Influence of pH and corrosion inhibitors on the tribocorrosion behaviour of titanium in different tribological geometries
I dedicate this master dissertation to

my Mother, my Father,

and Luis
Acknowledgements

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**Influência do pH e inibidores de corrosão no comportamento à tribocorrosão do titânio em diferentes geometrias tribológicas**

Nos últimos anos, o titânio tem sido utilizado em aplicações dentárias, devido às suas óptimas propriedades mecânicas, resistência à corrosão e biocompatibilidade. Contudo a falha do componente metálico do implante e o desgaste dos materiais dentários continuam a ser um motivo de preocupação. Quando o implante dentário é colocado na cavidade oral, este é sujeito a solicitações mecânicas como resultado de micro-movimentos cíclicos na interface osso/implante ou implante/abutment ou mesmo abutment/porcelana e também solicitações químicas como consequência do contacto do implante com a saliva ou substâncias orgânicas. Podemos afirmar então que o implante está inserido num sistema de tribo-corrosão, consistindo este numa degradação do material devido a interacções mecânicas e corrosivas. Como consequência a investigação dos mecanismos de tribo-corrosão destes sistemas tornaram-se essenciais.

Neste trabalho, o estudo do comportamento tribo-corrosivo de titânio em contacto com saliva artificial foi investigado. Os testes foram realizados numa geometria de deslizamento linear alternativo, com diferentes amplitude de movimento (200 μm e 6 mm) e diferentes cargas aplicadas (2 e 10 N). Para simular a cavidade oral, uma solução de saliva artificial foi utilizada. Tal como ocorre na saliva humana, variações no pH foram testadas com a adição de ácido cítrico. Foram adicionados também inibidores de corrosão com o intuito de verificar a possibilidade de adição destes produtos a determinados dentífricos e avaliar o seu efeito no comportamento à tribo-corrosão de titânio.

Os resultados demonstraram que o comportamento tribo-corrosivo do titânio em contacto com as diferentes salivas artificial são fortemente afectados pelos parâmetros mecânicos bem como pelos químicos. A adição de ácido cítrico promoveu a formação de um filme passivo com superiores propriedades de resistência à corrosão em ambas as geometrias, contudo após o desgaste, em regime de deslizamento linear alternativo, uma quantidade anómala de material foi removido para cargas mais elevadas (10 N) devido à elevada velocidade de corrosão que o Ti apresenta nesta solução. A adição de
inibidores de corrosão demonstrou afectar negativamente o comportamento tribo-corrosivo do titânio em ambas geometrias de desgaste.
Influence of pH and corrosion inhibitors on the tribocorrosion behaviour of titanium in different tribological geometries

In recent years, titanium has become widely used in multiple dental devices, such as dental implants, because of its excellent mechanical properties, resistance to corrosion and biocompatibility. The failure of the metallic component of the implant and the excessive degradation of dental materials is still relevant and it is a reason for concern. When placed in the human body, dental implants are submitted to mechanical solicitations, as results of cyclic micro-movements at the implant/bone or implant/abutment interface or even at the abutment/ceramic crown interface and also chemical solicitations as a consequence of contact with saliva and other organic substances. Consequently, it can be said that dental implants become part of a tribocorrosion system, which consists in a complex materials degradation phenomenon due to the interaction between mechanical and chemical solicitations. As a consequence, the investigation of the tribocorrosion mechanisms in such systems becomes essential.

In this work the tribocorrosion behaviour of titanium grade 2 in contact with an artificial saliva solution was investigated. Tests were performed in two different sliding geometries with different movement’s amplitude (200 μm and 6 mm), and also with different normal loads (2 and 10 N). To reproduce the oral environment, artificial saliva solution was used as electrolyte. As it occurs in human saliva, variations in pH were simulated by the addition of citric acid. Also, corrosion inhibitors were added in order to understand their influence on the tribocorrosion behaviour of titanium and to investigate the possibility of introducing these products as components of special teeth cleaning agents or medicines.

Results demonstrate that the tribocorrosion behaviour of c.p. Ti in contact with artificial saliva solutions is significantly affected by the mechanical and chemical parameters. The addition of citric acid promotes the formation of a passive film with superior corrosion resistance in both geometries, however after reciprocating sliding tests with higher loads (10 N) an anomalous amount of material was removed, due to
the high corrosion rate of titanium in this solution. The addition of corrosion inhibitors negatively affects the tribocorrosion behaviour of titanium in both geometries.
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Motivation
Motivation

Why this work?

In recent years, there has been a general need to develop new biomaterials that can be inserted in the human body without causing any adverse reactions. The main biomaterials used for specific biomedical applications such as artificial hip joints, drug delivery systems, prostheses and dental implants are metallic, ceramic and polymeric[1].

In dental implant applications, the metallic biomaterials used are stainless steel, Co based alloys, pure titanium and titanium alloys. Lately, titanium has been the most commonly used material in dental implants because of its excellent mechanical properties, biocompatibility and resistance to corrosion, which is provided by a spontaneous formation of a native oxide film on its surface[2]. When placed in the oral cavity, dental implants are subjected to biochemical and biological events. The mouth is thought to be an environment undergoing a wide range of physical and chemical circumstances such as, foods, variations in pH, temperature (ranging from 5 ° to 55 °C), and various bacteria which can corrode the metallic component of the implant[3]. The attack of the implant by corrosion can cause the release of metallic ions to the human body compromising their mechanical integrity and also the biocompatibility of the surrounding tissues[2-4].

Also, in the oral environment the high magnitude of forces due to mastication can lead to wear of dental implants. In adult humans, the average biting load is between 100-150N, being the maximum biting force reported 443 N. However it cannot be disregarded that biting forces can be different between individuals and in different regions of mouth. In the case of patients containing dental implants placed after 3.5 years, biting forces are around 50.1 N[5]. All these forces developed by mastication can generate micro-movements on the implant/abutment, abutment/ceramic crown or in the implant/bone interface.
As a result of these biochemical and biomechanical interactions, it is possible to conclude that dental implants become part of a tribocorrosion system, which is characterized by the materials degradation due to combined chemical and mechanical solicitations which do not act separately. As a consequence, the investigation of the tribocorrosion mechanisms in such systems becomes essential. It is important to point out that in this area few reports have been published. Consequently this is an important innovative approach to be followed in this master dissertation[6-9].

One of the main purposes of this master dissertation was to study the tribocorrosion behaviour of titanium grade 2 in contact with artificial saliva solutions in two different sliding geometries (fretting and reciprocating sliding). As it was referred before, low and high magnitude forces can be formed during mastication, so two different loads were used to perform tribocorrosion tests. Fretting corrosion tests were performed with an amplitude movement of 200 μm and with 2 N of normal load, and reciprocating sliding tests were performed with amplitude of 6 mm at a normal load of 10 N. All the experiments were performed in specific artificial saliva solutions.

The influence of pH and corrosion inhibitors in artificial solution was also considered in the purpose of this study. Regarding this, citric acid was added to artificial saliva, in order to understand how changes in pH can influence the tribocorrosion behaviour of titanium. Corrosion inhibitors were also introduced, in a way to understand the contribution of anodic and cathodic reactions on the tribo-electrochemical behaviour of titanium. Also, the study of effect of corrosion inhibitors, was aimed at investigating if corrosion inhibitors may be introduced in tooth cleaning agents or other medicines in a way to prevent corrosion of dental implants.
Chapter 1
Summary

The main aim of the first chapter is to characterise the problem that was at the origin of the experimental work that will be described later in this master dissertation. The employment of titanium as a biomaterial used in dental implants applications, its corrosion, wear and tribocorrosion behaviour will be focussed in detail.

Chapter 2 and 3 are related to experimental work, which will be presented in the form of 2 papers already published or to be submitted to an international journal with the following titles:

- **Influence of pH and corrosion inhibitors on the tribocorrosion of titanium in artificial saliva** (Wear 261 (2006) 994–1001)

- **Reciprocating sliding – corrosion behaviour of titanium in artificial saliva solutions in presence of corrosion inhibitors and variations of pH** (to be submitted to Wear)

Dental implants that are most of the times subjected to cyclic micro-movements as a result of mastication phenomena. These micro-movements are very well characterized by fretting contacts. As a result, in chapter 2, the tribocorrosion behaviour of titanium in fretting contacts was studied. Changes in pH and the addition of corrosion inhibitors to artificial saliva were performed in a way to understand their influence on the tribocorrosion behaviour of titanium.

Chapter 3 looks upon the influence of pH and corrosion inhibitors on the tribocorrosion behaviour of titanium in reciprocating sliding contacts. It seems that high amplitude movements as a result of mastication may be very well described by the reciprocating sliding motion. Tribocorrosion experiments were performed in the same artificial saliva solutions used in chapter 2 but in a different tribometer.

In chapter 4, the discussion of the results of the two papers produced will be presented. The results obtained in the two different geometries, fretting and reciprocating sliding will be correlated. The final conclusions and futures works will be presented in chapter 5 and 6.
Introduction

We are living in an era of longer life expectancy, and thus dental care becomes an especial target for better quality of life in old age. As the population average increases, and the lifespan appears to be longer, the replacement of natural teeth with artificial ones (dental implants) will increase.

At the moment the materials used for biomedical applications are metallic, ceramic and polymeric[1, 3]. When inserted in the human body, they must have specific properties which vary with the particular application. They should have specific mechanical and chemical properties, be non-toxic, non-irritant, and also resistant to corrosion, in order to ensure patients health[1, 3]. An inappropriate material choice may lead to a strong inflammatory response, and also to eventual failure of the implant[1, 2].

In general, the requirements that biomaterials are expected to cover are divided in three groups, as we can follow in table 1.1.

**Table 1.1: Requirements for implant materials[10].**

<table>
<thead>
<tr>
<th>Requirement of implants</th>
<th>Biocompatibility</th>
<th>Mechanical Properties</th>
<th>Manufacturing</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>- Tissue reactions</td>
<td>- Elasticity</td>
<td>- Manufacturing methods</td>
</tr>
<tr>
<td></td>
<td>- Changes in properties</td>
<td>- Yield stress</td>
<td>- Raw material quality</td>
</tr>
<tr>
<td></td>
<td>- Degradation leads to:</td>
<td>- Toughness</td>
<td>- Sterilization capability of</td>
</tr>
<tr>
<td></td>
<td>• Local deterioration</td>
<td>- Hardness</td>
<td>materials</td>
</tr>
<tr>
<td></td>
<td>• Harmful systemic effects</td>
<td>- Fatigue strength</td>
<td>- Superior technique to</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Wear resistance</td>
<td>obtain excellent surface</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Ductility</td>
<td>finish or texture</td>
</tr>
</tbody>
</table>

In dental implant applications, the clinical goal is to establish the adequate interface between tissues and implantable materials in order to obtain a long term secure
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Bone anchorage, which will sustain dynamic and static loads of the implant, as a result of mastication and other phenomena[11]. The tissue-implant interaction is managed by the surface characteristics of the biomaterial present at around 1 nm of the biomaterial surface, for that, the importance of the surface science of the implantable device is obvious[1].

In the early history of teeth replacements, natural materials such as minerals, and parts from dead animals were used to replace lost teeth. In the 18th and 19th century some efforts were conducted in the design and the development of synthetic materials. With the scientific and technological advances of the 20th century a new concept of implantable materials was developed, as far as designs and biomaterials were concerned[3]. Nowadays in dental implants, the uses of metallic biomaterials are the most usual to replace the teeth lost by periodontal disease or injury.

The dental implant system was developed by Branemark[1] in 1952, and was first placed in the human body in 1965. Nowadays, dental implant designs can be divided into two categories, the endosteal (endosseous), which enter in direct contact with bone tissue, and the subperiosteal which contact with the exterior of bone surfaces[1, 3]. In Fig.1.1 it is possible to observe a common dental implant in contact with bone tissues (Fig.1.1 (a)), and their main components (Fig.1.1 (b)).

![Diagram](image_url)

**(a)**

**Fig. 1.1:** Schematic representation of (a) dental implant in mouth, (b) the components of dental implantable device[1, 12].
The system consists of a ceramic crown that is attached to a metallic screw made of titanium, which is in direct contact with bone tissues[11]. Implants are commonly cylindrical and constituted by a screw thread in the outside and another in the inside. The coronal part of single tooth abutments needs to provide adequate retention and resistance to the crown, to be retained by cement to the abutment[1].

In Fig.1.2 it is possible to observe the several steps that occur to replace a single tooth by a dental implant. Before the introduction in the oral cavity the complete restoration can be observed in master cast (see Fig. 1.2 (b)).

**Fig. 1.2:** Schematic representation of (a) the completed crown and abutment, (b) the completed restoration on master cast, (c) standard abutment in place, (d) the completed restoration, (e) the abutment shapes (try-in kit)[13].
After the connection of the implant to the bone (see Fig.1.2 (c)), the implant must be protected during healing by a cover that is screwed into the internal thread. After a specific period of 3-6 months, the cover screw is removed and the abutment is introduced and attached to the implant. It is important to refer that abutments can have several shapes as we can see in Fig.1.2 (e), and it is selected depending of each specific case. Then the abutment is subsequently adapted for the final attachment of the prosthetic tooth, and the final result can be seen in Fig.1.2 (d)[1].
1.1. Application of titanium in dental implants

The use of titanium for implant applications dates from the 1930s. In dentistry it has been used for over 30 years[1]. Nowadays it is commonly used as the metallic component of a dental implant, as shown in Fig.1.1 and 1.2 (a). It is important to denote that all the tests performed in this master dissertation used in c.p. titanium in the form of plate. The idea was to study the material used in the metallic screw of a dental implant.

There are four grades of pure titanium for biomedical applications; their main differences appears from the percentage of impurity contents, as we can see in table 1.2[14].

<table>
<thead>
<tr>
<th>Element</th>
<th>Ti Grade 1</th>
<th>Ti Grade 2</th>
<th>Ti Grade 3</th>
<th>Ti Grade 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen</td>
<td>0.03</td>
<td>0.03</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>Carbon</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>0.015</td>
<td>0.015</td>
<td>0.015</td>
<td>0.015</td>
</tr>
<tr>
<td>Iron</td>
<td>0.20</td>
<td>0.30</td>
<td>0.30</td>
<td>0.50</td>
</tr>
<tr>
<td>Oxygen</td>
<td>0.18</td>
<td>0.25</td>
<td>0.35</td>
<td>0.40</td>
</tr>
<tr>
<td>Titanium</td>
<td>Balance</td>
<td>Balance</td>
<td>Balance</td>
<td>Balance</td>
</tr>
</tbody>
</table>

**Mechanical properties**

<table>
<thead>
<tr>
<th></th>
<th>Yield Strength (MPa)</th>
<th>Elongation (%)</th>
<th>Ult. Tensile Strength (Mpa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti Grade 1</td>
<td>692</td>
<td>24</td>
<td>785</td>
</tr>
<tr>
<td>Ti Grade 2</td>
<td>275</td>
<td>20</td>
<td>345</td>
</tr>
<tr>
<td>Ti Grade 3</td>
<td>380</td>
<td>18</td>
<td>450</td>
</tr>
<tr>
<td>Ti Grade 4</td>
<td>485</td>
<td>15</td>
<td>550</td>
</tr>
</tbody>
</table>

Regarding table 1.2 is possible to see that small variations in oxygen % significantly affect the ductility and strength of the material, hydrogen and nitrogen may also have an enbrittlement effect on titanium[14].
Titanium is known to have two allotropic structures, one hexagonal close-packed (hcp, $\alpha$-Ti) up to 882 °C and body-centred cubic (bcc, $\beta$-Ti) above that temperature. As a result of the allotropic transformation from $\alpha$ to $\beta$ phase, titanium alloys fall into three classes: $\alpha$ alloy, $\alpha+\beta$ alloys, and $\beta$ alloys\cite{14, 15}.

The addition of alloying elements such as aluminium and vanadium, to commercially pure titanium enables it to obtain a wide range of properties\cite{14, 15}. Aluminium tends to stabilize the $\alpha$ phase, increasing the temperature of transformation from $\alpha$ to $\beta$ phase improving the strength characteristics and oxidation resistance at high temperatures. Vanadium, however stabilizes the $\beta$ phase lowering the transformation temperature (from $\alpha$ to $\beta$ phase). The addition of vanadium at controlled amounts causes a higher strength of $\beta$ phase to persist below of the transformation temperature\cite{15}.

In table 1.3 is presented the mechanical properties of pure titanium and titanium alloys.

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|}
\hline
\textbf{Alloy designation} & \textbf{Microstructure} & \textbf{Young Modulus (GPa)} & \textbf{Yield Strength (MPa)} & \textbf{Ultimate Strength (MPa)} \\
\hline
c.p. Ti & $\alpha$ & 105 & 692 & 785 \\
\hline
Ti-6Al-4V & $\alpha/\beta$ & 110 & 850-900 & 960-970 \\
\hline
Ti-6Al-7Nb & $\alpha/\beta$ & 105 & 921 & 1024 \\
\hline
Ti-5Al-2.5Fe & $\alpha/\beta$ & 110 & 914 & 1024 \\
\hline
Ti-12Mo-6Zr-2Fe & Metastable $\beta$ & 74-85 & 1000-1060 & 1060-1100 \\
\hline
Ti-15Mo-5Zr-3Al & Metastable $\beta$ & 82 & 771 & 812 \\
\hline
Ti-Zr & Cast $\alpha'/\beta$ & N/A & N/A & 900 \\
\hline
Ti-13Nb-13Zr & $\alpha'/\beta$ & 79 & 900 & 1030 \\
\hline
Ti-15Mo-3Nb-0.3O & Metastable $\beta+$ silicides & 82 & 1020 & 1020 \\
\hline
Ti-35Nb-5Ta-7Zr & Metastable $\beta$ & 55 & 530 & 590 \\
\hline
Ti-35Nb-5Ta-7Zr-0.4O & Metastable $\beta$ & 66 & 976 & 1010 \\
\hline
Bone & Viscoelastic composite & 10-40 & - & 90-140 \\
\hline
\end{tabular}
\caption{Mechanical properties of titanium and titanium alloys\cite{18}.}
\end{table}
In biomedical applications, some of the mechanical requirements for titanium are high tensile strength as well as low Young modulus, because of the large and cyclic stresses to that dental implants are subjected and because higher values of Young modulus can result in bone resorption\[16]. The Young modulus of titanium is much lower than those of stainless steel and Co based alloy, however their value is still higher than bone, as we can see in table 1.3\[16-19].

Nowadays there already exists some titanium alloys (Ti-35Nb-5 Ta-7Zr, Ti-35Nb-5 Ta-7Zr-0.4O) with a Young Modulus lower than pure titanium with values approaching bone. As it was said before, this is a characteristic of extreme importance in such a way that it can avoid bone resorption\[2].

