EVALUATION OF BIOIMPLANTS SURFACE NANO-MICRO DESIGN BY CHEMICAL MECHANICAL POLISHING AGAINST ALTERNATIVE METHODS

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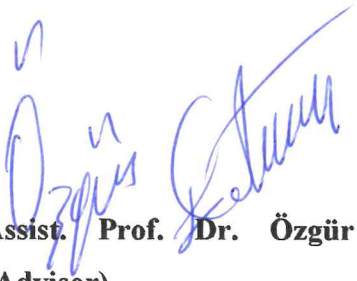

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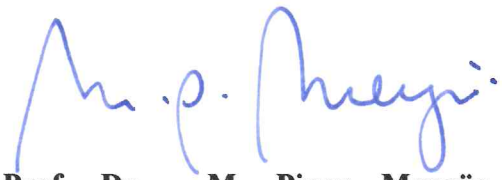

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To my family,

To my wife and children (Abdulrahman and Kahramana),

& to my parents, my brother and my sister

ABSTRACT

Biomaterials comprise a representative fraction of the products used in the health area. Biomedical devices (such as biosensors, blood circulation tubes, hemodialysis systems) can be cited as examples. Biomaterials can be of internal or external placement which must be pharmacologically inert and designed to be implanted or incorporated into the living system (such as sutures, plaques, bone substitutes, tendons, screens or meshes, heart valves, lenses, teeth), devices for the release of medications (in the form of films, subdermal implants and particles), artificial organs kidney, liver, pancreas, lungs, skin) and dressings.

The term biomaterial has been defined in different ways by different authors over the last years. In the scope of this review, biomaterials are defined as devices that come in contact with biological systems (including biological fluids), with diagnostic, vaccine, surgical or therapeutic applications, and may consist of compounds of synthetic or natural origin, as well as chemically natural materials both in the form of solids and gels, pastes or even liquids, not necessarily manufactured, such as pig heart valves and human skin flaps treated for use as implants.

The most biocompatible material in this field is titanium and its alloys have been widely used as biomaterials, especially in prostheses, devices for cardiovascular use and for fixation of fractures, due to their high biocompatibility, low density, low modulus of elasticity and superior corrosion resistance compared to stainless steel. Titanium has the additional advantage of a greater tendency for osseointegration, an important characteristic for long-term implants. The reduced or non-existent reaction of the titanium with the tissues surrounding the implant is due to the passivation formed by the titanium dioxide film (TiO_2), usually of nanometric thickness, on the surface of the metal. Surface processing techniques for the implant materials also affect its properties and may lead to

contaminated surface which can affect on the biocompatibility which may cause infection in implantation. The surface roughness and chemistry are the most important factors that can affect the long-term successful of the implant. Forming a protective surface oxide layer have been introduced through different methods in the literature to increase the biocompatibility and to assure the mechanical anchoring and hence the primary stability as a result the success and survival of the bio-implant. the method of choice in recent manufacturing processes is sand blasting correlated with chemical etching are commonly used for engineering the titanium surfaces to give a desired surface roughness to be accepted in the host. The sand blasting method consist of jetting specific particles to induce a micro roughness to the surface being treated, these particles may adhere to the implant surface which can cause surface contamination. However, the other alternative surface structuring methods such as high temperature plasma coating and laser peening are costly.

In this dissertation, Three-Dimensional Chemical Mechanical Polishing (3-D CMP) process is established as an alternative technique to process non-flat bioimplant surfaces such as dental implant cylindrical-threaded surfaces in addition to the existing methods in the literature to alter the implant surface properties. Originally CMP process is one of the methods used in the semiconductor manufacturing industry to assure surface planarization through simultaneous mechanical cutting and chemical actions associated with the presence of the abrasive particles in the polishing slurries which provides the mechanical cutting effect through the process enabling the surface cleaning through the nanometer level erosion process. The unified set of variables including the chemical components of the slurry stabilizers, pH adjusters and oxidizers are combined to stimulate the formation process of the passive oxide film that can cover the surface and enhance the biocompatibility. Generally, the CMP is used to polish the surfaces and

induce smoothness, but here it has been shown that changing the process variables includes the slurry particles concentration, the pad material properties, pad-sample velocity oxidizer type and concentration gives the possibility to engineer and control the surface roughness on the treated surfaces. The main purpose of the CMP treatment is to produce a uniform protective film. The application of 3-D CMP is believed to reduce the organic and inorganic contamination on the surface of the bio-implants which is in contact with the human body environment and limiting the periimplantitis and infection risk by reducing the reject reactions in-vivo due to ion release processes. The application of CMP on titanium alloys has been shown in the literature the ability of producing TiO_2 films and creating a smooth surface. However, its native oxide is a self-forming process, but it is a slow process and the CMP treatment is accelerating this process. Titanium oxide film is known to promote the biocompatibility, cell adhesion, osteo-formation and bacteria growth prevention. Yet, the oxide films produced in similar treatments such anodization method resulted in thick-porous films structures which have the advantage of using these cavities as drug releasing spots. In the other hand this porosity can affect the corrosion prevention process. Therefore, in this study, the 3-D CMP process has been implemented to the Ti-based implants to eliminate the organic and inorganic contaminations on the implant surface and provide the desired roughness on the implant surfaces. Furthermore, biocompatibility of the CMP treated surfaces have been evaluated through surface wettability and corrosion resistance through electrochemical analyses and optimal surface parameters through biomechanical evaluations as a result determine the desired surface roughness according to the surface responses.

ÖZETÇE

Yaklaşık 10 yıldır, biyomalzemeler, sağlık alanında kullanılan ürünlerin 300,000 olarak tahmin edilen temsili bir kısmını oluşturmaktadır. Biyomedikal cihazlar (biyosensörler, kan dolaşım tüpleri, hemodiyaliz sistemleri gibi), implante edilebilir malzemeler (sütürler, plaklar, kemik ikameleri, tendonlar, meshler veya ekranlar, kalp kapakçıkları, lensler, diş gibi), ilaçların salınması için ürünler (filmler, deri altı implantlar ve parçacıklar şeklinde), böbrek, karaciğer, pankreas, akciğerler ve deri gibi yapay organlar, pansuman ürünleri gibi birçok ürün biyomalzemelere örnek verilebilir.

Biyomalzeme terimi, son yıllarda farklı yazarlar tarafından farklı şekillerde tanımlanmıştır. Bu inceleme kapsamında, biyomalzemeler; biyolojik sistemler (biyolojik sıvılar da dahil), teşhis, aşı, cerrahi veya terapötik uygulamalar ile bağlantılı cihazlar olarak tanımlanmaktadır ve kimyasal veya kimyasal kaynaklı olduğu kadar sentetik veya doğal kökenli bileşiklerden de oluşabilir. İmplant olarak kullanılmak üzere işlenmiş domuz kalp kapakçıkları ve insan derisi flapları gibi çok fazla üretilmeyen hem katı hem de jel, macun ve hatta sıvı formundaki doğal malzemeler bunlara örnek verilebilir.

