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This thesis is dedicated to my parents, my grandparents and my boyfriend.

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ABSTRACT

Co-Cr alloys are widely used fabrication of removable partial dentures (RPDs), particularly as a dental framework. These alloys replaced noble metal alloys, due to better mechanical properties, corrosion resistance and lower cost. The oral cavity is a complex environment that frequently changes in response to the intake of food, beverages, and drugs. The use of mouthwashes is known as an effective method of preventing dental caries. Several studies have been carried out on the electrochemical corrosion and metallic ion releasing on titanium, titanium alloys, and Co-Cr alloys. However, studies related to the effect of mouthwash on electrochemical behavior of Co-Cr alloys are still limited. Even a wash with a mouthwash tooks approximately 30 seconds, the mouthwash is kept in the mouth during more time. Thus, the micro-movements between the framework and the teeth or even some particles of food in contact with the framework can lead to wear. So, it is important to study the tribocorrosion behavior due to the combined action between the wear and corrosion with the presence of mouthwashes.

Four different commercial mouthwashes were chosen and artificial saliva was used as control group in order to investigate the corrosion and tribocorrosion behavior of Co-Cr dental alloy. Results showed that there was no significant influence of the mouthwashes on the corrosion behavior of the Co-Cr dental alloy. However the tribocorrosion behavior of Co-Cr alloy in mouthwash containing solutions presented both higher open circuit potential values and lower coefficient of friction. Thus, it can be stated that the presence of mouthwashes did not affect negatively the tribocorrosion behavior of Co-Cr dental alloy.

Key-words: Co-Cr dental alloy, Mouthwash, Corrosion, Tribocorrosion

RESUMO

As ligas de Co-Cr são bastante usadas para produzir próteses parciais removíveis (PPRs) e especificamente no caso do framework dentário. Estas ligas vieram substituir ligas metálicas nobres, devido a apresentarem melhores propriedades mecânicas, resistência à corrosão e baixo custo. A cavidade oral é um ambiente complexo que frequentemente se altera devido à interação com alimentos, bebidas e medicamentos. O uso de elixires dentários é conhecido como sendo um método efetivo para a prevenção de cáries. Existem vários estudos relativos ao comportamento eletroquímico e à libertação de iões metálicos de titânio, ligas de titânio e ligas de Co-Cr. Contudo, estudos relativos ao efeito da presença de elixires dentários no comportamento à corrosão de ligas dentárias é ainda escasso. Mesmo que uma lavagem com um elixir dentário dure aproximadamente cerca de 30 segundos, o elixir dentário permanece na boca durante mais tempo. Assim, os micro-movimentos entre o framework e os dentes ou mesmo algumas partículas de comida em contacto com o framework poderão levar ao desgaste. Deste modo, é importante estudar o comportamento de tribocorrosão devido a uma ação combinada entre desgaste e corrosão com a presença de elixires dentários.

Quatro elixires dentários disponíveis no mercado foram escolhidos e saliva artificial foi usada como grupo de controlo, de modo a estudar o efeito desses elixires no comportamento à corrosão e à tribocorrosão de uma liga de Co-Cr. Os resultados mostraram que não existe uma influência significativa da presença de elixires dentários no comportamento à corrosão da liga de Co-Cr. Contudo, sob ação mecânica o comportamento à tribocorrosão da liga de Co-Cr na presença dos elixires dentários apresentou valores de potencial de circuito aberto mais altos e valores de coeficiente de atrito mais baixos. Assim sendo, pode ser dito que a presença de elixires dentários não afeta negativamente o comportamento à tribocorrosão da liga de Co-Cr.

Palavras-chave: Co-Cr, Elixires Dentários, Corrosão, Tribocorrosão

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

ABBREVIATIONS

$\bar{A}_W$	Average Wear Loss
$\bar{D}$	Average Depth
$\bar{W}$	Average Width
®	Trademark
AC	Alternating Current
AS	Artificial Saliva
ASTM	American Society for Testing and Materials
A_w	Wear Loss Area
BSA	Bovine Serum Albumin
c.a.	Approximately
CAC	Colgate Plax® Alcohol-Containing
CAD	Computer Aided Design
CAF	Colgate Plax® Alcohol-Free
CE	Counter Electrode
COF	Coefficient of Friction
CPE	Constant Phase Element
CP	Cyclic Polarization
cp-Ti	Commercial Pure-Titanium
E	Potential
E_b	Breakdown Potential
EDS	Energy Dispersive Spectroscopy
EIS	Electrochemical Impedance Spectroscopy
et al.	And Others
FEG	Field Emission Gun
HC	High Carbon
HP	Hot Pressing
HV_5	Hardness Vickers
Hz	Hertz

I	Current
i_{corr}	Corrosion Current Density
i_{pass}	Passive Current Density
ISO	International Organization for Standardization
LAC	Listerine® Alcohol-Containing
LAF	Listerine® Alcohol-Free
LC	Low Carbon
N	Newton
OCP	Open Circuit Potential
OM	Optical Microscopy
Pa	Pascal
PBS	Phosphate buffered saline
PD	Potentiodynamic
ppm	Parts Per Million
Qox	Constant Phase Element of the Native Oxide Film
RDP	Removable Dental Prosthesis
RE	Reference Electrode
R_e	Electrolyte Resistance
R_{ox}	Resistance to Polarization or Native Oxide Film Resistance
SCE	Satured Calomel Electrode
SEM	Scanning Electron Microscopy
WE	Working Electrode
WHO	World Health Organization
XRD	X-Ray Diffraction
$E_{(i=0)}$	Corrosion Potential

CHEMICAL FORMULAS

Al_2O_3	Alumina
$C_{12}H_{19}Cl_3O_8$	Sucralose
$C_{12}H_{25}NaO_4S$	Sodium Lauryl Sulfate
$C_{18}H_9NNa_2O_8S_2$	Disodium 2-(1,3-Dioxoinden-2-yl) Quinoline-6,8-Disulfonate
$CaCl_2 2H_2O$	Calcium Chloride Dihydrate
KCl	Potassium Chloride
M_xC_y	Metal Carbide
Na_2S9H_2O	Sodium Sulfide Nonahydrate
$NaCl$	Sodium Chloride
$NaH_2PO_4 2H_2O$	Sodium Dihydrogen Phosphate
SiC	Silicon Carbide
TiO_2	Titanium Dioxide

MOTIVATION

Along the time, new materials have been developed in the dental materials field in order to increase the quality of dental restorations. Dental restorations are used to substitute or repair the lost or damaged teeth [1].

A dental framework is a piece that supports the artificial teeth. In the beginning, gold was used for dental applications. However, the price of gold increased in the 70’s. Thus, other alternative materials appeared on the market. Co-Cr alloys are one of these solutions and are being used in prosthetic dentistry as removable partial denture frameworks as well as in implant structures. These alloys present good mechanical properties and low weight, having a good balance between strength, wear, and corrosion resistance. Therefore, these alloys have been used specifically in removal partial denture frameworks [2–4].

In the dental healthcare field it is recommended the use of mouthwashes to prevent caries. Some studies [5–7] showed that flouride-containing solutions like toothpastes or mouthwashes are an acidic environment that may decrease the corrosion resistance of materials used in dental applications. However, most of the studies in the literature are related to the influence of fluorides on the corrosion behavior of Ti and its alloys. Rincic et al. [3] explained that the pH value of the fluids in contact with a Co-Cr-Mo dental alloy may have a stronger effect on decreasing corrosion properties. On the other hand, Rezende et al. [8] showed that for titanium alloys the mouthwash type has a stronger influence on corrosion behavior than the composition or microstructure. Souza et al. [9] used electrochemical impedance spectroscopy technique to show that the corrosion resistance of titanium decreases with increasing of fluoride concentration in artificial saliva.

Tribocorrosion is a process of degradation that involves a synergism between corrosion and wear phenomena. It has been reported that 20-30% material loss can be related to this synergism of corrosion and wear [10]. Thus, it is important to investigate the influence of mouthwashes on corrosion and tribocorrosion behavior of Co-Cr dental alloy used in removable partial dentures (RPDs).

OBJECTIVE

The main objective of this work is to study the effect of commercial mouthwashes on the corrosion and tribocorrosion behavior of a Co-Cr dental alloy.

1. FUNDAMENTAL ASPECTS OF DENTAL RESTORATIONS

1.1. Human dentition

Humans have two dentitions during their life: one during childhood, called the primary (deciduous) dentition, and a new one in adulthood, called the permanent dentition (also known as secondary dentition), being these two types of dentition showed in figure 1. The teeth in the upper jawbones collectively form an arch shape called the maxillary arch, and those teeth in the lower jawbone collectively are the mandibular arch. Each arch can be divided into the left and right halves (also known as left and right quadrants) [11,12].

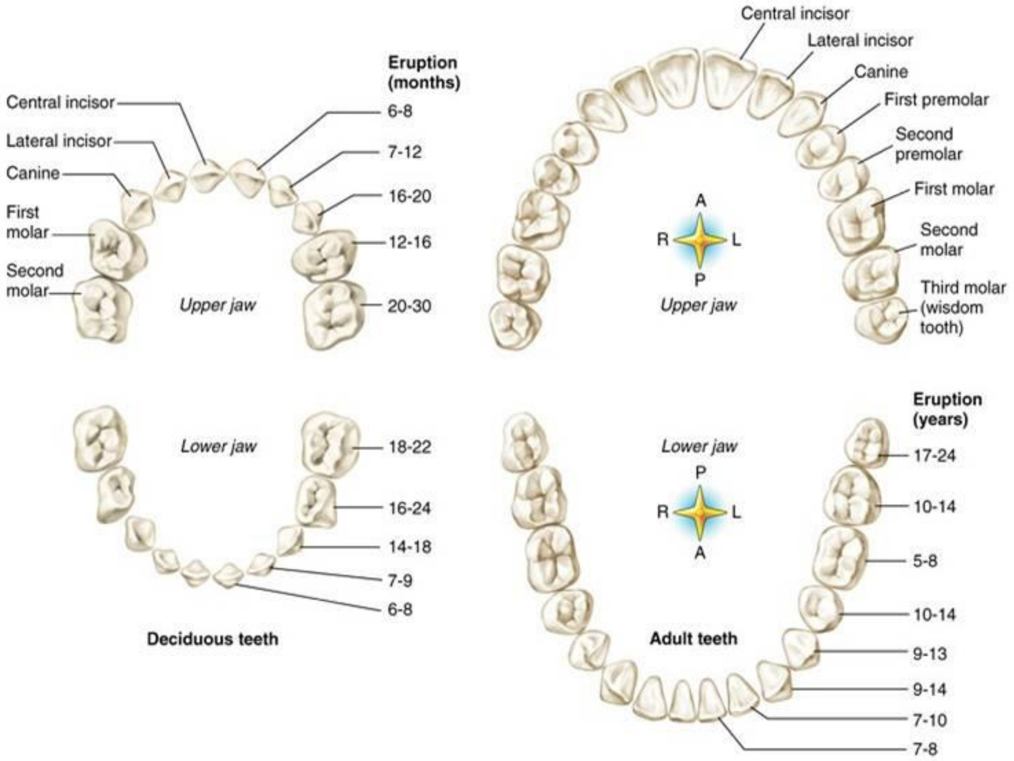

Figure 1 Deciduous (primary) teeth and adult (permanent) teeth, with denominations of teeth and the age of eruption of each teeth [12].

Figure 2 are represents the constituents of a tooth. The enamel is the white and protective external surface layer of the anatomic crown. It is highly calcified or mineralized, and it is the hardest substance in the body. Its mineral content is 95% calcium hydroxyapatite (which is calcified) and the remaining substances include 5% water and enamel matrix [11].

The cement is the dull yellow external layer of the tooth root. The cement is very thin, having only 50–100 μm of thickness [11].

The dentine is the hard yellowish tissue underlying the enamel and cement, and makes up the major bulk of the inner portion of each tooth crown and root. It extends from the pulp cavity in the centre of the tooth external to the internal surface of the enamel (on the crown) or cement (on the root). Mature dentin is composed of about 70% calcium hydroxyapatite, 18% organic matter (collagen fibres), and 12% water [11].

The pulp is the soft (not calcified or mineralized) tissue in the cavity or space in the centre of the crown and root called the pulp cavity. The pulp cavity has a coronal portion (pulp chamber) and a root portion (pulp canal or root canal). The pulp cavity is surrounded by dentine, except at a hole (or holes) near the root tip. The pulp has as main functions: protection (by producing reparative dentine), nutrition (blood vessels transport nutrients from the bloodstream to cells of the pulp and the odontoblasts that produce dentin) and sensivity (the nerve endings relay the sense of pain caused from heat, cold, drilling, sweet foods, decay, trauma, or infection to the brain) [11].

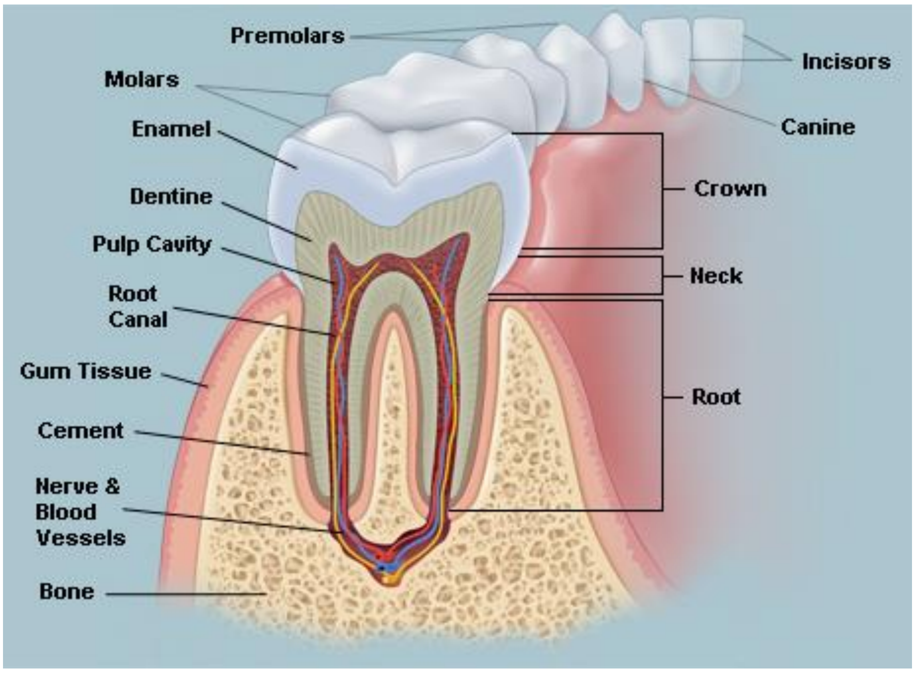

Figure 2 Representation of a tooth [13].

1.2. Causes for the dentition lost

There are different reasons related to dentation lost: diseases, age, diet, accidents, teeth quality, caries status, etc. It is important to avoid four types of possible interactions among dental restorative material and biological environment: post-operative sensitivity, toxicity, corrosion and hypersensitivity or allergy. Between the diseases the most relevant are: cavities (caries), tooth decay, periodontitis, gingivitis, plaque, tartar, overbite, underbite, teeth grinding (bruxism), tooth sensitivity. Dental caries are still a major public health problem affecting 60-90% of school-aged children and the great majority of adults [1,13,14]. According to a report of the meeting convened at WHO HQ, Geneva, Switzerland, in 2009, the distribution and severity of dental caries changes in different parts of the world and within the same region or country [15].

In addition, along the time, the population is increasing drastically and the life time as well. Moreover, since 1960 it is estimated that in 2025, 70 million of people will be older than 65 year. Thus, the number of people that need a dental restorations is also increase due to the increasing of population and the life time of a natural tooth [16].

1.3. Dental restorations

1.3.1 Types of dental restorations

There are many types of dental restorations that can be applied in different cases. The dental restorations can also restore a part or the entire tooth and they can be removable or fixed. The types of dental restorations are:

- inlay (figure 3a) consists in cover centre of the crown damaged with a dental material and onlay (figure 3b) that is similar to inlay but covers a major area of the tooth [11,17–19];
- crowns (figure 3c and 3d) cover the entire natural tooth crown [11,17,19];
- veneer (figure 3e) consists of bonding thin ceramic laminates onto the labial surfaces of affected teeth [11,17,19];
- dental amalgam (figure 3f)that is a hard mass used for restorations on the chewing surfaces of posterior teeth and to restore posterior proximal contacts [11,15,18–20];
- removable partial denture (RPD - figure 3g) is an artificial partial denture that can be removed and replaced in the mouth by the patient. The dental framework that is explained in item 1.3.2. is the metal part of the figure 3g [11,19,21,22];
- bridge (figure 3h) that is a false tooth, called a pontic, are attached at two healthy teeth on either side of the gap must be ground down to anchor the bridge (the bridge covers the prepared teeth that are left after grinding and the pontic sits in the missing tooth space above the gum) [11,19,21,23–25];

- dental implant (figure 3i) that replaces the root of a natural tooth that is the support of the new artificial tooth [11,19,21,25–28].

According to a study made by Zitzmann et al. [22] approximately half of the adult population in almost all European countries have some type of dental restoration. In countries of lower income, restorations are less frequent, although it is assumed that the need for treatment is still high.