The integration of the dental implants into bone is a paramount of real importance for the proper functioning of the implant and therefore, extensive studies have been carried on the osseo or osteointegration process\[20, 21, 22]. The osteointegration concept was initially associated with root form implant and it was introduced by Branemark et al.\[3, 20], and by Schroeder et al.\[20]. This concept is described as the direct contact of bone with the biomaterial surface (without fibrous tissue) for a functioning implant. However, in 1993, Jovanovich et al.\[20] suggested that this term should be used to describe the difference between implants that promote bone growing in the proximity of the implant and those that have a identified band or connective tissues between the implant and the adjacent bone. It is known, nowadays that a range of biomaterials have been shown to exhibit a type of tissues or fibrous interface for functional dental systems\[3].

Little is known about the influence of surface topography of titanium on cell metabolism or differentiation, but it seems that surface topography have a marked influence on ossoeingtegration process. Mythili et al.\[23] studied the influence of the titanium surface treated with two different treatments (sandblasted and acid-etched) on osteoblasts-like primary cells evolution during 7 days. Results demonstrate that groove surfaces offer better cell attachment and proliferation.

Biocompatibility is considered to be the major requirement for materials that are inserted in the human body. In general, biocompatibility concerns the relationship
between the biomaterial and the host environment; it covers all aspects of the interfacial reactions between the material and tissues[11]. The term biocompatibility also focuses on the host response, which is the reaction of the tissues to the implant. It is important to considerer that this interaction can be considered adverse if there is evidence of degradation of the surround tissues or in any other part of the human body[1, 11, 23].

Titanium biocompatibility has also been studied by several authors. Clauídia et al.[20] developed a research based on the study of tissue responses around smooth pure titanium implant after a healing period of eight weeks. The formation and the amount of bone formed inside the implant threads were analyzed. Histological results show a remodeling and new bone formation near implantable surfaces[20].

1.2. Corrosion

Corrosion, wear and fatigue are considered the most frequent causes of biomaterials degradation[11]. In this master dissertation the corrosion and wear of titanium used in dental implants application will be focused in detail.

Corrosion can be defined as the materials degradation due to electrochemical attack. It is a consequence of the interaction of the material with its surrounding environment, which may lead to a degradation of materials properties, such as the loss of structural and chemical integrity[3, 14]. All metallic materials used as biomaterials has one characteristic in common, their corrosion resistance is due to the formation of a passive oxide film on their surface[11, 14]. However this oxide film seems not to be stable, because of the incorporation of ions and/or molecules as a result of the contact with body fluids[24].

If the human environment where they are inserted is aggressive, this oxide film might be disrupted and corrosion will be enhanced. It is thought that the oxide film has the ability of being partially dissolved and reprecipitated in body fluids. If the dissolution process is higher than the reprecipitation rate, metal ions will gradually be released into the human body, however their release is very slow, because potential
changes of the material in vivo are relatively small[25]. This ions, can be accumulated on the tissues surrounding the implant or in other part of the body[11, 24].

Concerning dental implants, if the metallic component of the implant is corroded by body fluids, it may lead to its weakening, and also the liberation of metallic ions. Furthermore, if these ions are combined with biomolecules an adverse reaction such as toxicity or allergy or even carcinoma may occur in the patient[25, 26].

Metallic ions released from dental materials have been identified in saliva, oral tissues, and in cell culture media after incubation. T. Hanawa et al.[26] reviewed the metallic ionic species that can be released in human body by titanium, stainless steel and cobalt-chromium. Specific reactions occur there, and just a small amount of ions will combine with biomolecules originating biological reactions such as allergy and citotoxicity [26]. Several released elements have been shown to be cytotoxic during in vitro studies[27].

The oxide passive film formed on metallic materials seems to play an inhibitor role on the release of ionic species in vivo. Bianco et al.[28], also show that the transport in vivo of degradation species of titanium was limited, i.e. they are accumulated locally. Titanium serum and urine levels in rabbits with a titanium implant were analyzed by Bianco et al[28]. In this work the tissues that surround the implant were analyzed. Results demonstrate that titanium dissolved from the oxide film is not transported in noticeable amounts via serum proteins and it is not measured in rabbit’s urine[28].

1.2.1. The oral environment

The biological environment is surprisingly harsh and can lead to rapid or gradual degradation of biomaterials. When a dental implant is inserted on the oral cavity it will be consequently in contact with saliva.

Saliva is the fluid present on the oral cavity, constituted by biochemical compounds and with a great deal of individual variations[29, 1]. It is considered to play
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an important role on the initial breakdown of food, on the lubrication of the oral tissue facilitating manipulation of food in the oral cavity and also on swallowing. [30, 31]

Saliva is produced by three pairs of salivary glands, the parotid, submandibular and sublingual, and it consists for more than 99 % of water and contains a large number of organic and inorganic compounds. The organic constituents of saliva are a wide variety of proteins which have specific biological functions and which intervene on oral health. Concerning the inorganic constituents of saliva it consists on sodium, chloride, calcium, phosphate and bicarbonate[32].

A review of the literature on human saliva composition, flow rates and some health benefits of saliva was performed by M.W.J. Dodds[32] and his colleagues. Results show the importance of saliva in maintaining the oral healthy environment.

Human saliva is thought to have an unstable nature, which does not permit the duplication of its properties. This instability makes natural saliva unsuitable to be used for in vitro studies, and so the development of artificial saliva compositions was found necessary. A requirement for artificial saliva is that it has to react with the test material in a similar manner to natural saliva[33].

The use of artificial saliva for testing dental materials dates back to 1931 and it has been reported in several specific studies with different kinds of compositions[32, 33, 34, 35, 36]. Jean Gal et al.[35] have performed a study based on 60 different artificial saliva’s, with similar composition compared to natural saliva. In this work, the role of some compounds, such as CO₂ gas, calcium ions, hydrogenocarbonates, hydrogenophosphates and thiocyanates was evaluated. In vitro tests of dental materials was evaluated on the saliva’s reviewed and compared with a medium proposed some years ago, the SAGF medium. For physicochemical studies, this medium has some advantages; it allowed us to specify the mode of fluoride ions release from glass ionomer cements and the corrosion behavior of the dental amalgams[35].

So it can be said that dental implants, when inserted on the oral cavity are exposed during a prolonged period to saliva whose main constitution present a wide range of biochemical compounds which may enhance corrosion[4].
1.2.2. Fretting Corrosion

There are several forms of corrosion that can occur in biomaterials[11, 14, 37, 38], however in dental implants, fretting corrosion is considered to be the most relevant, and it will be studied in detail. Fretting corrosion occurs when two surfaces are in contact and experience a small amplitude oscillatory motion, resulting in the damage of the surfaces in the contact region (see Fig 1.3)[11, 14, 37, and 38].

Fig. 1.3: Schematic representation of fretting corrosion a form of corrosion[37].

Every time the two surfaces rub against each other, their protective passive film can be removed and they must heal by reaction with the environment[11, 14, 37, 38]. Fretting corrosion appears to be observed at the implant/abutment or implant/bone or even in abutment/ceramic crown interface of a dental implant, where cyclic micro-movements or micro-motions take place commonly as a result of mastication[1, 3].

The micro-motion concept was introduced in 1973. Literature suggests that there exist a critical threshold for micro-motion, remaining this value somewhere between 50 μm and 150 μm. Micro-motion that did not interfere in bone ingrowth was estimated to be around of 50 μm, however movements around 100 μm may be tolerated for implants with a bionert surface, as suggested S. Szmukler et al [39, 40]. Nowadays it is known that excess of movement at the implant interface affects the healing sequence affecting bone ingrowths[39, 40].

Another biomedical system that is under fretting corrosion is the orthopedic plate/screw. Lalor et al.[41] describe five cases of failure due to fretting corrosion in chrome-cobalt plates are fixed to bone by Ti6Al4V screws, where the motion between the two materials caused fretting corrosion of the titanium alloy.
As a result of fretting corrosion, metallic debris can be released from the implant surface. M. Franchi et al. [42] studied the biological evolution in vivo of tissues around dental implant and the detachment of Ti debris from their surfaces. For that, titanium screws with different surfaces were used. Results show that metal particles were released in the early phases after implant fixation, and their release was related to the morphology of the implant, and to the frictional force between titanium surfaces and the pre-existing bone [42].

Fretting corrosion will be focus in detail in chapter 2, where the tribocorrosion behaviour of titanium in artificial saliva and in fretting contact will be studied.

1.2.3. Corrosion of titanium and Ti alloys in oral environments

As it was referred before, the corrosion behaviour of titanium in any kind of medium is controlled by a protective oxide layer (up to a depth of 10 nm) on its surface. The characteristics of films grown at room temperature on pure titanium are schematically represented in Fig. 1.4 [43].

![Schematic representation of the oxide film formed on titanium at room temperature and schematic illustration of their cross section](image-url)

**Fig. 1.4:** (a) Schematic representation of the oxide film formed on titanium at room temperature and (b) schematic illustration of their cross section [44, 45].
The film growth is influenced by the natural characteristics of the bulk material and by the surrounding environment (air, or some physiological solution), resulting in a formation of a very stable and adherent film[43, 44, 45].

The nanocrystalline or amorphous oxide film has 3-7 nm of thickness and it is mainly composed by TiO$_2$; amorphous titanium dioxides are the most common. The TiO$_2$/Ti interface has O to Ti ratio that changes gradually from 2 to 1, i.e from TiO$_2$, and with much lower ratio in the bulk. Hydroxides and chemisorbed water has the tendency to be strongly bound to Ti cations at the outermost surface[43]. The surface oxide stops growing for kinetic reasons, i.e, due to increased difficulty of the transportation of oxygen and metal atoms across the formed film[43, 44, 45].

Titanium can develop several oxides with different stoichiometries (TiO, Ti$_2$O$_3$, TiO$_3$ and TiO$_2$); so the contact between the dental implant and the physiological fluids will occur on these oxides[11].

In Fig.1.5 the potential-pH diagram of titanium in water is presented.

![Fig. 1.5: Pourbaix diagram[11].](image)

The Pourbaix diagram for titanium, demonstrate that oxide passive films are very stable for a wide range of potentials. Several titanium species, such as Ti metal,
Ti$^{2+}$, Ti$^{3+}$, TiO, Ti$_2$O$_3$, TiO$_2$ and TiO$_3$.H$_2$O, can be stable under specific potential and pH conditions[11].

In recent years, there has been a considerable amount of scientific knowledge published on titanium corrosion properties; it is thought to be a result of the chemical stability and structure of titanium oxide formed. The oxide film provides corrosion resistance and also contributes to the biological performance of titanium (contributes for the osseointegration process) when in contact with some tissues as suggested by Branemark and colleges[6, 11, 46, 47].

The electrochemical behaviour of titanium that is under mechanical and chemical solicitations is an important parameter for the performance of the dental implant. For this reason studies on the corrosion behaviour of biomaterials, in particular for dental implants applications in oral environments, have been performed in the recent years.

*C. E.B. Marino et.al.*[4] studied the electrochemical behaviour of titanium grade 2 (a dental screw), in artificial saliva and in a phosphate buffer solution during a period of 1500 min. Electrochemical impedance spectroscopy, open circuit potential and potentiodynamic (-1 to 1.5V at 50 mV/s$^{-1}$) measurements were performed. Results demonstrate that the surface oxide is stable on titanium grade 2, protecting it against corrosion up to 1.5 V at 25 ºC in artificial saliva. The resistance of the passive film decreased as the exposure time increased, due to the breakdown of the oxide film followed by dissolution process. Analysis of the chemical composition of titanium indicates that the maximum limits of interstitial elements (C, N, Fe and O) are altered influencing its corrosion resistance[4].

Alloying titanium has pronounced effects on its chemical properties. *Gonzales and Mirka-Rosca et al.*[45] study the corrosion behaviour of titanium and Ti alloys (Ti-10Mo, Ti-10Mo-10Al, Ti-15Mo-5Al, Ti-7Al-4.5V, and Ti-5Al-2.5Fe in Ringer solution (pH=7.8). The results obtained by potentiostatic and potentiodynamic techniques, were compared with EIS results. All titanium alloys demonstrate a spontaneous passivation. Mo, V and Fe appeared to improve passivity while the Al enrichment was found to be detrimental to passivity and corrosion resistance[45].
The effect of alloying on the structure of the oxide film was investigated also by Ibris et al.[43] in Ti, Ti7Al4.5V and Ti5Al2.5Fe alloys in Hank’s solution and in Fusayama Mayer solution + 0.1 F⁻. The addition of alloying elements resulted in an increasing of the resistance of the oxide film and on its growth kinetics[43].

The electrochemical properties of titanium-silver alloys and the surface characteristics of the passive film formed in artificial saliva, was investigated by H.M Shim.[48]. Titanium silver alloys were produced with silver contents ranging from 0 to 5 at. %. Results demonstrate that they maintain low current density and show a passive region very stable and also high open circuit potentials when compared with pure titanium. They conclude that it was a formation of a thick oxide film which improved corrosion resistance and electrochemical stability[48].

1.2.4. Factors affecting the corrosion behaviour of titanium and Ti alloys

As it has been referred before, the oral environment with all hostile conditions and variations, can compromise titanium corrosion resistance. Some variations can be observed in the oral environment and they can have a strong influence on titanium behavior. They can be: changes in pH and the presence of fluorides in saliva, the contact of titanium with H₂O₂ and the eventual presence of corrosion inhibitors.

1.2.4.1. Changes in pH and presence of fluorides in saliva

When inserted in the oral cavity, dental implants can experience environments with different pH. Our attention will be brought to the influence of citric acid which can be found in some drinks and which can bring about variations in saliva pH.

In human body, the pH of blood and interstitial fluids are considered to be between 7.35-7.45. The insertion of implantable devices however results in alteration of pH to 5.2, but after two weeks the pH recovers to its steady-state value (between 7.35-7.45)[49]. It seems that proteins and bacteria present in human body can alter the pH of the local environment through the production of acid metabolic products[3]. So, when a
dental implant is inserted in the oral cavity, local pH changes occur, which can compromise the efficiency of titanium.

The pH of mouth seems to be different between individuals. A.J. Preston et al.[36] reviewed several methods that can be used to determine the dental plaque pH. The oral environment also has strong variations of pH as a result of ingestion of food and drinks. Case reports were developed on gross tooth destruction as a result of consumption of juices, which modify pH of saliva[50].

Citric acid is a weak organic acid found in citrus fruits, which has strong influence on pH changes of saliva. It exists in a variety of fruits and vegetables, but it is most concentrated in lemons and limes, where it can comprise as much as 8% of the dry weight of the fruit. Studies using citric acid and ascorbic acid, suggested that these acids may be particularly harmful, and can enhance the erosion of natural teeth[50].

T. Akova et al.[51] investigate the influence of food simulating liquids on the mechanical properties of composite restorative materials. In this study the specimens were conditioned for 7 days at 37 ºC as follows: water, 0.02 N citric acid, heptane and 75 % ethanol aqueous solution. Results demonstrate that the mechanical properties of composite restorative materials are strongly influenced by environmental conditions. The mechanical properties of some of the composites such as hardness were reduced after immersion during 7 days at 37 ºC in citric acid[51].

It is thought that in the oral cavity, all these interactions of saliva with food components and beverages (containing citric acid) with the dental implant occur and may degrade and age the dental implant[51]. In relation to dental implant applications, few reports exist, which take into account the influence of variations in pH on the corrosion behaviour of pure titanium. Despite of the significant practical benefit, also there have been almost no reports taking into account the influence of variations in pH applied in tribocorrosion behaviour of dental materials. This is an innovative aspect of this thesis.

There has been in recent years an increase in the use of dental gels and rinses containing fluoride for caries dental prevention. The use of these dentals gels, results in
an increase of fluorides in the oral cavity which may affect the corrosion behaviour of titanium[52, 53, 54].

A.M. Mayouf et al.[52] studied the effect of fluoride and pH on the corrosion behaviour of Ti, Ti6Al4V and Ti30Cu10Ag alloys in artificial saliva solution. It could be observed that fluorides ions attack Ti and Ti alloys, but the severity of the attack was strongly dependent on the pH. Increasing fluoride ions concentration leads to an increase of thickness and porosity of the oxide layer reducing their corrosion resistance [52].

The presence of fluorides and the influence of pH variations in Fusuyama Meyer artificial saliva was also evaluated by N. Schiff[55]. OCP, linear sweep voltametric analysis, polarization resistance and corrosion current measurements were performed. In Fig. 1.6 it is possible to observe the evolution in corrosion potential in the different media.

![Fig. 1.6: Evolution of corrosion potential versus time for titanium in different media](image)

As it can be observed in the Fig. 1.6 in an acidified medium the potential obtained was slightly lower than in the original solution. In a fluoridated medium it seems that the characteristics of the passive film changes leading to a decrease of the corrosion resistance. In fluoridated-acidified saliva results suggests a strong reduction of the corrosion resistance of titanium[55].
Influence of pH and corrosion inhibitors on the tribocorrosion behaviour of titanium in different tribological geometries

In Fig. 1.7 potentiodynamic polarization curves suggest that current densities increase indicating that corrosion resistance decreases when the medium changes from acidified, fluoridated to fluoridated-acidified. Furthermore in some circumstances fluoride ions, can induce localized corrosion phenomena, and can cause the breakdown of protective passive film, leading to pit corrosion[55].

1.2.4.2. Contact with H$_2$O$_2$

The high corrosion rate that sometimes is observed in titanium might be due to the presence of H$_2$O$_2$, which is produced as the result of the inflammatory response caused by surgical trauma after the implantation in living tissues.[56, 57].

The electrochemical behaviour of titanium in presence of artificial saliva which was prepared by dissolving in 1l of water of 0.340 g KH$_2$PO$_4$, 0.445 g Na$_2$HPO$_4$.2H$_2$O, 1.5 g KHCO3, 0.58 g NaCl, 0.0305 g MgCl$_2$.6H$_2$O, 0.0315 g citric acid and 0.016 g CaCl$_2$ at pH 7.2 and 3. OCP, polarization and EIS studies were performed. The corrosion resistance of titanium decreased with the presence of hydrogen peroxide due to the increase of the dissolution/oxidation rate. When titanium is put in contact with hydrogen peroxide, two specific processes occur at metal interface: titanium catalyzed decomposition of H$_2$O$_2$, and the corrosion of titanium. It seems that H$_2$O$_2$ decomposes
into oxygen and water at titanium surface. Because H₂O₂ is a physically powerful oxidizer it can cause some changes on the titanium oxide[58]. In this study it was possible to conclude that the effect of H₂O₂ on the electrochemical behaviour of titanium is strongly dependent on its concentration as well as pH, leading to a decrease of the corrosion behaviour of titanium. The polarization resistance increases in neutral artificial saliva with H₂O₂, but the opposite behaviour occurred in acidic medium. Polarization resistance decreased, when the ratio of H₂O₂ was increased, but it increased when the pH was equal to 7.2[58].

### 1.2.4.3. Influence of corrosion inhibitors

Corrosion inhibitor is considered to be a chemical substance that when added in small concentration to an environment, effectively decreases its corrosivity[59].

The insertion of corrosion inhibitors may alter the pH of saliva, but the idea of researching this possibility is that, depending on their behaviour, they may be introduced in tooth hygienic products, such as toothpastes, as a way of protecting dental implants from corrosion degradation. This is considered to be another innovative aspect of this dissertation[59].