Bu alanda en biyouyumlu materyal titanyumdur. Yüksek biyouyumluluk, düşük yoğunluk oranı, düşük esneklik katsayısı ve paslanmaz çeliğe kıyasla üstün aşınma direnci sayesinde titanyum alaşımı, özellikle protezlerde, kardiyovasküler ve kırıkların sabitlenmesi için kullanılan cihazlarda yaygın olarak kullanılmaktadır. Titanyum, uzun süreli implantlar için önemli bir özellik olan osseintegrasyon için daha uygundur. Titanyumun, implantı çevreleyen dokularla azaltılmış veya var olmayan reaksiyonu, genellikle metal yüzeyinde nanometrik kalınlıkla olan titanyum dioksit filmi (TiO_2) tarafından oluşturulan pasivasyondan kaynaklanmaktadır. Implant materyalleri için yüzey

işleme teknikleri materyalin özelliklerini de etkiler, ve implantasyonda enfeksiyona neden olabilecek ve biyouyumluluk oranı üzerinde etkili olabilecek kontaminasyona sebep olabilir. Başarılı, uzun ömürlü bir implantı etkileyen en önemli faktörler yüzey pürüzlülüğü ve kimyadır. Biyouyumluluğun arttırılması ve mekanik bağlanmanın (ankraj) sağlanması ve bunun sonucunda birincil stabilitede başarılı bir biyo-implant için, literatürde farklı yöntemlerle koruyucu bir yüzey oksit tabakası oluşturulmuştur. Son yıllarda üretimde kullanılan yöntem, kimyasal dağlama ile ilişkilendirilen kumlama yöntemidir ve istenilen oranda yüzey pürüzlülüğü elde etmek için titanyum yüzeylerin düzenlenmesinde yaygın olarak kullanılır. Kumlama yöntemi, işlem yapılan bölgeye mikro bir pürüzlülük kazandırmak için özel parçacıkların püskürtülmesinden oluşur. Bu parçacıklar, implant yüzeyine yapışabilir ve bu da kontaminasyona neden olabilir. Bununla beraber, yüksek ısıda plazma kaplama veya lazerle yüzey işleme gibi diğer alternatif yüzey yapılandırma yöntemleri de maliyetlidir.

Bu araştırma kapsamında, silindirik yüzeyli diş implantı gibi biyoimplant yüzeylerini işlemek için implant malzeme yüzeylerinin işlenmesi için literatürde var olan yöntemlere alternatif olarak, Üç Boyutlu Kimyasal Mekanik Cilalama/Düzlemleme (3-D CMP) prosesi oluşturulmuştur. Aslında CMP prosesi, aynı anda yüzeyi hem mekanik hem de kimyasal olarak düzlemleyebilen yarıiletkenler endüstrisinde kullanılan yöntemlerden biridir. İşlem sırasında kullanılan slurry içerisindeki aşındırıcı kimyasallar mekanik kesme etkisi yaratarak yüzey temizliğinde nanometrik seviyede aşınım sağlar. Slurrynin kimyasal bileşenlerini oluşturan stabilizatörler, PH ayarlayıcılar ve oksitleyiciler, yüzeyi kaplayabilen ve biyouyumluluğu artırabilen pasif oksit filminin oluşum sürecini hızlandırmak için birleştirilirler. CMP genel olarak pürüzsüz yüzeyler oluşturmak amaçlı kullanılmaktadır, fakat bu araştırmada; slurry partiküllerinin yoğunluğu, cilalama pedi

materyalinin özellikleri, ped materyali türü, oksitleme hızı ve yoğunluğu olmak üzere işlem bileşenlerinin değişkenleri, mühendise, tedavi edilen bölgedeki pürüzlülük oranını kontrol etme imkanı verir. CMP tedavisinin asıl amacı, tek tip bir koruyucu film oluşturmaktır. 3-D CMP uygulamasının; insan vücudu çevresiyle temas halinde olan biyo-implantların yüzeyindeki organik ve inorganik kirlenmeyi azalttığına, peri-impantitis oluşumunu engellediğine ve iyon salınımı sayesinde vücut içinde yan etkileri azaltarak enfeksiyon riskini azalttığına inanılmaktadır.

Literatürdeki çalışmada, titanyum alaşımları üzerinde CMP uygulamasının TiO_2 filmleri ürettiği ve pürüzsüz bir yüzey oluşturduğu belirtilmiştir. Ancak, bu bileşim doğal yolla oksitlenir ve bu süreç de yavaş bir süreçtir ve CMP uygulaması bu süreci hızlandırmaktadır. Titanyum oksit filminin biyouyumluluğa, hücre adezyonuna ve bakteri ve osteo-oluşumunun önlenmesine katkı sağladığı bilinmektedir. Fakat, anotlama yöntemi gibi benzer yöntemlerde oluşturulan oksit filmler; oluşan boşlukları ilaç bırakma noktaları olarak kullanma avantajına sahip olan kalın gözenekli film yapılarına yol açmıştır. Diğer bir yandan, bu gözeneklilik korozyon önleme sürecini etkileyebilir. Bundan dolayı, bu araştırmada, 3-D CMP yöntemi, implant yüzeyinde istenilen pürüzlülük oranını sağlamak ve organik ve inorganik kontaminasyonu önlemek için implant malzemesi olarak kullanılan Ti-plakalar üzerinde uygulanmıştır. Bunun yanı sıra, CMP ile tedavi edilmiş yüzeylerin tepkilerine göre istenilen yüzey pürüzlülüğü oranı ve biyouyumluluğu; yüzey ıslanabilirliği ve korozyon direnci, elektrokimyasal analizler, optimal yüzey parametreleri ve biyomekanik değerlendirmeler yollarıyla değerlendirilmiştir.

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CHAPTER I

INTRODUCTION

Biomaterials are widely used in dentures as orthopedic implants, heart valves and catheters as implant materials in the body. As a result of the researches carried out to date, titanium and alloys are among the most biocompatible materials with their exceptional mechanical properties as well as their surface properties. The processing of the implant material also affects the surface properties and can lead to contamination, which reduces biocompatibility and causes infections that can be detected later the implantation process which may appear as a number of diseases related to the ions release process [1]. Changing the surface roughness of the material to increase the biocompatibility and bioinformity of the implant materials and the formation of the oxide film on the surface have been given the literature by various methods. Chemical abrasion methods commonly used in patterning to modify surface roughness cause contamination on the surface of the implant material. In addition, other alternative methods, such as high temperature plasma coating and laser patterning, cause high costs.