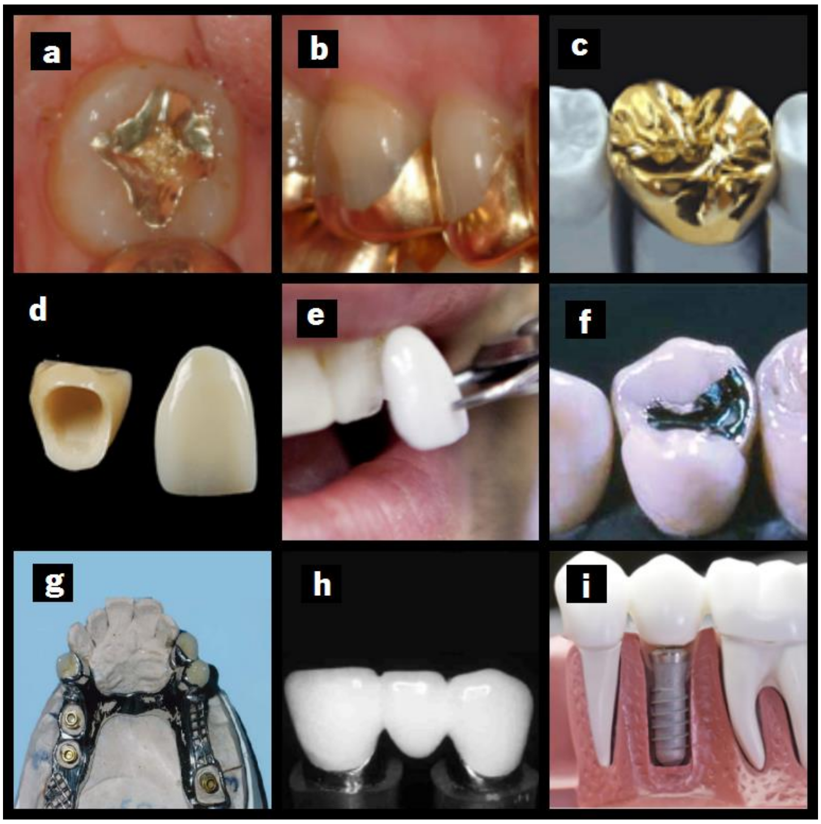

Figure 3 Dental restorations types: a) inlay b) onlay c) golden crown d) ceramic crowns e) venner f) dental amalgam g) removable prosthesis h) Bridge i) Dental implant [11,23,29–34].

1.3.2. Metal frameworks

In this master thesis a Co-Cr dental alloy used in removable dental frameworks was studied. A dental framework is the base that supports the prosthesis (removable restoration – metal part of figure 4a) or it can be supported by oral implants placed in the jawbone or by remaining teeth (fixed restoration - figure 4b) [2,4].

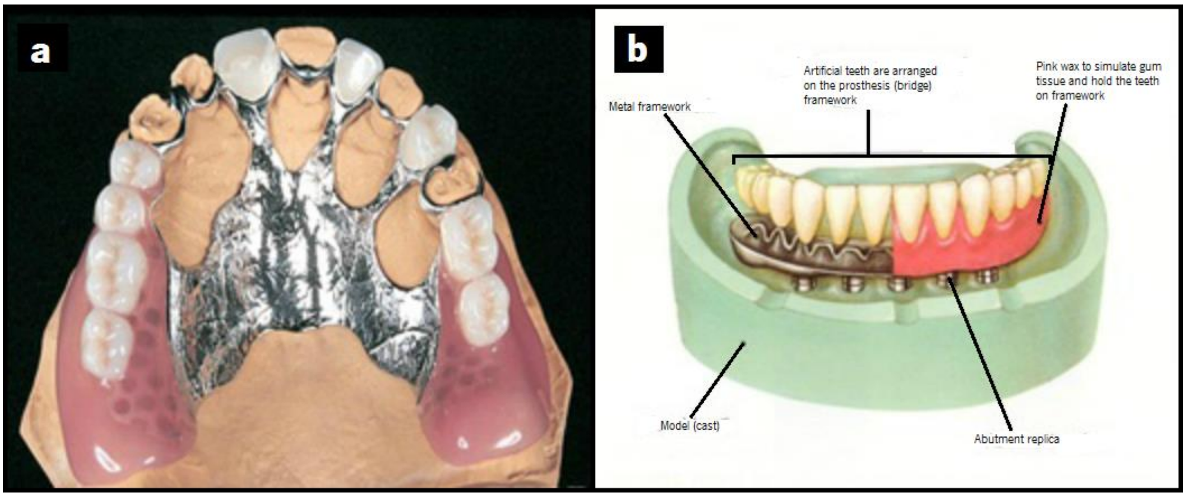

Figure 4 a) Scheme of a removable restoration b) scheme of a fixed restoration [35,36].

Nowadays full-cast and metal-ceramic restorations have been used together with the removable partial dentures. It is estimated that 90% of all removable partial dentures are now cast from non-precious alloys [37].

1.4. Dental materials

In dental applications it is required that the use of biomaterials. Biomaterials can be synthetic or natural and they are used in contact with biological systems, commonly applied in Medicine. This type of materials has to be compatible with the living tissues and must have good physical properties, avoiding the corrosion in the tissue environment and having a good surface quality and low potential for eliciting inflammation or rejection response [28,38,39].

Metals and alloys have been used in dental industry for hundreds of years. Metals and alloys are more suitable for load-bearing applications compared with ceramics and polymers, combining high mechanical strength with higher fracture toughness [40,41].

Initially, noble metals and their alloys were used for dental applications as Pd-Ag alloy for prosthetic elements. These alloys have good mechanical, biological properties, and corrosion resistance. The high price of these metals and alloys limited their use and some cheaper alternatives appeared. The non-precious metals and alloys rapidly replaced the precious or noble alloys in dentistry. In this way, base metal alloys have a good clinical performance due to high elastic modulus, hardness and low cost. Nowadays, several dental alloys are available on the market. One of the advantages of using these dental alloys for casting prostheses is the good combination between the properties: such as high hardness, strength and resistance to tarnish, low weight and also corrosion resistance [3,19,37,42–44]

At the beginning of the XX century, I. Gotman [45] showed that alloys as aluminium, copper, zinc, iron and carbon steels, silver, nickel and magnesium were tested for biomedical applications, being all of them too reactive in body and unsuitable for this application.

Although some base alloys present lower corrosion resistance compared with noble alloys, they present better mechanical properties. Manaranche et al. [43] concluded that the Pd-based and Au-Pt-Pd dental alloys are the most resistant to corrosion, even higher than gold in a sodium chloride solution at 37°C. However, most of the used metals in implants are stainless steel, Co-Cr alloys and Ti alloys. Titanium and its alloys are used for this application because of their biocompatibility and they have been used for the castings of metal-ceramic crowns. Viennot et al. [4] concluded that Co-Cr alloy has a much negative corrosion potential than Pd-Ag alloys in *Fusayama* artificial saliva, being less passive, but it is not significant. In addition, the palladium content can cause allergic reactions in patients. Titanium and its alloys have higher corrosion resistance. However, Ti and its alloys present lower mechanical properties than stainless steel or Co-Cr alloys [19,37,44,46].

Ni-Cr and Co-Cr alloys have been used in dental structures and orthopedic implants due to their corrosion behavior. These alloys have low cost of casting process, a coefficient of thermal expansion identical to ceramic used in the crown and good mechanical and tribological properties [47].

However, Ni-Cr alloys are susceptible to corrosion and can cause allergies to the users. Thus, due to this fact, Co-Cr alloys have been used because of their good electrochemical properties. Another fact is the allergic properties of metal ions of Co-Cr based alloys, although they are still very popular for dental applications [40,42].

The table 1 shows the main properties of the most used biomedical alloys. The open circuit potential (OCP) and electrochemical breakdown potential of these alloys (in 0.17 M NaCl) are presented in table 2.

Table 1 Comparison between the properties and applications of Co-Cr, Ti-6Al-4V and 316L SS [1,19,45,46,48,49].

Material	Cast Co-Cr alloys	Ti6-Al-4V alloys	AISI 316L Stainless Steel
Density (g/cm³)	8.3-9.2	4.5	7.9
Tensile Strength (MPa)	690-1800	860-1100	650
Yield Strength (MPa)	490	795-970	280
Vickers Hardness	300-430	-	190
Young's Modulus (GPa)	210-248	110-121	211
Fatigue Limit (GPa)	0.30	-	0.28
Applications	Cranial plates, orthopaedic fracture plates, dental implants, spinal rods, joint replacement prostheses, stents, catheters	Orbit reconstruction, dental implants, orthopaedic fracture plates, heart valves, spinal rods, joint replacement prostheses	Cranial plates, orbit reconstruction, maxillofacial reconstruction, dental implants, dental wires, orthopaedic fracture plates, joint replacement prostheses, ablation catheters

Table 2 OCP and Breakdown Potential in deaerated 0.17 M NaCl [45].

Material	OCP after 480h (V)	Breakdown potential (V)
AISI 316 stainless steel	≈0.30-0.50	0.40-0.48
Cast Co-Cr alloy	≈0.50	0.87
Typical titanium alloy	0.23	≈25.00

For AISI 316 both OCP and breakdown potential are in the same range of values, showing that this material may present pitting corrosion. Regarding Co-Cr alloy the breakdown potential is higher than OCP, so pitting corrosion or localized corrosion may occur just under exceptional conditions. For titanium and its alloys the differences between the two potentials is too high that it makes impossible to occur pitting or localized corrosion. Thus, titanium and its alloys present the best corrosion behavior. The OCP values from Co-Cr and 316 stainless steel are about the same which can be due to the presence of Cr in both that leads to form a passive protective layer. [45,50].

In non-precious alloys, chromium is added in the range of 15-30% in non-precious alloys to obtain the best balance between corrosion resistance and mechanical strength. Nickel addition also increases corrosion resistance and mechanical properties. In addition, molybdenum can increase the corrosion resistance of the alloy [37].

The addition of elements as Co, Cr and Ni increases the mechanical properties and it can improve the cast process into thinner shapes as crowns, bridges, fixed or removable partial dentures without compromising the rigidity [37].

1.4.1. Co-Cr alloys

Cobalt-Chromium alloys were introduced in the 30’s in order to substitute gold alloys (Type IV) in partial denture bases, and in the 70's to substitute gold in crowns and bridges due to the their low cost [1,40]. Cobalt-based alloys are widely used in biomedical applications because of their properties: good corrosion resistance and good mechanical properties as high ultimate tensile and fatigue strength combined with sufficient elongation at fracture [51,52].

Co-Cr alloys have a higher balance between its properties like strength and wear resistance compared to the other materials used for the same applications. However, the carbon content affects the hardness, strength and ductility. Co-Cr alloys can be high carbon (HC) (>0.15% weight) or low carbon (LC). The carbon forms carbides with any of the compounds and a high presence of these carbides lowers the ductility. The carbides precipitate in the interdendritic regions. The main difference is the existence of chromium carbides in the HC alloys, increasing the hardness. However, these carbides affect the corrosion stability by depleting the metal matrix in chromium. The high carbon alloys present higher wear resistance, as result the $M_{23}C_6$, M_7C_3 and M_6C carbides are formed during the solidification. The distribution of carbides is also affected by the processing and it is favourable a discontinuous carbide formation to continuous carbide formation [1,14,19,53,54].

Dobrzański et al. [41] concluded that the increase of Co content may increase the hardness. The cobalt and chromium form a solid solution for up to 30% chromium, which is the limit of solubility of chromium in cobalt; additional chromium would produce a highly brittle second phase. Molybdenum and beryllium can be added in order to refine the grain structure and improve the behavior during the casting. Co-Cr-Mo alloys form on their surface a mix of cobalt, chromium and molybdenum oxides. This thin passive film (1-4nm) can be damaged due to mechanical loading, resulting from scratches and fretting. In this way, the oxide damage is caused by wear, exposing a reactive surface to contact with corrosive environment. In fact, Cr and Mo improve the corrosion behavior, forming a protective oxide film on the surface in a corrosive environment and in general, the higher the chromium content, the better the corrosion resistance of the alloy. It has the added benefit that produces a significant solid solution hardening effect, an effect shared by the addition of iron. Co-Cr-Mo alloys are susceptible to mechanical disruption of passive film in case of dental skeletal structures and orthopaedic implants as screws, pins and plates [1,19,40,55].

Alifui-Segbaya et al. [56] studied some Co-Cr alloys and concluded that the level of metallic ions releasing for Co, Cr and Mo is according to the ISO definition.

Co-Cr alloys can be processed by different routes leading to different microstructures, and consequently different properties [48].

1.4.2. Titanium alloys

Some of the most attractive properties of titanium alloys are: high strength with low density, excellent biocompatibility and corrosion resistance. The aluminium and vanadium increase the strength in small quantities, being α-stabiliser and β-stabiliser, respectively. The α-phase is relatively soft and ductile while the β-phase is harder by changing the proportion between α-phase and β-phase, it can be obtain different properties [1].

The biggest disadvantage of titanium and its alloys are related with the problems that happen during the processing. Titanium has a high melting point, which can lead to create cooling contraction. This kind of material is very reactive, thus, it is required a special equipment with high vacuum or inert atmosphere to process it.

1.5. Processing methods for dental metal frameworks

Saji et al. [47] concluded that there was a marginal influence on the variation of morphology by casting method in Co-Cr and Ni-Cr dental alloys on the overall corrosion rate. The possibilities to produce dental metal removable frameworks of Co-Cr are the following:

1.5.1. Flame Casting

Metals and non-noble alloys have being used in full-cast and metal-ceramic restorations in addition to removable partial dentures. Nowadays, approximately 90% of all removable partial dentures are now cast from non-precious alloys containing Co, Cr, Ni [37].

The casting process for dental alloys can be performed by flame (with gas/air) or electric current The technique with flame (figure 5a) is performed by directing the flame produced from the gas/oxygen combination at the dental alloy to be melted. In this way the heat produced from this flame is radiated in all the dental alloy. The alloy is melted by a torch flame in a glazed ceramic crucible attached to the "broken arm" of the casting machine [57,58].

The torch flame can be generated from a mixture of propane and air, natural gas and air, acetylene and air, or acetylene and oxygen [57].

The flame can be divided in 4 zones (figure 5b): mixing zone (consists of unburnt gas), combustion zone (it is an oxidizing zone where a partial combustion takes place), reducing zone (that is the hottest area of the flame) and the oxidizing zone (the final combustion between the gas and the surrounding air occurs). The best area considered for melting an alloy is showed in figure 5b [58].

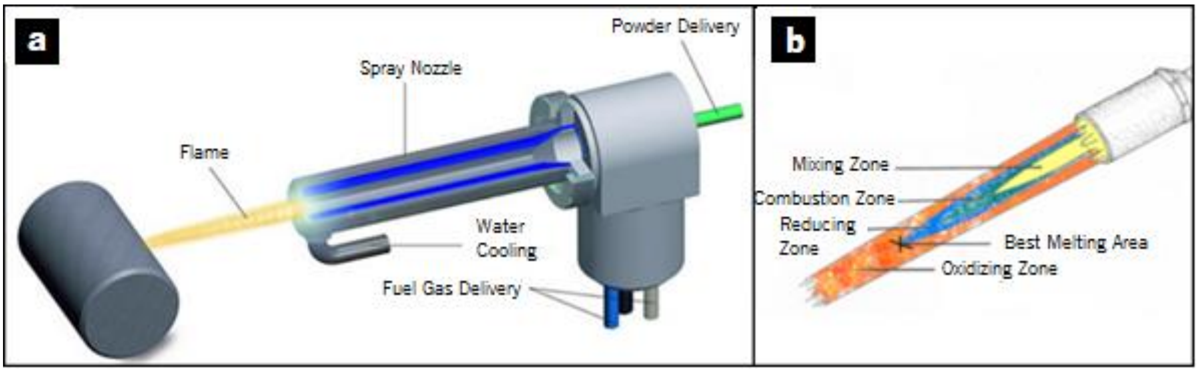

Figure 5 a) Flame Casting Technique b) zones of the flame from flame casting [58,59].

There are two types of casting machines: the first one uses the principle of centrifugal force being the metal accelerated outward by rapid spinning and it is called centrifugal casting machine (figure 6). When the metal is completely molten, the hot casting ring is placed behind the crucible that contains the molten alloy and the crucible-ring assembly is turned rapidly, which accelerates the entrance of the metal into the casting ring, by occupying the space previously occupied by the wax pattern. The other type of casting machine uses pressure over the molten alloy, called pressure/vacuum casting machine. The vacuum is applied to the bottom of the mold: the molten alloy is “pushed and sucked” simultaneously into the mold [58].

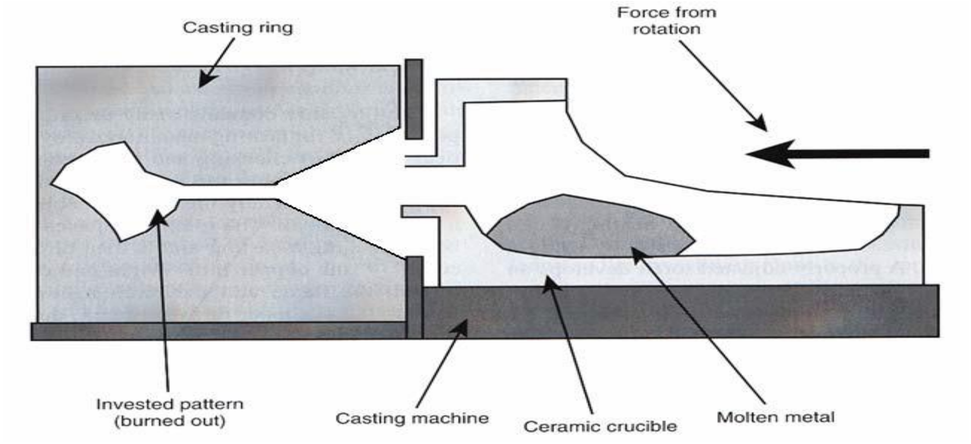

Figure 6 Scheme of a centrifugal casting machine [58].

