaces can be unidirectional or reciprocating, being the amplitude of movement relatively large [54]. On the other hand, fretting involves a motion with the same relative contact, but the movement amplitude is not greater than 500 μm [56], [57]. Surface deterioration might release wear particles which can lead to the presence of a third body, which is considered to be abrasive wear [6], [58]. Abrasion is usually caused either by particles which are embedded or attached to some opposing surface, or by particles which are free to slide and roll between two surfaces and can be easily observed when the surface is placed in contact with another which hardness value is equal or greater. A material undergoes fatigue wear when a cyclic loading is applied in it, and this phenomenon can be observed in sliding, rolling, or impact [56]. The mechanisms that mainly affect dental implants are fatigue; abrasive and chemical wear [3], [6], [21]. Abrasion processes may be subdivided into two-body and three-body abrasion processes. Two-body abrasion involves damage caused by the particles and asperities that are attached to another surface. On the other hand, three-body abrasion wear process involves damage caused by hard particles that are not fixed on a surface but instead move between the two contact surfaces [49].

2.5.3. Corrosion

It is estimated that the annual cost of corrosion, only in the USA, range from 9 billion to 90 billion dollars[18]. Premature failure of structures or equipment can result in human injury or even life loss.

Most of metals commonly used are unstable in the atmosphere. They tend to return to their original state, the lowest thermodynamic state [59]. For most materials, this means the formation of oxides or sulfides from which they were initially extracted, being refined for engineering purposes [60]. The changes mentioned are electrochemical reactions that follow the laws of thermodynamics. The understanding of the interactions of materials with environment depends on the understanding of the chemistry and electrical changes between both.

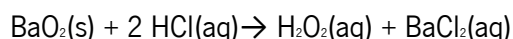
The oxidation of a pure metal when exposed to water is one of the basic corrosion reactions. The oxidation part of the reaction is normally called anodic reaction, while the reduction is called the cathodic part.



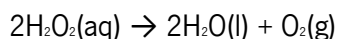
Anodic reactions in metallic reactions are simple to predict. In these, the metal is always oxidized to a higher valence state [18]. This higher valence state can be understood as the formation of metallic ions, sometimes with several valence states, showing several stages of the corrosion process [53]. An important aspect to be noticed is the importance of both anodic and cathodic part of reaction, since, the liberated electrons in the first process are consumed on the second, a corroding metal does not accumulate charge [18], [61]. This neutral charge is maintained with the same rate in both branches of the reaction. With this in mind, an important feature can be highlighted; the retarding or stopping of the reduction part will affect directly the corrosion rate. Although, not all this processes have a negative aspect. As already said before, titanium forms almost instantly an oxide layer on its surface. The formation of this oxide provides a protective film against further degradation.

2.6. Hydrogen Peroxide

Hydrogen peroxide was first produced by Louis Jaques Thenard in 1818. He acidified Barium Peroxide (BaO_2) with Nitric Acid (HNO_3). This pathway is replaced by a new one, which leaves a relatively pure aqueous solution of H_2O_2 .



The worldwide production of H_2O_2 was estimated to have reached more than 1.6 million metric tons. The major part of this production is intended to be used in bleaching processes [62]. Hydrogen peroxide is a reactive substance in the presence of other substances [63], elements [25], radiation [64], materials [65] or cells [66]. Both biotic and abiotic degradation processes are important routes in the removal of hydrogen peroxide in the environment. Biological degradation of hydrogen peroxide is an enzyme-mediated process [67]. Abiotic degradation of H_2O_2 is due to reaction with itself (disproportionation), reaction with transition metals, organic compounds capable to react with H_2O_2 , reaction with free radicals, heat or light. When exposed, H_2O_2 rapidly decomposes to oxygen gas, following equation:



The presence of a catalyst has to be faced as an important factor to be pointed out. Most transition metals, especially Fe, Mn and Cu may have significant influence on degradation rates of hydrogen peroxide in aqueous solutions [68]. Regarding the photodecomposition of it, radiation over a wide continuous spectrum 280-380 nm is absorbed (visible and infrared) but is not decomposed by exposure to light of wave length greater than about 380 nm [64].

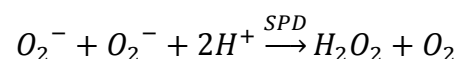
Solutions used for bleaching and wound treatment varies from 3-30% in volume [62], [69]. Higher concentrations (70-98%) are used as monopropellant in rocket engines. Its decomposition, a highly exothermic reaction (-98.30 kJ/mol), is followed by enough heat to convert water in steam [63].

Even though H_2O_2 is usually a short live substance, when degradation processes are inactive it can persist in the environment [68].

2.6.1. Hydrogen peroxide in the human body

Hydrogen peroxide is commonly described as a cytotoxic to a wide range of animal, plant and bacterial culture [67]. It is dangerous to mucosal cells, easily penetrating through membranes and causing, depending on their concentration, their apoptosis and necrosis [24]. The LD50 (lethal dose of a compound that is needed to kill half of the population) value depends on the cell type, physiological state, length of exposure and concentration [70]. Even though, it is a normal metabolite aerobic cells. Hence, the elimination must be a quick process, engaging enzymes as catalases or peroxidases [42], [66].

The reason for this harmful behavior leads to the production of superoxide anion radical (O_2^-) as an intermediate compound in hydrogen peroxide production [29], [66], [71], [72]. Indeed, the presence of hydrogen peroxide is due to superoxide dismutase (SPD), produced during inflammatory response, which catalyze O_2^- by the following chemical reaction.



Some tissues are more often in contact with H_2O_2 . Its presence, besides the inflammatory process mentioned before, can be detected in freshly voided human urine and in exhaled air [67]. The continuous production of hydrogen peroxide after the end of the inflammatory response, might lead to DNA damage, additional inflammation and changes cellular metabolism [71].

Hydrogen peroxide can also be present in some beverages, as instant coffee or green tea [67], [73], in mouthwashes and tooth whitening products [70], [74].

2.6.2. Hydrogen Peroxide in dentistry

As already said before, dentistry plays an important role in aesthetics of oral cavity. The appearance of teeth depends on the combined intrinsic and extrinsic characteristics. Color appears as one of the most important concern on this matter. This characteristic can be influenced by both intrinsic and extrinsic color. Intrinsic one is the result of the color of enamel and underlying dentine [75]. On the other side, extrinsic comes from staining on the tooth

surface and on the salivary pellicle [74]. Discolorations can appear related to a number of reasons, as injury, antibiotic use, fluorosis, aging (in intrinsic color) and ingestion of tea, coffee, red wine, smoking, metal salts or a bad oral hygiene in general (for extrinsic color) [22], [71], [76], [77]. The extrinsic factors can be contained in part by the use of toothpaste abrasives. Some chemical agents as peroxides have been used to improve intrinsic tooth color. These kinds of treatments can be performed professionally or homely, with a wide range of peroxide based products available [74].

In 2003, The Scientific Committee on Cosmetics and Non Food Products intended for Consumers (SCCNFP) had stated that: “It is known that the use of tobacco, and alcohol abuse, cause an increased risk of oral cancer. Hydrogen peroxide may enhance this risk. This effect cannot be quantified. It is not anticipated that the tooth whitening products will represent a risk of oral cancer in people neither using tobacco nor abusing alcohol. Tooth whitening products should only be used under the surveillance of a dentist. These teeth whitening product should not be freely available to consumers” [70] Although, three years later, in 2006, the same commission stated that : “The proper use of tooth whitening products containing > 0.1 to 6.0 % hydrogen peroxide (or equivalent for hydrogen peroxide releasing substances) is considered safe after consultation with and approval of the consumer's dentist. Particular care should be taken in using tooth whitening products by persons with gingivitis and other periodontal diseases or defective restorations. Conditions such as preexisting oral tissue injury or concurrent use of tobacco and/or alcohol may exacerbate the toxic effects of hydrogen peroxide”. The same commission had also referenced some counter indications on the use of hydrogen peroxide based products, as tooth sensitivity, irritation, pathological effects on oral tissues, changes in amalgam surfaces, although any of these was related to titanium dental implants [78]. The lack of study related to this matter is a fact and the importance of this study is emphasized at this point.