As an alternative to the methods available in the literature for the processing of implant material surfaces within this project, the Chemical Mechanical Polishing (CMP) process has been introduced. The CMP process is one of the methods used in the semiconductor industry and the surface can be leveled both mechanically and chemically. The abrasive chemicals in the slurry used during the process provide mechanical effect and provide abrasion at the nanometer level on the surface and remove the surfaces from potential contamination It is formed. On the other hand, the stabilizers, PH adjusting agents and oxidizers forming the chemical components of the slurry form a passive oxide film coating

on the surface. Although CMP is generally used to create smooth surfaces, it has also been shown in previous studies that the suspensions used on the polished surfaces may be used to create a coarse roughness by changing the grain size and the texture of the polishing pad. This Chemically Modified Film in reaction provides a leveling effect in semiconductor applications because it is a stopping protective oxide layer. The application of CMP to implants is thought to reduce the risk of contamination and infection on the surface by stopping chemical reactions. In the limited literature in the literature, it is stated that CMP applications on Ti films used as implant materials produce a smooth surface and TiO_2 oxide films. However, while the protective properties of titanium oxide film on the CMP process bioimplant are not characterized, the passivating properties of Ti films used in semiconductor technology are known during CMP. It is known that titanium oxide films formed increase cell adhesion, bioavailability and adhesion to hydroxyapatite, but most of the oxide films formed have a thick and porous structure as they are obtained by artificial oxidation methods. These films cannot provide the inertia of the underlying metal material in the lower layer due to their porous structure and cannot prevent contamination. Therefore, in this study, the CMP process was applied to the upper layer which could be exposed to contamination on the Ti plates used as implant material. In addition, the structure of the metal oxide layers, which are formed on the metal surfaces by CMP are characterized in terms of limiting the chemical reaction. CMP treated surfaces are also characterized in terms of biocompatibility and resistance to biofilm formation and attempts have been made to determine optimal surface properties to increase cell adhesion, depending on the compatibility of the cells. Considering the consequences of the thesis work in the future, it is the most important requirement to develop a CMP process that can work 3-D, taking into account the three-dimensional structure of implant materials. Three-dimensional applications of CMP technology on

titanium-based bio-implants are considered to be both more economical and more effective than other alternatives. Nano-patterned surfaces formed by CMP on titanium and titanium alloy biological implants are intended to prevent chemical and bacterial reactions with the self-protecting oxide layer and also to increase biocompatibility by surface patterning.

MOTIVATION

The mechanical properties of metals and their alloys, compared to polymeric and ceramic biomaterials, make the former indispensable for the manufacture of components subject to loading, with orthopedic surgery and traumatology as the main field of application, as well as the sector of dental and maxillofacial implants.

The metallic materials used in the unbonded prosthesis bone attachment area must interact with the tissue surrounding them, promoting their osseointegration, that is, the intimate, direct and functional connection between the bone and the implant. The "primary stability" or absence of movement of an implant after its surgical insertion is a critical factor to ensure bone apposition or "secondary stability". It seems that micro-movements above a certain margin (100-150 nm) can prevent the surrounding bone formation because after implantation the metal prostheses are spontaneously encapsulated by a fibrous tissue, without direct binding to the bone. This surrounding tissue allows the diffusion of ions and even microparticles to the physiological medium, which has often been related to clinical complications. For this reason, the creation of bioactive surfaces, through the generation of coatings with ceramic or polymeric materials, is a widely used alternative to improve the biological fixation of implants, since it does not entail fibro-encapsulation. However, these coatings often do not adhere sufficiently well to the metal surface, also causing clinical complications. Therefore, obtaining metallic biomaterials that facilitate osseointegration is one of the key objectives in the development of the new generation of orthopedic and dental implants.

BCP is one of the methods most used industrially to improve the stability of the implant consists in the creation of rough surfaces that increase the area available for bone

apposition. The data obtained in vivo show that the rough surfaces produce a greater fixation than the smooth ones, without this compromising their good corrosion behavior. Jetting calcium derivatives (Biphasic calcium phosphate) which is called by authors and companies as RBM (Resorbable Blast Media) treatment currently used by the industry, causes an increase in roughness, whose magnitude depends on the size, shape and kinetic energy of the particles reaching the surface. Chemical etching This technique consists of increasing the thickness of the oxide layer and the roughness by immersion of the metallic implant in an etching solution, which erodes the surface producing micro pores with sizes ranging from 0.5 to 2 μm. The factors that determine the result of the chemical attack are the concentration of the etching solution, time, and temperature. The main advantage of chemical etching treatments is that they provide homogeneous roughness, a larger area of active surface and improve cell adhesion, and therefore osseointegration. These treatments causes, in some cases, a loss of biofunctionality (resistance to fatigue). Since the values obtained are within the limits established by the standards this does not pose a problem of use. However, recently, it has been shown that these surfaces lead to a worse in vitro behavior against corrosion and the release of metal ions, which justifies the need to minimize these effects to improve the quality of life of the affected patient.

In order to try to solve some of the problems that comes with conventional surface treatments (release of ions to the physiological environment and, in some cases, decrease in resistance to fatigue), in this work we propose a surface modification strategy based on an alternative treatment on dental implants, to enhance the surface against ion release and / or modify the biomechanical properties.

OBJECTIVES

General objectives

Comparative study of the conventional surface modification techniques to the 3-D CMP.

- Machining (baseline)
- Sand blasting
- Chemical etching

Specific objectives

Technological objective

Obtain surfaces with rugosity levels of clinical interest, without compromising the bio-functionality and the release of ions from the surface of the treated materials.

Scientific objectives

Design optimal Ti-based dental implant to promote:

1. Surface integrity.
    - Control the surface Nano/Micro structure.
    - Composition.
    - Corrosion resistance.
2. Mechanical integrity
    - High fatigue life.
    - High hardness (decreases the incidence of wear of implant material).
3. Mechanical compatibility: show favorable response in given biological environment (Osseointegration interaction.)
    - pull-out force

- Removal torque

4. Improved interface for alternative coatings.
    - Sol gel silica coating
5. Study the behavior against ion release in vitro in a simulated physiological medium.

CHAPTER II

PRESENT STATE OF SURFACE ENGINEERING OF METALLIC BASED IMPLANTS

2.1 Introduction

Research in metallic biomaterials has been directed towards the development of superficial modifications that allow to improve their mechanical, biological properties or their resistance to Wear and corrosion [2]. An important aspect to take into account when modifying the surface of a material is to consider the specific requirements of the clinical application for which it has been designed. For example, some implants used as temporary devices require minimal interaction with bone tissue to facilitate removal [3]. However, the materials used in the area of attachment to the bone of uncemented prostheses should interact with the tissue around them promoting their osteointegration [4]. In this case the long-term efficacy of the implant will depend to a large extent on the first phase of interaction enters the osteo-forming cells and the material, as well as its capacity of proliferation, differentiation and mineralization on its surface. In order to improve the performance of implants, superficial modifications have been investigated in recent years to control the adhesion of bone cells to the material, through the development of techniques and methodologies aimed at modifying the Chemical or topographical properties of conventional biomaterial surfaces.

2.2 Biomaterials

The biomaterials comprise a representative fraction of the products used in the health area, estimated at about 300 thousand about 10 years ago [5]. Among them can be cited as

examples of biomedical devices (biosensors, blood circulation tubes, hemodialysis systems), implantable materials (such as sutures, plates, bone substitutes, tendons, screens or meshes, heart valves, lenses, teeth); devices for the release of medications (in the form of films, subdermal implants and particles), artificial organs (such as heart, kidney, liver, pancreas, lungs, skin) and dressings, among many others.

The term biomaterial has been defined in different ways by different authors over the last years. In the scope of this review, biomaterials are defined as devices that come into contact with biological systems (including biological fluids), with diagnostic, vaccine, surgical or therapeutic applications, and may consist of compounds of synthetic or natural origin, as well as chemically natural materials both in the form of solids and gels, pastes or even liquids, not necessarily manufactured, such as pig heart valves and human skin flaps treated for use as implants [6].