Generally the flame casting is performed by centrifugal casting machines (figure 6) and the resistance melting and induction melting is done by centrifugal or vacuum/pressure casting machines [58].

Bauer et al. [60] stated that the mechanical properties of Ni-Cr-Mo and Co-Cr alloys were significantly improved when processed by flame casting compared with other casting techniques. Compared with laser sintering this process is simpler, it does not need high skilled human resources and expensive machines, being more economical. Furthermore, the impurities from the cast process in the alloy could lead to heterogeneity. Other problems from this process are porosity and shrinkage, that can lead to the initiation of corrosion [56,61].

1.5.2. Laser sintering

The laser sintering technique is able to generate complex 3D pieces controlled by computer from a CAD file, by consolidating successive layers of powder material, using thermal energy supplied by a focused and computer controlled laser beam, being a process used as rapid prototyping. Comparing with the cast process, the porosity is controlled [2,62].

This technique is also used for the processing of cobalt-chromium (Co-Cr) removable partial denture (RPD) frameworks [56]. A schematic representation of the operation of this machine is represented in figure 7.

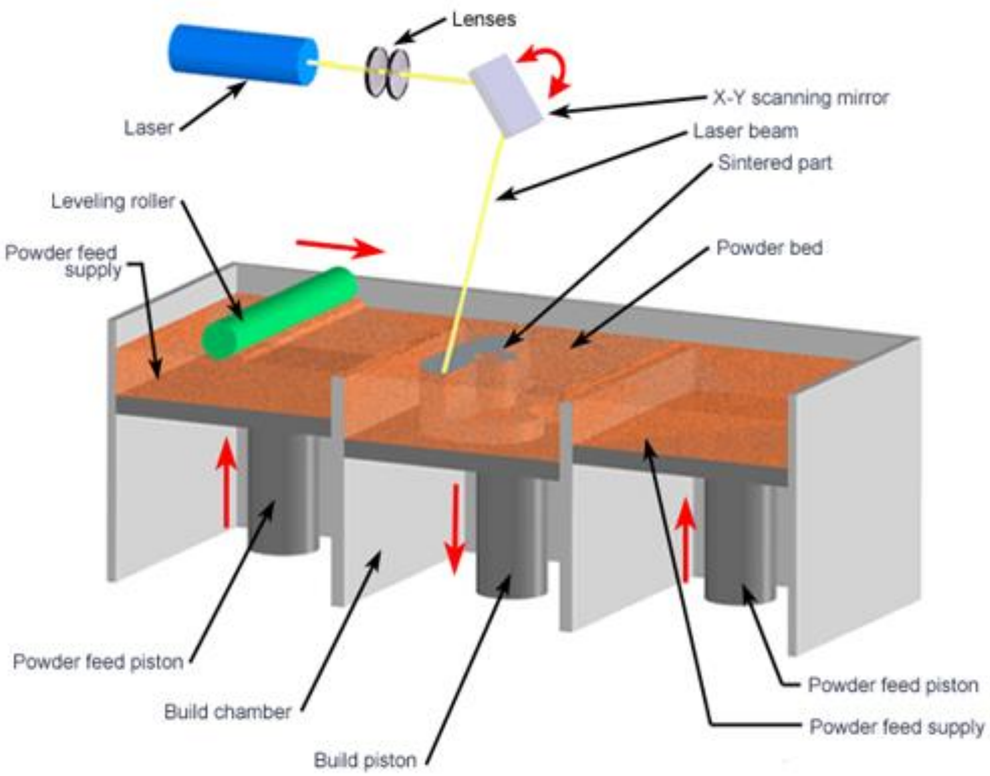

Figure 7 Scheme of laser sintering process [63].

This process is suitable for dental applications due to the complex geometry that is always different from patient to patient and low production volume of pieces required in this process. Another advantage is the digital control and the final product is obtained just in one-step. However, no scientific data are available about the physical properties of laser-sintered dental metals [2,56,62].

Some disadvantages of this process are [64,65]:

- the model may become too high and the time of the process may increase significantly;
- the powder out removal must be previously designed, the non-sintered powder may remain inside and consequently the part will not become lightweight;
- the complete powder compaction is rarely achieved and thus a post-treatment is often required, relatively small building area, few different material possibilities;
- relatively high costs associated with the process.

2. THEORETICAL ASPECTS OF METALLIC DENTAL MATERIALS DEGRADATION

2.1. Corrosion

In dental alloys the corrosion reactions might exhibit biological, functional and aesthetics effects. Adverse biological reactions due to metallic ion releasing during the corrosion process are usually detected. Another problem is tarnish that is a surface discoloration due to the formation of hard and soft deposits. However it does not cause deteoration of material. Thus, it is needed to study the corrosion behavior of dental alloys once they can induce adverse biological reactions as gingival swelling and erythema, mucosal pain and lichenoid reactions. Oral cavity is an aggressive environment due to the humidity level, saliva and temperature and pH changes. Corrosion is defined as deteoration of materials by the aggressive action of environment. This process can lead to loss of some mechanical and physicochemical properties. The corrosion behavior can be an indicator of biocompatibility (being the biocompatibility the mutual coexistence between the biomaterials and the physiological environment). A dental material is daily exposed to degradation caused by humidity, temperature and pH changes [1,40,43,66–69].

Nonferrous metals and stainless steel materials usually have great corrosion resistance due to a protective passive layer formed on its surface [44].

The corrosion process decreases the free energy when metal reacts with an environment. It can happen oxidation reaction, occurring the dissolution of the metal as metallic ions at the anode [1,69]:

$$M \rightarrow M^{n+} + ne^{-} \text{ (1)}$$

Being M a metal.

Or it can occur a reduction of hydrogen ions to hydrogen gas at cathode, [1,69]:

$$O_2 + 4H^{+} + 4e^{-} \rightarrow 2H_2O \text{ (2)}$$

When a metal or an alloy is in aqueous solutions, corrosion occurs on the surface as a result of electrochemical reactions, resulting in dissolution of metal and/or loss of ions [68].

The tendency to corrosion of metals is shown by standard electrochemical series of Nernst potentials (presented in table 3) [46].

Table 3 Standard electrochemical series of Nernst potentials [46].

Reaction	**ΔE_0 (V)**
$Li \leftrightarrow Li^+$	-3.05
$Na \leftrightarrow Na^+$	-2.71
$Al \leftrightarrow Al^{3+}$	-1.66
$Ti \leftrightarrow Ti^{3+}$	-1.63
$Cr \leftrightarrow Cr^{2+}$	-0.56
$Fe \leftrightarrow Fe^{2+}$	-0.44
$Cu \leftrightarrow Cu^{2+}$	-0.34
$Co \leftrightarrow Co^{2+}$	-0.28
$Ni \leftrightarrow Ni^{2+}$	-0.23
$H_2 \leftrightarrow 2H^+$	0.00
$Ag \leftrightarrow Ag^+$	+0.80
$Au \leftrightarrow Au^+$	+1.68

Noble metals have a higher potential than the standard hydrogen electrode and base metals have lower potentials. In this way, noble metals, as gold, are almost considered inert, and the metals that have a more negative potential difference as Co and Ti form on the surface oxide film for their corrosion resistance [46,69].

The corrosion of metals or alloys depend on the composition, surface roughness, temperature, pH, and presence of inhibitors. [70].

2.1.1. Types of corrosion

There are different types of corrosion:

- Uniform corrosion occurs on the whole surface of the metal, affecting all metals even though at different corrosion rates. It is the most common type of corrosion [71,72];
- Galvanic corrosion occurs due to the galvanic coupling of different metals involved. The less noble metal becomes anode and usually corrodes. For example, in dental applications, galvanic corrosion can occur when two dissimilar metals or alloys are joined for construct a bracket or a posted archwire. This can also occurs in removable prosthesis, when two metals or alloys are joined, and this situation is aggravated when this joint is welded [39,71,72];
- Crevice corrosion occurs in crevices on the material surface causing regions of stagnant solutions that will attack the material. An example of crevice corrosion happens on orthodontic wires or brackets in saliva due to their surfaces not being perfectly smooth and thus they can exhibit many crevices at microscopic level [39,71,72];

- Pitting corrosion is a form of extremely localized corrosion resulting in small pits or holes. A consequence of this corrosion type is a low material loss until the failure occurs, which cannot be detected. For example, pitting corrosion can occur in an implant with a small surface pit placed in a solution [28,71,72];
- Intergranular corrosion due to more reactive nature of grain boundaries to some alloys and in particular environments. The stainless steel is particularly susceptible to intergranular corrosion in brazed and welded pieces [71,72];
- Erosion corrosion is the acceleration or increase in rate of deteoration or attack on a material due to the relative movement between a corrosive fluid and material surface [71];
- Stress corrosion is caused by simultaneous presence of tensile and a specific corrosive environment. An example of stress corrosion is when an archwire is linked to orthodontic brackets increasing the reactivity of the metal alloy due to the loading in specific sites [71,72].

The pitting and the crevice corrosion increase the susceptibility to continue the corrosion process because of the accumulation of microorganisms that can cause reduction of pH and depletion of oxygen, which affects the passivation process (formation of the protective passive layer) [72].

2.2. Tribocorrosion

Tribocorrosion is a material deteoration or transformation resulting from simultaneous action of wear (tribology) and corrosion. Tribology is the science of friction, wear and lubrication and corrosion is related to chemical aspects of material degradation [73].

There is a synergism of mechanical and environmental effects that results in degradation of materials and consequently loss of material can be much large than only one of two processes of degradation separately. The metals passivate in case of corrosion only due to their highly reactive nature. However, in a situation where wear occurs, the material loss due to mechanical action is much higher than the result of wear and corrosion separately [73,74].

Tribocorrosion phenomenon occurs in large variety of applications leading to a material loss, durability loss, reliability loss, safety loss, worst performance, less energy efficiency, health harmful, etc.. Thus, some properties of a material, necessary to correspond to specific requirements, can be lost. Tribocorrosion is presented in living systems like metallic implants in human body such joints, plates, crews, dental and orthopaedic implants [73,74].

The factors that affect tribocorrosion phenomena are: properties of the contacting materials, mechanics of the tribological contact and physicochemical properties of the environment, being these factors interrelated and correlated with synergism existing on tribological system. The microstructure, the presence of defects, the topography and the chemical composition of the surfaces in contact are critical factor on tribocorrosion behavior. The environment of tribocorrosion can also influence, due to some variables such as: phase state, viscosity, conductivity, pH, temperature, etc. [73].

The corrosion resistance of many materials can lead to an oxide film formation on the surface, meaning that the material has a passive behavior. However, within the tribological contacts, this film can be removed by wear or impingement processes, increasing the mass loss of material [73].

The study of tribocorrosion in dentistry is important because in the masticatory process exists a phenomena of rubbing between teeth and food particles in presence of saliva.

2.2.1. Contact modes of tribocorrosion

A schematic representation of different tribological contacts is shown in figure 8.

- Sliding is a two or three body contact between sliding surfaces the relative motion of the surfaces can be unidirectional or reciprocating [73,75];
- Fretting is a special type of tribological contact involving a reciprocating motion of small amplitude (a few micrometres) [73,75]. This phenomenon results of a combined effect at small scale of cyclic wear and corrosion. An example is the archwire/bracket-slot interface when a load is applied leading the two metals to undergo a process of cold welding from the pressure at the interface between them. Continuing this load, the protective oxide layers on the surface of the material can be damaged leading these metals or alloys to corrosion [39,55,72].
- Rolling contacts that is typical for ball bearings [73,75];
- Particle impingement can result in a combined mechanical and chemical attack of the material; a well-known example is erosion corrosion of pumps and pipes carrying slurries [73,75].

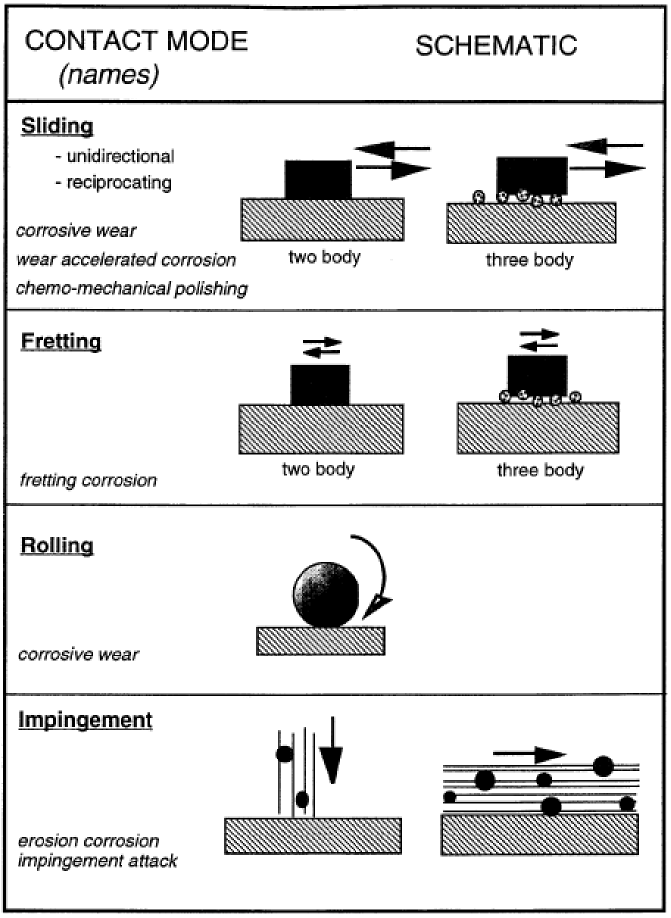

Figure 8 Schematic representation of different types of tribological contacts involving simultaneous mechanical and chemical effects [75].

3. STATE OF ART ON CORROSION AND TRIBOCORROSION OF DENTAL ALLOYS

3.1. Corrosion

Alves-Rezende et al. [70] studied the corrosion resistance of Ni-Cr with different compositions in 3 different commercial mouthwashes with different active ingredients. The authors concluded that the corrosion behavior of Ni-Cr alloys was more affected by their composition and microstructure than by mouthwash type. A spontaneously passive film was formed on Ni-Cr alloy surface independently of the mouthwash.

In another study of Alves-Rezende et al. [8], the authors concluded that the chemical composition of the same three commercial mouthwashes affects more than the composition of the alloy in case of Ti alloys. Thus, the authors recommend that patients with Ti alloys restorations should use non-fluoridated mouthwashes due to the protective characteristics of passive film.

Mareci et al. [40] studied the corrosion behavior of a Co-Cr-Mo alloy in artificial saliva. It was concluded that the Co-Cr-Mo alloy has a passive behavior and a high corrosion resistance, leading to a good biocompatibility of this alloy. On the other hand, Viennot et al. [42] compared the corrosion behavior of a noble alloy and a Co-Cr alloy and concluded that Pd-Ag alloy has more passive behavior than Co-Cr alloy in *Fusayama* artificial saliva. However, no significant differences on corrosion currents were found between Pd-Ag and Co-Cr alloys. Another study by Mareci et al. [76] compared the corrosion behavior of four different alloys (Ag-Pd, Ni-Cr, cp-Ti and Ti-12Mo-5Ta) in artificial saliva with Oral B solution. It was concluded that all the alloys have a good resistance to corrosion. However, Ag-Pd alloy did not show a passive behavior when compared with the other alloys for all electrolytes.

Jaffer [67] studied the effect of different mouthwashes on the metallic ion releasing of Co-Cr alloy denture and it was concluded that Cr ion releasing was lower than Co ions.

Schiff et al. [5] studied the corrosion resistance of three orthodontic brackets (Fe-Cr-Ni, Co-Cr and Ti alloys) on three fluoride mouthwashes. Regarding the Co-Cr alloy the corrosion behavior was not influenced by the different mouthwashes. However, the corrosion behavior of Fe-Cr-Ni and Ti alloy was affected by the mouthwashes. The authors stated that Elmex® and Ancorea® mouthwashes were the less corrosive environments compared with Meridol®.

Lassila et al. [77] concluded that the fatigue resistance of three Co-Cr dental alloys is reduced by testing in air, artificial saliva and distilled water and this can be due to of corrosion fatigue of the alloy. By Electrochemical Impedance Spectroscopy (EIS) tests, for Co-Cr, Ni-Cr and cp-Ti in artificial saliva was formed a stable passive film except Cu-Ni-Al, where porous film was formed in artificial saliva [37].

Souza et al. [9] studied the corrosion behavior of titanium in *Fusayama* artificial saliva with addition of different concentration of fluorides. The authors concluded that a compact passive film was formed in artificial saliva without fluorides presence and up to 227 ppm F^-. In these solutions the OCP increased to more noble values that suggest the growth of a passive film. On the other hand, a decrease of the OCP values was noticed on immersion in artificial saliva containing 12,300 ppm F^-.