Chapter 3

Materials and Methods

3. Materials and Methods

3.1. Materials and Solution

3.1.1 Samples

CP-Titanium Grade 2 (Goodfellow Cambridge Limited, UK) squared samples (20mm x 20mm x 1mm) were used to perform the tests. The samples were acid-etched (H₂O: HF: HNO₃ (1:1:1)). After the attack the samples were ultrasonic cleaned for 10 min in propanol followed by 10 min in distilled water. The samples were ground down to 1200 mesh size SiC paper. After grinding, the samples were ultrasonic cleaned in the same conditions as before. The samples were kept in desiccator for 24 h before starting the tests in order to obtain similar surface conditions.

3.1.2. Artificial Saliva

The chosen electrolyte was Fusayama's artificial saliva. It was chosen due to the previous reported works [3], [4], and also by the electrochemical similarity with the oral environment [11], [79]. On Table 4 is given the chemical composition of the solution.

Table 4 – Fusayama's artificial saliva composition [3], [4], [11], [79]

| Compounds | Artificial Saliva (g/L) |
|---|----------------------------|
| NaCl | 0,4 |
| KCl | 0,4 |
| CaCl ₂ .2H ₂ O | 0,795 |
| Na ₂ S.9H ₂ O | 0,005 |
| NaH ₂ PO ₄ .2H ₂ O | 0,69 |
| Urea | 1 |

3.1.3. Hydrogen peroxide

Two different amounts of hydrogen peroxide were used to understand the corrosive and tribocorrosive behavior of CP-Ti. Concentrations of 0,1% and 6% (%vol.) of hydrogen peroxide were added to the artificial saliva in order to mimic the two boundaries that are mentioned in a directive of European Commission, in a plenary meeting on 28th of March, 2006 [78]. This guidance states that the use of tooth whitening products up to 0,1% hydrogen peroxide are safe and that an amount of 6% is also considered safe but it should only be used with an approval of a dentist.

All solutions were kept agitated using a magnetic stirrer up to the moment of the beginning of the test.

After this point the solutions will be called as the Table 5 suggests.

Table 5 – Abbreviations of solutions' denomination

| Solution | Denomination |
|---|--------------|
| Artificial Saliva | AS |
| Artificial Saliva + 0,1% of H ₂ O ₂ | AS-0.1 |
| Artificial Saliva + 6% of H ₂ O ₂ | AS-6 |

3.2. Methods

3.2.1. Tribocorrosion Measurements

The tribocorrosion measurements were conducted on polished CP-Ti samples immersed in AS, AS + 0,1% and AS + 6% hydrogen peroxide. These solutions were prepared recurring to Fusayama's Artificial Saliva recipe. It was prepared and maintained in rotation to avoid deposition. The addition of the hydrogen peroxide was done right before the beginning of the tests. The used electrochemical cell was designed for this purpose. The exposed area in this case is 4,52 cm² and the cell can hold a solution volume of approximately 40 mL. The tests were performed at body temperature of (37^o±1^o C).

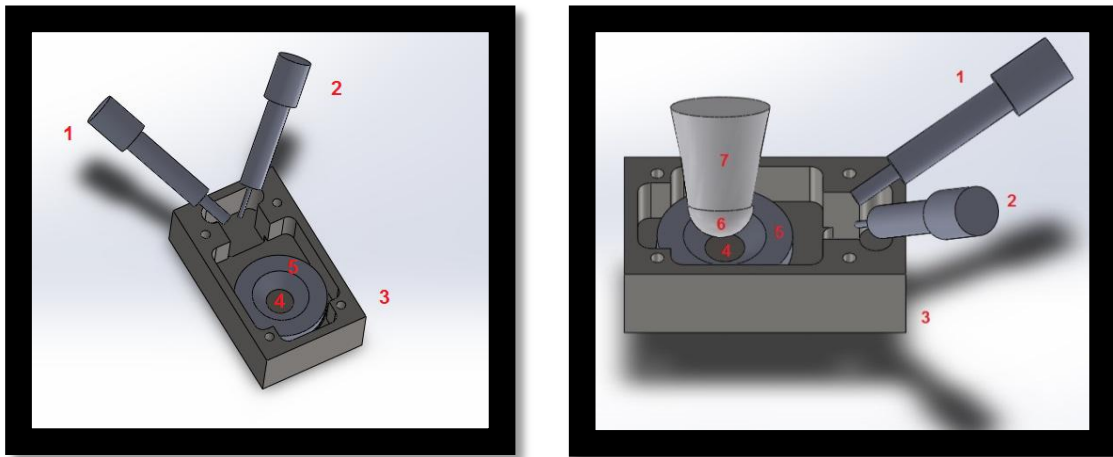


Figure 4 – Schematic representation of the test apparatus

Legend:

- | | |
|--------------------------------------|--------------------------|
| 1- Saturated Calomel Electrode (SCE) | 5- Acrylic Sample Holder |
| 2- Platinum (Pt) Electrode | 6- Alumina ball |
| 3- Acrylic Cell | 7- Alumina ball support |
| 4- CP-Ti Sample / Working Electrode | |

A CETR tribometer (UMT-2, Campbell, USA) was used in ball-on-plane configuration (Figure 4) and for the reciprocating sliding parameters were:

- 1000 cycles;
- 1 mm of stroke length;
- 1,5 N of normal load;
- 1 Hz of frequency

The sliding tests were performed against an alumina ball (Al_2O_3) (Ceratec Technical Ceramics BV) with a diameter of 10 mm. A fresh part of the alumina ball was used for each trial to avoid contamination by transfer of wear debris from one test to another. The applied load, tangential force and COF were recorded and analyzed by the UMT-2 software (Campbell, USA). The initial Hertzian contact pressure was calculated based on the materials properties and dimensions. The initial value for the contact pressure was 0.47 GPa.

Electrochemical tests were performed recurring to a Gamry Potentiostat/Galvanostat (Model Reference 600).

A conventional three electrode set up was mounted to measure all the electrochemical aspects on the trials, although, two different configurations were used. A saturated calomel electrode (SCE) was used as reference electrode, a platinum (Pt) electrode was used as a counter electrode and the CP-Ti sample was placed as working electrode. The sample was connected to the potentiostat through an electrical copper connection placed under it.

The Open Circuit Potential (OCP) was measured right after the temperature of 37° C was reached. As soon as a stable potential plateau was reached on the OCP, the value is used as a corrosion potential in the Electrochemical Impedance Spectroscopy (EIS), over a frequency range from 63 kHz to 10 mHz, with 10 points per decade, and a sinusoidal wave of 10 mV of amplitude. OCP was measured before, during the reciprocating sliding contact and after it. At the end, another EIS was measured to understand the differences between the pre-sliding electrochemical characteristics of the system and its differences after of it. At least three samples were tested per condition in order to guarantee the reproducibility of the results.

After tests, a wear track analysis was performed using Leica DM2500 optical microscope.

3.2.2. Potentiodynamic Measurements

A standard three electrode electrochemical cell (adapted from ASTM: G3-89) with an electrolyte volume of 200 mL.

The solutions used were the same mentioned before, AS, AS + 0,1% H₂O₂ and AS + 6% H₂O₂. To avoid any kind of decomposition of hydrogen peroxide, the addition of H₂O₂ happened in the moment right before the electrochemical test.