The use of biomaterials is not recent, and their application in correcting the most diverse types of problems related to human health goes back to antiquity [6]. There is record, for example, of the use of linen and gold sutures in Ancient Egypt (2000 BC) and cat intestines in Europe during the Middle Ages, as well as artificial teeth made of shells by the Maya (600 BC), iron by the French (200 BC) and gold and wood by the Romans, Chinese and Aztecs. Bone substitutes made of wood were also found in Ancient Egypt and Europe in the Middle Ages, and efficient osseointegration was observed.

Initially, and up to the last century, the approach adopted in the development and application of biomaterials was fundamentally of the trial and error type, but, more recently, sharply systematic approaches have been the focus in studies in this area. At the beginning of the use of the biomaterials in a more systematized way, in the vicinity of the 50's, the bioenergy materials (focus on the material itself) were sought. Over time, the goal has

become the bioactivity of biomaterials, and more recently, the goal has been the regeneration of a functional tissue in fact, with a focus on the biological aspect [6]. That is, initially the objective was to obtain biocompatible materials that could replace a damaged tissue and provide mechanical support, with minimal biological response of the patient. Over time, it was sought to increase the life of the implant by its interaction with the interface of the host tissue; and then focused on the development of biodegradable materials, which are capable of being incorporated or absorbed (after dissolution) by the host tissue, and, more recently, the concept of biomimetics has been worked on, looking for materials that participate in active in the recovery process, acting on the tissue in a specific way, with stimulation at the cellular level. Such an evolutionary concept in the development and use of biomaterials is illustrated in Figure 2-1, which also indicates that the materials most used clinically at the present time are mainly of the categories biocompatible, bioactive and biodegradable, and the most researched, bioactive, biodegradable and biomimetic [7].

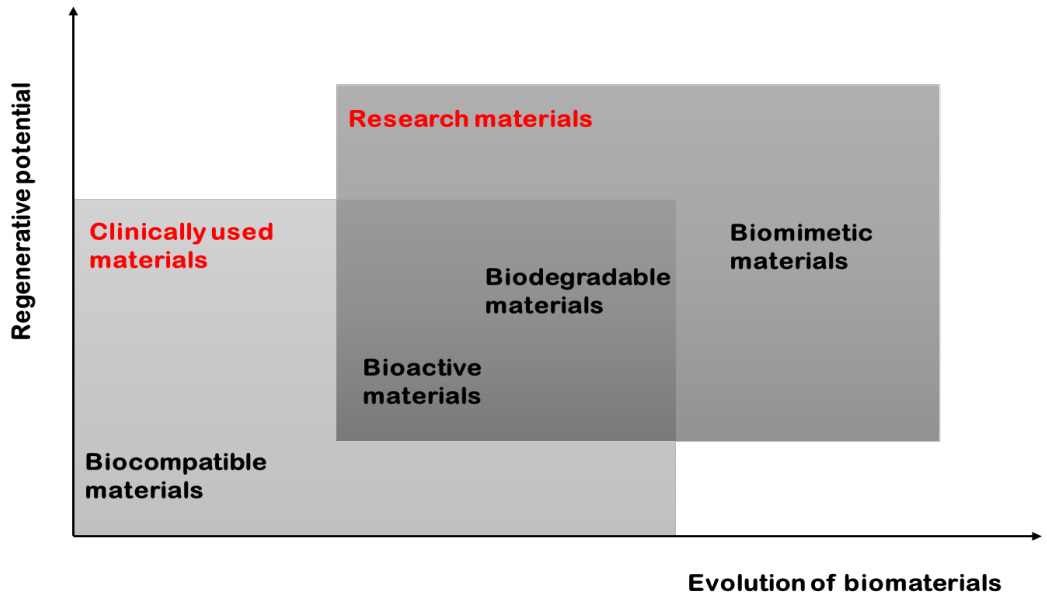


Figure 2-1. Evolution of the functionality and regenerative capacity of biomaterials throughout their development (based on Ref. 19)

The process begins with the identification of the need for a biomaterial for a given application, which may be the treatment of a disease, the replacement of an organ or merely cosmetic use. The following is the design and synthesis of materials for various tests (composition, structure, mechanical properties, toxicology, bioremediation to the material, biostability) and, based on the choice of those that are most appropriate, manufacturing followed by sterilization and packaging of the biomaterial which is then directed to more detailed tests of toxicology, bio- *in vitro* and *in vivo*. Next, regulatory aspects related to pre-approval in the market, to initial clinical studies, to clinical screening and to long-term follow-up are addressed. The development has a sequence even after the approval and clinical use of the biomaterial, with the analysis and registry of explanations extracted from patients aiming the understanding of eventual flaws for its correction. In all stages, it is necessary to have professionals with varied formations so that the analysis can be made to cover the various aspects required, especially the role of chemists, pharmacists, engineers, physicists, biologists, doctors and dentists. Thus, one can safely say that the biomaterial development approach is, by its nature, multidisciplinary and that it prioritizes the convergence of goals.

Although it is not possible to generalize the required characteristics of the biomaterials, since these depend fundamentally on their application, some types of properties are often evaluated so that the design of the device can be performed in an effective and economically attractive way. In this sense, biological properties such as biocompatibility, frequently associated with hemocompatibility, cytotoxicity, allergenicity, adhesion stimulation and cell proliferation are highlighted; physical properties such as surface morphology, surface energy, anatomical fit, roughness, porosity, color, transparency and permeability, mechanical properties such as tensile strength, elongation, fatigue life and

flexibility, and chemical properties such as density,

As regards the biological properties, implantable biomaterials can be classified into four categories, according to the type of reaction they cause in the cells with which they come into contact. Those that result in the death of the cells surrounding the implant are considered to be toxic, and non-toxic or virtually inert ones that cause the formation of a fibrous tissue around the implant. Biomaterials that arouse biological recognition because they present adhesion factors, polyanionic sites similar to those of regulatory polysaccharides or sites for enzymatic cleavage involved in cell migration, are considered as non-toxic and bioactive. Such devices may also undergo phase change in situation for example, including precursor to solid transformations [8]. In the latter category, of the biomaterials classified as non-toxic and degradable, there are those that allow the healthy cells surrounding or present in them to grow and replace the matrix that constitutes the biomaterial.

Among the different types of raw materials available to obtain biomaterials, the metals class stands out because it presents excellent mechanical performance, such as high resistance to fatigue and fracture. Due to these characteristics, metals have been widely used as structural components for the replacement, reinforcement or stabilization of rigid fabrics, which are constantly subjected to high tensile and compression loads. In this context, the most common applications include wires, screws and plates for fixation of fractures, dental implants and prostheses for joint replacement [5, 9].