Inhibitors are considered to be chemical compounds which react with a metallic surface, or the surrounding environment to which the surface is exposed, giving to the surface a certain level of protection. They frequently work by adsorbing themselves on the metallic surface, protecting the metallic surface by forming a film. They slow the corrosion processes by increasing the anodic or cathodic polarization behaviour, by reducing the movement or diffusion of ions to the metallic surface and by increasing the electrical resistance of the metallic surface[59].

The way that inhibitors act on the corrosion kinetics can be by inhibiting the cathodic, anodic reactions, or by a combination of both. In accordance to this, they can be classified such as anodic, cathodic and organic inhibitors. The effectiveness of these inhibitors depends on the chemical composition, their molecular structure, and their affinities for the metal surface.
Influence of pH and corrosion inhibitors on the tribocorrosion behaviour of titanium in different tribological geometries

In the case of anodic or passivating inhibitors, they have the ability of suppressing anodic reactions, by supporting the natural passivation of the metal, forming a layer impermeable to metal ions[59]. They have the ability of forcing the metallic surface into a passivation range, causing a large anodic shift on corrosion potential[48, 59]. If the insulating layer becomes damaged, corrosion begins and the passivator acts on the new products to repair the layer[59]. There exist two types of anodic inhibitors: oxidizing anions, such as chromate, nitrite, and nitrate, that can passivate in the absence of oxygen and the nonoxidizing ions, such as phosphate, tungstate, and molybdate that require the presence of oxygen to passivate. These inhibitors are the most effective and consequently the most widely used. When concentrations fall below minimum limits anodic inhibitors can act causing pitting and accelerating corrosion[38, 59, 60].

Cathodic inhibitors either slow the cathodic reaction itself or selectively precipitate on cathodic areas to limit the diffusion of reducible species to these areas. Cathodic inhibitors have the ability of producing a barrier to oxygen diffusion that prevents the transfer of electrons from the metal surface. Cathodic inhibitors are compounds of arsenic and antimony, ions such as calcium, zinc or magnesium, or also sodium sulfite[38, 59, 60].

Both anodic and cathodic effects are sometimes observed in the presence of organic inhibitors. Organic inhibitors affect the entire surface of a corroding metal when present in sufficient concentration; they are usually designated as film-forming, protecting the metal by forming a hydrophobic film on the metal surface. The adsorption of organic inhibitors depends on the ionic charge of the inhibitor and the charge on the surface. Cationic inhibitors, such as amines, or anionic inhibitors, such as sulfonates, will be adsorbed preferentially depending on whether the metal is charged negatively or positively. The strength of the adsorption bond is the dominant factor for soluble organic inhibitors[38, 59, 60].

Chemical compounds such as benzotriazole have been studied as a specific organic corrosion inhibitor, and has been satisfactorily used for the last 25 years as corrosion inhibitor of copper[61]. However J.L. Yao et al.[62] developed a study based on the use of benzotriazole for the protection of Fe. The protection of Fe was confirmed, but pH of the solution revealed to have a influence on the inhibition efficiency.
Although great efforts have been made, a better understanding of the mechanisms of inhibition for titanium corrosion is still to be achieved. Mansfeld et al. [63] study the addition of organic corrosion inhibitors containing nitro-groups for the protection of titanium. The tests were performed in HCl solutions, and results show that these additives act as passivators reducing the corrosion rates of titanium. It seems that the nitro-groups are reduced on titanium surface, causing polarization of Ti to more noble potentials.

The influence of corrosion inhibitors, such as potassium chromate and hexamethyleneimine, on the electrochemical and corrosion behaviour of freshly formed metal surfaces in specific electrolyte solutions was studied by Rozenfel’d et al.[64]. Apparently the action of the corrosion inhibitors depends on the time, and they can promote a formation of a primary film with better protective properties[63].

One study related to corrosion inhibitors, shows that they were developed for the control of titanium dissolution in sulfuric acid. The more effective inhibitors seem to form permanent complexes with titanium atoms within the lattice structure[65].

1.3. Wear

One of the most important tribological problems of the human body is the wear of teeth and consequently of dental implants, as a result of the forces and motions that they are submitted on the oral environment, which can lead to their loss. In materials science, wear can be defined as the progressive loss of material resulting from mechanical interaction occurring between two contacting surfaces. These surfaces will be in relative motion (either sliding or rolling), and under load [66, 67, 68]. Wear variations includes load, speed, temperature, counterbodie, and type of contact.

There are four principal wear processes:
- Fatigue wear
- Adhesive wear
- Abrasive wear
- Corrosive wear
Fatigue wear is defined as a contact between materials accompanied by high local stresses and repeated a large number of times in one specific course. As a result the generation of wear particles and also crack initiation occurs. It is considered to be associated with rolling contacts because of the cycling nature of the load. The formations of cracks and their propagation are a result of cyclic stress in sliding contacts which leads to stress concentration. The environment can determine not only the stress required for surface crack nucleation, but more significantly the rate of crack propagation once a crack has reached the surface[68, 69].

Adhesive wear refer to the ability of atomic structures to hold themselves and form surface bonds with other atoms or surfaces with which they are in contact. Two surfaces of similar crystal structure will adhere strongly on to another simply by placing them in contact as shown Fig.1.8. No normal stress is required to ensure a complete bond.

![Fig. 1.8: Schematic representation of adhesive wear [68].](image)

Plastic deformation frequently occurs at the contacting areas because of the high loading generated in these regions, resulting in the disruption of oxide films[68].

Many wear processes start with adhesive mechanisms, but the fact that the wear process leads to the generation of debris inevitably means that there is always a possibility that it may change to abrasion.

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 contact surfaces[68]. It is a physical contact between two surfaces and one of them is significantly harder that the other, resulting in the loss of material by the passage of hard particles over a surface (see in Fig.1.9).
There is a relatively simple relationship between abrasive wear resistance and hardness, where for instance, pure metals show an almost linear relationship between wear resistance and hardness. Wear caused by hard particles is very similar and can be compared to that occurring during grinding materials[68, 69].

Corrosive wear is a general term relating to any form of wear dependent on a chemical or corrosive process. The fundamental cause of this form of wear is a chemical reaction between the worn material and a corroding medium which can be a chemical reagent, reactive lubricant or even air[68, 69].

### 1.3.1. Tribological contacts in wear

Materials degradation by wear can occur in different tribological contacts as shown in Fig.1.10. They can be reciprocating sliding, fretting, rolling and impingement[70].

<table>
<thead>
<tr>
<th>Contact mode</th>
<th>Schematic presentation</th>
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<tbody>
<tr>
<td>Sliding</td>
<td>Two body</td>
</tr>
<tr>
<td>- Unidirectional</td>
<td></td>
</tr>
<tr>
<td>- Reciprocating</td>
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<tr>
<td>Fretting</td>
<td>Two body</td>
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<tr>
<td>Rolling</td>
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<td>Inpingement</td>
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Fig. 1.10: Schematic representation of the different types of tribological contacts [70].
Influence of pH and corrosion inhibitors on the tribocorrosion behaviour of titanium in different tribological geometries

Reciprocating sliding occurs when two surfaces are in contact and experience an oscillatory reciprocating motion with high amplitude when compared with fretting. As a result in the contact region the surface is damaged. The motion can be in one direction (unidirectional) or reciprocating[70, 71, 72, 73, 74, 75, 76, 77].

Fretting which was explained before is considered to be a small amplitude oscillatory motion. In both geometries of contact (fretting and reciprocating sliding), the contact between the surfaces may be two or three body (third body particles formed as a result of rubbing), and as a result it can occur the initiation of cracks by cyclic stresses.

Rolling occurs when a cylindrical or spherical object rolls across a smooth surface of sufficient hardness to support it. It is generally observed that there is only a small amount of friction to oppose the rolling motion. It generally occurs in many vital mechanical components such as roller or ball bearings, railway wheels and rubber tyres[69].

Impingement, usually occurs as a result of impact of particles with a materials surface. It is a result of combined mechanical and chemical attack of the material. An example is the erosion corrosion of pumps[70].

1.3.1.1. Fretting versus reciprocating sliding wear

Studies related with fretting led to the determination of several regimes of displacement accommodation characterized by different shapes of tangential force ($F_T$) vs. displacement ($D$) cycle, which are related with different wear processes[71, 72, 74, 78, 79, 80].

When two bodies are in contact, under imposed fretting conditions, an effective relative motion between the two surfaces occurs, consequently friction occurs and a tangential force ($F_T$) may be measured[80, 81, 82, 83]. A direct plotting of the tangential force evolution versus displacement ($D$) can be performed. The three different fretting regimes can be observed in Fig.1.11.
The first regime is considered to be the elastic regime in Fig. 1.11 (a). It is a closed cycle where it is not observed wear and no dissipation of energy. This linear relation results in very little surface damage, where there is no indication of interfacial sliding at the interface[80, 81, 82, 83].

The second regime is characterized to be slightly open and thus called elliptic. It characterizes the partial slip fretting condition, one part of the surface slips whereas the other sticks Fig. 1.11 (b). The relation between the tangential load and the displacement seems to be not longer linear, a hysteresis loop occurs corresponding to a transition of elastic to plastic shear. Generally this wear process corresponds to failure by crack initiation and propagation[80, 81, 82, 83].

The last regime is considered to be a gross slip, characterized by a parallelogram cycle as shown Fig.1.11(c). In this regime the entire surface slips and it corresponds to a gross slip condition and abrasive wear, it is a dissipative mechanism[80, 81, 82, 83].

The overriding difference between fretting and other sliding wear processes lies in the small reciprocating nature of the motion. A correlation between sliding condition in fretting and damage evolution can be regarded in Fig.1.12.
Influence of pH and corrosion inhibitors on the tribocorrosion behaviour of titanium in different tribological geometries

By applying a normal load and maintaining sliding conditions, it has been showed that crack occurs in partial slip regime and wear is observed for larger amplitudes in gross slip conditions. The damage tends to be of a localized form and any debris which are generated has some difficulty in escaping from the rubbing zone. The oscillatory character of the movement introduces a strong fatigue element into the wear pattern and the reversed shearing of localized material inevitably gives rise to fine surface cracks which may initiate a low stress fatigue failure[84].

In fretting conditions, wear occurs by several mechanisms, such as adhesive, abrasive, oxidative, fatigue wear, in which two or more mechanisms may act simultaneously. In reciprocating sliding conditions the wear mechanisms seems to be simpler. One main characteristic of this system is that wear volumes for different amplitudes are kept constant for identical sliding distance and reciprocating movements[85].

The regimes of wear which are dependant of the amplitude of reciprocating sliding can be observed in Fig.1.13.
1.3.2. Wear in dental implants

Although reports show high success rates of dental implants, cases of failure, sometimes as a result of wear, are still unavoidable[1, 71]. The different kinds of wear that can be found in dental implants will be presented in detail.

The wear of human teeth, at different ages was evaluated by Zeng et al.[87]. It was found that wear can be in form of erosion and/or abrasion, and it is accompanied by delamination and ploughing mechanisms changes according to the age of the teeth. A better wear resistance was found in permanent teeth in young and middle aged in comparison to permanent teeth at older ages[87]. It is possible to suppose that in dental implants wear by abrasion and by erosion may also occur.

Nowadays there already exist methods to quantify wear of materials used in dental implants applications[88]. In this application the correct choice of biomaterials is
of extremely importance, because after the insertion on the oral cavity, it will occur the contact of an artificial tooth (dental implant) with an opposing natural tooth. If we have a hard material in contact with a natural tooth, a severe wear will happen as a result of the contact between them.

There are combined forces that act on the mouth as a result of the mastication process which depends on the location of teeth [89]. The most common forces in dental implants are the compressive (V) as a result of chewing. These forces produce a lateral force (H) component that will cause a bending moment that is related to specific distances as Fig. 1.14. can show, these moments have also a large action on bone[89].

![Fig. 1.14: Lateral forces produced from a compressive force on an oblique plane][89].

These lateral forces can also be a result of motions during mastication but can also be due to teeth grinding (bruxism). This disorder has increased in recent years, and it is considered to be a cause of wear of teeth[90]. The action of a lateral force on the crown of the implant will lead to a torsional force. The loading of dental implants can be visualized as repeated cycles of different magnitude and combination of different forces (compressive, bending and torsional) which can lead to the wear of biomaterials[90-93].

Wear by fatigue is considered to be one of the causes of failure of dental implants. Fracture of the screw by fatigue as a result of biomechanical and physiological processes also occurs. Furthermore screws are considered to be possible locations, where concentration of stresses occurs inducing the initiation of fatigue failure. The loosing of the screw can also be a result of cyclic loads that enhanced the alternating contact and separation between the screw head base and the crown[92]. Juneseok et al.
studied the mechanism of screw loosening in simulated mastication. The main mechanism responsible for the screw loss was the torque\cite{93}.

*Scot A. Hoyer et al.*\cite{94} studied the fatigue life of dental implant/abutment interface with different diameters. Results shows that the adjustment of the interface decreased the life time of the abutment screw joint\cite{94}.

The fracture of the implant can also occur as a result of physiological loads. Some studies reveal that implant overload may lead to implant failure. It can occur due to pathologic overloads; as a result, stress and strain exceeded the physiologic tolerance of the bone, causing micro-fractures at the bone-implant interface. Overloading can also occur by repeating single loads causing micro-fractures within the bone tissue, and continuous applications of low loads may lead to fatigue failure\cite{95}.

A different origin of wear in dental implants can be observed due to the use of oral hygiene products, such as toothpastes. In order to maintain oral hygiene, natural and artificial teeth are subjected to toothbrush abrasion using toothpastes containing abrasive materials, such as SiO$_2$ or CaHPO$_4$.2H$_2$O in order to clean and remove dental plaque, pellicle and food debris. In general brushing forces varies from person to person, and their effect may mechanically degrade the dental device, by abrading through an extended period. It is important to point out, that the action of the personal hygiene has a strong influence on the superficial state of the dental device, which may lead to a formation of grooves. Some researches use toothbrush machines in order to study body abrasion of natural and restorative materials\cite{96, 97}. The effect of toothbrushing on titanium surfaces was studied by A. Hossain et al. It is clear that the toothbrushing of titanium alters surface morphology and composition; depending on the content of abrasive agents. It seems that dentifrices with lower contents of abrasive agents are advisable for patients with titanium implantable devices\cite{96}.

It may be said therefore that dental implant wear as a result of mechanical action results on a reduction of the efficiency of mastication, and also oral disorders.
### 1.3.3. Wear of titanium

The wear of dental materials such as titanium are of extremely importance, because excessive wear may lead to clinical complications as a result of incorporation of worn material into body cells or tissues[90].

*In vivo* wear measurements are difficult; however wear testing simulating machines have been developed to study the wear behaviour of materials[88, 89]. For dental implant applications, simulating wear machines should have into consideration the force profile, contact time, sliding movement, and the clearance of the worn material. However, in the studies already performed, there was no concern about these wear parameters[90].

Over the past 50 years, investigations have been performed on the tribological performance of restorative materials, such as composite, amalgam, ceramic and also metallic[87, 98]. In this chapter the tribological performance of titanium will be reviewed in detail.

Although titanium presents excellent properties such as good mechanical properties, biocompatibility, resistance to corrosion, in relation to wear it presents poor wear resistance which limits its application[17, 18]. Recent studies have shown that the wear resistance of titanium depends on its structure, surface topography, oxide thickness and tribological parameters used during testing.

The wear resistance of pure titanium and titanium castings used in dental prostheses was evaluated by *D. Tijima et al.*[99]. Titanium grade 2, 3 and Ti6Al7Nb was subjected to a simulated wear test; the wear resistance of the materials was evaluated by weight loss measurements. Results show that the weight loss of Ti6Al7Nb alloy was lower than that titanium grade 2 and 3[99].

*M. Niinomi et al.*[100] studied the corrosion wear fracture of new β-titanium alloys in Ringers solution. For that a pin-on-disk tribometer was used. The wear
characteristics were evaluated by weight loss and by the width of the groove of each specific specimen. At the end, the weight loss and the width of the groove of the alloys was when lowered compared with titanium alloys for biomedical applications such as Ti6Al4V and Ti6Al7Nb[100].

Also M.A.Khan et al., use a sliding wear test machine to study the wear behaviour of titanium and titanium alloys (Ti6Al4V, Ti8Al1Mo1V, Ti15Mo, Ti6Al7Nb, Ti3Al2.5V and Ti13Nb13Zr) in both corrosive and non corrosive environments. Results shows that Ti6Al4V presents the best combination of corrosion-wear behaviour, although pure titanium, Ti13Nb13Zr and Ti15Mo exhibit also good corrosion resistance[101].

1.4. Tribocorrosion

Tribocorrosion is considered to be an irreversible transformation of a material which results from the simultaneous action of chemical, mechanical (wear) and electrochemical (corrosion) surface interactions presented in a tribological contact[70, 71, 102, 103, 104, 105]. A tribocorrosion system includes a variety of mechanical and chemical degradation phenomena such as corrosive wear, wear accelerated corrosion, oxidative wear, fretting corrosion and impingement attack[70].

1.4.1. Mechanistic interpretation of synergy effects in tribocorrosion

The corrosion and wear processes that act on a tribocorrosion system are controlled by the properties of the oxide layer formed on the titanium surface and the interaction of the oral environment with the surface.

The role of the passive film on the mechanical degradation of metals in an aqueous environment is not very well understood[70, 105, 106]. Some theoretical models have already been developed to describe the passive film growth[70, 105, 106, 107]. A theoretical model was developed taking into account that the degradation process is proceeded by successive stages of build-up and removal of the passive oxide film[70, 105]. The kinetics of film formation and the ohmic effect was evaluated by
Influence of pH and corrosion inhibitors on the tribocorrosion behaviour of titanium in different tribological geometries

Jemmely et al.[105]: the proposed model allows the calculation of the current transients measured in electrochemical reciprocating motion. In recent years the scratch test has been used to study the repassivation mechanism of passive metals [108].

Sliding a hard material, such as alumina (in a way to simulate the crown) against a passive metal such as titanium (to simulate the metallic component of the dental implant), may increase the corrosion rate of the latter by two mechanisms[103]. At the beginning of rubbing disruption of the passive film that protects titanium against corrosion may occur, exposing the bare metal to the aggressive body fluids, as we can see in Fig.1.15.

![Tribocorrosion model, pin in contact with titanium substrate and scratching the passive film](image)

**Fig. 1.15** Tribocorrosion model, pin in contact with titanium substrate and scratching the passive film[109].

As the pin moves on, the metal reforms the passive film increasing, at the same time, the internal energy of the metal due to severe plastic deformation. This action will interfere with the electrochemical behaviour of the metal[70, 105, 108]. A consequence of this local destruction of the passive film is the formation of submicrometric debris (third body particles) from titanium which may be released, as shown in Fig.1.16.
Fig. 1.16 Schematic illustration of a tribocorrosion contact involving a ductile metal sliding against a hard inert counter piece[103].

The concept of third body particles was introduced by Godet to describe the velocity of accommodation in tribological contacts due to the presence of fluids or of particles or both. Their role is critical because they can act as an abrasive which accelerates wear, or as a solid lubricant which may decrease friction and wear[110].