First, the immersion of the electrochemical cell in a bath, in order to achieve the desired temperature, 37° C. as soon as reached, an OCP was performed for an hour (3600 s) in order to get a stabilized state of the system's potential. The stabilized potential is observed and a potentiodynamic test is set up. With the value of stabilized potential, it starts at 0,5 V below E_{ocp} and moving into anodic direction up to 1 V. The potential scan rate used for these tests was 1 mV/s.

At least three samples were tested under each condition. The surface exposed to the solution was 0,64 cm².

Chapter 4

Corrosion

4. Corrosion

The study of corrosion behavior of the electrochemical system has an enormous importance, not only in dentistry but also in industrial field. In this chapter, results obtained from potentiodynamic curves are going to be showed. Some curves as OCP and EIS, are going to be presented only on Chapter 5 due to its relation with the tribocorrosion tests. Potentiodynamic curves were measured to obtain information related to the corrosion rate and passivity of the electrochemical system.

4.1. Potentiodynamic Polarization

Potentiodynamic measurements are a very important tool to understand how both cathodic and anodic reactions influence the active/passive behavior of the material [80], [81]. Figure 5 shows the potentiodynamic curves of the three CP-Ti samples in artificial saliva containing H_2O_2 or not.

These curves were obtained by increasing the potential, dV/dt while the current was recorded. The magnitude of the measured current is related to the driving force of the reactions taking place on the working electrode. It shows which electrochemical processes take place at the anode and cathode, as well as their rate.

The curves show a similar behavior, typical of passive materials. All samples present a large passivation region which goes in concordance with the fact that titanium can get protected by a protective oxide film [82], [83], Corrosion parameters obtained from potentiodynamic polarization scan can be found in Table 6.

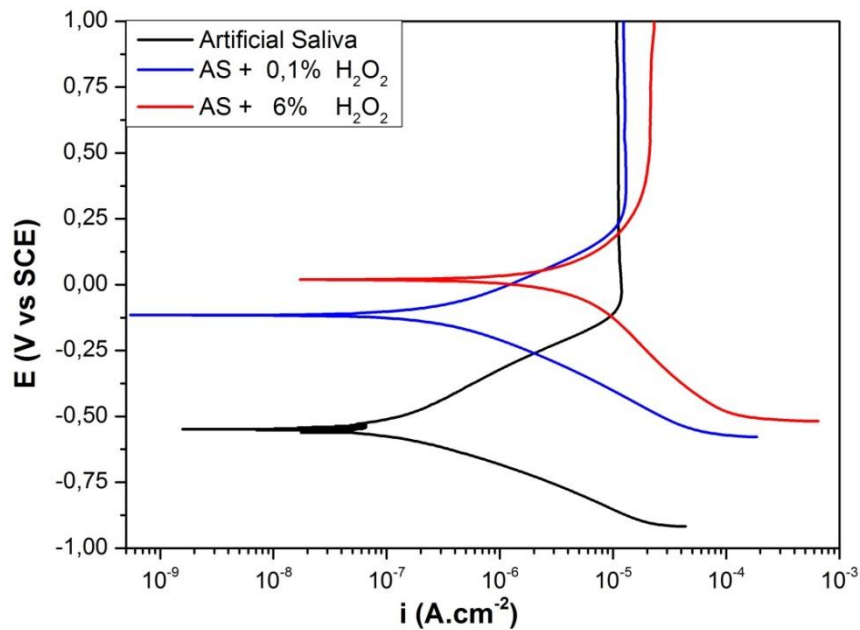


Figure 5 – Potentiodynamic polarization curve on CP-Ti immersed in AS with different amounts of H_2O_2 . Surface area: $0,38 \text{ cm}^2$, potential scan rate: 1 mV/s , potential scan rate from OCP – $0,5 \text{ V}$ to 1 V vs SCE

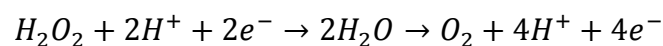
Table 6 – Corrosion potential and passive current density for potentiodynamic measurements on CP-Ti immersed on different AS solutions

| Electrolyte | Corrosion potential (E_{corr} vs SCE) | Passive current density $i_{\text{pass}} (\mu\text{A}/\text{cm}^2)$ |
|-------------|--|--|
| AS | $-0,48 \pm 0,05$ | $8,67 \pm 2,44$ |
| AS-0,1 | $-0,03 \pm 0,07$ | $8,34 \pm 4,22$ |
| AS-6% | $0,05 \pm 0,03$ | $14,2 \pm 7,44$ |

The tests started in the cathodic part of the curve (range differ for each condition, potentials below E_{corr}). Under these conditions of potential, the reduction of the oxide film of the

surface takes place [83]; the reduction of oxygen takes place [20]. When the potential reaches E_{corr} , the current density that is measured has a value near 0. Under these conditions a steady state is achieved where the cathodic and anodic reactions happen at same but opposite rate [59]. Regarding the corrosion potential for all the samples, an increase of this value with the addition of H_2O_2 , takes place leading to a nobler titanium surface potential. The potential shift in the positive direction is attributed to an enhanced oxide film growth rate according to the high-field theory which relates the oxide thickness to the potential difference across the film [65], [76]. On the contrary, the samples immersed only in AS showed a negative corrosion potential, near -0,5 V vs SCE, the ones in contact with H_2O_2 suffered an increase of about 0,5 V, getting a corrosion potential near 0 V vs SCE. This increase gives information related to the corrosion tendency, although, it doesn't contribute with any information related to the reaction rate. This kind of information can be obtained by the analysis of passive current density values.

The anodic part of the curve, unrolls from E_{corr} until the passivation *plateau* is achieved (this concept applies only if an oxide layer is formed on the surface). In Figure 5, it is possible to observe that the different curves don't correspond it. The increase of the H_2O_2 concentration leads to a quicker oxidation of the surface. It is also possible to observe that the passivation *plateau* had moved to the right, to higher current densities. It can be said that the presence of hydrogen peroxide increases the corrosion rate of titanium. Comparing the values of E_{corr} and I_{pass} , they seem to point out in different directions. On one hand the tendency to corrosion seems to decrease but on the other hand the corrosion rate increases. This can be explained by a non-stabilized element on the surface. This result suggests that the film growing on is not TiO_2 but a hydroxy-titanium- and titanium-peroxy rich layer that is porous [29]. This aspect can be due to the variation on electrical properties, which suggests the presence of residual currents, created by the reduction followed by oxidation of H_2O_2 [29], as suggested on the next equation.



Tengvall proposed in 1989 a model to explain the interaction between titanium and hydrogen peroxide. When in contact, a different chemical state is achieved; the oxidized titanium surface is covered with a hydrated $TiOOH$ matrix.

As a conclusion, regarding only potentiodynamic polarization results so far, it can be said that, the immersion of titanium in hydrogen peroxide decreases the tendency to corrosion of

the material but on the other hand, it increases the reaction rate. It is also important to keep in mind that the outer porous layer that is formed might not be completely composed by TiO_2 .

Chapter 5

Tribocorrosion

5. Tribocorrosion

The understanding of tribological and corrosive mechanisms on dental implants has a huge importance. Since the interactions between mechanical, chemical and electrochemical phenomena are not well known, a full understanding is needed to avoid implant failure. The extension of the study of these systems includes tribocorrosive and corrosive behavior in several physiological fluids, although, the influence of hydrogen peroxide as an agent in tribocorrosion of titanium implants had never been studied.

In Chapter 4, the influence of the concentration of H_2O_2 was studied based on potentiodynamic curves. The results showed that the presence of the H_2O_2 decreases the tendency to corrosion of CP-Ti but it increases its susceptibility. In this chapter, the influence of a reciprocating sliding applied on the sample surfaces is studied based on the analysis of the coefficient of friction, the wear volume loss, as well as OCP and EIS measurements.