3.2. Tribocorrosion

Some studies on tribocorrosion of biomaterials have been done. Contu et al. [78] enhanced the need and importance of a better understanding of the corrosion behavior of metallic implants of pure titanium, Ti-6Al-4V, Ti-6Al-7Nb, and Co-Cr-Mo after mechanical disruption of both the passive film and the stability of the protecting oxide film when exposed to physiological solutions. The influence of fluorides in artificial saliva on the tribocorrosion behavior of cp Ti was investigated by Souza et al. [9]. Even though a decrease on COF was observed when the fluoride concentration increased and an increase on material loss was noticed by the higher concentration of fluorides. On the other hand, the presence of fluorides concentration on Ti can significantly influence the corrosion resistance. Thus, the degradation of the protective titanium oxide layer may lead to failures in dental implants and prostheses. This negative effect can also lead to inflammations and toxic effects on the human body.

Vieira et al. [79] studied the influence of the pH and corrosion inhibitors in artificial saliva on the tribocorrosion behavior of cp Ti. It was concluded that the addition of citric acid or anodic inhibitor to artificial saliva results in a slight improvement of the tribocorrosion behaviour of Ti. Regarding the wear rate, no significant differences were observed. However, a lower wear volume loss was obtained, which can be due to the slightly lower corrosion rate detected in these solutions during the fretting tests. Ti had a lower wear volume loss in the AS containing citric acid, indicating that some protection was provided by the addition of citric acid to the solution. In solutions containing citric acid or anodic inhibitor generated protection due to the nature of the oxidation and reduction reactions occurring in the contact area during fretting test. Tribo-layers were formed in the contact region during the tribocorrosion test and become more stable after 7000 cycles in solutions with citric acid or anodic inhibitor, as noticed by a lower coefficient of friction and a lower corrosion current. The addition of a cathodic or an organic inhibitor to artificial saliva, has a dangerous effect on the tribocorrosion behaviour of titanium. Both an increase in the wear volume loss and a significant higher corrosion rate during fretting test were noticed.

It was not found more information about tribocorrosion on dental applications. However, it was done a review of some scientific information of in other biomedical applications.

Yan et al. [80], in their work on tribocorrosion behavior of a HC Co-Cr-Mo, a LC Co-Cr-Mo and the 316L Stainless Steel in 3 different electrolytes (50% calf bovine serum, Dulbecco's Modified Eagle's Medium (DMEM) and 0.36% NaCl solution), at 37°C, concluded that the influence of the corrosion was more significant than the wear. Another study from Yan et al. [81] using the same alloys in 50% bovine serum and 0.36% NaCl solutions, concluded that proteins and amino acids can influence the corrosion and tribocorrosion behavior, accelerating the corrosion rate and acting as lubricants enhancing the degradation due to the increase of corrosion behavior. In these two works it was concluded that the material with the best behavior was HC Co-Cr-Mo [80,81].

Doni et al. [10] studied the tribocorrosion behavior of Co-Cr-Mo alloy processed by casting and hot pressing and Ti-6Al-4V alloys used in orthopedic and dental implants in NaCl solution at 24 ± 2 °C and 37 ± 2 °C. It was concluded that the temperature did not influence COF (coefficient of friction) and OCP (open circuit potential) values during the sliding in NaCl solution. Moreover, both Co-Cr-Mo alloys presented similar behavior in terms of worn surface features, COF, and OCP. However, Co-Cr-Mo samples presented lower tendency to corrosion under sliding compared with Ti-6Al-4V. The wear rates after tribocorrosion tests presented different values; while wear rates of Co-Cr-Mo samples presented similar values, wear rate of Ti6Al4V was found approximately 45 times higher than the both Co-Cr-Mo samples.

Arenas et al. [82] showed that the Co-Cr-Mo alloy have a good corrosion behavior in a simulated physiological solution, PBS. A big decrease in the total wear volume loss was observed under anodic control when compared with the OCP condition. On the other hand, the wear volume loss under anodic control is nearly double in relation to that obtained under OCP. This result shows that the oxidizing conditions imposed during sliding greatly accelerate the overall tribocorrosion process of the Co-Cr-Mo alloy. The morphology results indicate that corrosion aggravates the wear of the Co-Cr-Mo alloy in PBS, generating an important increase of total wear volume.

4. CORROSION AND TRIBOCORROSION TECHNIQUES

4.1. Corrosion techniques

4.1.1 Open circuit potential (OCP)

By open-circuit potential technique it is possible to get information about the electrochemical state of a material. However, this method just provides limited information on the kinetics of the surface reactions. The potential of metal is measured with respect to a reference electrode, when no current flows. “Corrosion potential” is defined as the potential of a corroding surface in an electrolyte relative to a reference electrode. Open-circuit potential technique is appropriate for monitoring corrosion-wear of passive metals in a corrosive environment. However, the information of OCP is not sufficient to identify the corrosion-wear mechanisms for unknown corrosive wear systems. On the other hand, by monitoring the OCP of a metal it can be indicated whether a metal is undergoing a depassivation or a repassivation process [83].

Figure 9 represents a typical behavior of the OCP evolution with time in physiological solutions (such as Hanks' or Ringer's solution) [45].

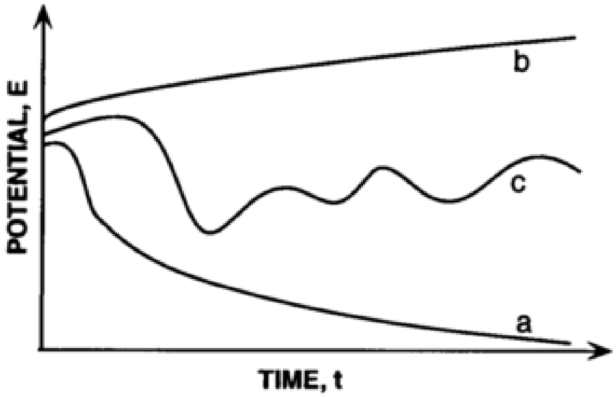

Figure 9 Evolution of potential with time: a) the material exhibits film breakdown after immersion, b) the material have an intact passive film, c) the material exhibits film breakdown after initial thickening [45].

The curve a) in figure 9 shows a sharp drop on potential at the beginning of the immersion and after some time the potential remains constant. This behavior indicates a complete film breakdown after immersion and shows that general corrosion is taking place. In the curve b) the potential rises and is continuously increasing with time. This is a typical behavior of a passive metal. Regarding the curve c) fluctuations on potential evolution are observed, meaning that the metal is susceptible to the localized corrosion or pitting corrosion, in which small areas on the metal surface are rapidly attacked while the remainder of the surface remains passive and unaffected [45].

4.1.2. Potentiodynamic polarization (PD)

Potentiodynamic polarization measurements can be used to derive the dependence of anodic or cathodic current, I, on the electrode potential, V, measured versus a reference electrode (figure 10). This technique is useful to determine the active/passive behavior of materials at different potentials [83].

When anodic current is equal to the cathodic current, the net current measured on the surface will be zero. The equilibrium potential at which this occurs is called corrosion potential ($E_{(i=0)}$). The corrosion current density (i_{corr}) is determined at the $E_{(i=0)}$. Then, the potential increases and the curve moves to active zone. In this zone, metal oxidation is the dominant reaction and general corrosion and sometimes pitting occurs. Above passivation potential, E_p, the applied potential increases and the current density is constant and, thus, passive current density (i_{pass}) is achieved (passive zone). Once the potential reaches a sufficiently positive value (sometimes termed the breakdown potential E_b) the applied current rapidly increases forming a transpassive zone where pitting corrosion can occur. This increase may be due to a number of phenomena, depending on the alloy/solution combination. For some alloys, typically those with a very protective oxide, such as cobalt, the sudden increase in current is due to oxygen evolution [50,83–85].

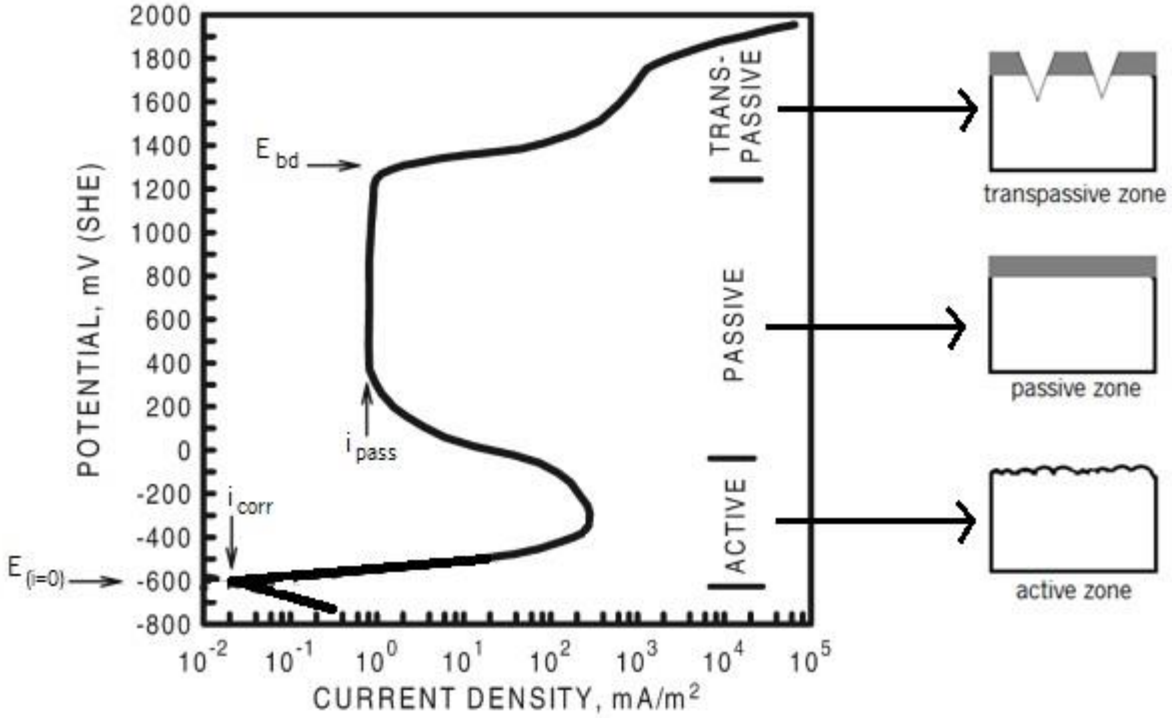

Figure 10 Representative polarization curve adapted from [86].

i_{corr} and $E_{(i=0)}$ are obtained by the interception of the anodic and cathodic Tafel branches on the polarization plot as it is shown in figure 11.

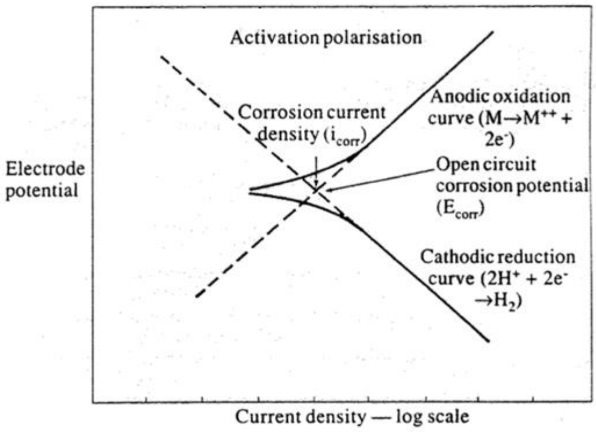

Figure 11 Example of polarization plot, showing intersection of anodic and cathodic Tafel [87].

4.1.3. Electrochemical impedance spectroscopy (EIS)

Electrochemical impedance spectroscopy (EIS) is a non-destructive technique for studying many chemical and physical processes, which is a result of a material in contact with an electrolyte. By applying a small AC voltage across the metal/electrolyte interface, EIS is able to examine the interfacial properties of a metal in an electrolyte. By knowing the response of the system material/electrolyte to the applied potential, the interface is changed by adsorbed species onto the surface and/or metal dissolution can be studied [84].

The EIS measurements consists on applying an AC small amplitude signal, usually a voltage between 5 to 50 mV, to a specimen over a range of frequencies of 0.001 Hz to 100,000 Hz, recording the real (resistance) and imaginary (capacitance) components on impedance response of the system, resulting in two types of diagrams: the Nyquist diagram that is a graph of real and imaginary impedance amplitudes and the Bode diagram that is a graph with X-axis which contains logarithmic values of frequencies and two Y-axis: one contains logarithmic values of total impedance and the other the phase angle for resistance and capacitive resistance [85].

In order to understand the electrochemical system it is fitted an equivalent circuit model. This equivalent circuit model is constituted by electrical parameters (resistances and capacitors, for example) that represent the electrochemical properties of the system [85].

4.2. Tribocorrosion techniques

This kind of tests is important to understand the relationship between corrosion and mechanical damage of a material immersed in a corrosive solutions and simultaneously exposed to wear.

The OCP of the system is measured up to achieve a stable potential. Then the sample is exposed to sliding and it is simultaneously measured the OCP. The results from this test can be presented as in the Figure 12. The potential decreases when the sliding happens and recovers when the applied force stops.

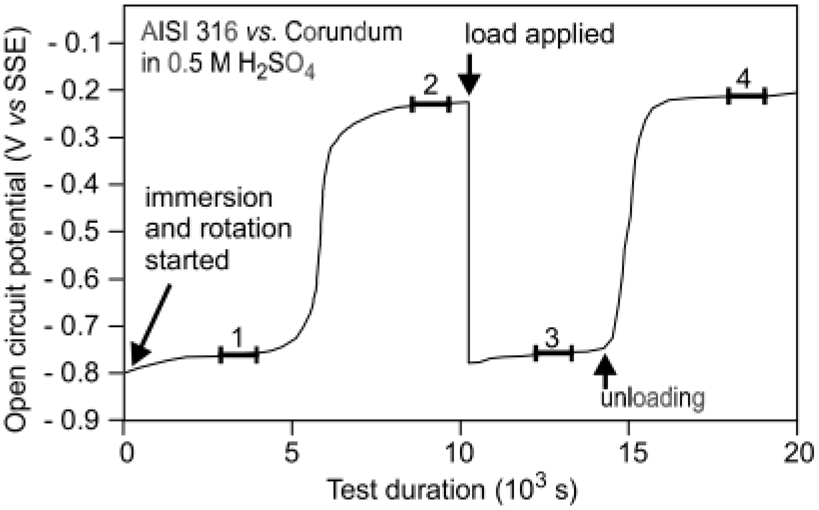

Figure 12 Example of variation of the open circuit potential of a stainless steel disk immersed in 0.5M H_2SO_4 before (e.g. areas 1 and 2), during (e.g. area 3), and after loading (e.g. area 4) against a corundum ball [83].

Many factors can influence the tribocorrosion behavior. In case of local abrasion of passive film, it can lead to wear accelerated corrosion due to a rapid dissolution of the locally depassivated film, followed by repassivation. The repassivation is a film reforming process on the broken surface film as it showed in figure 13. The repassivation phenomenon occurs by a process of nucleation and growth of a passive film on the bare surface of an alloy, mechanisms proposed for the formation of a passive film can be applied to repassivation kinetics [88,89].

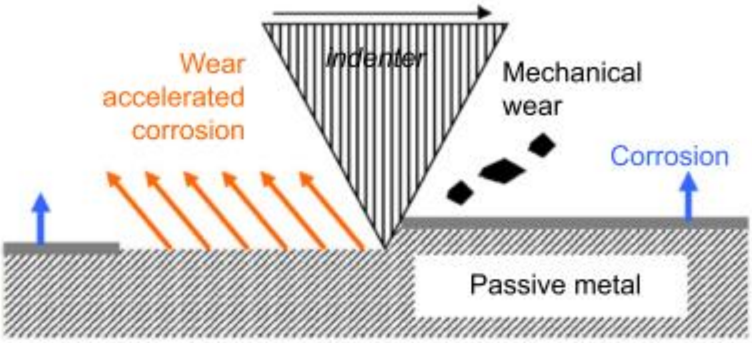

Figure 13 Schematic illustration of the degradation mechanisms of passive metals subject to tribocorrosion [90].

After the end of sliding, when the mechanical damage is interrupted and the OCP value increases, the repassivation phenomenon occurs. The repassivation rate is calculating by OCP graph showed in figure 14 and the logarithmic law showed in equation 3.

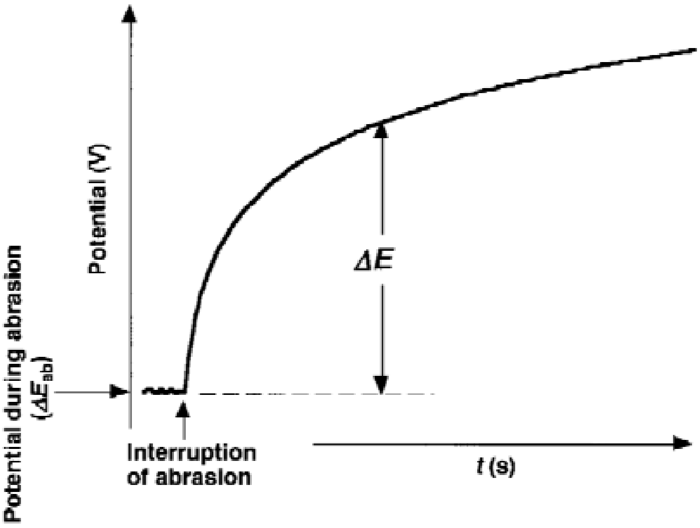

Figure 14 Change in potential in titanium during and after abrasion [91].

$$\Delta E = k_1 \log t + k_2 \quad (3)$$

Where ΔE is the potential in V, t is the time, k_1 is the repassivation rate and k_2 is log t when E=0 V, being a constant. k_1 is calculated from the slop of ΔE. The considered time is the time after the abrasion interruption. High k_1 values mean a larger increase of potential at the initial stage of repassivation and a high repassivation kinetics [91,92].