Before leaving the contact region this debris may form a transfer film on alumina surface or can even be spread on the titanium surface. The effect of the third body particles depends on their physical properties but also on their number. The amount of third body particles depends on sliding conditions, their ability to be ejected, experimental design of the equipment, the geometry of contact and of the type of motion[70, 103].

In dental implants, the formation of these third body particles must be considered. In fact titanium debris is detected in tissues around the implant as a result of the repetitive destruction of the oxide film by wear. Like metallic ions, this debris can be very harmful to patients[25, 26].

To predict the rate of tribocorrosion it is necessary to understand the mutual contribution of wear and corrosion, and how they depend on the parameters of the tribocorrosion system. For that theoretical models were developed. Theoretical models took into account the electrochemical and mechanical effects developed to understand
the scientific knowledge of the tribocorrosion phenomenon[70, 105]. Mischler et al. [111] purpose a model for the description of the rate of wear accelerated corrosion taking into account the effect of normal load and the repassivation behaviour of the metal. A. Walters et al., for instance, take account the mechanical factors that act on the tribocorrosion system [112]. The interaction between corrosion and sliding wear of metals was presented a theoretical model proposed by J. Jiang et al.[113]. This model takes into account all the factors affecting corrosion and wear such as the environmental and the experimental ones. It seems to be an interesting model which provides information about wear map construction[113].

1.4.2. Wear quantification in tribocorrosion systems

The quantification of wear in rubbing contacts can be determined by the Archard wear criterion. Related models were also developed by Rabinowicz, Mulhearn and Samuels[73, 83].

The total wear volume in an electrochemical tribocorrosion experiment can be determined by measuring the worn material before and after an experiment, or by measuring the rate of descent of the pin during rubbing. It is considered to be the sum of two terms, the wear volume characterized by materials loss (due to electrochemical oxidation) and the mechanical wear volume[70, 103]. However it can be measured taking into account the dissipated energy.

In gross slip regimes, as it is possible to observe in Fig.1.17, the fretting cycles display a quadratic shape. Each fretting cycle is characterized by a tangential load-displacement; the continuous recording of these two parameters during the entire test will represent the dissipated energy[73].

Depending on the fretting regime that operates in the contact, a characteristic shape of the hysteresis loop is obtained. The dissipated energy during a test may be obtained by summing this fretting loop, for instance the area of the fretting loops corresponds to the dissipated energy during each specific cycle.
The wear of materials in sliding contacts can be a result of a dissipated energy due to friction between two bodies in contact. The dissipated energy in the contact generates surface damage and contact heating. The evolution of the mechanical contact response is monitored by acquiring force-displacement hysteresis loops at closely spaced time intervals during fretting tests.

This energy approach permits to obtain an intrinsic correlation between the single variable energy and one main parameter such as the normal force, the friction coefficient and the displacement[83]. The wear volume of materials based on the concept of energy dissipation can be a tool to gain information about possible changes in wear damage.

The calculation of the dissipated energy in different tribological contacts has already been performed. M.Z. Huq et al.[114] developed a research based on the expression of wear rate based on dissipated energy in sliding contacts. They suggested a method to correlate the volumetric wear loss with the dissipated energy for unidirectional and bidirectional ball-on-flat configuration[114].

In Fig.1.18, the way in which the dissipated energy interferes in wear process is illustrated.
Integrating all the degradation through the wear volume measurements results in a linear relationship with total dissipated energy. It is possible to predict the volumetric wear per unit area from the dissipated energy versus wear loss diagram[83, 114]. Most of the dissipated energy is consumed in tribo-mechanical processes such as third body particles formation, heating, ejection of debris and plastic deformation of the material in contact[83]. A question arises in relation to the distribution of this energy in all process[74].

From the point of view of dental implant applications, the quantification of wear which is a result of two independent process (corrosion and wear), by means of dissipated energy, permit to obtain a idea how many cycles the implant will sustain. However it is important to stress, that this prediction for in vivo conditions is very different, because the types of forces change continuously (as a result of mastication), also the insertion of the implantable device is different for each patient (the reaction of the body might be different). In future advances of mechanical and electrochemical techniques it appears to be possible to predict the lifetime of the dental implant.
1.4.3. Equipment for study tribocorrosion

Different types of equipment have been developed to study the tribocorrosion behaviour of implantable materials[71, 75, 76]. Typically, in all cases they involve an antagonist material rubbing against a flat plate. It should be noticed that this antagonist might be a cylindrical pin, a truncated cone or a sphere (see Fig.1.19 (I, II, III)[70].

![Fig. 1.19 Experimental arrangement used in tribocorrosion studies][108]

In Fig.1.19(b) it is possible to see the configuration that was used in the tribocorrosion experiments carried out in this work. It is constituted by an alumina ball, which simulates the ceramic component of the dental implant (the crown) rubbing against a flat plate of titanium, which simulates the metallic component of the implant (the screw).

New equipment based on fretting-corrosion experiments was developed by S. Barril et al.[109] to test metallic implant materials used in dental implants. Micro-movements are very well defined by a rigid structure, an electrochemical cell is used and during all the tests the mechanical and electrochemical parameters are monitored. The apparatus developed allows in vitro experiments with mechanical and electrochemical control. Results confirm the good reproducibility of the measurements [109].
A new concept of simulating apparatus for fretting wear experiments was described by H. Mohrbacher et al.\cite{76} and their colleagues. The data acquisition system developed characterizes the mechanical contact response based on the measurements of contact displacement, tangential force and normal load. Experimental tests using hard coatings show the high performance and precision of the equipment\cite{76}.

### 1.4.3.1. Electrochemical techniques in tribocorrosion systems

The tribocorrosion mechanisms can be very well followed by electrochemical techniques\cite{103}. The immersion of a material in one electrolyte allows the in situ characterization of the surface state of the material and its evolution during sliding. The surface state can be determined by different electrochemical techniques such as, open circuit potential, polarization and impedance measurements (EIS)\cite{104}.

Open circuit potential (OCP) measurements gives information about the electrochemical state of a material, if it is on an active or passive state. Kinetics of the surface reactions are a kind of information limited for this technique\cite{104}. During a tribocorrosion test, OCP is an average value determined by factors as the ratio active-to-passive material in the wear track, the repassivation kinetics of the base material in the wear track, the contact frequency and load. Variation of the open circuit potential of materials in tribocorrosion systems can thus be correlated with variations in the surface of the material\cite{104}.

Potentiodynamic polarization tests are useful in tribocorrosion studies because they give information on changes in electrochemical reactions kinetics induced by sliding, and also the influence of surface reactions on sliding conditions in the contact region. Polarization tests can give detailed information about mechanical depassivation of worn surfaces, corrosive wear rates, and the mechanism of mechanical wear\cite{104}.

Electrochemical impedance spectroscopy is a technique for a detailed analysis of electrochemical reactions, mechanisms and kinetics. It gives information about the properties of the passive film, and allows the study of the intermediate species adsorbed on the materials surface. In tribocorrosion tests, EIS permit the determination of the electrochemical reactions and the interaction between friction and corrosion. However
as in polarization measurements, the interpretation of impedance measurements is difficult because of the heterogeneous state of the surface[104].

In the specific case of titanium, with electrochemical techniques it is possible to measure in real time the amount of titanium transformed into oxide or into dissolved ions, by using current measurements during the entire tribocorrosion test.

The electrochemical noise technique is a promising technique that was recently used to monitor the corrosion wear process[115, 116, 117]. The modes of measuring the potential and current may be by means of two identical working electrode, one working electrode coupled to a microelectrode or two identical working electrodes with a bias potential. Noise measurement works in free corrosion condition and does not apply any kind of perturbations to the electrochemical system[115]. It consists in the analysis of the spontaneous fluctuations of potential and current occurring in the electrodes in a corrosion-wear system, as we can see in Fig.1.20.

![Electrochemical noise measurements recorded before, during, and after a fretting test on SS 3M stainless steel orthodontic wire sliding against corundum ball in a Ringer’s solution[7].](image)

**Fig. 1.20:** Electrochemical noise measurements recorded before, during, and after a fretting test on SS 3M stainless steel orthodontic wire sliding against corundum ball in a Ringer’s solution[7].

Following the evolution of corrosion potential and current it is possible to denote the starting of rubbing (the open-circuit potential suddenly decreases to lower values, and an increases in current), with the disruption of the oxide film allowing the fresh active titanium surface to be exposed to the electrolyte.
Actually Faraday’s law has been used to provide a quantitative relation between the measured anodic charge and the amount of electrochemically oxidized metal [103, 70]. Landolt et al. [70] have made a critical review focusing on the use of electrochemical methods in tribocorrosion studies. Recent electrochemical impedance spectroscopy has been used by some researchers to monitorize the surface modification of passive films during corrosion-wear tests.

Some works have been done using electrochemical noise techniques applied to tribocorrosion systems [115, 116]. P. Quiang et al. [115] use the electrochemical noise technique on corrosion wear tests in sliding contacts with stainless steel. It appears that this technique has the capacity of identifying the process modification of materials that occurs during corrosion-wear tests [115].

1.4.4. Tribocorrosion in dental implants

It is widely recognized that wear and corrosion of metallic biomaterials is one of the most important aspects in implant surgery. In recent years, innovative work has been developed in biomaterials with specific cases of tribocorrosion, for example, in dental implants and hip-joint applications. In both cases the wear-corrosion is caused by fretting, reciprocating sliding and/or by micro-abrasion [71].

The joint degradation process caused by corrosion and wear (tribocorrosion) on titanium surfaces are clearly of great importance in the development of dental devices. As in other systems, the tribocorrosion of dental implants depends on a large number of parameters. As presented in Fig.1.21, they may be classified according to their relation with: materials, mechanical operational, solution and electrochemical.

Concerning materials, in a tribocorrosion system we may have the contact between two different surfaces, with different hardness, roughness, morphology and with a presence or not of an oxide film.
In the specific case of this study, we have the contact between the metallic component of the implant (the screw), which is simulated by titanium, and the abutment where the crown (a ceramic material) is attached. These materials will be in contact, and slides one against each other with a specific movement, amplitude, frequency, and load.

In dental implants, mastication will endorse the formation of cyclic micro-movements at the interface implant/bone or implant/abutment or even abutment/ceramic crown, as shown Fig.1.22. The type of movement may be fretting or reciprocating sliding, depending on the amplitude of micro-movements[1].
In saliva. Temperatures and mena[1, 29]. So it might be said that in the oral environment, dental implants are under mechanical and chemical solicitations, which do not act separately, and can degraded the implant until its failure. This mechanical and chemical conditions have the ability of affecting the electrochemical behaviour of the materials in contact[70, 103, 109]. Theoretical models with experiments under mechanical and electrochemical control have been already developed in a way to understand the contribution of all parameters that constitute and interfere on the tribocorrosion system.

Another tribocorrosion system which may occur in dentistry is the presence of an environment with micro-abrasive particles, as it happens, for instance, due to the presence of silica particles in toothpastes which can damage dentine. Also some movement may occur at the interface between the metallic component of the crown and ceramic, as show Fig.1.22 (b). So it is possible to conclude that mouth is thought to be a local with several examples of tribocorrosion systems which should be taken into account when considering the development of a new biomaterial.
1.4.5. Tribocorrosion studies in fretting conditions

The fretting wear rate is strongly dependent on the substrate materials and also on the corrosive environment which contact them. Great developments on testing, damage mechanisms, and modelling on fretting have been reported since 1911 (date of the first report on fretting)[81].

Fretting corrosion of titanium and its alloys has been studied in simulated body fluids, the synergism between wear and corrosion seems to increase metal degradation [119, 120, 121, 122]. Godet et al.[123] has been discussing fretting using the third-body concept. The influence of fretting regimes on the tribocorrosion behaviour of Ti6Al4V has been discussed by S. Barril et al.[122]. Results demonstrate that the electrochemical response of Ti6Al4V to tribocorrosion is affected by the prevailing fretting regime. Wear and increases of the anodic current just occurs in the presence of slip regime[122].

The fretting-fatigue damage was characterized for surface modified and unmodified medical titanium (PVD TiN coatings, plasma nitride and thermally oxidised Ti6Al4V and Ti6Al7Nb contact pairs) by A. Variraj et al[119]. Results are compared with uncoated alloys. The friction coefficient curves apparently explain the progression of the damage during fretting. In terms of fretting fatigue, PVD TiN pairs present the better results. Thermally oxidised samples exhibit early failures due to high oxide thickness[119].

The fretting of metallic materials for orthopaedic implants was evaluated in different environments by L. Duisabeau et al.[120]. The aim of the work was to study the damage mechanism at the head-neck contact of a total hip joint with Ti6Al4V and stainless steel as contact materials. The tests were performed in air and in artificial physiologic medium, results show that fretting regime, accumulate dissipated energy and corrosion are interdependent[120].

The tribocorrosion behaviour of c.p Ti, Ti6Al4V, Ti5Al2.5FE, Ti13Nb13Zr and Co28Cr6Mo in fretting contacts in Hank’s balanced salt solution was evaluated by A. Choubey et al.[121]. This work was carried out in order to understand the tribological behaviour of some metallic alloys. Results demonstrate that the lowest friction profile
was obtained for Ti5Al2.5Fe. The wear mechanisms present in all tribocorrosion tests were tribomechanical wear as a result of abrasion and cracking[121].

### 1.4.6. Tribocorrosion studies in reciprocating sliding conditions

In recent years there has been a general progress on the understanding of corrosion-wear mechanisms during reciprocating sliding in aqueous environments. It seems that the level of sliding wear in aqueous environments is a complex function of materials and the corrosive environment.

Recent work on sliding has concentrated on the corrosion contribution to total weight loss. *J.P. Celis et al*[124] has introduced the concept of active wear track in a way to explain the mechanisms of corrosion-wear of passive materials in sliding conditions. The wear track looses temporarily its passive film due to the mechanical action. By repassivation kinetics measurements using a potential pulse method and from anodic current measurements during sliding the evolution of the passive state may be investigated[124].

*Mischler et al.*[106] have developed work based on sliding wear in aqueous environment. The degradation of carbon steel sliding against alumina pin in borate solution (pH=8.4) was evaluated. It was found that the presence of a passive film influences the degradation mechanisms and lead to a increase in wear, by two degradation mechanisms: wear accelerated corrosion and mechanical surface degradation[106].

*A. Berradja et al.*[7] studied the dependence of the applied load, normal force and sliding velocity on the tribocorrosion behaviour of stainless steel applied to orthodontic archwires in ringer’s solution. In this study an electrochemical noise technique was used. Results show that sliding wear affects the repassivation behaviour of stainless steel AISI 304L and SS3M (tested materials), by increasing the anodic current in the wear track area[7].
The friction behaviour of titanium for orthopaedic applications was studied in a reciprocating sliding against hardened steel by M. Long[6]. Results show that friction behaviour depends on the cyclic count, sliding velocity, contact stress and alloy phase structure. The evolution of friction involves localized asperity deformation and fracture, surface ploughing with formation of wear debris and transfer between titanium and the counterpart as shown by surface observations. The extensive plastic deformation indicates that dynamic friction of titanium surface is controlled by its surface behaviour[6].

1.4.7. Tribocorrosion maps

In recent years, some efforts have been made to characterize tribocorrosion regimes. An important advance on the research of material degradation in specific environments is the application of the wear-corrosion map approach. Generally wear maps tend to express the mode of wear, wear mechanisms and regions of their dominance. These maps present the wear data in the form of graphics which provide information about material behaviour in different amplitude conditions[125].

The first wear map, which is considered to be a very simple diagram, was developed in Japan. In this diagram (sliding velocity vs. applied load) wear mechanisms were not described. Latter, in 1987 Lim and Ashby built a comprehensive wear map taking into count published wear data and providing mathematic basis for the transition regimes. This wear map was the basis for the development of wear maps for other materials such as steel, ceramics, composites and coatings[126]. The development of fretting maps has influenced the way wear processes were interpreted. As it was possible to observe before, in fretting wear various regimes may operate. Fretting maps were developed to describe interactions between the regimes (stick, slip and wear); to provide two dimensional representation of wear, but also to predict the evolution of fretting behaviour under combined conditions[81]. Vincent et al[126] have developed the fretting map based on two concepts, materials response and running conditions.

Fretting maps can be developed and constructed based on normal load and tangential forces as well as frequency and displacement amplitude. Z.R. Zhou and
Vincent have proposed separately two kinds of fretting maps, the running conditions fretting map (RCFM) and materials response fretting map (MRFM). Both fretting maps can be visualized in Fig.1.23 and 1.24. The fretting maps presented correlate the dynamic description of fretting loading with damage development[84].

![Fretting Map](image)

**Fig. 1.23:** Fretting map with a combination of fretting regimes (RCFM) [84].

These fretting maps present the different fretting regimes as a function of the normal force-displacement amplitude, and compare to a similar loading representation, the range of fretting damage evolution.

![Fretting Map](image)

**Fig. 1.24:** Fretting map with materials response (MRFM)[84].

These fretting maps have been used to analyse materials such as metals, polymers and composites, they present however a high difficulty. It is not possible to visualize the relative impact of each parameter involved on the phenomena[84].
In relation to sliding maps, some research has been developed by Jiang et al.[113] which provides information about the construction of a simple map based on mathematical models of wear-aqueous-corrosion in sliding contacts[113]. M.M. Stack[77] has also performed a study related to sliding-wear corrosion of steel in pin-on-disc equipment in carbonate/bicarbonate solution. In this work electrochemical techniques and microscopic techniques were used to evaluate the effect of velocity and load. Wear corrosion mechanisms were identified in wear-corrosion maps, where differences in tribocorrosion regimes were identified as function of velocity, electrochemical potential and applied load[77].

The advances on wear-corrosion mapping in the last years are remarkable, but there are still important areas to be covered in this approach. An important issue is the development of tribocorrosion maps, but it is important to point out that a large number of variables must be considered, and it might be difficult to combine these in specific groups.

1.5. References

Influence of pH and corrosion inhibitors on the tribocorrosion behaviour of titanium in different tribological geometries


Influence of pH and corrosion inhibitors on the tribocorrosion behaviour of titanium in different tribological geometries

Influence of pH and corrosion inhibitors on the tribocorrosion behaviour of titanium in different tribological geometries

[118] www.cicdental.net/servicios.html
Chapter 2
Summary

Chapter 1 consists of a brief overview of corrosion, wear and tribocorrosion behaviour of titanium applied in dental implants. The main aim of this chapter was to characterize the problems that may occur in dental implants when inserted in the human body.

Chapter 2 will be presented in the form of a paper already published in Wear, with the following theme:


It is important to point out, that the fretting corrosion experiments were performed in the Department of Metallurgy and Materials Engineering (MTM) Faculty of Engineering of Katholieke Universitait of Leuven in Belgium. The research work was performed in the group of Prof. Jean-Pierre Celis who acts as supervisor.