5.1. Reciprocating Sliding Contact

Figure 6 shows the recorded OCP values before, during and after reciprocating sliding on polished CP-Ti samples immersed in artificial saliva containing different amounts of hydrogen peroxide.

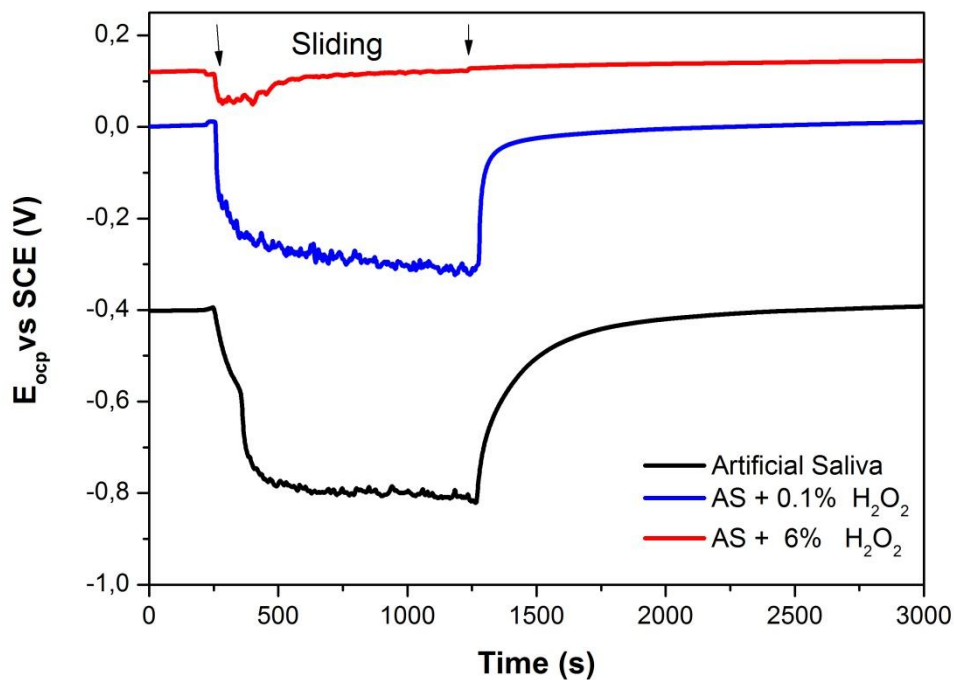


Figure 6 – OCP evolution of CP-Ti polished samples immersed in AS with different amounts of H_2O_2 (Reciprocating sliding at a frequency of 1 Hz, applied normal load of 1,5 N, amplitude of displacement – 1 mm, 1000 cycles)

The open circuit potential of the samples stabilized at different values. Samples immersed in AS had the lowest electrochemical potential (stabilized $\approx -0,4$ V vs SCE), followed by AS-0,1(≈ 0 V vs SCE) and, the highest electrochemical potential is recorded on the samples immersed in AS-6. The presence of H_2O_2 shifts gradually the potential value to a nobler one. The stabilization time involves the transformation of the naturally formed passive film in a solution formed one [4], [53].

At the beginning of the contact it is possible to observe a decrease of potential in all the curves. This behavior can be explained by the contact pressure of the alumina ball on the sample' surface, which is smaller than the yield strength of titanium causing the destruction of the outer layer, but smaller enough to avoid plastic deformation [6], [84]. The process of destruction and removal of the oxide layer on the surface is known as depassivation [84], allowing the exposition of an active titanium surface part, increasing the tendency to corrosion of the sample. Regarding the decreasing of the electrochemical potential, this phenomenon didn't occur with the same impact in all the samples. The one immersed in AS suffered a potential decrease of almost 0,4 V, in contrast with the 0,3 V and 0,1 V of the ones immersed in AS-0,1 and AS-6, respectively. Actually, the fact that neither of the samples in contact with H_2O_2 ever reaches the potential displayed in AS, indicates that the passive layer hasn't been completely removed. The oscillations in this part of the plot can be explained by the constant depassivation and repassivation of the outer layer.

At the end of the sliding tests, when the counter body is lifted away from the surfaces, the increase of the potential happens, recovering the stabilized electrochemical values observed at the beginning of contact, although, this happens at different rates. The sample immersed in AS took approximately 1000 s to reach the same potential while the one in AS-0.1 took half of that time, namely 500 s. The sample in contact with the higher concentration of hydrogen peroxide, AS-6, had a different behavior, reaching the initial potential even before the sliding test ended. Two explanations can be introduced in here. First it can be said that the repassivation rate is higher than the depassivation one [85]–[87]. The observation of the detachment of some wear debris can be pointed out, which might expose some fresh titanium area, accelerating the decomposition of H_2O_2 . The presence of bubbles on the surface of the samples shows the model explained on Chapter 4, regarding the reduction and oxidation of hydrogen peroxide leading to the release of molecular oxygen.

An interpretation of OCP values should not be enough to fully characterize an electrochemical system. Since the OCP is a mean value determined by the ratio between active to passive, material in the wear track depending on, repassivation rate, contact frequency and normal load [81], some more detailed information regarding the kinetics of reactions should be taken into account. EIS measurements are such a good complement to OCP.

5.2. COF

Concerning the COF evolution, Figure 7, no significant differences were found between the samples immersed in AS and in contact with 0,1 % of H_2O_2 . The mean values under these conditions were 0,46 ($\pm 0,02$) and 0,50 ($\pm 0,02$) respectively. On the other hand, the curve related to AS-6 has a different shape, acquiring a mean COF of 0,57 ($\pm 0,06$).

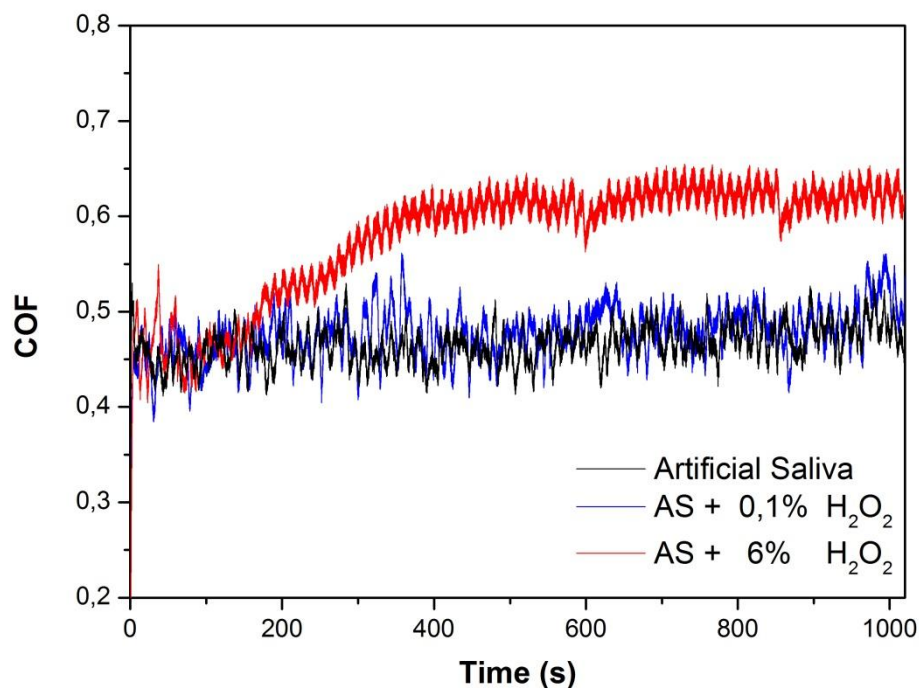


Figure 7 – Evolution of COF of CP-Ti polished samples immersed in AS containing different amounts of H_2O_2 (Reciprocating sliding at a frequency of 1 HZ, applied normal load of 1,5 N, amplitude of displacement – 1 mm, 1000 cycles)