In addition to the structural components, metals can be used in the manufacture of artificial heart valves and expandable stents , which require, in addition to adequate mechanical resistance, durability and the possibility of visualization in X-ray images [9, 10]. The good electrical conductivity, another common attribute of these materials, has favored the obtaining of neuromuscular stimuli devices, such as cardiac pacemakers [11]. The great

versatility of metals for biomedical use is also due to the possibility of surface polishing and abrasion, as well as the ease of sterilization. The latter feature becomes responsible for the extensive application of metals in surgical instrumentation (ultra-fast biomaterials) such as scissors, needles, forceps, tweezers and retractors.

Currently, the most commonly used metals in the medical field are the groups of stainless steels, titanium alloys and commercially pure titanium, and cobalt-chromium based alloys [12]. In Table 2-1 details the major types of metals or alloys and examples of their most frequent applications.

Table 2-1 Main metals and alloys and their applications in the biomedical area (adapted from Ref. 24)

Metal or alloy	**Applications**
316L stainless steel	Fixation of fractures, stents, surgical instruments
CP-Ti, Ti-Al-V, Ti-Al-Nb, Ti-13Nb-13Zr, Ti-Mo-Zr-Fe	Replacement of bones and joints, dental implants, pacemaker encapsulation
Co - Cr - Mo, Cr - Ni, Cr - Mo	Bone and joint replacement, dental restorations and implants, heart valves
Ni-Ti	Bone plates, stents, orthodontic wires
Gold alloys, Hg-Ag-Sn amalgam	Dental Restorations
Talk	Antimicrobial agent
Platinum and Pt-Go	Electrodes

The properties of metals are governed primarily by their crystalline lattice structure and bond strength. The high density comes from the grouping of atoms in a three-dimensional crystalline pattern, in an orderly and repeated way. The positively charged ion nuclei are immersed in a cloud of electrons that can move freely, being responsible for the good thermal and electrical conductivity of the metals. The tensile strength is a consequence of the strength

of the metal bonds and the plastic deformation occurs due to the non-directed bonds, which allow the position of the metal ions to be altered without destroying the crystalline structure [13, 14].

In order for them to be safely applied to the human body, metals or alloys must meet a number of requirements. Fundamentally, they must be biocompatible so as not to produce inflammatory, toxic or allergic reactions [15]. still must be chemically stable and provide suitable corrosion resistance in order to prevent degradation in the biological environment. In the case of bone implants, high adhesion strength between the osteoblasts and the implant is required. Appropriate mechanical properties, such as modulus of elasticity similar to that of human bone and resistance to fatigue, should also be considered.

Once implanted, the biomaterials remain in contact with the body fluid, which consists of an aqueous solution containing dissolved oxygen, proteins and various ions, such as chloride and hydroxides [16]. In the case of dental implants or orthodontic materials, metal alloys are still susceptible to variations in temperature and PH, the presence of microbial biofilm and the physical and chemical properties of food. These media can be aggressive to the metals, causing their corrosion. In addition to these factors, most implants work under the action of mechanical loads that generate friction, slip and, consequently, the possible release of metallic particles [17].

As a result of these mechanisms of wear and corrosion, the mechanical and structural integrity of the implant can be compromised, leading to premature failure or fracture. Implant degradation products have been associated with complications such as osteolysis, inflammation, allergic reactions and vasculitis, and may lead to metallic ions accumulating in organs, teratogenicity and cancer [6, 18].

Noble metals, such as gold and silver, are not susceptible to corrosive

processes. However, other attributes such as high density, insufficient resistance and high cost make the orthopedic applications impossible [13]. All other metals for medical use are susceptible to corrosion when in contact with biological systems [19]. In general, the resistance to this process comes from a thin film of oxide formed spontaneously by exposing the metal surface to the air. This film, in the form of passivation layer, prevents the exchange of ions, protecting the surface. Some factors, however, may compromise corrosion resistance, such as lack of homogeneity in the microstructure related to variation in composition, surface deformation, presence of impurities, precipitates, segregations and inclusions. Thus, during the manufacturing process, in order to improve the corrosion resistance by strengthening the protective film, the implants may undergo further treatments and deposition of oxides on their surface [9].

Once the passivation layer has ruptured, the corrosion process begins, and the release of the metal ions will occur until the film is regenerated if this is possible. The repassivation time, therefore, is decisive for the determination of the corrosion rate and varies according to the material. Titanium based alloys, for example, have less repassivation time than stainless steels [20].

Among the most common forms of corrosion in metal implants are pitting, cracks and wear corrosion. Pitting corrosion is extremely localized and is characterized by the formation of deep and small-diameter cavities in metals that are exposed to media containing aggressive ions such as chloride [19]. Slot corrosion occurs in cracks between metallic material in contact with another component, metallic or non-metallic. It may start, for example, in the space created by fastening a metal plate by screws [19]. In these environments, the diffusion of chemical species is difficult, but once they enter, they become stagnant, promoting changes in this space. If this process is initiated, the oxygen present in the gap is consumed,

acidifying the solution and causing corrosion. On the other hand, wear corrosion is the result of the damages produced by metallic components in direct physical contact, in the presence of vibratory movements and repetitive loads, damaging the surface of the material and favoring the appearance of fractures [21].

The favorable side of metal implant corrosion is to use such a phenomenon for the development of biodegradable materials with very attractive applications in orthopedic, pediatric and cardiovascular surgeries in which it would be difficult to remove the device without damaging the healthy tissue. One of the main metals with potential for this application is magnesium, which has good mechanical properties and low resistance to corrosion, and its degradation products are rapidly excreted from the body and do not show appreciable toxicity [22]. With materials having controllable rates of corrosion, implants that do not require subsequent removal, such as vascular stents , screws and stems used in the treatment of fractures, may be available [23].

In addition to the possible corrosion and release of metal ions, as already mentioned, another limitation observed in metals relates to the disparity between the modulus of elasticity of metals and the bone. The modulus of elasticity of bones generally ranges from 3 to 20 GPa [24], whereas in stainless steel and cobalt-based alloys this value can be up to 10 times higher. In cases where the modulus of elasticity of the implant is much greater than that of the bone, the implant will assume the load and the bone will not receive the stimulus necessary to maintain its mass [7], leading to the clinical phenomenon known as *stress-shielding*, with reduction in bone density and loosening of the implant. Modifications in metals, such as the insertion of pores, contribute to the approximation of values. This strategy has been successfully applied to the tantalum, the porous medium, has modulus of elasticity similar to cortical bone, with values of about 3 GPa [24].

Another disadvantage of metals is related to the possible noise resulting from friction in implants composed of two metals in contact. The incidence of this problem in patients with hip implants, for example, can reach 10% and usually starts between 6 months and 2 years after surgery [21]. In addition, the high density of metals may imply high mass implants that are uncomfortable for the patient.

2.2.1 Classification of biomaterials

The choice of a material to be used as biomaterial depends on the analysis of a series of requirements that must be found. In this sense, biocompatibility (effect of the organic environment on material and effect of the material in the body), biodegradability (phenomenon in which the material is degraded or solubilized in tissue fluids, disappearing from the site of implantation), as well as the rate of degradation of the material are developmental and fundamental characteristics for the choice of a biomaterial [25].