This work was developed with collaboration with Eng. Catarina Vieira, who studied the influence of corrosion inhibitors on the tribocorrosion behaviour of titanium. The influence of changes in pH on the tribocorrosion behaviour of titanium was focused by me.
Influence of pH and corrosion inhibitors on the tribocorrosion of titanium in artificial saliva

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Abstract

Dental implants are used to replace teeth lost due to decay, trauma, or periodontal diseases. Dental implants are most of the times subjected to micromovements at the implant/bone interface or implant/porcelain interface (due to the transmitted mastication loads) and chemical solicitations (oral environment). Such implant becomes part of a tribocorrosion system, which may undergo a complex degradation process that can lead to implant failure. In this work, the fretting–corrosion behaviour of titanium grade 2 in contact with artificial saliva was investigated under fretting test conditions. Citric acid was added to artificial saliva to investigate a pH variation on the tribocorrosion behaviour of the material. Additionally, three different inhibitors were added to investigate cathodic and anodic reactions on the electrochemical response. Also, the influence of inhibitors included in the formulation of tooth cleaning agents or medicines was investigated.

Degradation mechanisms were investigated by electrochemical noise technique that provided information on the evolution of corrosion potential and corrosion current during fretting tests. Depassivation and repassivation phenomena occurring during the tests were detected and discussed. Considering the influence of corrosion inhibitors, it was observed that the degree of protection varies with the nature of the inhibitors.

Keywords: Tribocorrosion; Dental implants; Titanium grade 2; Artificial saliva; Inhibitor
2.1. Introduction

In dentistry, metallic materials are used as implants in reconstructive oral surgery to replace a single tooth or an array of teeth, or in the fabrication of dental prosthesis such as metal plates for complete and partial dentures, crowns, and bridges, essentially in patients requiring hypoallergenic materials[1,2].

Due to its mechanical properties, good resistance to corrosion in biological fluids and very low toxicity, titanium is the most commonly material selected for dental implants and prosthesis[1–4]. Corrosion of metallic implants is of vital importance, because it can adversely affect the biocompatibility and mechanical integrity of implants [3–5]. The stability of titanium under corrosion conditions is essentially due to the formation of a stable and tightly adherent thin protective oxide layer on its surface[5–7]. The passive film stability depends on its structure and composition, which in turn are dependent on the conditions in which it was formed[5–7]. For instance pH is known to have a strong influence on the corrosion resistance of Ti and Ti alloys[8].

Ion release to the surroundings takes place when the dissolution of the surface passive film is accompanied by corrosion of the underlying base material. Extensive release of ions from implants can result in adverse biological reactions, and can lead to mechanical failure of the device [4–6]. It should be referred that an accumulation of Ti ions in tissues adjacent to implants has been reported in conditions not totally attributed to wear[6,9].

Despite their attractive corrosion and toxicological properties, titanium and titanium alloys generally exhibit poor fretting and wear resistance[4,10,11]. In fact, when used as implants or prosthesis, cyclic micro-movements at the implant/bone interface or implant/abutment interface may occur, inducing wear[1,4]. The low fretting and wear resistance of Ti and Ti alloys is attributed to the poor integrity of the TiO₂ surface passive layer, or to the plastic deformation of surface and subsurface layers [11]. Additionally, under sliding wear conditions Ti alloys have a strong tendency for transferring material to their counter faces, and tribochemical reactions at the contact surface are likely to occur[10]. Also, the release of wear debris may lead to cellular
damage, inducing inflammation or encapsulation of the implant by fibrous tissue[4]. These environmental alterations may also alter the corrosion behaviour of the material.

Therefore, Ti dental implants and prostheses exposed to the combined degradation by corrosion and fretting, constitute a tribocorrosion system. It should be stressed that the two mechanisms of degradation do not proceed separately, but depend on each other in a complex way. Normally corrosion is accelerated by wear and, similarly wear may be affected by corrosion phenomena[12,13]. In fact, wear may lead to local removal of the passive film resulting on the exposure of the metal surface to the aggressive environment. Consequently, the corrosion rate will increase (wear accelerated corrosion) leading to a rapid degradation of a contact. Eventually, corrosion products will accumulate in the mechanical contact region, influencing the wear regime[12,13].

Several recent studies have focused on the fretting–corrosion behaviour of Ti alloys. Barril et al. [14] investigated the effect of the displacement amplitude, normal force, and tribometer stiffness on the tribocorrosion behaviour of Ti6Al4V/Al2O3 pairs, in contact with a 0.9 wt % NaCl solution. They concluded that wear accelerated corrosion would only occur, if the amplitude of the displacement was enough for causing slip between the materials. They proposed a model describing the influence of mechanical parameters (normal force, elasticity, and speed) on the wear accelerated corrosion of materials. Duisabean [15], studied the tribocorrosion behaviour of Ti6Al4V/316L stainless steel pairs in a Ringer’s solution, under gross slip conditions. They concluded that the dissipated mechanical energy and fretting regimes are strongly affected by the presence of a corrosive lubricant, because of the electrochemical phenomena caused by the electrolyte. The effect of the electrochemical conditions on the tribocorrosion behaviour of Ti6Al4V/Al2O3 contacts was investigated by Barril et al.[13,16]. They observed that under gross slip conditions, friction and wear are critically dependent on the applied potential, affecting the thickness, composition, and stoichiometry of the passive film. They concluded that the degree of oxidation of the plastically deformed metallic material would influence the extent of wear.
In this work, the tribocorrosion of titanium grade 2, under fretting regime, in contact with artificial saliva solutions, is investigated. The influence of pH and corrosion inhibitors in the artificial solution are considered.

2.2. Experimental

Samples made of Ti grade 2 (all from the same sheet) were cut in size as 2.5 cm × 2.5 cm, and mechanically polished down to 0.25 μm. The initial sample roughness was $R_a = 0.03 \, \mu m \pm 0.004 \, \mu m$. All the samples were polished 1 day before the experiments in order to allow the formation of an oxide surface layer. After polishing they were ultrasonically cleaned with ethanol and distilled water and finally dried. The nominal chemical composition of Ti grade 2 was 0.25 wt % O, 0.03 wt % N, 0.08 wt % C, 0.015 wt % H, 0.3 wt % Fe, and residuals (0.4 wt %).

Fretting–corrosion behaviour was investigated using a triboelectrochemical approach, in which the electrochemical noise technique was used to monitor the fluctuations of corrosion potential and corrosion current during the fretting tests. Corundum balls (Ø 10 mm) were selected as counter body material (Ceratec, The Netherlands) because of high wear resistance, chemical inertness, and electrical insulating properties. Titanium grade 2 specimens used as working electrode (WE) were covered with an adhesive tape to leave an area of 1 cm$^2$ exposed to the test solutions. A Ag/AgCl reference electrode and a microelectrode consisting in a Pt electrode with a diameter of 0.25 mm and a tip length of 1.2 mm were used. The experimental set-up used for electrochemical noise measurements during corrosion–wear tests on immersed samples is schematically shown in Fig.2.1.

As described elsewhere[17], the configuration of the experimental set-up was optimised to improve accuracy and minimize external noise. A potentiostat (Solartron electrochemical interface model 1287) was used, which allows voltage and current measurements at a resolution of 1 μV and 1 pA, respectively. The microelectrode coupled to the working electrode was used to sense the current flowing between them. The counter body was lifted away from the WE at the end of fretting tests. The electrochemical noise data are reported according to ASTM conventions[18].

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Fig. 2.1: Schematic representation of the experimental set up used for the tribocorrosion experiments.

The bidirectional sliding (fretting) test equipment was described elsewhere[19]. The sliding conditions correspond to a fretting test performed at a normal load of 2N, an oscillating frequency of 1 Hz, and a linear displacement amplitude of 200 μm. These fretting tests were performed for 5000 and 10,000 cycles at an ambient temperature of 23 °C. The number of cycles, the tangential force, the normal force, the displacement amplitude, and the coefficient of friction were recorded at equally spaced time increments during the whole test duration.

The solutions used during the experiments were artificial saliva (AS), with different chemical compositions (Table 2.1).

Table 2.1: Chemical composition of the artificial saliva solutions used (wt %).

<table>
<thead>
<tr>
<th>Solution Compound</th>
<th>Artificial saliva (AS)</th>
<th>AS + citric acid</th>
<th>AS + anodic inhibitor</th>
<th>AS + cathodic inhibitor</th>
<th>AS + organic inhibitor</th>
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<tr>
<td>Sodium Chloride, NaCl</td>
<td>0.70</td>
<td>0.70</td>
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</tr>
<tr>
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<td>1.20</td>
<td>1.20</td>
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<tr>
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<tr>
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<tr>
<td>Calcium Carbonate, CaCO₃</td>
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<tr>
<td>Benzotriazole, C₆H₅N₃</td>
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<tr>
<td>pH</td>
<td>5.5</td>
<td>3.8</td>
<td>5.5</td>
<td>5.5</td>
<td>5.5</td>
</tr>
</tbody>
</table>
Citric acid was added in order to investigate the influence of a pH variation on the tribocorrosion behaviour of the contact. Three different kinds of inhibitors were added in order to investigate the action of the cathodic and anodic reactions on the electrochemical response. Also, it was found useful to analyze the influence of corrosion inhibitors, which may be included in the formulation of tooth cleaning agents or medicines.

After the tribocorrosion tests, the samples were ultrasonically cleaned with ethanol and distilled water during 10 min. The wear scars were investigated by reflected light microscopy with Nomarski contrast, laser profilometry (Rodenstock RM 600), and SEM-EDX (Philips XL 30 ESEM FEG). The wear volume was determined by a profilometric method as described earlier[19].

2.3. Results and discussion

2.3.1. Tribological measurements

The evolution of the mechanical contact behaviour was investigated by acquiring force–displacement hysteresis loops at certain time intervals during the fretting tests. For tests performed during 5000 fretting cycles, loops at 20, 1000, and 5000 cycles were obtained. As these tests were performed at a frequency of 1 Hz, the number of cycles corresponds to the testing time in seconds. Moreover, during tests performed for 10,000 fretting cycles tests, the loop at 10,000 fretting cycles was also recorded.

In Fig.2.2 representative fretting log diagrams (AS and AS + citric acid) are presented. The shape of the tangential force–displacement ($F_t$–$D$) cycles is, in all cases, a parallelogram, indicating that the accommodation of displacement occurs under a gross-slip regime[15,19,20].
Fig. 2.2: Fretting logs recorded during tests conducted for 10,000 cycles in (a) AS and (b) AS + citric acid solution. Fretting test parameters: 2N, 1 Hz, 200 μm, and 10,000 cycles.

In fact, under the imposed fretting conditions, the elastic deformation of the material and the stiffness of the apparatus do not accommodate the imposed displacement, and an effective relative motion between the two contacting materials takes place. Consequently, friction occurs between the two materials, resulting in a measurable tangential force. $F_t$ increases during the test, and reaches a steady state after 5000 cycles. This behaviour was observed under all test conditions.

In Fig.2.3 the average coefficient of friction monitored in the AS and artificial saliva plus organic inhibitor (AS + organic) is presented.

Fig. 2.3: Evolution of the average coefficient of friction during fretting tests performed for 10,000 fretting cycles in AS and AS + organic inhibitor solutions. Fretting test parameters: 2N, 1 Hz, 200 μm, and 10,000 cycles.
In the other solutions, the evolution of the coefficient of friction with fretting cycles is similar to the one noticed in the AS solution. In the AS solution three regions can be identified during the fretting tests. A first region extends up to ca. 2000 cycles where an increase of the coefficient of friction is observed. This region corresponds to the running-in period in which an adjustment of the two contacting surfaces occurs by crushing and smearing of the asperities [14]. A second region expands up to ca. 6000 cycles, during which the coefficient of friction remains fairly stable. Finally, after ca. 7000 cycles, a monotonic decrease of the coefficient of friction is observed.

The coefficient of friction exhibits strong oscillations during the fretting test. After the running-in period, these oscillations may be attributed to the build-up and accumulation of third-body particles in the contact region. After the accommodation of the two surfaces debris are ejected out of the contact as rubbing keeps on [13].

Micrographs of the wear scars of Ti samples are presented in Fig.2.4. No significant differences were observed between samples tested in the different solutions. Under the imposed wear test conditions, two regions can be identified in the wear track. The central part is characterized by a relative severe material damage and the presence of wear debris. The surrounding external part of the wear scar is smooth and exhibits some material smearing [21].
Fig. 2.4: Micrographs of (a) the wear scar, and (b) of the interior of the scar: (1) AS; (2) AS + organic inhibitor; (3) AS + citric acid. Fretting test parameters used were: 2N, 1 Hz, 200 $\mu$m, and 5000 fretting cycles.

The wear scar is characterized by sliding wear marks aligned in the fretting direction. The central area of the wear scar reveals scales, most probably formed by an extensive plastic surface shear. These scales are likely to delaminate and detach from the surface, inducing the oscillations in $F_t$. Additionally, it is expected that during fretting under gross slip regime and oxidizing conditions, cracking, and delamination of wear particles will be accelerated by their oxidation[13,16].

As shown in Fig.2.2, the real displacement is inferior to the imposed displacement 200 $\mu$m, because a part of the displacement was accommodated by the elastic deformation of the fretting contact and the limited stiffness of the test equipment[20]. The area ($A$) in the fretting logs shown in Fig.2.2 can be expressed as[15]:

...
Influence of pH and corrosion inhibitors on the tribocorrosion behaviour of titanium in different tribological geometries

\[ A = \int F_t(D) \, ds \]

with \( F_t \) the tangential force and \( D \) is the displacement. Thus, area \( A \) represents the dissipated friction energy in the contact during each fretting cycle\[16,17\]. In Fig.2.5 (a) the evolution of the dissipated energy as a function of the number of friction cycles is presented. In all test solutions, the dissipated energy increases with fretting duration. In the artificial saliva with organic inhibitor (AS + organic) the dissipated energy is substantially higher than in the other solutions, attending a value of ca. 6.7 J, after 10,000 cycles due to the higher coefficient of friction (Fig.2.2). Also, as observed in Fig.2.5 (a), the dissipated energy tends to reach a steady state as the number of fretting cycle’s increases.

![Graph of dissipated energy vs fretting cycles](image)

**Fig. 2.5:** (a) Evolution of the contact dissipated energy with testing time; (b)
evolution of the wear volume as a function of contact dissipated energy. Fretting test parameters used were: 2N, 1 Hz, 200 μm, and 10,000 cycles.

The evolution of the wear volume, calculated from profilometric measurements after 5000 and 10,000 cycles, is plotted in Fig.2.5 (b) as a function of the dissipated energy. These wear volumes account for the material removed from the contact region both by wear and corrosion. When the fretting contact is under gross slip regime, a linear relation between the wear volume and the cumulated dissipated energy is commonly observed[15,16]. In Fig.2.5 (b) the existence of a linear relationship is assumed. The slope of the wear volume/dissipated energy curves expresses the wear rate per unit of dissipated energy. Some differences are observed among the different solutions although these distinctions are dependent on the extent of the fretting tests. Regarding the test performed during 5000 cycles, it can be observed that the Ti sample tested in the AS + organic solution suffers a lower weight volume loss that is ca. 2 times lower than that the one noticed in the AS + cathodic inhibitor solution. However, after 10,000 fretting cycles, Ti has a lower wear volume loss in the AS + citric acid solution, indicating that some protection is provided by the addition of citric acid to the solution.

Regarding the wear rate per unit of dissipated energy, values between $7.2 \times 10^4$ and $7.8 \times 10^4 \, \mu m^3 \, J^{-1}$ have been reported in the literature for the Ti6Al4V alloy in contact with saline solutions[15,16]. However, such data for pure titanium are not yet available in literature. In this work, depending on the nature of the solution, values between $8.9 \times 10^3$ and $8.6 \times 10^4 \, \mu m^3 \, J^{-1}$ were derived. The nature of the solution appears to influence this behaviour. The AS + cathodic inhibitor and AS + anodic inhibitor solutions induce a higher wear rate of Ti per unit of dissipated energy than the other solutions. No significant differences in this behaviour were observed between the AS and the AS + citric acid solutions, while a rather slow evolution of the wear volume loss with dissipated energy was observed in the AS + anodic solution.

### 2.3.2. Electrochemical measurements

The evolution of the corrosion potential with fretting testing time is shown in Fig.2.6. Before the start of the fretting tests, the test samples were immersed in the different electrolytes to reach stabilization. Once stabilization was achieved, fretting
tests were started. A significant drop in potential is observed immediately after the start of the mechanical action, indicating the destruction of the passive film (depassivation), and the exposure of fresh active titanium to the test solutions[12–17].

**Fig. 2.6:** Evolution of open-circuit potential: (a) AS and AS + organic inhibitor solutions; (b) AS + citric acid and AS + anodic and cathodic inhibitor solutions. Fretting test parameters: 2N, 1 Hz, 200 μm, and 10,000 cycles.

The evolution of the corrosion potential at the start of the fretting test is shown in Fig.2.7.
Fig. 2.7: Evolution of open-circuit potential values during the running-in of the fretting tests: (a) AS and AS + organic inhibitor solutions; (b) AS + citric acid and AS + anodic and cathodic inhibitor solutions. Fretting test parameters: 2N, 1 Hz, 200 μm, and 10,000 cycles.

In the AS (Fig.2.7 (a)), AS + citric acid and AS + anodic inhibitor (Fig.2.7 (b)), the potential reaches very low values within a short period of ca. 100 s, before it evolves to more noble values. Concerning the behaviour of Ti in the AS + organic inhibitor (Fig. 2.7 (a)) and in the AS + cathodic inhibitor (Fig.2.7 (b)) solutions, it can be observed that the drop in potential is significantly lower attending, after some time, a steady state value that remains almost unchanged during the remaining fretting test cycles (Fig.2.6 (a) and (b)).
In all the other solutions, an abrupt increase in potential occurs after the first stage. Then, the corrosion potential slowly evolves to more noble values, indicating a decrease in corrosion susceptibility as the fretting tests go on. As shown in Fig.2.4, this behaviour may be attributed to the build-up of a tribolayer in the contact region that creates a barrier between the Ti surface and the test solution. As observed in Fig.2.6 (a) and (b), the slow increase in potential is sometimes interrupted by abrupt potential drop events, probably due to the sudden partial delamination of the tribolayers. The sample tested in the AS + citric acid solution is the one exhibiting the highest electrochemical potential before, at the beginning, during, and after the fretting test (see Figs.2.6 (b) and 2.7 (b)).

A representative evolution of the coefficient of friction and of the corrosion potential as a function of the fretting time is plotted in Fig.2.8 for Ti in AS + anodic solution. The potential drop events are accompanied by a sudden decrease of the coefficient of friction. As explained above, the delamination of the tribolayers formed in the contact region may explain this behaviour.

**Fig. 2.8:** Evolution of the open-circuit potential and of the coefficient of friction during the fretting test. AS + anodic inhibitor. Fretting test parameters: 2N, 1 Hz, 200 μm, and 10,000 cycles.