If the COF curves are compared to the OCP curves, some interesting fact points out. Both curves follow the part, these means that AS and AS-0,1 remain constant during the contact, tough, the AS-6 samples' COF and OCP increase. In Figures 8, 9 and 10 show the curves and their evolution for each condition. The oscillations observed in all the curves might be explained by fluctuations in the normal force and/or the reciprocating movement [3]

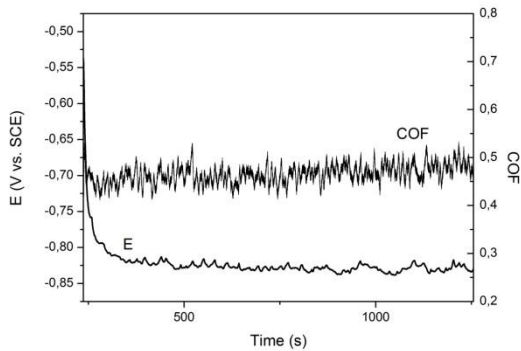


Figure 8 - Evolution of OCP and COF over time during contact sliding, for samples immersed in AS

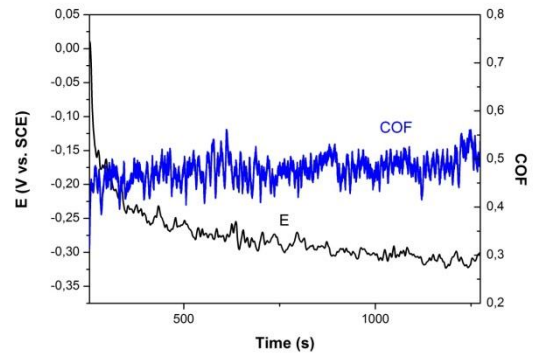


Figure 9 - Evolution of OCP and COF over time during contact sliding, for samples immersed in AS-0.1

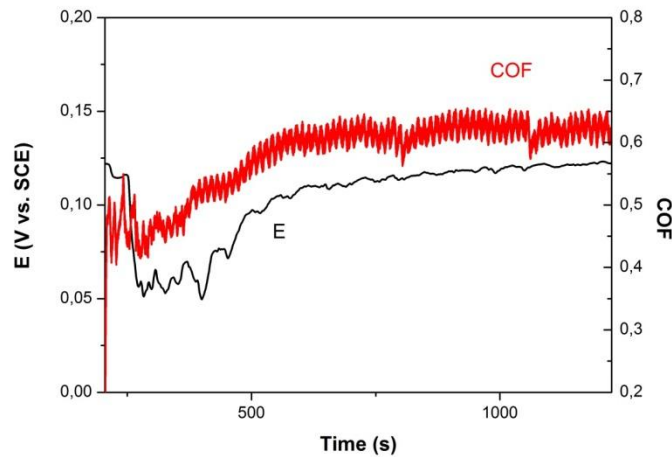


Figure 10 - Evolution of OCP and COF over time during contact sliding, for samples immersed in AS-6

The phenomena observed for each condition can be explained by the nature of the passive film and the chemical state of the surface. The adhesion of the passive film to the substrate and the resistance to delamination is shown by a stable COF which do not change considerably with potential [6]. Samples immersed in AS and AS-0.1 show a decrease on the measured potential, probably, bulk titanium was exposed. The fact that an active bulk titanium is in contact with the electrolyte lead to a synergism on the mechanism, the presence of a corrosive and mechanical part on the wear of the sample. On AS-6 samples, the potential never suffers such a drastic decreasing, which can indicate that the oxide film was never completely removed. The OCP and COF increase in AS-6 immersed samples can be explained by the reactions that took place on the surface. Several studies showed that the presence of H_2O_2 leads to the

formation of a porous surface [29], [76], [86], [88], [89]. As already said on *Chapter 4*, the possibility of a TiOOH formed layer can lead to different electrochemical and mechanical properties [90]–[92]. With the data showed in Figure 6 and 7, it is possible to admit that the newly formed layer has different properties than the oxide layer previously formed. Although, further tests are still needed to fully understand the differences between them.

5.3. Wear Track Analysis

In Figure 11, 12 and 13 it is possible to observe the wear track, observed in Optical Microscope (OM), of CP-Ti immersed on different solutions.

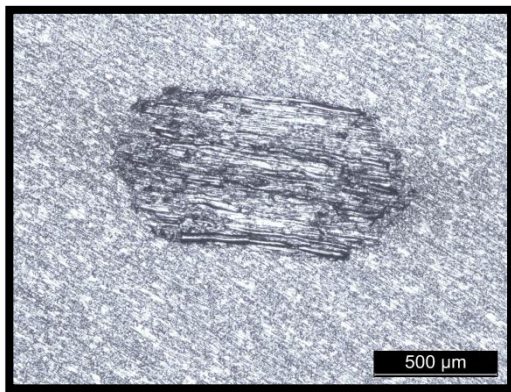


Figure 11 - OM image of CP-Ti wear tack immersed in AS

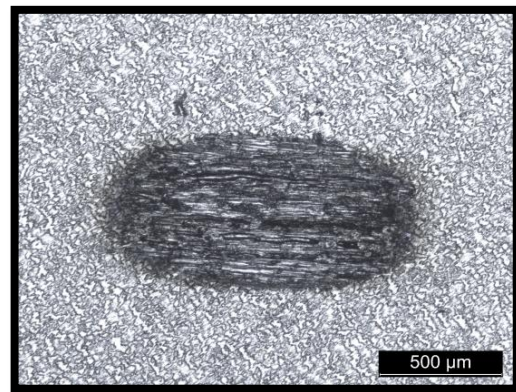


Figure 12 - OM image of CP-Ti wear tack immersed in AS-0.1

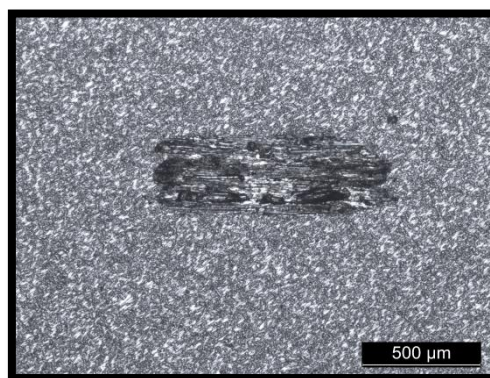


Figure 13 - OM image of CP-Ti wear tack immersed in AS-6

This observation technique can give information related to the scar dimensions, although, it is not possible to evaluate rigorously its depth. Also the wear mechanisms involved cannot be

derived from it. The wear track analysis was based on optical microscope images and the calculations for volume loss are theoretical, considering a perfect contact sliding. Figure 14 shows the wear scar obtained in a perfect contact.