These properties give the biomaterial a beneficial interaction with the organism where it is implanted, provided that:

1. The material does not elicit sustained or toxic inflammatory response upon in vivo implantation;
2. The degradation time of the material allows the occurrence of the process of regeneration or curing of the compromised site;
3. The material has mechanical properties appropriate to the application for which it has been indicated and any variation in the mechanical properties resulting from its degradation in vivo is compatible with the process of regeneration or restoration of the site of implantation;
4. Its degradation does not generate toxic products and is easily metabolized and released

from the body [26].

However, considering the evolution of biomaterials, these concepts of biocompatibility and biodegradability are part of a second generation of biomaterials. In the first generation, bioenergetic materials were developed, whose focus for their development was not to provoke a foreign body reaction in the organism [27]. The third generation includes the materials capable of stimulating specific cellular responses at the molecular level [28].

These three generations are interpreted conceptually and not chronologically, since each one represents an evolution in the properties of the materials involved, according to the needs and requirements that arose [29].

The use of biomaterials to replace bone loss has been a common practice for decades [30]. Initially, to restore bone losses, surgeons used autografts, considered ideal because they represent material from the individual. However, this procedure has drawbacks, such as a higher incidence of diseases in the donor site and limited size of donor material, which is often insufficient [30]. Faced with these limitations, allografts (composed of materials from another individual of the same species) and xenografts (materials obtained from another species) emerged as possible substitutes. However, they also present important limitations, such as risk of rejection or transmission of diseases [31].

2.2.1.1 Metallic biomaterials

The first metal biomaterials successfully used for bone repair were stainless steel and cobalt and chromium alloys around the middle of the 20th century [32]. The main characteristic of these biomaterials is their potential for high corrosion resistance in the in vivo environment, but they also have good mechanical strength, adequate conformability,

and high resistance to fatigue, traction and fracture [16]. From these first biomaterials produced, new alloy of stainless steel with the following properties:

1. they are structurally similar to the inorganic component of the bone [33];
2. In addition, they have been shown to be more efficient in the treatment of the disease,
3. have a high degradation time in vivo [34], allowing for bone remodeling at the implant site.

Their limitations are related to their low structural rigidity, so that they can not be used in regions of great mechanical stress, and to their porous nature, which increases the risk of fractures [35]. They are widely indicated in orthopedics and dentistry in the repair of bone defects, maintenance of the alveolar ridge and as orthopedic and dental implants [36]. Titanium have been used as a biomaterial due to its properties of mechanical resistance and anticorrosion [37]. However, some metallic elements have demonstrated a toxic action in the in vivo environment, such as Vanadium (V) and Nickel (Ni) [38-40].

The metal biomaterials in direct friction suffer marked wear, and their interaction with the adjacent tissue causes the release of metallic ions by dissolution, wear or corrosion [38]. Thus, their surfaces must undergo modifications and associations with other materials, such as polymers, which give it greater mechanical resistance, allowing adequate contact in regions of great friction, such as in hip prosthesis, for example, and minimizing the release of ions [41].

Another disadvantage of metal biomaterials is the loss of mechanical stimulus in the bone, site of implant of the material, and may induce local bone resorption, which may, in turn, lead to eventual failure and loss of the implant [42]. Besides that, many metallic biomaterials have ferromagnetic phases, producing adverse interactions in magnetic fields, currently widely used in diagnostic methods such as magnetic resonance imaging [43].

2.2.1.2 Non-metallic biomaterials

One of the important non-metallic biomaterials are ceramics which are composed between the metallic and non-metallic elements. They are often oxides, nitrides and carbides. The wide variety of materials that fall within this classification includes ceramics that are composed of clay materials, cement and glass. These materials are typically insulated from the passage of electricity and heat and are more resistant to high temperatures and abrasive environments than metallic and polymeric materials [44]. The ceramics are hard, have high compressive strength and are very brittle. They are difficult to manufacture, have low mechanical reliability and high density [44]. In the other hand, polymers they can be of natural or synthetic origin, and its main characteristic is the biodegradability. Synthetic polymers are generally degraded by simple hydrolysis, while the natural polymers are mainly enzymatically degraded [45]. Both natural and synthetic polymers have been used by tissue engineering to develop three-dimensional scaffolds for the preparation of cartilage, ligaments, meniscus and intervertebral discs, particularly synthetic biodegradable polymers [46]. The main polymers used for the purpose of repairing bone tissue are polyglycolic acid (PGA), polylactic acid (PLA), polyhydroxy butyrate (PHB) and polycaprolactone (PCL). Among its advantages are the easy control of synthesis, unlimited origin, no cell-mediated degradation, biodegradable and biocompatible. However, they have little mechanical resistance, they suffer a reduction in size over time, the cell-polymer interaction is questionable, they have a hydrophobic surface and there is the possibility of local toxic reaction by the release of acid degradation products [46]. They are indicated in orthopedics and as devices deployed for drug delivery [47].

In order to solve the disadvantages of ceramics and polymers, new studies have been carried out in order to develop hybrid or composite synthetic biomaterials, which have the

advantages of ceramics and polymers, but with better reabsorption rates after implantation and better mechanical resistance [48].

2.2.1.3 Biomaterials for bone repair

The demand for biomaterials to repair or replace tissues is justified by the degradation of their properties associated with trauma or a Diseases. In the case of bone tissues, this degradation results in a reduction of up to 40% in the mechanical resistance in people with more than 30 years, being able to be greater in the case of women. This decrease in mechanical properties is even more pronounced as a result of wear on joints and degradation in connective tissues such as cartilage and tendons [49].

In general, the period of use of a prosthesis or implant satisfactorily covered the expectations of patients ' life expectancy. Today, however, the increase in the quality of life of the population in advanced societies, the use of antibiotics and vaccines, as well as the improvement of surgical techniques, have led to a spectacular ageing of the population, which can exceed the Useful time in service of the prosthesis or implant necessitating replacement. These substitutions are technically very complicated and sometimes unpredictable clinical outcomes. If we consider that the patient list is increasing with more and more young people due to the practice of high-risk sports or traffic accidents, the likelihood of needing a second or third implant replacement is very high. The expectations of this replacement are an increase from the current 7% of prosthesis for revision to 60% in the coming years, which justifies the need to develop biomaterials with better properties that guarantee a greater time in service.

The interface between the tissue and the implanted material is of vital importance for the development of biomaterials or biomedical devices. The physical connection between

two independent systems such as the surface of the implant and the tissue Adjacent biological. The study of various interfaces (implant-bone, implant-blood, etc.), as well as studies In vitro of adhesion and cell proliferation of different biomaterials, has shown that biological systems have the ability to recognize details at the molecular level [50-53]. The superficial physical-chemical properties affecting the cellular response include: wettability, surface energy, roughness, texture, chemical composition, surface electrical load and morphology [54-56].

2.2.1.4 Titanium and its alloys in orthopedic surgery

The low density of titanium, 4.5 g/cm3, compared with 7.9 g/cm3 of stainless steel, together with its good mechanical and electrochemical properties, are the most outstanding characteristics of this material with a view to its application as osteo-articular implants. In addition to its low density, titanium-based alloys present an elastic modulus of 105-120 GPa, lower than that of stainless steels, so their mechanical behavior is more similar to bone [57]. They also present good resistance to corrosion in the biological environment due to the spontaneous formation of a layer of oxide on the surface (TiO_2), which passively electrically and chemically to the material [58].