Remarkable is the evolution of the corrosion potential towards higher potential values, observed after ca. 7000 cycles in the AS solution and in the AS + citric acid or + anodic inhibitor (Fig.2.6). As shown in Fig.2.8, this variation in potential is accompanied by a decrease of the coefficient of friction. This new regime might be attributed to the stabilization of the three body contact area, after 7000 cycles. In other
words, as the mechanical action proceeds in the contact area, wear debris become smeared out and entrapped into the surface. Consequently, a delamination of the tribolayers at the contact area becomes less probable, and the formed mechanical mixed layer acts as a protective film both in terms of wear and corrosion.

Finally, it should be noticed that at the end of the fretting test, the corrosion potential recovers its original value of before the test or becomes even slightly higher. This behaviour indicates that the newly formed passive film, after a total removal of the naturally formed passive film by the fretting action, together with the mechanical mixed layer has quite similar characteristics as the naturally formed film present on titanium before mechanical loading. The exception to this behaviour are the Ti samples tested in the AS + cathodic inhibitor and AS + organic inhibitor, in which such a recovery of the corrosion potential is not observed after the fretting tests. These solutions by inhibiting the cathodic reaction(s), probably hinder the formation of a new passive film on the surface of worn Ti.

The evolution of the corrosion current monitored by the electrochemical noise technique during the fretting tests is presented in Figs. 2.9–2.13. The behaviour of Ti in the AS, AS + citric acid, and AS + anodic inhibitor solutions (Figs. 2.9–2.11) differs from that observed in the AS + cathodic inhibitor and AS + organic inhibitor solutions (Figs. 2.12 and 2.13).

![Fig. 2.9](image.png)

Fig. 2.9: Evolution of the corrosion current during the fretting tests in AS solution.

Fretting test parameters: 2N, 1 Hz, 200 μm, and 10,000 cycles.
Nevertheless, as it can be observed, in all samples the depassivation of the materials during the initial stage of fretting is accompanied by a sudden increase in corrosion current density. This increase is much higher in the AS + cathodic inhibitor and AS + organic inhibitor solutions than in the other solutions (see current scale in the graphs), indicating that these solutions have a much stronger corrosive action on fresh (depassivated) titanium surfaces than the other ones. In fact, the presence of organic and cathodic inhibitors, at concentrations used in this work, significantly affects the corrosion rate of titanium.

Fig. 2.10: Evolution of the corrosion current during the fretting tests in AS + citric acid. Fretting test parameters: 2N, 1 Hz, 200 μm, and 10,000 cycles.

Fig. 2.11: Evolution of the corrosion current during the fretting tests in AS + anodic inhibitor. Fretting test parameters: 2N, 1 Hz, 200 μm, and 10,000 cycles.
Actually, as shown in Figs. 2.12 and 2.13, the corrosion current monitored during the fretting tests on samples immersed in these solutions, is much higher than the one found in other solutions.

**Fig. 2.12:** Evolution of the corrosion current during the fretting tests in AS + cathodic inhibitor. Fretting test parameters: 2N, 1 Hz, 200 μm, and 10,000 cycles.

Also, after the first increase in current, arising from the removal of the passive film in the contact region when sliding starts, no significant variation in the corrosion current is observed during the fretting tests. Nevertheless, the organic inhibitor seems to be somewhat more effective based on the corrosion current results. That is in accordance with the slightly lower wear volume loss noticed on Ti in this solution (Fig. 2.13).
Influence of pH and corrosion inhibitors on the tribocorrosion behaviour of titanium in different tribological geometries

2.5 (b)), in comparison with the AS + cathodic inhibitor solution, notwithstanding the higher coefficient of friction (Fig.2.3).

In all the other samples (Figs.2.9–2.11), after the initial increase in corrosion rate caused by the destruction of the passive film, the corrosion current monotonically decreases during the fretting test. Again, as the corrosion potential evolution revealed (Fig. 6 (a) and (b)), some current peaks are observed, which are in good agreement with the oscillation in the coefficient of friction, as appears from Fig.2.14. The delamination of the tribolayers formed at the contact surface, by exposing or facilitating the access of the solution to the metallic Ti, may explain this behaviour.

![Graph: Evolution of the corrosion current and of the coefficient of friction during the fretting tests in AS + anodic inhibitor. Fretting test parameters: 2N, 1 Hz, 200 μm, and 10,000 cycles.](image)

**Fig. 2.14:** Evolution of the corrosion current and of the coefficient of friction during the fretting tests in AS + anodic inhibitor. Fretting test parameters: 2N, 1 Hz, 200 μm, and 10,000 cycles.

A decrease in the corrosion current is observed after ca. 7000 cycles, in the AS, AS + citric acid, and AS + anodic inhibitor solutions indicating the formation of a third-body protective layer in the contact region, as already referred. However, the decrease in corrosion current is more pronounced in the AS + citric acid and AS + anodic inhibitor solutions, indicating that these additives provide some protection to titanium. The slightly lower wear volume loss of Ti in these solutions, in comparison to the AS solution (Fig.2.5 (b)), may be attributed to the corrosion protection afforded by the presence of the citric acid or the anodic inhibitor.
In other words, the wear and corrosion behaviour of Ti is influenced by the oxidation and reduction reactions occurring in the contact area during fretting, depending on the chemical composition of the test solutions.

2.4. Conclusions

In this work, the influence of pH and corrosion inhibitors in artificial saliva on the tribocorrosion behaviour of pure Ti under fretting was investigated.

The addition of citric acid or anodic inhibitor to artificial saliva results in a slight improvement of the tribocorrosion behaviour of Ti. No significant differences were observed in the wear rate per dissipated energy, but a lower wear volume loss was obtained that can be attributed to the slightly lower corrosion rate observed in these solutions during the fretting tests.

The protection noticed by the addition of citric acid or an anodic inhibitor to artificial saliva is probably due to the nature of the oxidation and reduction reactions occurring in the contact area during fretting. Tribolayers are formed in the contact region during the tribocorrosion test. These tribolayers become more stable after ca. 7000 cycles in solutions containing citric acid or anodic inhibitor, as revealed by a lower coefficient of friction and a lower corrosion current.

The addition of a cathodic or an organic inhibitor to artificial saliva at concentrations tested in this work has a hazardous effect on the fretting–corrosion behaviour of titanium. Both an increase in the wear volume loss per unit-dissipated energy and a significant higher corrosion rate during fretting tests, were observed in these solutions.

2.5 References

Influence of pH and corrosion inhibitors on the tribocorrosion behaviour of titanium in different tribological geometries

Chapter 3
Summary

In chapter 2, the influence of pH and corrosion inhibitors on the tribocorrosion behaviour of titanium in artificial saliva solutions in fretting contacts was studied.

Chapter 3 will be related with the influence of changes in pH and the presence of corrosion inhibitors on the tribocorrosion behaviour of titanium in artificial saliva solutions in a different contact geometry: reciprocating sliding. This chapter will be presented in the form of a paper which will be submitted for publication in Wear with the following title:

- Reciprocating sliding – corrosion behaviour of titanium in artificial saliva solutions in presence of corrosion inhibitors and variations of pH

It is important to remark that the experimental work was developed at the Research Centre in Interfaces and Surface Performance (CIICS) of the University of Minho. The scientific activity of the Research Centre is concentrated on the development of interfaces/interphases and surfaces with superior wear and/or corrosion resistance. Also, special attention is given to the understanding of the mechanisms of interaction between wear and corrosion (tribocorrosion) with the aim of optimizing the performance of the materials in which interfaces were created or surfaces were modified.
Reciprocating sliding - corrosion behaviour of titanium in artificial saliva solutions in presence of corrosion inhibitors and variations of pH

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Abstract

The failure of the metallic part or of the metal/ceramic interface existing in dental restorations (crowns or bridges), is still relatively frequent. Most of the failures result from the simultaneous action of mechanical action (wear, fretting and/or fatigue, as a result of mastication) and chemical solicitations (due to the contact with saliva and/or other organic species). As a consequence, such materials becomes part of a tribocorrosion system.

In this work the tribocorrosion behaviour of titanium in reciprocating sliding conditions, in contact with artificial saliva (AS) solutions was studied. Some additives were added to artificial saliva in order to understand how variations in pH and how the action of corrosion inhibitors influence the tribocorrosion behaviour of titanium. During the reciprocating sliding tests, the degradation mechanisms were evaluated by electrochemical techniques.

Results demonstrate that in reciprocating sliding the AS + citric acid shows an $E_{corr}$ significantly higher than that observed in the other solutions. However after sliding, the amount of material removed from the Ti is higher, which is due to a high $i_{corr}$. In view of the addition of corrosion inhibitors to the artificial saliva solution, they do not have any beneficial effect on the tribocorrosion behaviour of the titanium.

Keywords: Tribocorrosion; Commercial pure titanium; Dental implants; Artificial saliva; Corrosion inhibitors.
3.1. Introduction

The general term that can describe the synergism due to the combined action of corrosion and wear is tribocorrosion. This phenomenon is defined as the mechanical and chemical or electrochemical interactions that can cause degradation of materials in relative displacement[1-4]. This mutual action occurs in a diversity of biomaterial components such as dental implants and also in other orthodontic or orthopaedic devices[5].

Concerning dental implant applications, in the oral environment, they are subjected to mechanical solicitations as a result of mastication. This mechanical solicitation may lead to cyclic micro-movements at the implant/bone or implant/abutment or even at the abutment/ceramic crown interface. These micro-movements are very well simulated by fretting motions which are characterized by the contact between two surfaces in a small amplitude oscillatory motion. However reciprocating sliding movements (higher amplitude of motion) may be considered to describe the relative motion of teeth and consequently, the contact with dental implants during mastication[6-11]. Also in the oral environment, dental implants are in contact with saliva, which is considered to be an environment with a wide range of parameters affecting its characteristics (chemical constituents of foods, variations in pH, temperatures, and bacteria). This host environment may corrode the metallic component of the implant[12-14]. In fact, this corrosion-wear phenomenon that may occur in dental implants, can introduce additional ions and debris into the human body, causing harmful effects on health such as allergy, inflammation and/or carcinoma[10,14,16,17]. Metallic elements from dental alloys (namely titanium) have already been found in saliva, oral tissues, and in cell culture media after incubation[15].

In conclusion, dental implants and dental materials are exposed to a combined process of degradation by corrosion and wear, i.e. tribocorrosion. As a consequence, the investigation of the tribocorrosion mechanisms in such systems becomes essential.
The friction behaviour of titanium for orthopaedic applications was studied in the reciprocating sliding configuration against hardened steel by M. Long[18]. Results show that friction behaviour was a function of several parameters such as: cyclic count, sliding velocity, contact stress and alloy phase structure. The extensive plastic deformation observed indicated that dynamic friction of titanium surface was controlled by the surface behaviour[18]. Recent work performed with reciprocating sliding motion was also performed by Mischler et al.[19]. In this work the relative contribution of mechanical and chemical mechanisms on metal degradation was studied. The experiments were performed using carbon steel sliding against alumina in borate solution, using a reciprocating ball on plate equipment. It was found that the presence of the passive film strongly influences the degradation mechanism. Results suggests that wear accelerated corrosion and mechanical surface degradation, contribute to the overall material loss[19].

In last year’s, titanium has been widely used as a biomaterial (restorative surgery) owing to its excellent mechanical properties, good resistance to corrosion in biological fluids, and very low toxicity. The corrosion resistance of titanium arises from the formation of a thin (10nm) passive oxide layer on its surface, which prevents the contact of the bare metal with the human fluids[17, 20-24]. The composition of the passive oxide film, determines the integrity of the implant and plays an important role during the osseointegration process[5]. However pH is known to have a strong influence on the corrosion behaviour of Ti and Ti alloys.

When inserted in the oral environment, dental implants are consequently in contact with saliva, which has strong variations of pH as a result of food and drinks ingestion. Case reports on gross tooth destruction as a result of consumption of juices, which can modify pH of saliva have already been published[25, 26]. Citric acid although being a weak organic acid found in citrus fruits can cause strong variations in pH. On the other hand, there are other chemical substances that when added to an environment, in this case saliva effectively decreases the corrosion rate of specific materials. The general term used for these substances are corrosion inhibitors, and it is important to point out that depending on their specific protection properties, they can be proposed for being introduced in teeth hygienic products, such as toothpastes or rinses,
in a way to protect dental implants from the corrosion degradation that they may undergo when placed in the oral environment. The influence of pH variations and the action of corrosion inhibitors were studied by A.C.Vieira et al.[27]. Fretting–corrosion experiments on titanium grade 2 in contact with artificial saliva solutions were performed. Citric acid and corrosion inhibitors were added to artificial saliva to investigate their influence on the tribocorrosion behaviour of titanium. The addition of citric acid or anodic inhibitor to artificial saliva results in a slight improvement of the tribocorrosion behaviour of Ti. The addition of a cathodic or an organic inhibitor to artificial saliva had a hazardous effect on the fretting–corrosion behaviour of titanium[27].

In dental implant applications, a few reports take into account the tribocorrosion behaviour of dental materials. So the aim of the present work is to study the tribocorrosion behaviour of titanium in reciprocating sliding conditions in artificial saliva solutions, where variations on pH and the influence of corrosion inhibitors were also considered.

### 3.2. Experimental Work

#### 3.2.1. Materials and electrolytes.

The material used to perform tribocorrosion experiments was commercial pure titanium grade 2. Its nominal chemical composition is presented in table 3.1.

**Table 3.1:** chemical composition of titanium grade 2.

<table>
<thead>
<tr>
<th>Element</th>
<th>Oxygen</th>
<th>Nitrogen</th>
<th>Carbon</th>
<th>Iron</th>
<th>Residuals</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight %</td>
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<td>0.03</td>
<td>0.08</td>
<td>0.015</td>
<td>0.4</td>
</tr>
</tbody>
</table>

Samples, all from the same sheet, were cut and mechanically polished down to 0.25 μm one day before the experiment in order to control the characteristics of the oxide film which is naturally formed on titanium surface when in contact with air or other solution. After polishing, samples were ultrasonically cleaned with ethanol (10 minutes) distillate water (5 minutes), and finally dried. The surface roughness of titanium samples presented a Rₐ value of 0.03 μm ± 0.004 μm.
Corundum or alumina balls (Ceratec, The Netherlands) with 10 mm of diameter were used as a counterpart on reciprocating sliding tests. They were selected because their chemical inertness, resistance to corrosion and electrical insulating properties. Prior to corrosion-wear tests, corundum balls were ultrasonically cleaned following the same procedure used in titanium (10 minutes in ethanol and 5 minutes in distillate water).

After the adequate cleaning the weight of both, Ti samples and corundum balls, were measured in a microbalance Mettler AE240 with 0.01 mg of precision (the balance error is approximately 0.0000 ± 2 mg).

The chemical composition of the different artificial saliva (AS) solutions used in tribocorrosion experiments is presented in table 3.2.

**Table 3.2:** Chemical composition of the artificial saliva solutions.

<table>
<thead>
<tr>
<th>Solution Compound</th>
<th>Artificial saliva (AS)</th>
<th>AS + citric acid</th>
<th>AS + anodic inhibitor</th>
<th>AS + organic inhibitor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium Chloride, NaCl</td>
<td>0.70</td>
<td>0.70</td>
<td>0.70</td>
<td>0.70</td>
</tr>
<tr>
<td>Potassium Chloride, KCl</td>
<td>1.20</td>
<td>1.20</td>
<td>1.20</td>
<td>1.20</td>
</tr>
<tr>
<td>Citric Acid, C₆H₈O₇.H₂O</td>
<td></td>
<td>0.025</td>
<td></td>
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<tr>
<td>Sodium Nitrite, NaNO₂</td>
<td></td>
<td></td>
<td>0.16</td>
<td></td>
</tr>
<tr>
<td>Benzotriazole, C₆H₅N₃</td>
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<td></td>
<td></td>
<td>1.5</td>
</tr>
<tr>
<td><strong>pH</strong></td>
<td><strong>5.5</strong></td>
<td><strong>3.8</strong></td>
<td><strong>5.5</strong></td>
<td><strong>5.5</strong></td>
</tr>
</tbody>
</table>

A simple composition of artificial saliva, mainly constituted by NaCl and KCl, was used, because it was enough to study the tribocorrosion mechanisms. Some additives were added to artificial saliva. Citric acid in order to understand how variations in pH can influence the tribocorrosion behaviour of titanium and dissimilar inhibitors to investigate the action of the cathodic and anodic reactions on the electrochemical response of the titanium[27, 28].

***
3.2.2. Electrochemical tests in absence of wear

Potentiodynamic polarization tests in absence of wear were performed on titanium samples in contact with artificial saliva solutions, using a three-electrode set-up. This three-electrode set-up consists in titanium as a working electrode, a commercial platine electrode (wire B35M110 - Radiometer Analytical) as auxiliary electrode and saturated calomel (SCE) (B20B110 - Radiometer Analytical) as a reference electrode.

Tests were performed on titanium immersed in AS solutions with an exposed area of 0.385 cm². Anodic polarization curves were measured potentiodynamically from -900 mV vs. SCE to 2000 mV vs. SCE. at room temperature with a PG201 Potentiostat/Galvanostat (Radiometer Analytical, Denmark) controlled by the VoltaMaster-1 software. Before anodic polarization scanning, titanium was kept at open circuit potential for 90 minutes to allow dynamic stabilization between the working electrode and the AS solutions.

3.2.3. Reciprocating sliding–corrosion experiments

A reciprocating ball on plate tribometer Plint TE67/R was specially adapted for the tribocorrosion experiments. The schematic representation of the experimental set-up is presented in Fig. 3.1.

Fig. 3.1: Schematic representation of a tribocorrosion system using electrochemical techniques.
The system consists on a corundum ball mounted vertically and put in contact with titanium plate that was connected as working electrode. This contact was immersed in the solution (2.54 cm² of exposed area) contained in an acrylic electrochemical cell. Reciprocating sliding tests were conducted with the contact of corundum ball with top of the flat titanium sample at fixed normal load of 10 N, with a sliding stroke of 6 mm and with frequency of 1 Hz. Tests were performed at room temperature during 11160 cycles for all AS solutions. For each test condition the experiments were repeated at least two times for reproducibility.

During the entire test, open circuit potential (OCP) and corrosion current was followed using the three-electrode set-up that was already described for potentiodynamic polarization experiments. It is important to denote that both measurements were performed separately. In Fig.3.2 a schematic representation of electrochemical measurements performed during reciprocating sliding corrosion experiments is presented.

For OCP and corrosion current measurements, some periods of stabilization were achieved during tribocorrosion tests. At the beginning, when the contact of titanium with AS solutions occur, after the contact of corundum ball with titanium and consequent application of load and after sliding when the pin is lifted away from titanium surface. These periods allowed the stabilization of the oxide film formed on titanium surface after exposure with AS solutions.

An important aspect to stress is that corrosion current measurements were performed under potentiostatic control. Initially the samples were cathodically polarized.
at -900 mV vs. SCE during 3 min, for an *in situ* cleaning. After that, tests were performed at 1000 mV vs. SCE, potential that belongs to the passivation plateau of titanium.