5. MATERIALS AND METHODS

5.1. Materials

The chemical composition of Co-Cr alloy (DFS, Ländenstrabe, Riedenburg, Germany) is given in table 4. Co-Cr tablets (Ø – 12 mm x 2 mm thickness) were processed using conventional flame fusion technique and injected by centrifugation.

Table 4 Chemical composition (wt%) of Co-Cr alloy.

Material	**Co**	**Cr**	**W**	**Mo**	**Nb**	**Mn**	**Si**	**Fe**	**Others**
CoCr alloy	61	24	8	2.5	1	1	1	1	0.5

The samples were ground down to 2400 mesh size SiC paper followed by polishing with OP-S (0.04 μm) suspension. After polishing, samples were ultrasonic cleaned: 10 minutes in warm water, 10 minutes in propanol followed by 5 minutes in distillated water. Before each test the samples were kept in desiccator for 24 hours in order to homogenize the surfaces and obtain to similar surface conditions.

5.2. Solutions

Four different commercially available mouthwashes (*Listerine® alcohol-free and Listerine® alcohol containing - Johnson & Johnson Limitada, Barcarena, Portugal; Colgate Plax® alcohol-free and Colgate Plax® alcohol-containing - Colgate-Palmolive Unipessoal Lda, Porto-Salvo, Portugal*) were chosen and artificial saliva (*Fusayama* artificial saliva) was used as control.

The chemical composition of artificial saliva is given in table 5. The solutions were prepared as followed:

- AS: artificial saliva group – control: 100% artificial saliva;
- LAF: Listerine (alcohol-free group: 50% vol. mouthwash + 50% vol. artificial saliva);
- LAC: Listerine (alcohol-containing group: 50% vol. mouthwash + 50% vol. artificial saliva);
- CAF: Colgate (50% vol. mouthwash + 50% vol. artificial saliva);
- CAC: Colgate (50% vol. mouthwash + 50% vol. artificial saliva).

Table 5 Composition of artificial saliva *Fusayama* [9].

Compound	g/L
NaCl	0.4
KCl	0.4
$CaCl_2 2H_2O$	0.795
$Na_2S 9H_2O$	0.005
$NaH_2PO_4 2H_2O$	0.65
Urea	1

In table 6 is shown the pH of each solution.

Table 6 pH of solutions.

Solution	pH
AS	5.38 ± 0.30
LAF	4.09 ± 0.03
LAC	3.68 ± 0.06
CAF	4.96 ± 0.05
CAC	4.14 ± 0.12

5.3. Corrosion tests

All the corrosion tests were performed using a Gamry potentiostat/galvanostat (model Reference – 600). A standard three-electrode electrochemical cell (adapted from ASTM: G3-89) with an electrolyte volume of 200 ml was used for the corrosion measurements, where a saturated calomel electrode (SCE) was used as the reference electrode (RE), Pt electrode used as the counter electrode (CE), and samples having an exposed area of 0.38 cm^2 used as the working electrode (WE) as presented in figure 15. The tests were carried out at body temperature (37 ± 2 °C).

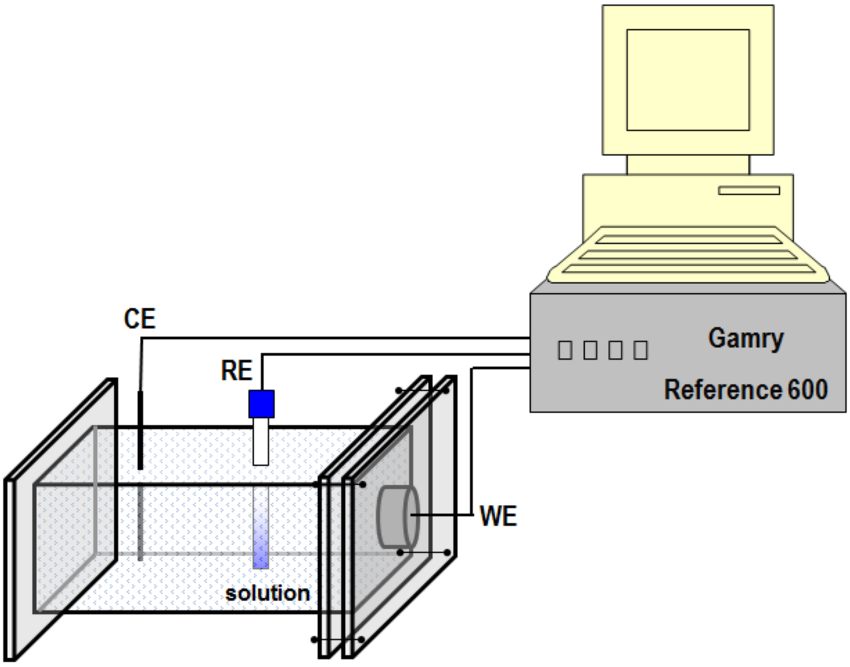

Figure 15 Schematic representation of electrochemical test, being CE the counter electrode, RE the reference electrode and WE the work electrode.

The Open Circuit Potential (OCP) versus time was measured during 1 hour to determine the tendency to corrosion.

In the Potentiodynamic Polarization (PD) test it was used an initial delay time at equilibrium state of 60 min in order to stabilize the surface at OCP. These tests were carried out in the anodic direction starting at 0.25 V below the OCP up to 1.5 V, at a scan rate of 5 mV/s. Before and after PD tests the pH of each solution was measured (EUTECH Instruments pH 510).

Electrochemical Impedance Spectroscopy (EIS) tests were carried out after monitoring OCP during 1 hour in equilibrium state. The impedance data acquisition was carried out by scanning a range of frequencies from 64 kHz until 10 mHz with 10 points per frequency decade and the amplitude of the sinusoidal signal was approximately 10 mV in order to guarantee linearity of the electrode response.

All the tests were repeated at least three times in order to have repeatability.

5.4. Tribocorrosion tests

The electrochemical cell was installed on a ball-on-plate tribometer (CETR-UMT-2), as it showed in figure 16, with the sample surface facing upwards, against the counter material (10mm diameter alumina ball, Goodfellow). The electrochemical measurements were carried out at body temperature using the same three-electrode set-up. In 30 mL electrolyte OCP evolution with time was monitored using a Voltalab PGZ 100 potentiostat. The OCP was measured before, during and after sliding. The sliding action started after reaching the stable OCP values for each test. The tribological parameters were: a frequency of 1 Hz, an amplitude of 5 mm, a load of 10 N and 1 hour of sliding. The maximum contact pressure was 4.2 GPa. After the test, the samples were ultrasonic cleaned with the following sequence: 15 minutes in warm water, 10 minutes in propanol and 5 minutes in distillated water.

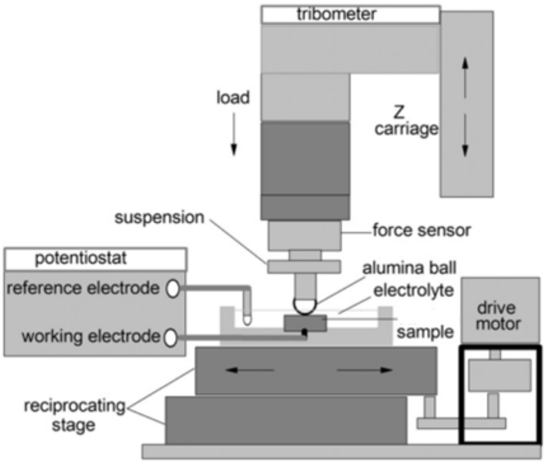

Figure 16 Example of modified tribocorrosion experimental setup with a reciprocating sliding tester [9].

All the tests were repeated at least three times in order to have repeatability.

5.5. Characterization techniques

It was performed a morphological, structural and chemical characterization of Co-Cr alloy, with the following characterization techniques:

- Optical microscopy (Leica DM2500 Optical Microscope) to study the surfaces morphology before and after corrosion and tribocorrosion tests;
- SEM/EDS FEI Nova 200 Field Emission Gun Scanning Electron Microscope (FEG-SEM) equipped with EDAX, energy dispersive X-ray spectroscopy (EDS). The SEM analysis were performed before and after the corrosion and tribocorrosion tests, and on the alumina balls after the tribocorrosion tests were also performed;
- X-ray diffraction (XRD) (Cu Kα radiation, Bruker D8 Discover) was used before and after the corrosion tests in order to identify the phases present in Co-Cr;

- Hardness (EMCOTEST DURASCAN), Vickers macro-hardness were determined by a mean of 5 indentations per sample at a 5 kg load with dwelling time of 15 s;
- Wear volume was calculated by profilometry (Veeco Dektak 150). This measurement was performed at the end of tribocorrosion each profile was taken with a scan rate of 0.185 µm/s.

The wear volume loss is determined by following the wear track model in figure 17. For each wear track, five 2D profiles were obtained, from the center of the wear track (lines b in Figure 17), and 1 and 2 mm away from the center for both sides (lines a1, a2, c1, and c2 in Figure 17) [10].

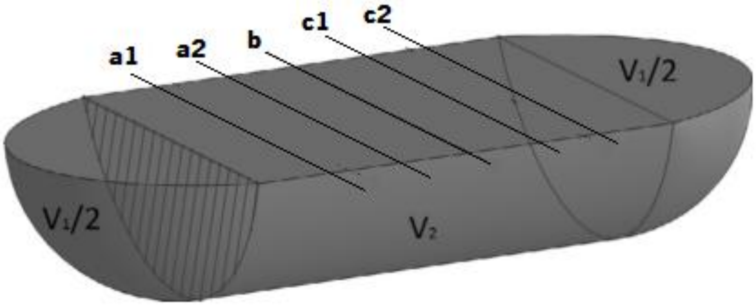

Figure 17 The estimated model used for calculating the wear loss volume. The lines a1, a2, b, c1 and c2 are indicating 2D profile lines - adapted from [10].

For the calculation of wear loss volume, first, wear loss area for each 2D profile is calculated with the following equation:

$$A_w = \sum_{i=0}^{n} 0.5(Y_i + Y_{i+1})(X_i + X_{i+1}) \quad (4)$$

Where A_w is the wear loss area for each 2D profile in mm^2, X is the width in mm, Y is the deepness in mm, and n is the number of counts. Then, average deepness values are calculated with the following equation:

$$\overline{D} = \frac{\bar{A}_w}{\overline{W}} \quad (5)$$

Where $\overline{D}$ is the average depth in mm, $\bar{A}_w$ is the average wear loss area of five 2D profiles for each wear track, and $\overline{W}$ is the average width of each wear tracks measured for five 2D profiles. Finally, wear volume is calculated with the following equation:

$$\Delta V = \left[\frac{1}{3} \times \pi \times \overline{D^2}(3R - \overline{D})\right] + \bar{A}_w \times l \quad (6)$$

where ΔV is the total volume loss for each wear track in mm^3, R is the radius of the alumina ball, and l is the total stroke length.

6. RESULTS AND DISCUSSION

6.1. Morphological and microstructural characterization of the surfaces

6.1.1. Optical microscopy (OM) and porosity

The morphology of the initial surface of Co-Cr alloy is shown on the low magnification OM images in figure 18. The casting processes are known by presenting defects as uncontrolled porosity, chemical inhomogeneity, large grain size and microstructure with hard precipitates in the interdendritic zones [10,47,93,94]. As it can be observed in figure 18 there is some porosity as a consequence of casting process. However, it is important to state that the porosity level is low regarding the testing surfaces. Viennot et al. [61] observed those defects could behave as starting points of corrosion processes.

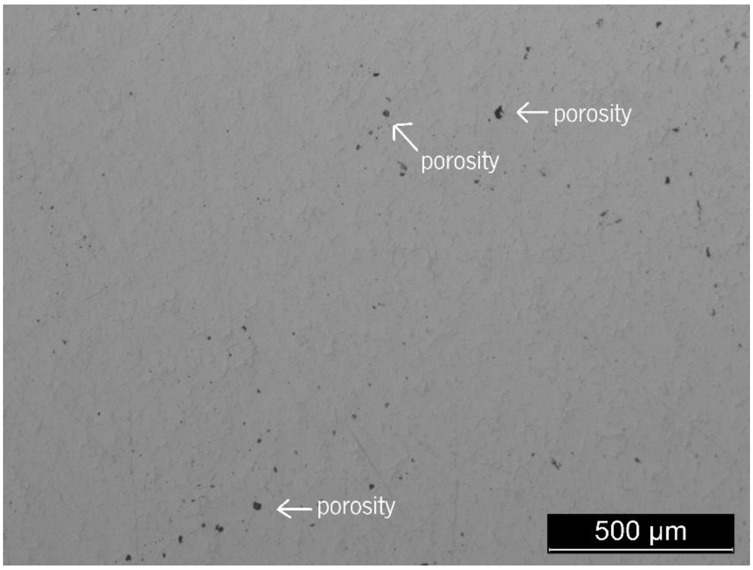

Figure 18 OM image of Co-Cr dental alloy surface.

6.1.2. XRD analysis

The XRD spectrum of Co-Cr dental alloy is shown in figure 19. As it can be observed on the spectrum, γ phase was obtained as matrix phase of the alloy. On the other hand, σ phase was identified as a second phase. σ phase was identified with data available for σ Co-Cr [95]. The γ phase has FCC structure and σ phase has a tetragonal structures.

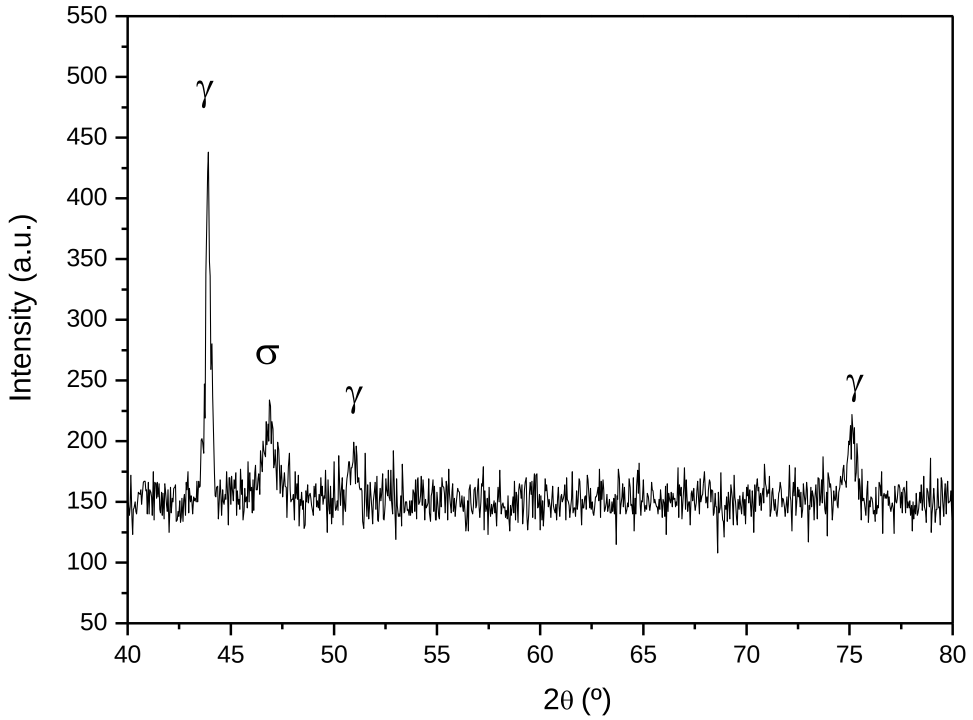

Figure 19 XRD spectrum of the Co-Cr dental alloy.

6.1.3. SEM and EDS analysis

In figure 20 is shown a SEM image of the microstructure of Co-Cr alloy. It can be distinguished the γ phase corresponding to matrix and a second phase σ corresponding to the eutectic.

In addition, a third phase was detected which is mainly rich in W and Nb as shown in EDS spectrum. Viennot et al. [4] mentioned that the W, an intermetallic compound in the alloy, it helps to reduce the formation of Cr-depleted zones and increases the corrosion resistance. Diomidis et al. [96] stated that Nb present in σ phase as well as Zr and Ta as alloying elements tend to form dense surface oxides, increasing the stability of passive layer.