Titanium in metallic state is allotropic material, i.e. it can exist in more than one form crystallographic. At room temperature it has a compact hexagonal structure, HC (phase α) and higher temperatures 882 º C underwent a reversible transformation to a centered cubic structure, CC (β phase). This transformation offers the possibility of obtaining alloys with different microstructures α, β or α + β by means of the addition of elements that stabilize one or another phase [59]. For example, aluminum tends a Stabilize the phase α while vanadium stabilizes the phase β. The addition of these alloying elements provides a greater resistance

to fatigue Currently, Ti6Al4V Alloy (90% titanium mass, 6% aluminum, 4% vanadium) is the most used in the manufacture of prosthetic components that will withstand load and require biological fixation, due to its high resistance to fatigue and corrosion , as well as its excellent biocompatibility [60]. The Ti6Al4V alloy is of the type α + β, in which the aluminum increases the temperature of the transformation between the phases α and β (it is a stabilizer of the phase α) and vanadium decreases that temperature stabilizing the phase β. In addition, aluminum decreases the density of the alloy and vanadium increases its ductility. It is produced in different degrees, being the most used those of grade 5, 23 and 29. The variety of degrees is related to the amount of oxygen, which makes the mechanical properties of the alloy vary. The lower the amount of oxygen, the greater the ductility and tenacity to the fracture, with some reduction in the resistance.

The microstructure of the Ti6Al4V depends on the heat treatment and the previous mechanical conformation. When heated above 1000 °c in the field of the β-phase, Figure 2-2, and then slowly chilled at room temperature, a two-phase structure is produced. The α phase, rich in aluminum and poor in vanadium, precipitates as plaques or needles with a specific crystallographic orientation within the grains of the β matrix. On the other hand, if the cooling from the β phase is faster (eg. in oil), a microstructure is produced acicular type due to the transformation martensitic or Bainitic. The Ti6Al4V alloy most used for bone replacement is the one that has a microstructure of the type "Mill annealed" consisting of equiaxial grains and α plaques, in an untransformed β matrix. This microstructure is the result of heating and deforming in the region α + β and cool then slowly, allowing the transformation of β to α. This type of microstructure allows for an excellent combination of mechanical strength, tenacity, ductility and fatigue resistance. Specifically, its elastic limit, tensile strength, percentage of elongation and necking are higher than those presented by the

alloy with microstructure type, Table 2-2, and the rate of spread of cracks due to fatigue is lower.

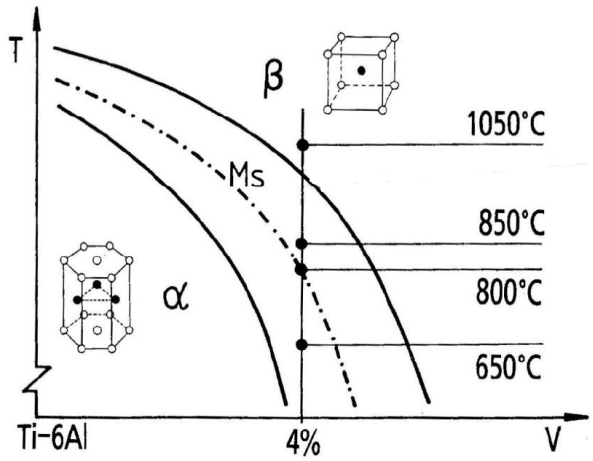


Figure 2-2 Schematic diagram of phases in the region α + β of interest in cold-working processes [61].

On the other hand, the Ti6Al4V is an alloy that quickly generates a passive layer of titanium oxide TiO_2 Spontaneously, in the presence of oxygen, with a thickness of the order of Nanometers [61]. This gives it excellent corrosion resistance in a wide variety of media, such as most aqueous solutions, oxidizing acid media, chlorides (in the presence of water) and alkalis. Part of the reason for the good biocompatibility of Ti6Al4V is due to its corrosion resistance. The body fluids are basically chlorides with a ph range from 7.4 to acid ph, another organic condition in which the Ti6Al4V is highly immune to corrosion. When the Ti6Al4V is subjected to certain temperatures, the oxide layer can grow up to the order of several microns [62]. This oxide, more stable, is bioactive and therefore of great interest in its application in implants, because it can generate a specific biological response in the interface of the material With The tissue, resulting in a direct link between both [63].

Table 2-2 Mechanical properties of the Ti6Al4V alloy.

Microstructure	**Elastic limit (MPa)**	**Tensile strength (MPa)**	**Elongation (%)**
Mill-annealed	880	945	18
Widmanstädter (Thomson structures)	750	885	15
Martensite	840	1070	7

Although all of these metals and metal alloys are often used without any superficial modification, recent studies consider it crucial to improve the stability of implants used to repair bone fractures in early states [33].

2.3 Overview of Surface Modification of Metallic Biomaterials

The modifications in the superficial chemistry of a metallic substrate allow to improve its physical, chemical and biological properties. The techniques used for this purpose include surface treatments and the deposition of coatings. Surface treatments such as thermal oxidation, ionic implantation, anodizing or acid or alkaline treatments alter the surface composition of the material With The purpose of improving its resistance to wear and corrosion as well as its biocompatibility [64, 65]. For example, the thermal oxidation of Ti6Al4V alloy results in the formation of an oxide layer on its surface that decreases ion release and improves adhesion and proliferation of osteoblastic cells (bone forming cells) [64]. On the other hand, the treatments of anodization on this same alloy induce an increase in the activity alkaline phosphatase (enzyme indispensable for the formation of the bone) of the cells osteoblastic [20]. While these surface treatments lead to changes in the chemical composition of the substrate, the deposition of coatings allows to generate surface compositions different from those of the base material without altering their mechanical

properties Intrinsic and improving its resistance to wear or corrosion.

On the other hand, the modifications in the topography of a metallic biomaterial allow the anchorage to the bone tissue, to reduce the times of osteointegration and to obtain a greater transmission of loads between the bone and the implant. Efforts to improve this osseointegration have been approached by creating rough surfaces that increase the surface area available for bone-to-implant binding (mechanical blockage) and optimize fixation and stability.

This dissertation focuses on topographical modification treatments, for which four superficial techniques have been used: as is or (machined) surface treatment, BCP processed by blasting beta-tricalcium phosphate BCP, which is called by authors and companies as RBM (Resorbable Blast Media) treatment [66] , Acid treatments or etching by acid is aimed at the detachment of metal particles from the surfaces of the implant by immersing them in acidic sources. Acid treatment tends to leave areas of higher corrosion in the peaks and valleys of the grooves left by surface fabrication. The advantages of this method lie in the fact that from it is possible to control the degree of porosity of the surface, as well as to allow an adequate method for cleaning the unwanted impurities generated during the manufacture of the implant [67]. implementing this method for implant surfaces had increased the cell adhesion and bone formation, thus enhancing the osseointegration due to the increase of the bonding into the implant surface [68].