Electrochemical Impedance Spectroscopy (EIS) measurements were performed before and after the sliding (when the pin is lifted away from titanium samples) by a Voltalab PGZ100 Potentiostat (Radiometer Analytical, Denmark), controlled by the VoltaMaster-4 software in the frequency range of 100 kHz to 15.8 mHz, applying an ac current with an amplitude of 10 mV, near the free open circuit potential.

After the reciprocating-sliding corrosion tests titanium samples and corundum balls were ultrasonic cleaned with ethanol, dried and the weight measured (*Mettler AE240* with 0.01 mg of precision and a error of approximately 0.0000 ± 2 mg). The morphology of the wear scars were evaluated by SEM and EDS equipment (*JEOL JSM-6301F Leica S360*). All the solutions obtained by tribocorrosion tests were analyzed by atomic absorption spectroscopy in a *GBC 904 AA* spectrometer.

### 3.3. Results and discussion

#### 3.3.1. Electrochemical measurements in absence of sliding

Potentiodynamic polarization curves of titanium on AS solutions have been recorded and presented in Fig. 3.3.

![Potentiodynamic polarization curves of titanium immersed in AS solutions without rubbing.](image)

**Fig. 3.3:** Potentiodynamic polarization curves of titanium immersed in AS solutions without rubbing.
Titanium in AS solutions presents a large passivation region, at potentials between 0.5 and 2 V vs. SCE which suggests that titanium is protected with an oxide film that could protect against corrosion. Some current density oscillations can be regarded for AS + citric acid (at 0.8 V vs. SCE) and in AS + anodic and organic inhibitor (at potential above 1.6V), which can be related to film breakdown and repassivation events[29, 30]. The corrosion current densities ($i_{corr}$) were obtained from the polarization curves, by extrapolation of the anodic and cathodic branch to the corrosion potential. The mean values and their standard deviation are shown in table 3.3.

**Table 3.3.** Corrosion current ($i_{corr}$) results of titanium in artificial saliva solutions.

<table>
<thead>
<tr>
<th>Solution Compound</th>
<th>$i_{corr}$ (µA.cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Artificial saliva (AS)</td>
<td>0.060 +/- 0.03</td>
</tr>
<tr>
<td>AS + citric acid</td>
<td>0.095 +/- 0.04</td>
</tr>
<tr>
<td>AS + anodic inhibitor</td>
<td>0.065 +/- 0.04</td>
</tr>
<tr>
<td>AS + organic inhibitor</td>
<td>0.043 +/- 0.02</td>
</tr>
</tbody>
</table>

It should be noticed that, titanium presents low values of $i_{corr}$, which is typical of passive materials. As it is possible to see regarding table 3.3, AS + organic inhibitor presents the lowest corrosion current density ($i_{corr} = 0.043$), and titanium in contact with AS + citric acid presents the highest value of corrosion current density ($i_{corr} = 0.095$). A wide range of $i_{corr}$ values may be obtained for potentiodynamic tests of titanium in artificial saliva solution. Z. Cai et al.[31] performed an electrochemical characterization of cast titanium alloys in aerated modified tani-zucchi synthetic saliva at 37 °C. Potentiodynamic results show that pure titanium presents an $i_{corr}$ equal to 0.091 µA.cm$^{-2}$[31]. However, results presented by N.A. Al-Mobarak and by A.M. Al-Mayouf [32, 33], show that no significant differences are observed on titanium behaviour in contact with artificial saliva with pH ranging between 3 and 7.2. ($i_{corr} \approx 0.03$ µA.cm$^{-2}$[32, 33]. Furthermore, it is also possible to see that the standard deviation results of $i_{corr}$ results are high, which is due to the high reactivity of titanium and its affinity with oxygen. It is
extremely difficult maintain the same titanium surface for each experiment. Small variations on preparation of the samples, changes in temperature, humidity that may occur during each test strongly influence its behaviour, and as a consequence increase the standard deviation results. Consequently it was not possible to have a definite view on the influence of the solutions chemical compositions on the corrosion behaviour of the material.

3.3.2. Reciprocating–corrosion measurements under potentiostatic control

Corrosion current measurements were performed during tribocorrosion experiments in order to elucidate the electrochemical processes taking place at titanium surface. The typical current response recorded before, during and after reciprocating sliding tests performed in titanium in AS solutions is shown is Fig. 3.4.

![Graph](image)

**Fig. 3.4:** Corrosion current density variation recorded on titanium during reciprocating sliding against alumina ball in (a) AS and AS + citric acid, (b) AS + anodic inhibitor and AS +...**
organic inhibitor. (Reciprocating sliding parameters used were: 10 N, 1Hz, 6mm, and 11160 cycles).

As we can follow, a significant rise in the anodic current through to the titanium samples is noticed at the start of reciprocating sliding tests. After a running-in period, the current fluctuates during the entire test, and at the end returns to the level observed before the start of the experiment. Similar results were reported by Wu et al[34] for AISI 304 stainless steel sliding in a reciprocating mode against a corundum ball, immersed in 0.5M NaCl, 0.02M Na₃PO₄ and 0.5M H₂SO₄. The fluctuations on potential and current during sliding were related with oxide film removal (depassivation) and re-growth (repassivation). Accordingly, current variations presented in Fig.3.4 suggest that titanium mainly undergo a removal of their passive film, at the start of sliding, it remains partially active during sliding (with depassivations and repassivations), and finally progressively repassivate on unloading. These fluctuations may be fluctuations in the normal force related to the mechanical stiffness of the tribometer[2].

The increase of corrosion current due to sliding of passive metals is related to the exposure of the native metal to the solution after the disruption of the passive film. In fact, during sliding, the passive layer is removed from titanium surface, and then at least partially rebuilt, till the next contact with the alumina ball. Since the applied potential lies in the passive range, the metal will oxidise until the new film is formed again. Plastic deformation of asperities, detachment of metal particles and spalling of the passive film, are mechanisms that yield depassivation[22]. In this study the corrosion current in the passive region increases under wear.

In relation to Fig. 3.4, it is possible to observe that there are no significant differences among all solutions tested. In fact, when the conditions of formation of the passive film are controlled, no significant difference on titanium behaviour is observed, indicating that variations on the chemical composition of the solutions do not have a significant influence on the characteristics of the passive film, at 1000 mV.
3.3.3. Reciprocating–sliding corrosion measurements

The evolution of the corrosion potential with the sliding time is shown in Fig. 3.5.

Prior to tribocorrosion tests, and before placing in contact the corundum ball with the metallic surface, titanium samples were immersed on different AS solutions in order to achieve stabilization. The stabilization of the passive film consists on the transformation of the naturally air-formed passive film into a solution-formed film[20]. Under unload conditions, the potential variations range from 0.05 to -0.3 V, results that are in a good agreement with the OCP results measured before potentyodinamic polarization tests. This behaviour can be explained by the influence of the chemical composition of the solution on the formation of the oxide film under titanium surface. During this stabilization period, AS + citric acid present the noblest potential and AS + organic inhibitor presents the lowest corrosion potential. Once stabilization was achieved, sliding started.

At the start of reciprocating sliding corrosion tests, a suddenly decrease on open-circuit potential is observed. This behaviour may be attributed to the disruption and removal of the oxide film allowing the fresh active titanium surface to be exposed to the electrolyte, as schematically showed in Fig.3.6[34]. In fact, when the pin is put in
contact with titanium surface, the passive film is partially destroyed in the contact area under sliding conditions. As the pin moves on, the passive layer would then reform, only to be subsequently removed during the next sliding contact with the alumina ball[35].

Fig. 3.6: Schematic representation of the removal and recovery of the passive layer.

During the entire test, potential fluctuates, as long as the reciprocating sliding corrosion tests goes on. These fluctuations are related with film depassivations (film removal) and repassivations (film re-growth) events.

In relation to the solutions tested, we can see that titanium in AS + citric acid presents a distinctive behaviour during the entire test. It presents the highest electrochemical potential (ca. - 0.7 V vs. SCE), before during and after reciprocating sliding tests. Regarding the action of corrosion inhibitors, it is possible to observe Fig. 3.5 (b) that there is no significant difference on their action, they present potential values near -0.86V vs. SCE. However, it is important to point out that, on the beginning of sliding, the decrease on corrosion potential is not gradual until stabilization is reached. This phenomenon can be related to the accommodation of the tribological pairs that normally occurs at the beginning of rubbing. It is possible that inhibitors are acting on titanium surface at the beginning of rubbing, but after the accommodation of the two surfaces, the oxide film is already disrupted and the action of inhibitors stabilizes.

At the end of the wear process, and when the counterbody is lifted away from titanium surface, the OCP increase to values between -0.23 V. SCE for AS + citric acid and -0.35 V. SCE for AS + organic inhibitor. AS and AS + anodic inhibitor present a similar behaviour. This increase in OCP values is due to the repassivation of the
Influence of pH and corrosion inhibitors on the tribocorrosion behaviour of titanium in different tribological geometries

material in the wear track, as was also suggested by corrosion current results[17]. It should be noticed that titanium surface recovers but the OCP values are lower than that obtained before sliding. This behaviour shows that the passive film formed under rubbed surfaces presents different characteristics from the naturally film formed on titanium surfaces before mechanical damage. OCP results suggest that the mechanical damaged and also the compositions of AS salivas influence the rebuilt of the oxide film after wear. It is possible to conclude that variations in pH result in a different thermodynamic tendency between all the solutions. AS + citric acid solution exhibit a lower tendency to corrosion, before, during and after rubbing. The addition of inhibitors seems to not have a beneficial effect on the tribocorrosion behaviour of titanium.

The evolution of the mechanical contact between titanium and corundum ball was investigated by acquiring the coefficient of friction (μ). The evolution of μ with the sliding distance for tribocorrosion experiments in artificial saliva solutions is presented in Fig. 3.7.

As we can see by the analysis of figure 3.7, at the beginning, the friction behaviour of the tribological pairs (titanium samples and corundum balls) exhibits a initial run-in period (1000 seconds) with μ values between 0.43 to 0.48, followed by a monotonically slight increase of the friction coefficient.

Fig. 3.7: Evolution of the coefficient of friction during reciprocating sliding tests involving a titanium flat disc immersed in AS solutions, sliding against alumina ball.

(Reciprocating sliding parameters used were: 10 N, 1Hz, 6mm, and 11160 cycles).
This running-in period is the result of accommodation of the tribological pairs, where microfragmentation or disruption and removal of the oxide film formed on the titanium surface occur. After the accommodation of the two surfaces, debris are ejected out of the contact and rubbing goes on[26].

Analysing Fig. 3.7, for all solutions tested μ remains between 0.43 and 0.58, and the friction profile stays quite similar for all the solutions tested. This behaviour can be explained, by the similar morphology obtained on titanium surfaces, after the same polishing procedure. Also the tribological parameters were maintained identical for all tribocorrosion tests; however the chemical composition of the AS tested were different. As a result it might be possible to conclude that the chemical composition of AS solutions tested do not have any effect on the mechanical interaction between the tribological pairs and as a consequence on the tribological behaviour of titanium.

During tribocorrosion tests it is also possible to see a small increase in the coefficient of friction. The coefficient of friction exhibits good reproducibility but some oscillations can be observed, which may be due to surface irregularities and/or of third-body particles in the contact region.
In Fig. 3.8 micrographs of the wear scars are presented.

![Representative micrographs](image)

**Fig. 3.8**: Representative micrographs (a) wear scar, and (b) interior of the wear scar, and (c) magnification of the agglomerated particles. (Reciprocating sliding parameters used were: 10 N, 1Hz, 6mm, and 11160 cycles).

As we can see the wear scar is characterized by sliding wear marks aligned in the sliding direction. The tribosurface exhibit localized asperity deformation, surface plowing, adhesive, abrasive wear with formation of larger surface debris (third body particles) as we can see in Fig. 3.8 (b). It is possible that the small increase on $\mu$ can be related with the formation of this third-body particles in the contact region, and that the oscillations observed in $\mu$ are related with the surface irregularities.

The weight of the sample is measured before and after each test, these results in the evaluation of the total loss of material for each sample. In Fig. 3.9 is presented the weight loss measurements, and also the % of titanium dissolved on the solutions after tribocorrosion tests, as a result of the combined action of wear and corrosion.
As it can be observed in Fig. 3.9 (a), titanium samples always lose more weight than corundum balls under identical wear conditions. This behaviour can be explained by the high wear resistance and chemical inertness of corundum balls.

For all the AS tested, the only solution which presents a distinct behaviour is AS+ citric acid solution with the highest weight loss as shown (see Fig.3.9 (a)). This result was confirmed by chemical analysis of the solutions obtained after tribocorrosion experiments. As it is possible to see, this same solution presents a considerable amount of titanium (near 2%) dissolved. In relation to other solutions, they present values under or very near of the detection limit of the machine (1.1 mg/l). The % of titanium on AS solutions is not enough to be detected by the equipment.
Weight loss results arise from both mechanical and electrochemical/chemical action in titanium surfaces. It is nevertheless possible to observe, analysing potential results, that the increase in corrosion tendency does not significantly affect the weight loss as shown Fig. 3.9 (a). It seems that the chemical composition of the AS solutions has a strong influence of the formation and consequently degradation of the passive film.

Titanium in AS + citric acid present a remarkable behaviour. This solution shows a lower tendency towards corrosion, before, during and after reciprocating sliding (as shown Fig.3.5); however it presents the highest weight loss. This result can be explained by the high corrosion current density that is observed on titanium in AS + citric acid in potentiodynamic tests (see table 3.3). It is possible that the film formed on titanium surface present a low thickness and it is easily removed, or its capacity of restoration as the pin moves on, is low accelerating the wear loss.

The characteristics of the passive film formed in AS solutions were analysed by electrochemical impedance spectroscopy (EIS). EIS data commonly presented in Bode plots, was analysed by fitting the experimental results to an electrochemical equivalent circuit model. The Bode plots for EIS tests performed before and after mechanical damage, the equivalent circuit model adapted for titanium immersed in AS solutions and polarization resistance results are presented in Fig.3.10.
Fig. 3.10: Schematic representation of (a) bode impedance diagram before and after mechanical damage, (b) equivalent circuit used for fitting EIS experimental data and (c) polarization resistance of the passive film for both measurements (before and after sliding)[36].
(Reciprocating sliding parameters used were: 10 N, 1Hz, 6mm, and 11160 cycles)

Regarding Fig.3.10 (a) it is possible to see that bode plots for all AS solutions tested are similar in nature. A highly capacitive behaviour, typical of passive metals, is indicated from the medium to low frequencies by phase angles approaching -90º. This is the capacitive response of a compact passive oxide formed on Ti-grade 2[36]. Bode diagrams suggests, that a compact passive film is formed on titanium for all AS solutions before mechanical damage with phase angles between -80 and -83º. AS and AS + citric acid present phase angles slightly higher, resulting in oxide films more compact and stable, which can enhance higher protection as suggest by OCP results. However, after sliding, as suggests Fig.3.10 (a), the film is less compact with phase angles between -78 and 80º. It seems that the repassivation of titanium oxide film is affected by the damaged titanium surface, as was also suggested by OCP results.

EIS data is commonly analysed by fitting the experimental results (Fig.3.10 (a)) to an electrochemical equivalent circuit model. For titanium samples analysed in this work, the equivalent circuit model schematized in Fig. 10(b) was proposed, where $R\bar{\Omega}$ is the resistance of the electrolyte and $R_p$ and $C_p$ are polarization resistance and the capacitance of the film, respectively. This model accounts the presence of a single layer on metal surface possessing resistance as well as capacitance[37]. $R_p$ is considered to be inversely proportional to the corrosion rate. With this simple circuit a satisfactory fitting
data was obtained. The $R_p$ estimated for all samples, before and after sliding, is represented in Fig. 10 (c).

The $R_p$ values obtained before mechanical damage, remain between $1.5 \times 10^6$ and $3.5 \times 10^6$ Ohm.cm$^2$ (see Fig. 3.10 (a)), indicating a good corrosion resistance, and as a consequence low corrosion rates\[22\]. The highest polarization resistance obtained before wear tests are due to the good protective character of passive oxide layer present at the surface. However during and after sliding, this passive layer highly degrades, resulting in a decrease of both $E_{corr}$ and $R_p$ values. It seems that the passive film formed after mechanical damage is modified altering the protection characteristics of it. Regarding $R_p$ results for titanium in contact with AS solutions, it is possible to see that the solutions that present a high resistance of the passive film, before and after sliding is AS, and AS + citric acid. Opposite behaviour present AS + organic inhibitor which is the solution that presents a passive film with less compact properties and a less protective film as suggested by open circuit potential results presented in Fig.3.5 (b).

The relative low corrosion rate of titanium in the artificial saliva solution can be attributed to the high polarisation resistance of the material when in contact with the solution. However, after the intense action of the mechanical damage, the corrosion resistance of the material is significantly decreased.

These changes in the passive film resistance can be attributed to a formation of a film under a rubbed surface which can raise structural changes. Also it has to be taken in account the influence of AS compositions. Although Ti in AS+ citric acid presents the high protection against corrosion, and its film is compact, it is possible that its capacity of repassivation and its thickness are low comparing with the other AS solutions increasing their removal and degradation due to sliding\[37\].

3.4. Conclusions

In this chapter the effect of reciprocating sliding wear on the corrosion behaviour of titanium grade 2 was investigated. OCP and corrosion current evolutions are in agreement.
The influence of variations in pH by the addition AS + citric acid (pH=3.8) was detected during tribocorrosion experiments by open-circuit results. Changes in pH result in a lower tendency to corrosion, before during and after mechanical damage. After sliding, however, the amount of material removed from the Ti is considerably higher when the material is in contact with this solution. This behaviour may be attributed to the high corrosion kinetics that this solution presents, which accelerate the degradation process of titanium. The restorative capacity of this oxide film under rubbed titanium surface may also be compromise accelerating wear. So it is possible to conclude that the addition of citric acid on AS solution has a harmful effect on reciprocating-sliding corrosion of titanium. However the addition of inhibitors to the artificial saliva solution does not have any beneficial effect (they do not provide the protection expected) on the tribocorrosion behaviour of the titanium.

Both actions of changes in pH and corrosion inhibitors in concentrations used in these work do not seem to have any effect on tribological behaviour of titanium. The behaviour of the Ti in the artificial saliva solutions appears to be governed by the characteristics of the passive film formed under open-circuit conditions. In fact, if the conditions of formation of the passive film are controlled (potentiostatic control in the passive plateau) no significant differences in behaviour are observed.

3.5. References

Influence of pH and corrosion inhibitors on the tribocorrosion behaviour of titanium in different 
tribological geometries

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Chapter 4
4.1. Results and discussion

4.1.1. Experimental conditions

The aim of this master dissertation was to study the tribocorrosion behaviour of titanium grade 2 in contact with artificial saliva solution in two different contact geometries, fretting and reciprocating sliding. Their main difference remains on the amplitude of reciprocating movement. Two different loads and test time were used in tribocorrosion tests: 2 N and 10000 cycles for fretting corrosion experiments and 10 N and 11160 cycles for reciprocating sliding corrosion experiments. The effect of amplitude and load was studied experimentally using two types of equipments: The bidirectional fretting test equipment with an electrochemical noise set-up which has been already described[1], and a tribometer PLINT TE 67/R that was adapted with a PG201 Potentiostat/Galvanostat (Radiometer Analytical, Denmark) controlled by the VoltaMaster-1 software. In Fig.4.1 is possible to observe the two different equipments.
Influence of pH and corrosion inhibitors on the tribocorrosion behaviour of titanium in different tribological geometries

Fig. 4.1: Photographic representation of the (a) bidirectional fretting test equipment with an electrochemical noise set-up and (b) tribometer PLINT TE 67/R with the electrochemical equipment, (c) three-electrode set-up.