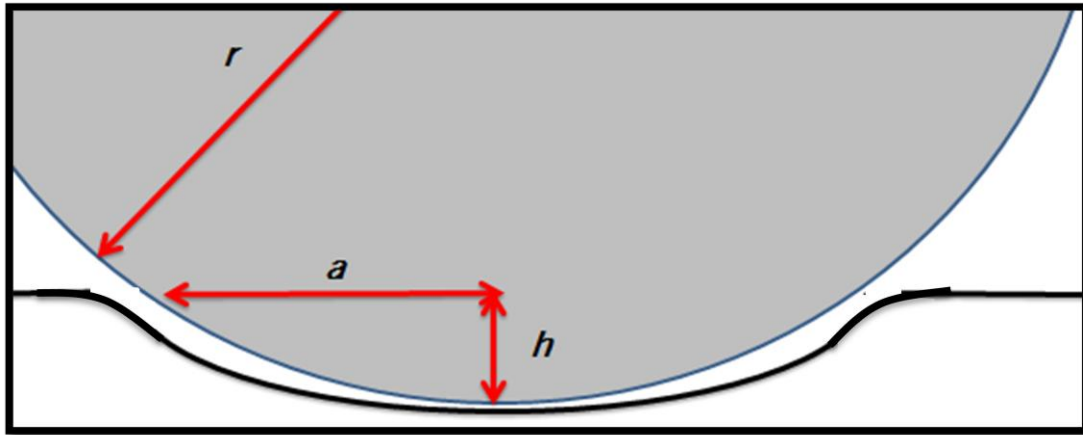


Figure 14 - Schematic representation of a perfect sliding contact

It is considered that when in contact, the counter body will scratch the sample surface in a certain way that, the widest part of the scar is indicative of the depth of the track. Since the radius of the counter body is known and the scratch can be measured, the depth of the contact can be calculated with the following equation:

$$r = \frac{a^2 + h^2}{2h}$$

In which, r is the radius of the counter body, a the distance between the center of the contact and the edge and h the depth. The equation can be arranged in order of h , being possible to solve it.

As soon as the value depth is known, the calculation of the wear volume can be done by the following equation:

$$V = \frac{2}{3} \pi a h b$$

This equation is derived from the volume calculation of a scalene ellipsoid, an ellipsoid with three different dimensions, which is the case. In this, a is the distance between the center and the edge, transversal, h is the deepness and b is the distance between the center and the edge, longitudinal.

The obtained results for the deepness and volume loss are shown on Table 7.

Table 7 – Contact deepness and wear volume loss for different conditions

| | Deepness (μm) | Wear Volume (mm^3) |
|--------|----------------------------|-------------------------------|
| AS | 8.3 ± 1.5 | 0.80 ± 0.26 |
| AS-0.1 | 8.5 ± 0.1 | 0.87 ± 0.12 |
| AS-6 | 3.5 ± 1.6 | 0.12 ± 0.03 |

It is important to reaffirm that the values on Table 7 are just indicative of volume loss, they don't have in consideration any wear mechanism that might involve.

With these values, another important concern can be pointed out. The differences on wear volume loss between AS and AS-0.1 are not statistically relevant, being in fact very similar. Regarding the increase of concentration of H_2O_2 , AS-6, the loss of material seems to be lower than the rest. With this information, some significant facts mentioned before get another relevant evidence. The fact that the wear volume loss has decreased but the COF has suffered an increase, goes in accordance with what had already been said, that the porous outer layer that is formed is not TiO_2 but some other compounds [29], [76]. The presence of a TiOOH layer, decreases the wear volume, which might indicate that, even it is a porous layer, it is more resistant to wear than the titanium oxide layer.

5.4. Electrochemical Impedance Spectroscopy

EIS can be considered the most important technique in kinetic characterization of an electrochemical system. It relies on the measurement of the impedance, a function of electrons' transference, a determinant aspect on a corrosive environment. The main objective of this chapter is to complete the information obtained before. The use of EIS as a tool for this objective had been widely used, even in the study of the influence of H_2O_2 . The main novelty is the introduction of the sliding contact.

5.4.1. EIS results

Figure 15 and Figure 16 show Bode and Nyquist plot with the respective fitting lines.

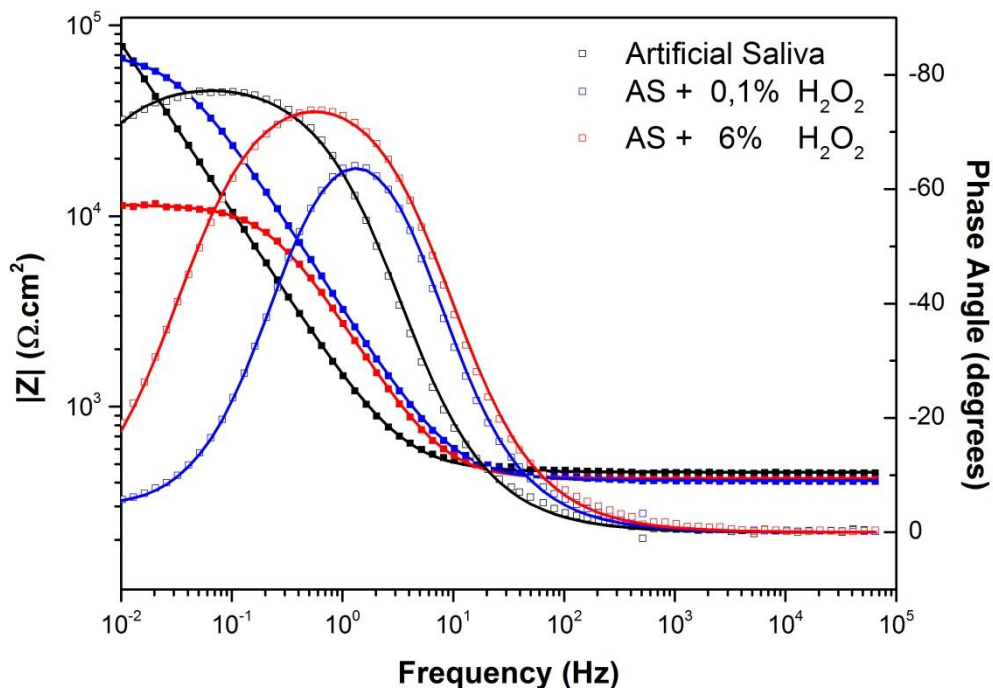


Figure 15 - Bode plot - CP-Ti in different AS solutions after 1.5h of immersion

In terms of $|Z|$ versus frequency (Figure 15), it is possible to observe the presence of a plateau at high frequencies. The high frequencies region reflects the transport of the charge in

the oxide layer, which has an electrical behavior similar to a capacitor [29]. This plateau is related to the phase angle of 0° , corresponding to the response of the electrolyte resistance, the resistance of the solution [10], [93]. Regarding the middle and lower frequencies, the differences between the curves, both impedance and phase angle, can be pointed out. From 10^1 to 10^1 Hz, the slope can give information about the stability of the passive film formed [4]. Slopes of -1 with a phase angle of -90° , the perfect capacitor, are representative of a very stable passive film. In this case, since the perfect capacitor is a rare case, it is replaced by a phase constant element (CPE). In all the cases the results are similar, with slopes of $-0,91$ for the samples immersed on AS and AS-0,1 and $-0,94$ for the ones on AS-6. The high values of impedance at the lower frequencies can be explained by the polarization resistance of titanium. It is also important to point out that the impedance value on the phase angle near -90° is representative of the sum of polarization resistance and solution resistance. The lowest frequencies in the plot are commonly associated with the mass transport in gas-diffusion layers.