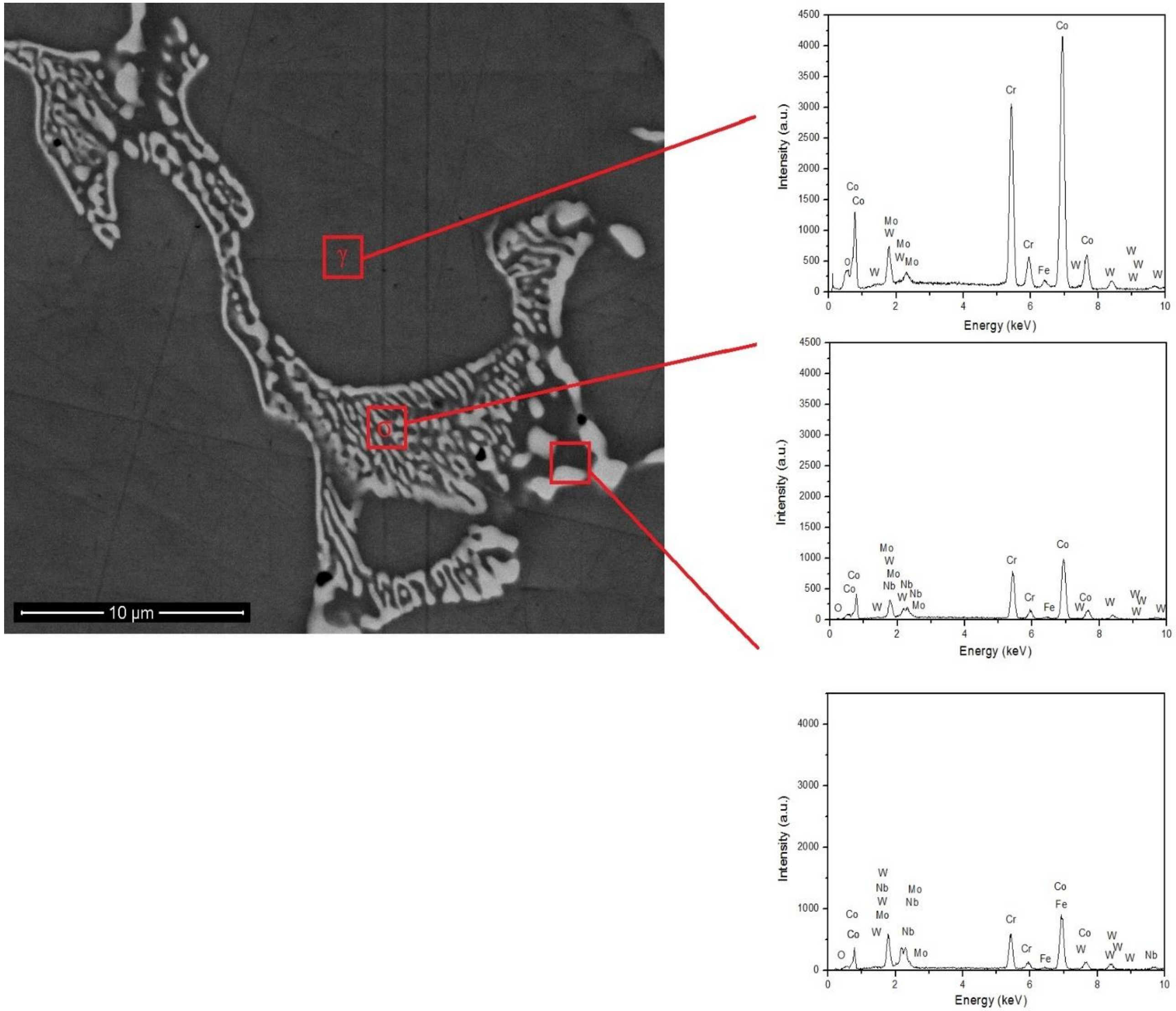

Figure 20 BSE SEM image of Co-Cr dental alloy and the EDS spectra taken from the marked areas.

In tables 7 to 9 are shown the chemical composition of the different phases founded in Co-Cr Alloy.

Table 7 Chemical composition of γ phase, obtained in Co-Cr Alloy by EDS technique.

Element	Weight (%)	Atomic Mass (%)
O	3.95	13.65
Mo	2.97	1.71
Cr	24.01	25.52
Fe	1.60	1.58
Co	58.46	54.83
W	9.01	2.71

Table 8 Chemical composition of σ phase, obtained in Co-Cr Alloy by EDS technique.

Element	Weight (%)	Atomic Mass (%)
O	3.73	13.89
Nb	7.12	4.57
Mo	5.94	3.69
Cr	20.67	23.71
Fe	1.15	1.23
Co	47.94	48.53
W	13.46	4.37

Table 9 Chemical composition of W-Nb rich phase, obtained in Co-Cr Alloy by EDS technique.

Element	Weight (%)	Atomic Mass (%)
O	2.44	10.35
Nb	14.52	10.60
Mo	9.74	6.89
Cr	15.09	19.69
Fe	1.00	1.22
Co	38.53	44.36
W	18.67	6.89

6.1.4. Hardness

The micro hardness tests show a value of 327 ± 11 HV_5. Some authors [10,66,94,97–99] found similar values.

6.2. Corrosion tests

The corrosion tests were performed on the Co-Cr alloy on the 5 different solutions in order to study the influence of the commercial mouthwashes on the corrosion behavior of this alloy.

6.2.1. Open circuit potential (OCP)

In figure 21 is shown the evolution of OCP for Co-Cr alloy immersed in different solutions. OCP gives information about the tendency to corrosion of material on a specific solution. The alloy had a stable behavior immersed in artificial saliva (c.a. - 0.188 V), showing a more stable passive film that protects the alloy from corrosion. On the other hand, the results obtained in the mouthwashes containing solutions showed a relatively unstable behavior. Once the OCP evolution of Co-Cr alloy immersed in mouthwashes containing solutions shows fluctuations through the immersion time, modifications in the formed passive layer can be taking place. These kind of modifications can be related to the formation and destruction of the passive film along the immersion time.

It was also observed that the Listerine containing solutions presented a higher instability, probably due to the more acidic environment of those solutions. However, some authors [5,8,76,100,101], who studied other commercial mouthwashes in contact with Co-Cr alloys at 37°C, showed that the OCP values initially increasing in a short period of time and then stabilized, forming a passive oxide film. However, in order to get a better stabilization in mouthwashes containing solutions a longer immersion time will be needed. The mouthwash producers [102,103] advise to keep the mouthwashes in mouth for approximately 30 seconds/use. In this way 1 hour of immersion was chosen to simulate a couple of days of use.

Souza et al. [9] showed that the OCP measurement is an important source of information on chemical reactivity of a material immersed in an electrolyte but it is just a tendency to corrosion and it is important to analyze other corrosion parameters in order to get more conclusive information.

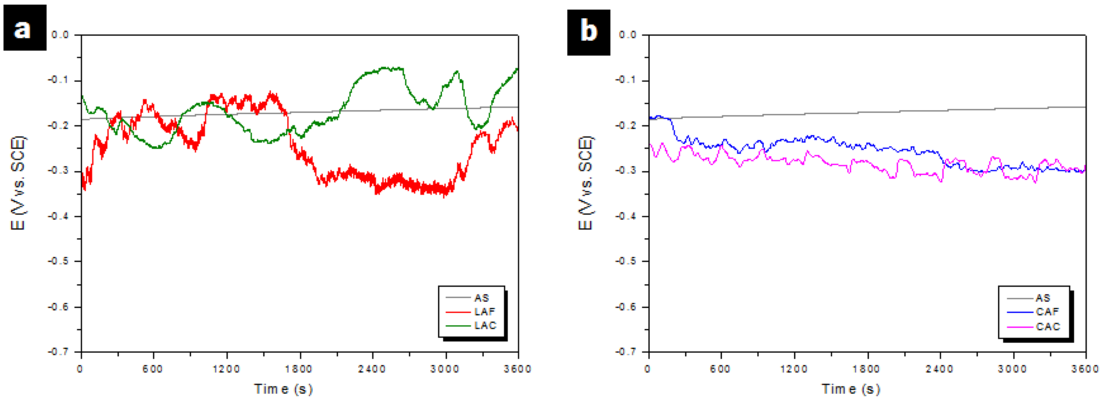

Figure 21 OCP evolution with the time for Co-Cr dental alloy in a) AS and Listerine containing solutions b) AS and Colgate containing solutions.

6.2.2. Potentiodynamic polarization (PD) tests

The PD method determines the kinectics of corrosion of a metal in contact with an electrolyte. Polarization curves of Co-Cr alloy in different solutions are presented in figure 22 and corrosion potential ($E_{(i=0)}$), breakdown potential (E_b), corrosion current density (i_{corr}), and passivation current density (i_{pass}) values are listed in table 10.

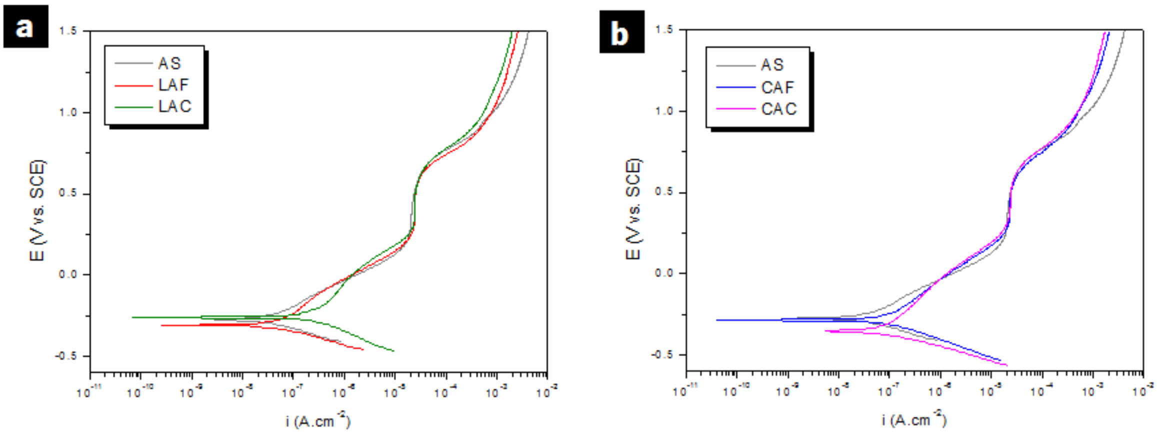

Figure 22 PD curves of Co-Cr dental in a) AS and Listerine containing solutions and b) AS and Colgate containing solutions.

Table 10 $E_{(i=0)}$, i_{pass} and E_b values of Co-Cr dental alloy in 5 different solutions.

	$E_{(i=0)}$ (V)	**i_{pass} (μA.cm^{-2})**	**E_b (V)**
AS	-0.279 ± 0.016	2.00 ± 0.27	0.581 ± 0.034
LAF	-0.283 ± 0.023	2.38 ± 0.05	0.551 ± 0.015
LAC	-0.222 ± 0.032	2.69 ± 0.24	0.575 ± 0.030
CAF	-0.289 ± 0.015	2.74 ± 0.43	0.594 ± 0.058
CAC	-0.303 ± 0.046	2.40 ± 0.18	0.625 ± 0.008

From the polarization curves, in all solutions, four different domains can be observed. The cathodic zone includes potentials below - 0.22 V for LAC that is the solution with higher $E_{(i=0)}$ and - 0.30 V for CAC that is the solution with lower $E_{(i=0)}$. In this zone the current is determined by the reduction of water and, partially, of dissolved oxygen. In this zone Co-Cr dental alloy present different behavior dependently on the chemical composition of the solution. The zone between these last values and c.a. 0.28 V is characterized by the transition from cathodic to anodic current at the corrosion potential. A small passivation plateu was found between c.a. 0.28 V and c.a. 0.55 V, where the current density remained approximately constant. Finally, in the transpassive zone, an increase on current appears at c.a. 0.55 V till 1.5 V, related to transpassive oxidation (water oxidation and metallic oxide oxidation).

Alves-Rezende et al. [70] studied the effect of commercial mouthwash on the corrosion behavior of Ni-Cr alloys. The authors stated that a passivation phenomenon was observed for the three mouthwashes, the main difference on the corrosion behavior of those alloys on the three mouthwashes was noticed on the i_{pass}, and this behavior was associated to the changes in the film porosity and thickness in each mouthwash. In cathodic domain the current is determined by the reduction of water and, partially, of the dissolved oxygen. On the other hand, Alves-Rezende et al. [8] noticed that anodic branches show passive and transpassive regions.

The $E_{(i=0)}$ is a parameter related with the thermodynamic of corrosion process and it can be observed that there are no significant differences between the solutions. These results are in accordance with the results obtained by OCP tests.

Corrosion potential ($E_{i=0}$) values were calculated by Tafel extrapolation method. As it is shown in figure 22, a passive region is formed in all solutions, that means that it was formed a passive layer of oxide on the surface of Co-Cr alloy that protects it. Schiff et al. [5] studied the corrosion behavior of Fe-Cr-Ti, Co-Cr and Ti for three different mouthwashes. The authors showed that in the case of Co-Cr there was no major influence on the electrochemical behavior. Another study of Alves-Rezende et al. [8] showed that the corrosion behavior of Ti-10Mo and Cp-Ti in three different mouthwashes and also concluded that these materials tend to become covered with and oxide film.

From the values in table 10 it can be noticed that the $E_{(i=0)}$ values have a similar tendency to corrosion in all solutions. In addition, the i_{pass} values, being the most important corrosion parameter to be considered in a material with passive behavior, is very similar in all cases. Thus, it can be assumed that there is no significant influence of the mouthwashes on the corrosion behavior of Co-Cr alloy, when compared with artificial saliva.

The pH values measured before and after corrosion tests are presented in table 11. There are some differences between the solutions, however there are not significant differences between the pH values before and after the corrosion tests.

Table 11 The pH before and after the potentiodynamic tests.

	pH before the test	**pH after the test**
AS	5.38 ± 0.30	5.70 ± 0.30
LAF	4.09 ± 0.03	4.11 ± 0.06
LAC	3.68 ± 0.06	3.67 ± 0.03
CAF	4.96 ± 0.05	4.92 ± 0.06
CAC	4.14 ± 0.12	4.12 ± 0.09

6.2.3. Microstructural characterization of the corroded surfaces

After PD test it was performed XRD for all the conditions. The γ and σ phases were identified as it was seen previously in a polished sample in figure 20. Figure 23 presents the SEM images of Co-Cr dental alloy before and after PD test for all solutions. It was shown the γ phase is the matrix and σ phase the second phase, presenting a dendritic structure. The differences on microstructure do not occur due to action of corrosion in the different electrolytes, but due to a heterogeneity of processing.

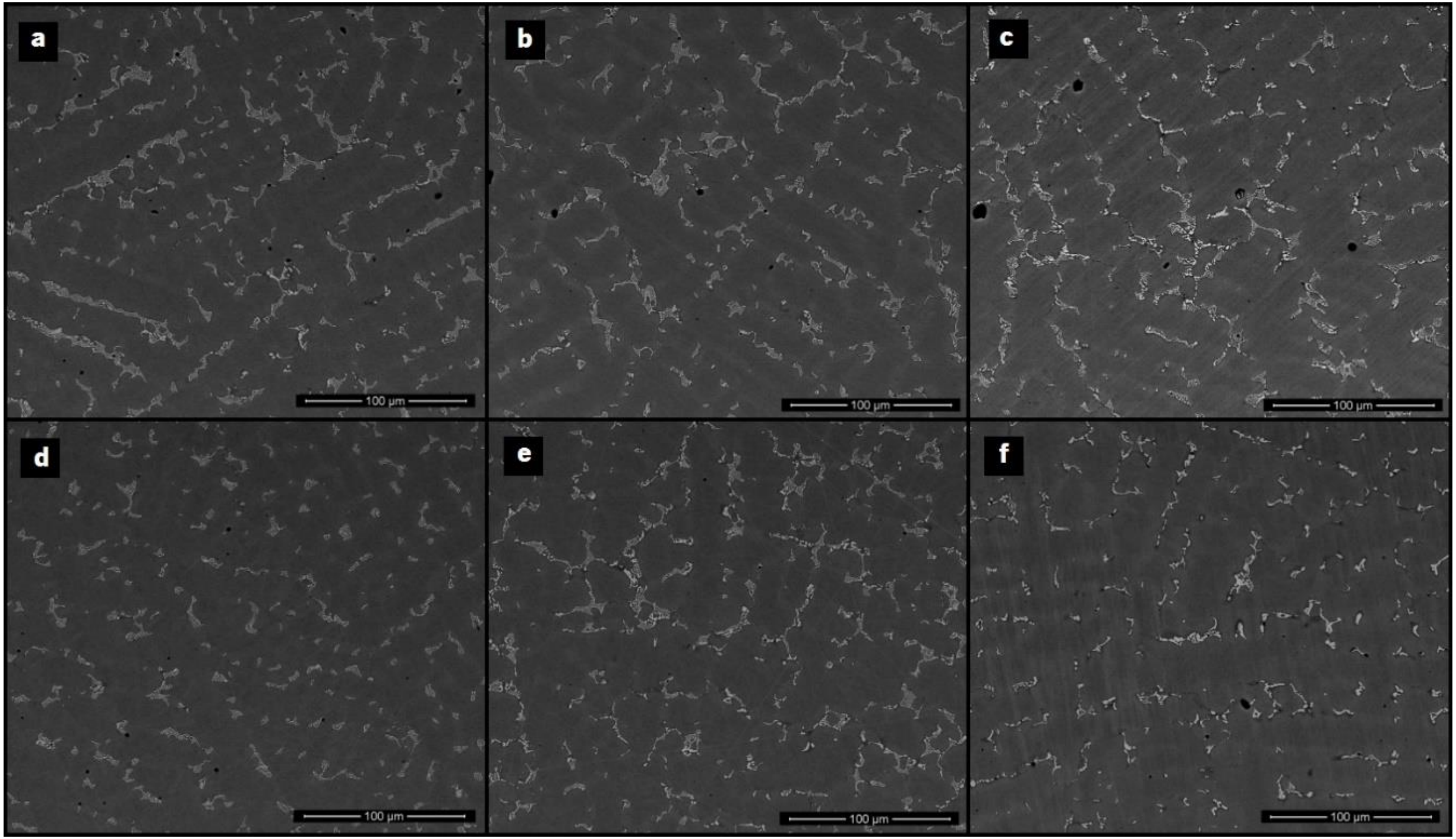

Figure 23 BSE SEM images of Co-Cr dental alloy a) polished and after PD in b) AS c) LAF d) LAC, e) CAF and f) CAC solutions.