The bidirectional fretting equipment allows the direct measurement of friction coefficient and variations in force-displacement. With these results, fretting lops for the different tests were performed and the dissipated energy calculated. With the tribometer PLINT TE 67/R just the friction profile was measured during reciprocating sliding tests. This was one limitation, in a way that dissipated energy will not be compared between both geometries. The tribological experimental conditions used in both kinds of experiments are summarized in Fig.4.2.

Fig. 4.2: Tribological conditions and contacts used in tribocorrosion tests, (a) in fretting and (b) in reciprocating sliding contacts.

After tribocorrosion experiments, in fretting tests, the wear scars were investigated by reflected light microscopy, by a laser profilometry and SEM-EDS. The wear volume was determined by the profilometric method. In reciprocating sliding tests the weight variation was obtained by the classical method of wear by weight loss and the morphology of the wear scars were evaluated by SEM-EDS. The solutions obtained in this tribocorrosion tests were analyzed by atomic absorption spectroscopy.

4.2. Tribological results

Friction coefficient

On the evolution of coefficient of friction in fretting contacts (see Fig.2.3 of chapter 2), it is possible to observe the influence of the chemical composition of the
different artificial saliva’s used. All the solutions with exception of AS + organic inhibitor which present the highest value of $\mu$ near 0.9, present $\mu$ values in the same order of magnitude. It is possible to conclude that for low loads and amplitudes the AS + organic inhibitor has a strong influence on the tribological behaviour of titanium. Regarding the friction profile for reciprocating sliding corrosion experiments in Fig.3.7 of chapter 3, it is possible to observe that $\mu$ remains similar between all experiments. It seems that the different composition of all solutions tested does not interfere with the mechanical contact between the two materials. The mechanical solicitation overlaps the chemical ones. In fact the higher load used in these tests leads to a strong mechanical degradation of the material, diluting any influence of the characteristics of the passive film.

In both contact geometries, it is possible to observe an initial running-in period followed by a steady state. This running - in is related with the accommodation of the tribological pairs, by crushing and smearing of the asperities. On both measurements strong oscillations occur in friction profile, which can be related with surface irregularities and the build-up and accumulation of third-body particles on the contact region.

Comparing both results it is possible to observe that for reciprocating sliding geometry $\mu$ present lower values comparing with fretting ones. Some results in literature suggest that the coefficient of friction depended of the applied load. The larger the applied force, the smaller the friction coefficient\[1\]. Friction results are in agreement with this theory. Also the higher $\mu$ results obtained in fretting corrosion experiments, suggest that different corrosion – wear mechanisms are active in the different tribocorrosion experiments\[2\].

Also it cannot be disregarded that the friction profile is strongly dependant of the topography of the tribological pairs. Surface roughness plays an important role on the tribocorrosion behaviour of passive metals because it affects the rate of depassivation and of mechanical wear. Typically, rubbing a hard body (corundum ball) with a rough surface against a passive metal (titanium) result in a predominant abrasive wear of the passive metal. Although there was a tendency to reproduce the same titanium surface
for tribocorrosion experiments in both contact geometries, it is known that it is very difficult to obtain the same final surface because of the high reactivity of titanium. Also the mechanical damaged that is formed during rubbing lead to different surface topographies. As it was possible to see, in fretting there was a generation of tribolayers and in reciprocating sliding there was just the formation of wear debris. In fretting corrosion experiments the formation of tribolayers influenced current and coefficient of friction results.

The role of debris (third body particles) is critical, because depending on their physical properties, they can act as abrasive which accelerates wear or as a solid lubricant diminishing friction and wear[3]. In this case, they are acting as abrasive accelerating wear. It is also possible that the tribolayers formed in fretting tests has higher roughness when compared with the wear particles formed in reciprocating sliding tests, increasing the $\mu$. These are parameters that can also influence the friction profile of titanium.

- **Dissipated energy / Wear rate**

During fretting corrosion experiments the values of force-displacement were measured. The parallelogram shape of the tangential force-displacement cycles show that the accommodation of the displacement occurs under a gross slip regime. The dissipated energy in the contact during each fretting cycle was calculated by the area of the fretting logs. Several studies have shown that in fretting it may be possible to establish a relationship between the dissipated energy and the volume of material removed by wear[4]. This association can also occur in reciprocating sliding. For fretting-corrosion testes, results demonstrate that dissipated energy tends to reach a steady state as the number of fretting cycles increase, and it appears that this energy increases with fretting duration. In relation to dissipated energy results, AS + organic inhibitor show a substantially higher values due to its higher coefficient of friction.

The wear volume account the material removed from the contact region by wear and corrosion. In gross slip regime a linear relation can be obtained between the wear volume and the cumulated dissipated energy. This linear relationship was assumed in
fretting corrosion experiments. Wear loss results suggest that for 5000 cycles Ti in AS + organic inhibitor suffers a weight loss 2 times lower that Ti in AS + cathodic inhibitor. However after 10000 cycles, some protection is provided by the addition of citric acid to AS. In relation to the wear rate per unit of dissipated energy results suggest that the nature of the solutions appears to influence this behavior. At sufficiently small oscillation amplitudes, however, the strain is accommodated by an elastic deformation of the contacting materials or by the equipment, leading to a reduction in tribocorrosion rate[5].

In reciprocating sliding experiments, it was not possibility to identify the regime, and to quantify the dissipated energy, because of the nature of the equipment. Some results in literature suggest that larger reciprocating amplitude results in higher values of dissipated energy and higher wear volume, because the wear volume increase linearly with the sliding distance[6].

The tribocorrosion of passive metals, such as titanium in sliding contacts is a result of the interaction between mechanical and electrochemical processes. Mechanical processes take in account the classic wear mechanisms of abrasion, adhesion and fatigue and the electrochemical processes include anodic dissolution and passive film formation. As a result the material loss due to tribocorrosion is the effect of this two processes acting independently. In literature this synergy effect has been studied by several authors[1].

Weight loss results due to the mechanical and electrochemical action obtained in reciprocating-sliding corrosion experiments, suggest that Ti in AS + citric acid loses its protection observed in fretting experiments. This behaviour is a result of the different contact and also applied load. In fact in these experiments, there is no formation of tribolayers on titanium surface. As suggested by fretting results, tribolayers gives some protection to titanium surface against corrosion and wear.

Also in potentiodynamic polarization experiments, AS + citric acid present the highest $i_{corr}$, which contribute for high weight loss results. Different mechanisms may also occur in the contact area resulting in a formation of a passive film with low capability to be reformed every time that corundum ball moves on and which is easily
removed by rubbing, accelerating wear loss. These results suggest that wear is a complex degradation phenomenon involving interaction not only between the two contacting surfaces but also the surrounding environment.

### 4.3. Wear morphologies

Several studies suggest that friction and wear behaviour of titanium is controlled by the presence of a oxide film and its breakdown during sliding[4]. In Fig.4.3 it is possible observe the wear scars formed by fretting and reciprocating sliding tests.

![Wear scars](image)

Fig. 4.3: Wear scars (a) in fretting and (b) in reciprocating sliding contacts.

The differences obtained in fretting and reciprocating sliding corrosion experiments can be understood by considering the differing initial surface, different contact geometry and different applied loads. The contact geometry is another important parameter in tribocorrosion, because it determines the size of the contact zone and the alignment of rubbing surfaces.

The elliptical dimension corresponds well with the dimensions of the Hertzian contact area summed, for the axis parallel to the motion direction, with the effective displacement[7]. Accordingly, the dimensions of the central part increase with increasing load, as we in Fig.4.3 (b). Also, increasing the time of testing (reciprocating sliding corrosion tests), increase the smeared area because of the increase of ball penetration due to wear of titanium. Both wear scars present marks aligned on the sliding direction.
Several different wear mechanisms are presented in both geometries, they can be observed in Fig. 4.4.

![Micrographs of the inside wear scars](image)

(a) (b)

**Fig. 4.4:** Micrographs of the inside wear scars (a) in fretting and (b) in reciprocating sliding tests.

Vingsbo and Söderberg et al.[8] described fretting regimes. At low amplitude the elastic deformation of the contact system accommodates the relative displacement between the two counter parts and only very limited surface damage occurs. At higher amplitudes, slip between the counterparts and plastic deformation result in severe surface damage by wear, as we can see in Fig. 4.4 (b). Experiments performed at 2N exhibited similar wear patterns characterised by less plastic flow and a slightly more disrupted surface structure compared to tests performed under 10N normal force. For both fretting and reciprocating sliding corrosion experiments no significant differences between all AS solutions tested were observed in wear morphologies.

One of the main differences in both experiments is the formation of tribolayers in fretting contact. When increasing the load (10N) increases the contact pressure and the destruction of debris and their ejection occur, without forming tribolayers. In both geometries there was a formation of third-body particles, however their number and size increase with the increasing of amplitude movement[1, 3].
4.4. Electrochemical results

4.4.1. Open circuit potential

The electrochemical conditions in the contact have marked influence on the formation rate and the properties of wear debris formed. Literature suggests that imposing a fixed potential can have a marked influence on mechanical wear mechanisms. An example is given by D. Landolt et al.[3] where the tribocorrosion behavior of stainless steel was performed in sulfuric acid and with electrochemical polarization. It was possible to observe that in the low passive range hardly any particles while in the high passive range particles were observed inside and outside of the wear scar. They speculate that for high potentials the metal passivates faster and therefore particles detached by mechanical abrasion dissolve less than at low potential[3].

In the tribocorrosion experiments performed in both contact geometries OCP measurements were performed in free potential. This measurement gives information about the electrochemical state of a material, for example, active or passive state in the case of titanium. The open circuit potential recorded during tribocorrosion tests, is a mixed potential reflecting the state of the unworn disk material and the state of the material in the wear track[9]. The general evolution of the open circuit potential results versus time for tribocorrosion tests is:

- A significant drop in potential is observed immediately after the start of the mechanical action, indicating the destruction of the passive film (depassivation), and the exposure of fresh active titanium to the test solutions[5-10].
- During the test it is possible that depassivations and repassivations events occur.
- At the end, when the pin is lifted away from titanium surface, the corrosion potential can recover or not to the original values. This recover is a result of the formation of a newly passive film on the rubbed surface.
During the stabilization period, it is possible to observed that for both contact geometries Ti in AS and Ti in As + citric acid present a less susceptibility to corrosion. Some protection is provided by the addition of citric acid to AS. When mechanical action start the drop in potential is different between AS solutions tested in both geometries. In fretting the drop in potential is significantly lower for Ti in the AS + organic and AS + cathodic inhibitor, remaining unchanged during all the rest of the test. In the others AS tested, the potential increases to more noble values indicating an increase on corrosion protection. This protection is given by the formation of tribolayres on the contact region, action as a barrier between Ti surface and the solution. In reciprocating sliding geometry, there is no evidence of formation of tribolayers.

Once a mechanical contact is established, a shift of the open circuit potential towards lower potentials (cathodic shift) is observed as it was referred before. The amplitude of that shift increases with increasing normal force, as it is possible to see in OCP results for fretting and reciprocating sliding corrosion experiments. The contact area between first bodies increases at increasing normal load. This generates a larger wear track area. As a consequence, a larger area of active material in the wear track causes a lowering of the open circuit potential[9].

During sliding OCP maintains quite stable values, but some oscillations occur, which are related with depassivations and repassivations events. Also the corrosion potential values are higher for reciprocating sliding experiments during mechanical damage, which is a result of the increase of applied load, which induce higher surface damage, higher removal of material and as a consequence a increase on susceptibility to corrosion.

At the end of the test, it should be noticed that titanium surface recovers (the oxide film repassivate) but the corrosion potential values are lower than that obtained before reciprocating sliding. The film formed under rubbed surfaces present a higher susceptibility to corrosion. However, in fretting test the corrosion potential recovers its original value or becomes even slightly higher. It seems that the film formed present characteristics similar or even better than the naturally film formed under Ti surface before mechanical damaged. The exception to this behaviour are the Ti samples tested in the AS + cathodic inhibitor and AS + organic inhibitor. These solutions are inhibiting
the cathodic reaction(s) probably hinder the formation of a new passive film on the surface of worn Ti.

These results demonstrate the increase on the severity of reciprocating sliding experiments. In both contacts geometries it is possible to observe that the samples tested in AS + citric acid solution is the one exhibiting the highest electrochemical potential before, during and after rubbing.

4.4.2. Current

Current measurements were performed in fretting tests using electrochemical noise technique. In all samples the depassivation of the materials during the initial stage of fretting is accompanied by a sudden increase in corrosion current density. This increase is much higher in the AS + cathodic inhibitor and AS + organic inhibitor solutions than in the other solutions, indicating that these solutions have a much stronger corrosive action on fresh titanium surfaces than the other ones.

After the initial increase on current, caused by the destruction of the passive film, the corrosion monotonically decreases for AS, AS + citric acid and AS + anodic inhibitor indicating the formation of a third body protective layer (tribolayer). The decrease in corrosion current is more pronounced in the AS + citric acid and AS + anodic inhibitor solutions, indicating that these additives provide some protection to titanium.

In reciprocating sliding corrosion tests, as it was referred before current measurements were performed under potentiostatic control. When the conditions of formation of passive film are controlled (at 1000 mV), no significant difference on titanium behaviour is observed. This behaviour indicates that a variation on the chemical composition of the solutions does not have a significant influence on the characteristics of the passive film. Regarding current results, nevertheless the presence of corrosion inhibitors at concentrations used in this work seems to be more effective.
The displacement amplitude and load clearly affects the corrosion current. Corrosion current results were higher for higher displacement amplitude and load, for reciprocating sliding corrosion experiments. Current is a consequence of exposing native metal to the solution, a phenomenon determined, at least in the case of very thin passive films, by plastic deformation, is therefore expected to yield higher currents for higher amplitudes of motions[1].

The load seems also to affect corrosion current during tribocorrosion experiments. M. Stemp performed a series of experiments at different applied loads by a constant potential of 250 mV. Results suggested that the wear track volume and the anodic current during sliding increase linearly with the increase of the normal force[1].

As it was possible to observe, the sharp potential drop and current increase in both fretting and sliding experiments are a result of the removal of the oxide film and subsequent exposure of fresh active material to the environment. The dependence of potential drop and current increase during tribocorrosion experiments on the applied load can be understood by considering the contact geometry between the two contacting surfaces. The real contact area depends on surface topography, materials properties and the applied force[10].

It appears that the normal load is transmitted by asperities, and increase their value will increase the contact area. Higher loads produce stress on asperities to cause the removal of oxide film, it may expect a lowering on potential till the oxide layer is removed from the entire contact[10]. As underlined in the electrochemical current increases with the mechanical loading. The difference is readily explained by the local depassivation / repassivation phenomena. It is more active under a larger load.

As our results show, an increase on the applied load from 2 to 10N, resulting in an increase in the removal of oxide film from a larger area, and may subsequently increase the exposure active material area leading to a lower potential and higher current.
4.5. References

Chapter 5
5.1. Final Conclusions

- Tribolayers with better characteristics than the naturally air-formed film appear in the contact region during fretting-corrosion experiments. This behaviour was not observed in reciprocating sliding conditions.

- The addition of citric acid to artificial saliva improves the protective character of the film in fretting-wear conditions, resulting in a high $E_{corr}$ and lower wear volume.

- In reciprocating sliding the AS + citric acid shows an $E_{corr}$ significantly higher than that observed in the other solutions. However, after sliding, the amount of material removed from the Ti is considerably higher, which is due to a high $i_{corr}$ of this solution in potenciodynamic polarization tests.

- The behaviour of the Ti in the AS solutions appears to be governed by the characteristics of the passive film formed under open-circuit conditions. In fact, if the conditions of formation of the passive film are controlled (potentiostatic control in the passive plateau) no significant differences in behaviour are observed.

- The relative low corrosion rate of titanium in the AS solution may be attributed to the high polarisation resistance of the material when in contact with the solution. However, after the intense action of the mechanical damage, the corrosion resistance of the material is significantly decreased.

- Corrosion inhibitors, by acting on the anodic or cathodic reactions, negatively affects the tribocorrosion behaviour of Ti, probably because they hinder the formation of a passive film. So in these concentrations they cannot be proposed to be introduced in oral medicine agents.

Results clearly demonstrate that the electrochemical and mechanical parameters jointly affect the tribocorrosion behaviour of titanium in contact with AS solutions.
6.1. Scientific challenges

The tribocorrosion behaviour of titanium in contact with AS was studied in two different geometries and loads. As it was referred in chapter 1, dental implants are subjected to a combined action of corrosion and wear.

The use of two different contacts was in a way to simulate mastication, where reciprocating sliding corrosion experiments are the most adequate (chapter 3), and to simulate the micromovement that might occur in implants, which is very well simulated by fretting (chapter 2). So taking into account these two distinct movements the tribocorrosion mechanisms presented in dental implants was evaluated.

Another important aspect to study in dental implants is their behaviour when in contact with saliva. When we are choosing the right biomaterial to use in biomedical applications such as dental implants, we cannot forget the behaviour of material when inserted in human body. As was referred in chapter 1, the human mouth is considered to be a multivariate external environment with a wide range of circumstances such as, foods, variations in pH, and bacteria which can corrode the metallic component of the implant. So it was important to study the effect of variations in pH, in a way to simulate the variations in pH that might occur in mouth with the consumption of some juices.

A different scientific parameter was studied; it is the influence of inhibitors on the corrosion behaviour of dental implants. The idea of this study was to try to evaluate the influence of inhibitors, in a possible way to provide some protection. They could be introduced in oral medicines, such as tooth cleaning agents to protect the dental implant against corrosion.
6.2. Suggestions for future works

As it was referred before, when placed in human body dental implants are subjected to a high variety of forces and movements, and are also in contact with saliva. So future work can be related to:

- The selection of a range of forces very low and high forces (in adult’s the average obtained was 100-150N);

- The study of the role of passive films on the degradation of titanium for dental applications in tribocorrosion systems;

- Study the different concentration of anodic and organic inhibitors influence on the tribocorrosion behaviour of titanium as a way to see if they could be introduced in oral medicines to protect against corrosion;

- Study the influence of other specific inhibitors on the tribocorrosion behavior of titanium;

- Investigate the tribocorrosion behaviour of titanium in different artificial salivas, example Fusayama that is the solution commonly used.

- Perform tribocorrosion experiments in the absence and presence of biofilms, in a way to understand their influence on the tribocorrosion behaviour of titanium;

It is important to point out, that a few reports take account the tribocorrosion behaviour of titanium for dental implants applications, so it is a scientific area to be pursued.