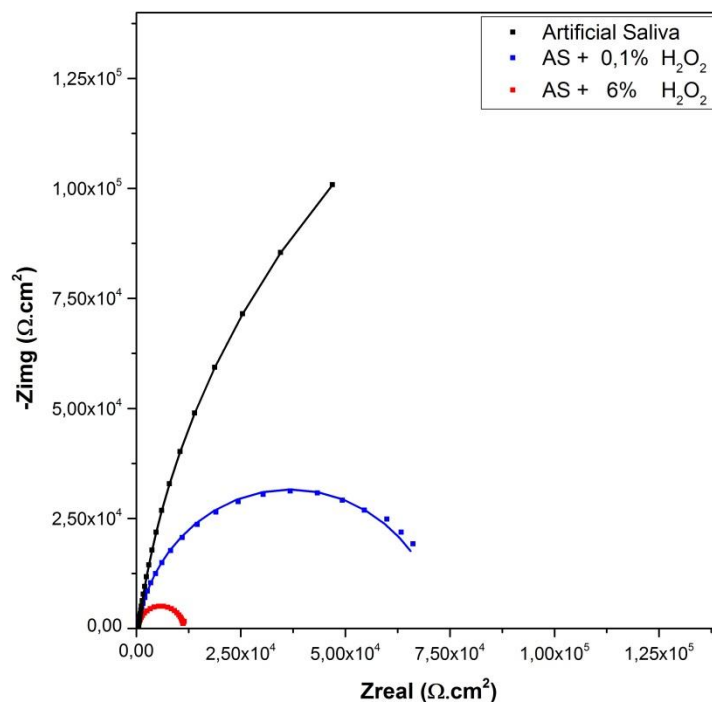


Figure 16 - Nyquist plot - CP-Ti in different AS solutions after 1.5 h of immersion

Nyquist impedance response, Figure 14, is normally identified as a semi-circle for metal/oxide/solution interface, illustrative of real and imaginary Impedances plotted against each

other. It can give important information about the total resistance of the system [94], [95]. The interception of the semi-circle with the Z_{real} axis is representative of the solution resistance and the total resistance of the system. The intersection on small values of Z_{real} (higher frequencies) gives information related to the solution resistance while the intersection for higher values (lower frequencies) shows the total resistance of the system. The difference between these two values is the polarization resistance. The cross of these results with the ones obtained in the Bode plot can give a full characterization of the system. As already said before, not always a Nyquist plot is a perfect semi-circle. The physical meaning of depression in the representation is attributed to either surface roughness, the presence of a porous corrosion product layer or the heterogeneous nature of the surface [96].

It is apparent that the corrosion resistance is strongly affected by the presence and concentration of H_2O_2 , as seen from both Bode and Nyquist plots. For frequencies below 1Hz. the impedance of the system suffers a decrease from $10^5 \Omega \cdot \text{cm}^2$ to $10^4 \Omega \cdot \text{cm}^2$. It is also possible to observe a decrease of the highest phase angle at the end of the slop. It is also possible to see that the total resistance of the system (Nyquist plot) decreases with the increase of H_2O_2 concentration. According to Tengvall [42], the decrease in the polarization resistance of the metal is related to the adsorption of intermediates with a strong oxidizing properties, such as HO_2^- or HO . The different curves observed indicate that the mechanisms that control the samples response to H_2O_2 are different.

5.4.2. EIS model and fitting

The analysis of EIS information is usually based on comparing of experimental results with results obtained by using an electrochemical equivalent circuit. In the presence of a compact passive protective layer, the first equivalent circuit to be tested is Randles. A schematic representation can be seen in Figure 17.

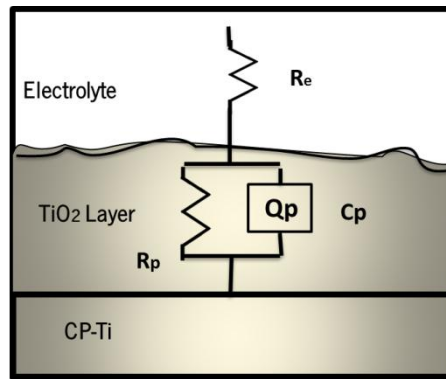


Figure 17 - Schematic representation of Randles equivalent circuit

Legend:

| | |
|--------------------------------|----------------------------------|
| R_e – Electrolyte Resistance | R_p – Polarization Resistance |
| | Q_p – Polarization Capacitance |

The electrolyte resistance measured between the working and reference electrode is represented by R_e , the non-ideal behavior of the passive film is represented by a constant phase element, polarization capacitance (Q_p). R_p represents the polarization resistance related with the system [3], [89].

The Randles circuit can be divided in two important parts, the electrolyte equivalent and the compact oxide layer. The parallel connected elements, R_p and Q_p represent the primarily capacitive effect on the oxide surface. From a physical point of view, it can be said that they represent the contribution of charged species through the oxide and how vacancies influence it [93], [97], [98]. Both of this variables are directly related to the amount of electrical charge accumulated in the titanium oxide and how it behaves when an electric current flow through it. This equivalent circuit was used to analyze the corrosion behavior of the samples immersed in AS and AS-0.1. The goodness of fitting, chi-square values, in this case vary between $4,34 \times 10^{-4}$ ($\pm 1,25 \times 10^{-4}$) and $4,01 \times 10^{-4}$ ($\pm 9,95 \times 10^{-5}$) for AS and AS-0.1, respectively.

Often, the system electrochemical behavior doesn't fit Randles equivalent circuit. The presence of a diffusion layer observed in the Nyquist plot is represented as a straight line, with an angle of 45° in the end of the semi-circle [99]. Literature relates the diffusion layer with a mass transport and a gas-diffusion layer [89], [93]. The interaction of H_2O_2 with a metal, titanium for instance, creates an inner compact oxide layer and an outer porous layer. Using this approach,

the model represented in Figure 15 shows the equivalent circuit considering this configuration of the passive film.

The equivalent circuit showed in Figure 18 was used by Fonseca et al. [89] , where the Warburg impedance is replaced by a resistance due the interactions between the outer porous layer and the decomposition of H_2O_2 . The other parts of the circuit represent: R_e is the solution resistance, as well in the Randles circuit; Q_{pr} the capacitance of the outer porous layer; Q_p and R_p represent the polarization resistance of the inner compact oxide layer as well the interfacial capacitance resistance.. This circuit shows better results regarding the tolerant deviation between the experimental and fitting results, with values ranging $2,12 \times 10^{-4}$ ($\pm 4,63 \times 10^{-5}$).

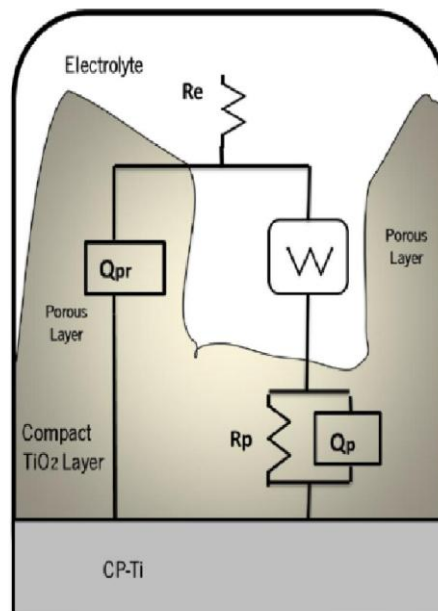


Figure 18 - Equivalent circuit for CP-Ti in contact with H_2O_2

Legend:

R_e – Electrolyte Resistance

Q_{pr} – Outer porous layer polarization resistance

R_p – Polarization Resistance

W - Warburg

Q_p – Polarization Capacitance

5.4.3. Influence of reciprocating sliding on EIS

Table 8 shows the different values for EIS obtained after using the equivalent circuits for fitting.

Table 8 – EIS different parameters values

| | | R_e ($\Omega \cdot \text{cm}^2$) | R_p ($\times 10^4 \Omega \cdot \text{cm}^2$) | Q_p ($\times 10^{-5} \text{s}^n \Omega^{-1} \text{cm}^2$) | Q_{pr} ($\text{s}^n \cdot \Omega^{-1} \cdot \text{cm}^2$) | W ($\Omega \cdot \text{cm}^2 \cdot \text{s}^{1/2}$) |
|--------|--------------|---|---|--|--|--|
| AS | Pre-sliding | 434.9±30.6 | 41.0±6.7 | 15.6±1.3 | - | - |
| | Post-sliding | 476.0±51.0 | 60.0±13.0 | 14.4±1.7 | - | - |
| AS-0.1 | Pre-sliding | 365.0±16.7 | 5.16±1.33 | 6.57±0.27 | - | - |
| | Post-sliding | 347.0±18.5 | 8.88±2.63 | 6.33±0.37 | - | - |
| AS-6 | Pre-sliding | 390.5±31.0 | 9.0±0.4 | 3.6±0.1 | 0.005±0.001 | 50.35±0.63 |
| | Post-sliding | 381.0±49.5 | 1.3±1.1 | 3.8±0.1 | 0.005±0.001 | 499.73±0.25 |

By observing the Table 8, it is possible to understand that samples immersed on AS had the higher values for all the parameters. Although, it is not statistical correct to assume that the addition of H_2O_2 lead to a decrease of the electrolyte resistance. In this case, the standard deviation overlaps the R_e of different conditions, Figure 19.