Figure 24 shows the differences of the surface before and after the PD tests. It can be observed a preferential dissolution of the matrix. Doni et al. [95], also showed that the γ matrix corroded homogenously and the σ phase appears not be significantly affected by corrosion.

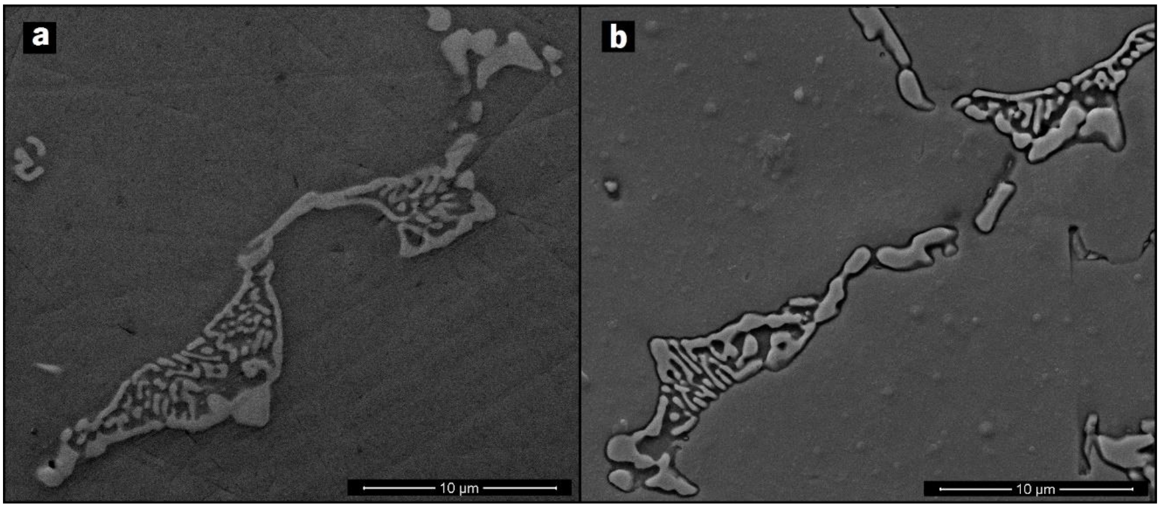

Figure 24 SE SEM image of Co-Cr dental alloy a) before and b) after the PD test in LAC.

There were no significant differences on the microstructure of Co-Cr alloy after corrosion tests when compared AS and mouthwashes containing solutions, meaning that the addition of these mouthwashes do not accelerate the corrosion process.

6.2.4. Electrochemical impedance spectroscopy (EIS)

The EIS test is important to understand the state of oxide film formed on the surface of a metal [9]. Figures 25 and 26 show the EIS spectra in the form of Nyquist and Bode diagrams, respectively for all conditions.

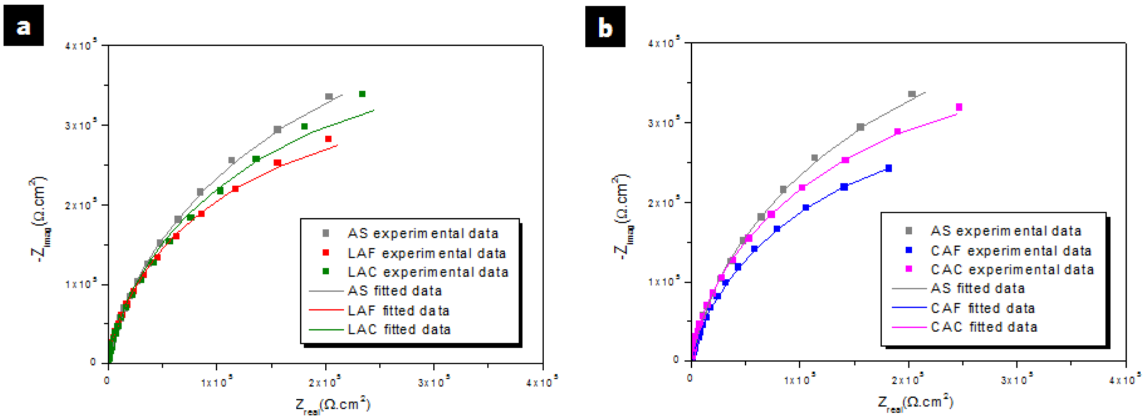

Figure 25 Nyquist diagrams of experimental data and fitted curves for Co-Cr dental alloy in 5 different solutions: a) comparison between AS, LAF and LAC b) comparison between AS, CAF and CAC.

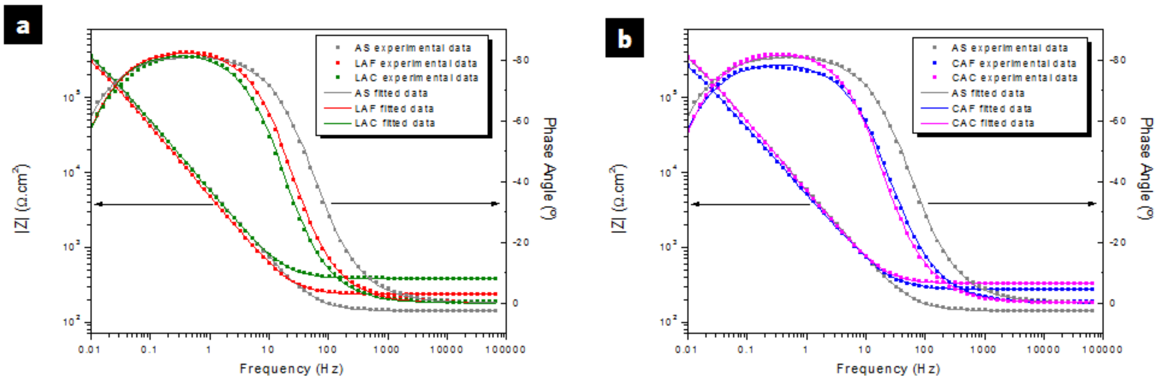

Figure 26 Bode diagrams of experimental data and fitted curves for Co-Cr dental alloy in 5 different solutions: a) comparison between AS, LF and LC b) comparison between AS, CF and CC.

Nyquist diagram can be evaluated by comparing the diameters of the semi-circles. Thus, the larger is the diameter, the better is the corrosion resistance of the sample [104]. As it can be observed in figure 25, the AS solution presented a bigger diameter of the semi-circle when compared with mouthwashes containing solutions.

The Bode diagram, observed in figure 26, shows constant values of |Z| in the high frequency range (100 Hz to 100 kHz) where phase angle is nearly to 0°, which is the response of the electrolyte resistance. However, in low and middle frequency ranges, the phase angle presents values that approach -80°in all cases, being almost capacitive, which indicates a good quality of the passive layer formed on the surface of Co-Cr dental alloy in all electrochemical solutions, especially in AS solution, in which the time constant is near to -90° during a larger range of low frequencies, showing a more stable passive film.

Mareci et al. [40] showed for two Co-Cr-Mo alloys tested in AS the values between -80° and -70° in low and middle frequencies, having a slight lower quality of passive layer. In addition, high impedance values (up to 10^5 Ω cm^2) from medium to low frequencies lead to a high corrosion resistance that is presented as well in the Bode diagrams for all the solutions.

The figure 27 presents the equivalent circuit used to fit the experimental data representing a native oxide film formed on the surface in contact with the electrolyte. The equivalent circuit contains the electrolyte resistance, Re, the native oxide film resistance, Rox, and assumes a non-ideal capacitance of the native oxide film, Qox, which is equivalent to a Phase Constant Element (CPE) replacing the ideal double layer capacitance. The proposed circuit has also been used by other authors [82,105].

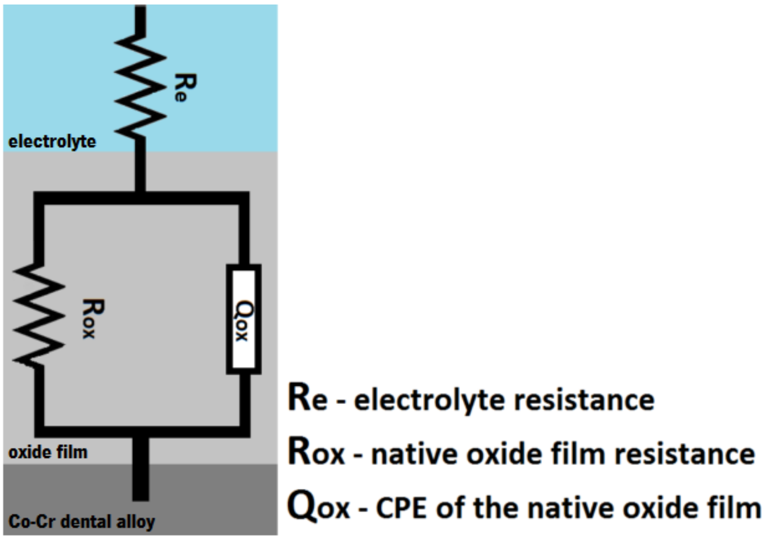

Figure 27 Equivalent circuit, adapted from Ribeiro [105].

The impedance spectra for the all solutions were fitted to the equivalent circuits using a Gamry Echem Analyst version 5.61 software and the quality of the fitting was evaluated through their goodness of fitting values. The proposed models described adequately the behavior of Co-Cr alloy in all solutions, with goodness of fitting bellow of 10^{-4}.

The values for the different elements of the equivalent circuit are presented in Table 12.

Table 12 Resistance to polarization (Rox) and CPE capacitance (Qox) of Co-Cr dental alloy in 5 different solutions.

	Rox (x 10^6 Ω.cm^2)	Qox (x10^{-5} s^n. Ω^{-1}.cm^{-2})
AS	1.26 ± 0.46	3.21 ± 0.62
LAF	0.79 ± 0.13	3.55 ± 0.14
LAC	0.64 ± 0.24	3.65 ± 0.70
CAF	0.77 ± 0.58	3.46 ± 0.80
CAC	0.57 ± 0.17	3.38 ± 0.17

Results of the native oxide film resistance show a slight better corrosion behavior in case of AS solution. The R_{ox} is a parameter proportional to the corrosion resistance of the material. As Mareci et al. [76] showed, large values of R_{ox} indicate the formation of a passive layer with high corrosion protection ability. Impedance is considered to be high with values up to 5 x 10^5 Ω.cm^2, which was verified for all the cases, suggesting high corrosion resistance. However it is observed a slight higher value for AS, which means a slight higher quality of the passive layer. After PD tests and comparing the SEM images obtained before and after PD tests, it is possible to note that EIS is a more sensible technique to detect small variations on the quality of passive films. In fact, by EIS it was possible to notice that in case of mouthwashes containing solutions more time of OCP is needed to form the same stable passive layer. The Q_{ox} parameter is the constant phase element obtained in all solutions. As it can be seen the passive film formed in all solutions has a very similar behavior in terms of corrosion protection as proved by the very similar Q_{ox} values.

The impedance of constant phase element (Q_{ox}) is defined as:

$$Z_{CPE} = [Y_0(jw)^n]^{-1} \quad (7)$$

Where -1 ≤ n ≤ 1, when n= 1, n= 0 and n= -1, the Q_{ox} responses correspond to those of a capacitor, a resistor or an inductor, respectively. When n≈ 1, a non-ideal capacitor may be described by this element the n value being influenced by the roughness and the heterogeneities of the surface. All solutions presented a range of n values between 0.90 and 0.94, approximately, indicating a non-ideal capacitor [106]. In addition the similar Qox values suggest a very similar insulating character of the passive layer formed on the surface of Co-Cr alloy immersed in all solutions. The corrosion behavior of Co-Cr dental alloy want not influenced by the presence of the mouthwashes. Thus, the tribocorrosion behaviour of Co-Cr alloy was investigated only using the Listerine containing solutions.

6.3. Tribocorrosion test

The tribocorrosion tests were performed on the Co-Cr alloy on 3 different solutions: AS and Listerine containing solutions (LAF and LAC) in order to study the combined action of wear and corrosion. Figure 28 presents the evolution of OCP with time before, during and after sliding, together with COF evolution during the sliding.

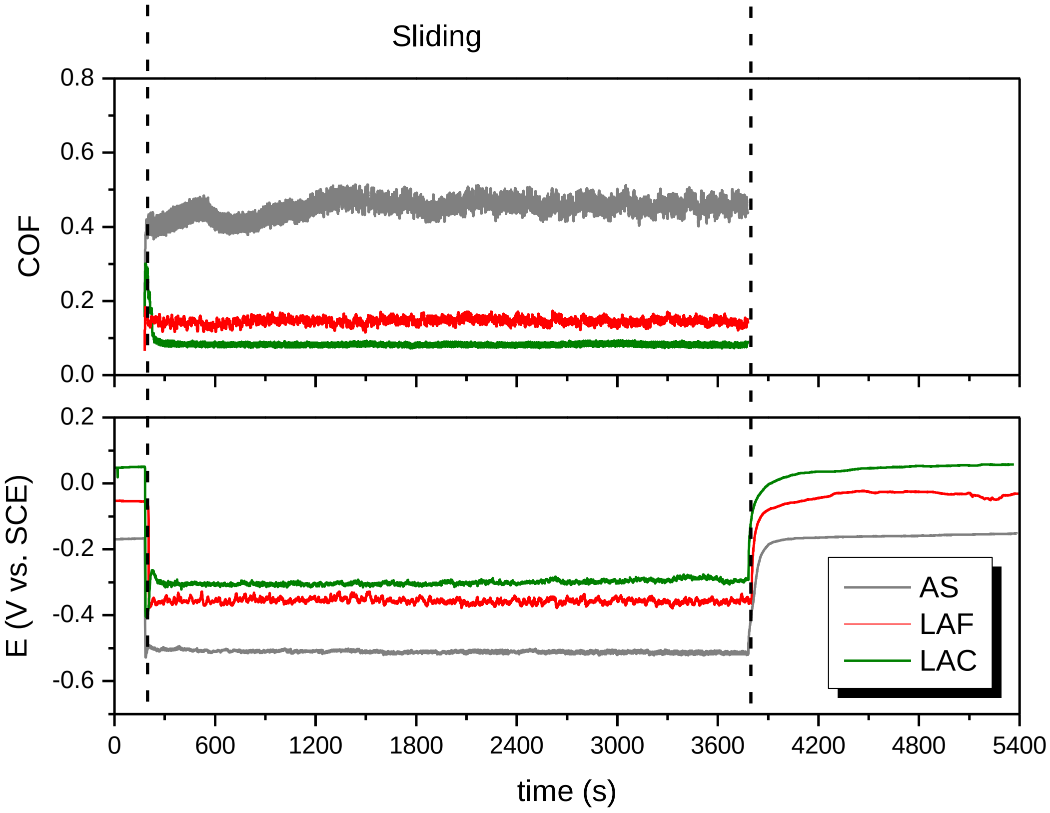

Figure 28 Evolution of COF and OCP of Co-Cr dental alloy.

Before the sliding OCP was stable at around -0.165 V, -0.06V, and -0.05V for AS, LAF, and LAC solutions respectively. It was noticed a sharp drop on OCP values when sliding started, which is due to the destruction of the passive film formed on the surface of the Co-Cr alloy (phenomenon known as depassivation) by the mechanical action. During the sliding action the OCP values remained almost stable for all solutions. However, the Listerine containing solutions presented always higher potential values under sliding, indicating a lower tendency to corrosion. In addition, the slight instability of OCP during sliding tests can be explained by the abrasive effect of the wear debris, destroying periodically the passive film on the wear track surface [9,10].

The differences observed in the tribocorrosion response of Co-Cr in all electrolytes, during the sliding, can be explained by the oxidation and reduction reactions occurring in the contact area during sliding, which depends of the composition of different electrolytes [79]. So, as it can be observed in figure 31, the AS solution has a higher coefficient of friction and more negative potential during the sliding, so it can be stated that the Co-Cr has a worse tribocorrosion behavior in AS solution. It can be observed that the mouthwashes containing solutions may act as a lubricant, once that the COF presents lower values.

It was noticed that the more acidic solution (pH=5.38±0.30 for AS, pH=4.09±0.03 for LAF and pH=3.68±0.06 for LAC) leads to a slight better tribocorrosion behavior, probably due to the nature of the oxidation and reduction reactions occurring in the contact area during the sliding, resulting in the formation of protective tribolayers that reduced the friction of coefficient as explained by Vieira et al. [79]. On the other hand, chemical composition changes in the mouthwashes in compounds as $C_{12}H_{25}NaO_4S$ and $C_{12}H_{19}Cl_3O_8$ for LAF and $C_{18}H_9NNa_2O_8S_2$ and ethanol for LAC. Thus these different compounds and, other common compounds probably are increasing the lubricant effect of the mouthwashes solutions when compared with pure AS.

Vieira et al. [79] showed that the potential of Ti in AS, AS + acid citric and AS + anodic inhibitor, after the sliding, recovers its original value. This behavior indicates that a new passive film was formed, after the removal of the naturally formed passive film when potential was stabilized in noble values before sliding action. This phenomenon is denominated repassivation.

6.3.1. Microstructural characterization of the wear tracks

Figure 29 shows the OM images of the wear tracks obtained after tribocorrosion tests. Important differences between the tests were observed. The samples in AS and LAF solutions exhibit higher degradation compared with LAC solution. The samples tested in this last solution presented smoother wear tracks, having less mechanical damage. This can be due to the lubricant effect in LAC and thus, this mouthwash can influence the tribocorrosion process, leading to a lower abrasion and consequently not so deep grooves. It is observed that the wear track of LAC presented lower width which confirms the lower degradation when compared with the other samples.

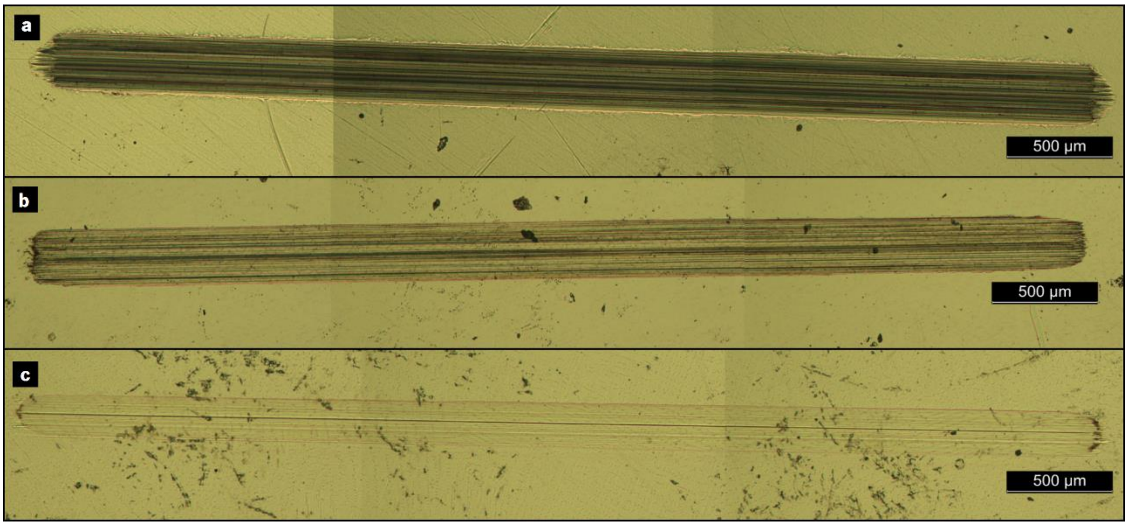

Figure 29 OM of wear tracks of Co-Cr dental alloy in: a) AS, b) LAF and c) LAC.

In figure 30 are shown the SEM images of the center of wear tracks for Co-Cr alloy in the three different solutions. Parallel sliding groves for all solutions were observed. The abrasive wear can be a result of the penetration of higher asperities of harder material, Al_2O_3 from the counter material [105].

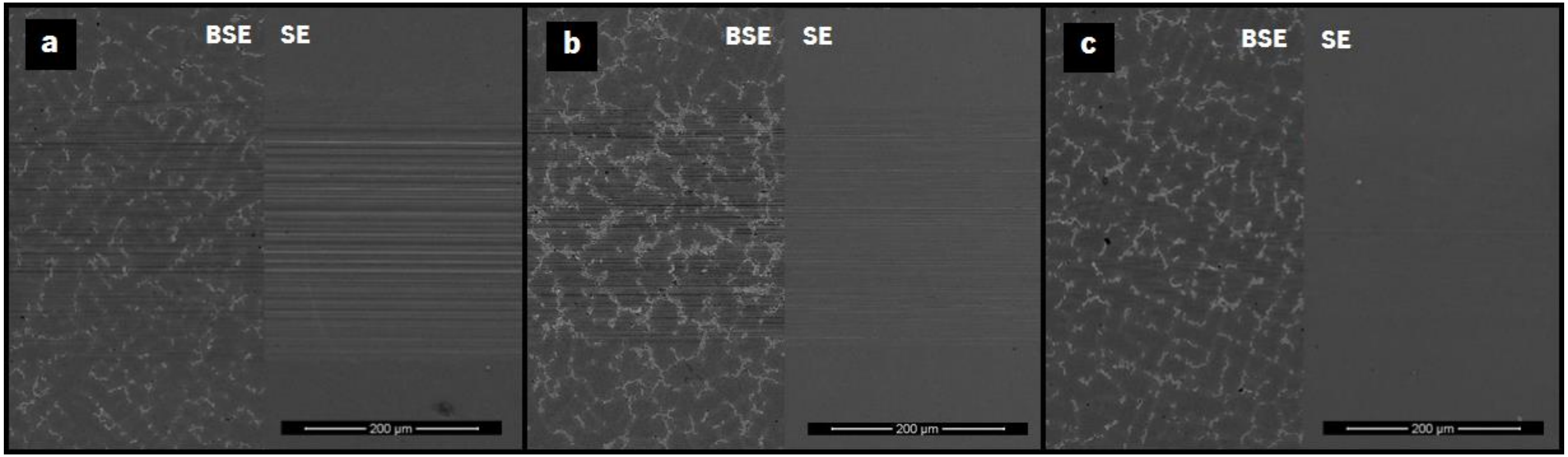

Figure 30 SEM images of the wear track of the Co-Cr dental alloy in a) AS, b) LAF and c) LAC.

Figure 31 presents the SEM images and EDS analysis of the Al_2O_3 ball slide against Co-Cr alloy in different solutions. As it can be observed on the images, an important amount of the alloy was transferred to the Al_2O_3 ball during the sliding, which indicates adhesive wear. It is observed that this degradation is lower in the case of LAC containing solution. Higher percentages of these two elements (Co and Cr) in AS can be observed. In the other two solutions Co and Cr contents are very small. These facts show a higher degradation in AS than in the other solutions.

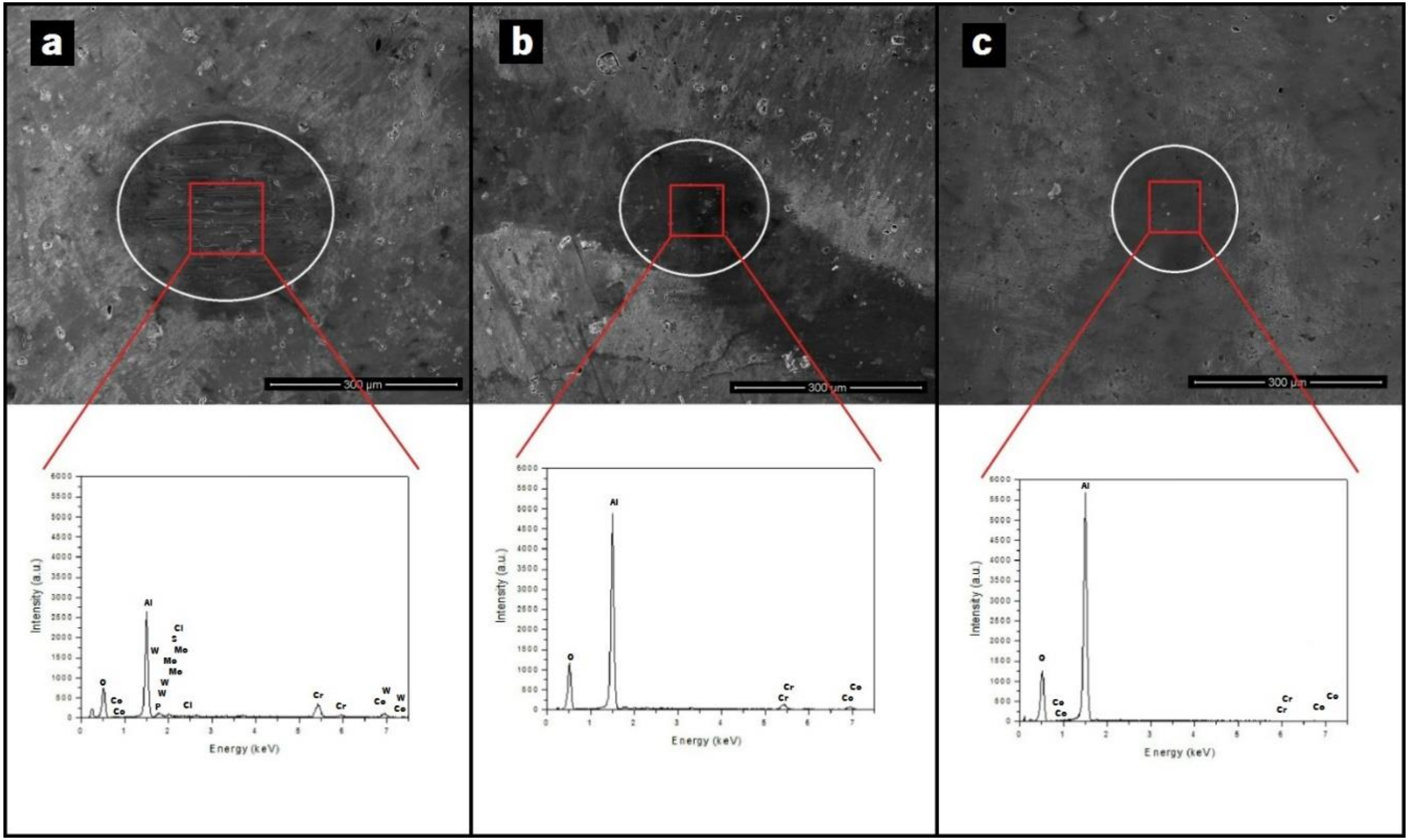

Figure 31 SEM images of mating counter material and EDS spectra taken from the marked and for a) AS, b) LAF and c) LAC.

6.3.2. Repassivation rate

At the end of sliding, the OCP increased progressively to achieve the OCP values recorded before the sliding. This behavior reveals a progressive repassivation of the wear track area according to Hawana et al. [91]. The evolution of the repassivation potential can be calculated using the following equation [91]:

$$\Delta E = k_1 \log t + k_2 \quad (8)$$

Where ΔE is the potential in V, t is the time in s and k_1 is the repassivation rate [91,92].

The values of the repassivation rate (k_1) and ΔE for each solution are presented in table 10. Alves et al. [107] showed that higher values of k_1 and ΔE show that the repassivation process proceeds to a stronger extension. As showed in table 13, the similar k_1 and ΔE values in all solutions show that the recovering of the potential after sliding occurs almost at the same rate for the three solutions. There are no significant differences in ΔE parameter, which confirms that fact. Thus, it can be assumed that there is not a significant influence of the addition of mouthwashes on the repassivation rate of Co-Cr alloy.

Table 13 Parameters k_1 and ΔE in equation 4 for 3 different solutions.

	k_1 (V s^{-1})	**ΔE (V)**
AS	0.14 ± 0.02	0.44 ± 0.07
LAF	0.12 ± 0.04	0.35 ± 0.04
LAC	0.09 ± 0.06	0.28 ± 0.06

6.3.3. Wear volume loss

The wear volume loss was calculated through the 2D wear track profiles with profilometry analysis. Figure 32 is shows the wear track profiles obtained for Co-Cr alloy in the three solutions. It was observed that the Co-Cr profile in AS solution is deeper and rougher than in mouthwashes containing solutions. Regarding the mouthwashes containing solutions smother wear tracks were observed. It can be observed a correlation between the wear volume loss results and the COF from figure 29. There is a higher COF for AS presenting rougher wear track (figure 32) and the other two solutions that present a smoother wear track, having a lower COF.

By the OM, SEM images and wear loss, a better tribocorrosion behavior was noticed for LAC solution.

The wear volume loss values are given in table 14. It can be noticed that AS solution presented the highest wear loss values. This result is in accordance with tribocorrosion tests in which a higher values of coefficient of friction were obtained in this solution.

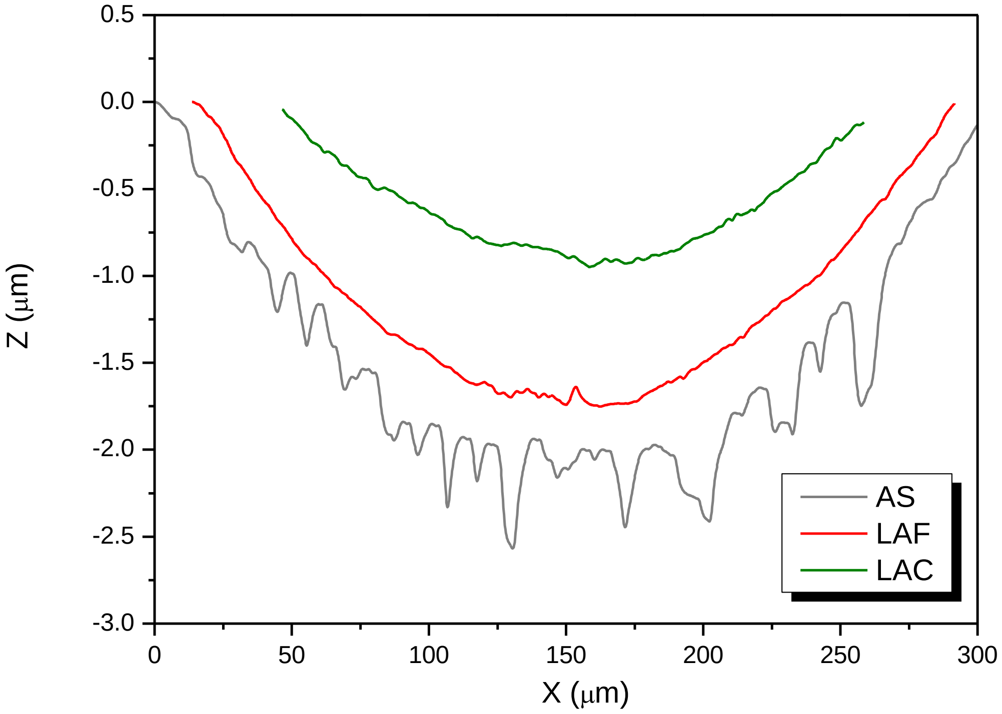

Figure 32 Wear track profiles.

Table 14 Wear volume from tribocorrosion test in 3 different solutions.

	Wear Volume (µm³)
AS	20.16 ± 0.98
LAF	14.35 ± 1.55
LAC	8.18 ± 0.39

CONCLUSION

The followings can be concluded after studying the influence of commercial mouthwashes on corrosion and tribocorrosion behavior of Co-Cr dental alloy:

- By potentiodynamic polarization tests it was possible to conclude that there is no significant influence of the mouthwashes containing solutions on the corrosion behavior of Co-Cr alloy when compared with artificial saliva. Once that, $E_{(i=0)}$ and i_{pass} presented similar values in all tested solutions;
- By EIS studies it was found that Co-Cr alloy immersed in artificial saliva shows a slightly higher resistance to corrosion and a constant behavior of phase angle close to -90° in middle and low frequencies range. That behavior is characteristic of metals and alloys that exhibit the formation of a very protective and stable passive layer on its surface when in contact with some electrolytes;
- After PD tests the Co-Cr dental alloy microstructures were similar in mouthwashes containing solutions and artificial saliva. Thus, it is possible to conclude that the addition of these mouthwashes to saliva solution do not accelerate the corrosion process;
- Regarding tribocorrosion tests, it was found that Co-Cr alloy the highest COF and a more negative OCP during the sliding test in artificial saliva;
- The wear tracks of Co-Cr alloy in AS presented the deeper wear track and a higher wear volume;
- Results obtained in the tribocorrosion tests lead to conclude that the presence of mouthwashes slightly improve the tribocorrosion behavior of Co-Cr Alloy. The slight decrease in the coefficient of friction and the increase on the corrosion potential can be explained by the formation of protective tribolayers which confer a lubricant effect to the mouthwashes during the sliding process;
- The wear mechanism of Co-Cr alloy in AS and a combination of abrasive and adhesion wear, while for the mouthwashes containing solutions was mainly abrasive wear;
- A clear repassivation phenomena was detected in all tested solutions. Results obtained allowed to conclude that no significant influence on addition of mouthwashes to the artificial saliva in the recovery of passive oxide layer after sliding.

Thus, the presence of mouthwashes in artificial saliva do not affect negatively neither the corrosion or tribocorrosion behavior Co-Cr dental alloy.

FUTURE WORKS

The work carried out during this thesis leads to the following suggestions in order to obtain a better understanding of the effect of mouthwashes on the corrosion and tribocorrosion behavior of Co-Cr dental alloys:

- to perform longer immersion periods, in order to understand the effect of mouthwashes on the corrosion behavior of dental alloys after a long period of immersion;
- to study the effect of mouthwashes on the metallic ion releasing ;
- to study the influence of fluorides on electrochemical behavior of Co-Cr dental alloys;
- to study the influence of mouthwashes on the corrosion and tribocorrosion behavior of Co-Cr dental alloys processed by other techniques.

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