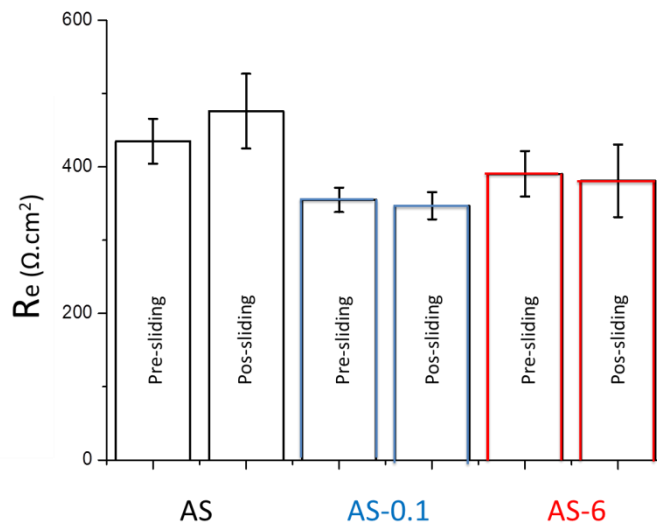


Figure 19 - Electrolyte resistance for different solutions containing H_2O_2 , before and after sliding

A decrease in R_p , Figure 20, and Q_p , Figure 21, values with the increasing of H_2O_2 concentration can also be observed. The immersion of CP-Ti in AS-0.1 and AS-6 lead to a lowering of the corrosion resistance as already detailed in *Chapter 4*. Pan et al. stated that titanium dissolution occurs at localized defects in the passive film rather than uniformly[76]. The presence of strong oxidizing agents and the existence of gaps in titanium structure (porous layer) can be pointed as the main reasons for this phenomenon. It is important to notice that, even though, AS-0,1 contains H_2O_2 , the fact that the concentration is so low, its influence is not so well defined as the influence of AS-6. Regarding the influence of the contact, no significant differences were found related to R_p and Q_p .

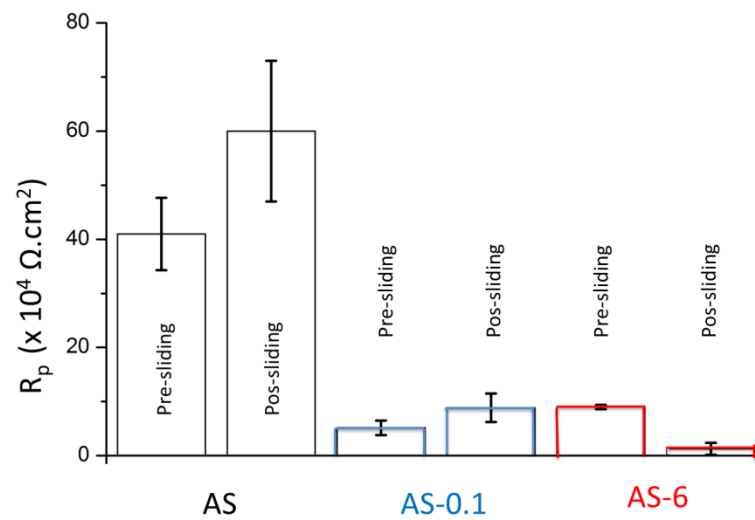


Figure 20 - Polarization resistance for different solutions containing H_2O_2 , before and after sliding

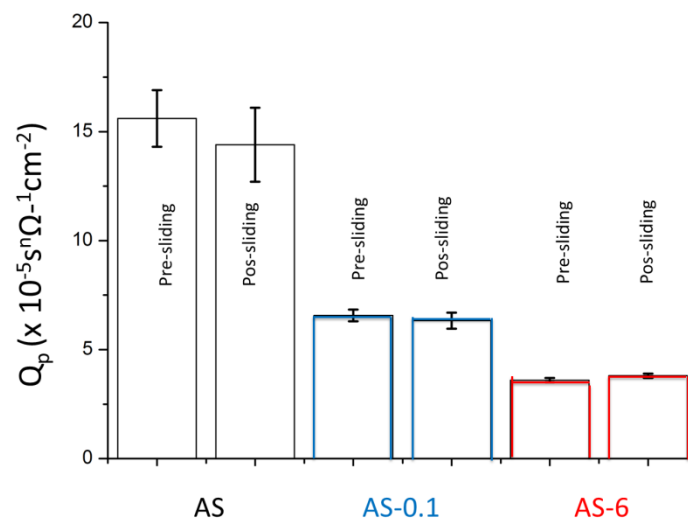


Figure 21 - Polarization capacitance for different solutions containing H_2O_2 , before and after sliding

Regarding the Warburg impedance, its presence is due to the diffusion of compounds, through the oxide layer, causing the adsorption of unstable ions. H_2O_2 drives Ti^{4+} diffusion through the oxide, leaving OH^- and PO_4^- on the surface [29]. The sliding increases the Warburg

impedance. This indicates that diffusion and surface heterogeneities have a predominant influence after sliding [100].

As a conclusion, the presence of hydrogen peroxide in artificial saliva influences the tribocorrosion behavior of titanium. The presence of a porous outer layer, formed by a different chemical state of titanium, namely TiOOH , decreases the overall corrosion resistance of the system. Also, its presence decreases the wear volume loss and increases the COF, probably due to different mechanical properties.

Chapter 6

Conclusions and Future Work

6. Conclusions and Future work

6.1. Main conclusions

Dental implants suffer relevant influence from the operating conditions, in a chemical and mechanical way. With this, tribocorrosion studies on materials used on these applications become clearly important.

The corrosive effect of hydrogen peroxide on titanium has already some studies dedicated to it. Its constant presence on the oral environment makes it attractive. The novelty of this work involves the study of the influence of hydrogen peroxide on the corrosion of titanium, but also to the use of it to a better understanding of the tribocorrosive behavior of implants.

The main conclusions of this work are summarized hereafter:

- The presence of hydrogen peroxide has an important influence on the corrosive behavior of CP-Ti. Higher concentrations of H_2O_2 lead the metal to a nobler state, although it accelerates its corrosion process;
- The corrosion resistance of the system is strongly affected by the presence of H_2O_2 , it decreases as the H_2O_2 concentration increases;
- The main conclusion of the work is that the presence of H_2O_2 has a strong impact on the tribocorrosion of CP-Ti. Its presence decreases the wear volume loss and decreases the needed time to achieve a stabilized state in a tribological contact. Even though its corrosive resistance is decreased in the presence of H_2O_2 , the tendency to corrosion is reduced.

6.2. Future Work

In this study, the influence of H_2O_2 on titanium was studied by the immersion of the samples in artificial saliva containing different H_2O_2 concentrations. During the development of this study, several questions had been raised, which needed to be answered by future work.

- To study the influence of hydrogen peroxide at concentrations between 0,1% and 6%, since the lower one had a weak effect on the surfaces. The understanding of the transition system would be important;
- To evaluate the influence of a higher concentration of H_2O_2 to understand if it follows a proportional behavior, the higher the concentration, the higher the influence;
- To investigate the colonization properties of surfaces immersed in artificial saliva containing different concentrations of H_2O_2 .

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