The term mechanical polishing is often used to describe the various final polishing procedures involving the use of special cloths, motions, products and suitable polishing abrasives. The rotational movements or vibratory movements are performed by hand or mechanically, or merely confined within the polishing area. For the reason of producing a non-contaminated Ti surface without reactive layers previous studies proposed the chemical

mechanical polishing method to prepare clean Ti surfaces [69]. When this method was applied to Ti polishing, no elements responsible for causing contamination were detected [69]. In light of the result obtained, this method showed itself to be an effective surface treatment for Ti based implants to render it to be more biocompatible. In this scenario the developed 3D (CMP) of titanium dental implants was carried out to study the optimal 3D CMP that decreases the unwanted side-effects and toxicity in pursuance of the strict modern criteria for a contemporary therapeutic agent. Hence, in this present study, the 3-D CMP was evaluated in attempt to provide a unified set of features to control the Process Variables (Sample down pressure, Sample velocity, Pad velocity, Pad characteristics, Process time, Particle characteristics, Slurry, chemistry, Substrate characteristics).

(USSP), "shot peening" high energy (HESP), Surface mechanical wear treatment (SMAT), Nano crystallization and surface hardening (SNH), shot peening [70] and water processing a High pressure (WJP, "Water Jet Peening") [71]. Several studies have shown that (Severe plastic deformation) SPD processes can improve the mechanical properties of the material, such as wear resistance in titanium [72], fatigue resistance [73] and the elastic limit [72], etc. Despite these advances, the mechanisms responsible for improving the mechanical properties induced by SPD are not entirely known. This situation is due to the fact that the formation of nanometric grains in the superficial area is usually accompanied by the introduction of a high density of dislocations, stacking defects and twins, and in many cases macroscopic residual stresses [74].

2.3.1 Surface Modification Techniques

Based on basic research that demonstrated the importance of controlling the physical, chemical and topographic properties of implant surfaces, a large number of surface

modification techniques and methodologies have now been developed [75]. These techniques vary from specific cleaning methods to the deposit of a thin film on the bulk material. According to Kasemo and Gold [76] the proposed surface modifications can be basically divided into three classes:

1- Topographic modifications, such as pore size and distribution, roughness, etc.,
2- Modification of the bio-chemical properties of the surface; release of chemical species (ions or drugs), adsorption of biomolecules (proteins or growth factors), etc., and
3- Modification of micro-mechanical properties or viscoelastic of the surface.

In the first case, it is sought to control the topography, since through different studies it has been elucidated that the topography, at both micrometric and nanometric scale, has relevant effects on cellular behavior. These effects include cell adhesion, proliferation, differentiation, cell morphology and spatial orientation, tissue organization, and even cell selection [77, 78]. While in (b) the objective is to achieve an active surface that interacts strongly with the surrounding tissue. A typical example is the development of stents with coatings that release drugs in a controlled manner [79, 80], which are injected directly into the bloodstream, acting as a blood thinning agent that reduces the formation of clots. Finally, in (c) it is sought to increase the life time of the implants through improving the resistance to wear, although the functionality of the implant can also be improved through a better distribution of the efforts mechanical [81]. Another possible classification is based on the structure of the modified layer [82]: nano-structured surfaces, surfaces with gradients and biomimetic surfaces.

2.3.1.1 Nano-structured surfaces

The nano-structured surfaces are of great importance in the design of biomaterials

since the biological response to materials is mainly controlled by structure and surface chemistry [83]. The nano-structured surfaces fall into two categories: (a) chemical or physical that alter the surface through a modification of surface chemistry (nitriding, ion implantation, surface functionalization) [84] or (b) coating the surface of the material in bulk with a different material (deposit of thin films) [85]. In both cases, the modified layer should be as thin as possible, because if the modification is very thick the properties of the package could be altered. In addition, very thick coatings can delaminate more easily. Alteration of only the outer molecular layer would be optimal for medical use, however, if the modification is extremely thin it is difficult to ensure that it is laterally uniform and could easily erode.

2.3.1.2 Surface modifications with gradients

The surface modification with gradients is a combination of two materials with different properties, such as polymer-metal or ceramic-metal. In the composite material, one material constitutes the matrix and the other forms a dispersed phase. A material with gradient (functionally gradient material) is one in which the dispersed phase is not uniformly distributed, but in the form of spherical particles, discs, bars, fibers or lamellae. In this way, properties that are not common in traditional composite materials are obtained [86].

2.3.1.3 Biomimetic surface modifications

Finally, the biomimetic surface modifications are those in which they try to imitate the multifunctional natural materials that have hierarchical morphologies [87, 88]. The bio-mimic involves the study of biological micro-structures to find the correlation between the structure with the physical and chemical processes that makes and use this knowledge to design and synthesize new materials. A well-known example of a hierarchical structure in nature is bone. Structurally, bone is a nanocomposite material made up of a natural polymer

(collagen) and an inorganic ceramic (hydroxyapatite, Ca5 (PO4) 3OH). The relationship between the organic and inorganic phases is not uniformly distributed, but varies with depth, so that it constitutes a nanocomposite with gradient, it is a FGM where the dispersed phase is hydroxyapatite and the distribution of this phase varies in depth. This structure provides the bone with optimal balance between hardness, fracture resistance, durability and shock absorption. The objective in the development of bio-mimetic surface modifications is to emulate nature to design biomaterials with greater functionality. Another example of bio-mimetic modifications to improve the bio-functionality of natural or synthetic materials is to promote the adhesion interactions between the cells and the surface. This can be achieved by means of immobilizing peptides or extracellular matrix components on surfaces that bind specific adhesion receptors of cells and promote cell adhesion [89]. Each of these proposals for surface modification has the basic objective of developing an ideal metallic biomaterial with improved properties of resistance to corrosion, fatigue and wear.

2.3.2 Methods of surface modification

Research in metallic biomaterials has been directed towards the development of superficial modifications that allow to improve their mechanical, biological properties or their resistance to Wear, corrosion and fatigue [90]. An important aspect to take into account when modifying the surface of a material is to consider the specific requirements of the clinical application for which it has been designed. For example, some implants used as temporary devices require minimal interaction with bone tissue to facilitate removal. However, the materials used in the area of attachment to the bone of uncemented prostheses should interact with the tissue around them promoting their osteointegration [67]. In this case the long-term efficacy of the implant will depend to a large extent on the first phase of

interaction enters the osteo-forming cells and the material, as well as its capacity of proliferation, differentiation and mineralization on its surface. In order to improve the performance of implants, superficial modifications have been investigated in recent years to control the adhesion of bone cells to the material, through the development of techniques and methodologies aimed at modifying the Chemical or topographical properties of conventional biomaterial surfaces [91].

The modifications in the topography of a metallic biomaterial allow the anchorage to the bone tissue, to reduce the times of osteointegration and to obtain a greater transmission of loads between the bone and the implant [92]. Efforts to improve this osseointegration have been approached by creating rough surfaces that increase the surface area available for bone-to-implant binding (mechanical blockage) and optimize fixation and stability [93]. There are few studies devoted to quantifying the biomechanical properties behavior simultaneously with the topographic changes in surface of the metallic bioimplants, in addition to a lack of experimental techniques with simple and well defined procedures that can offer the Integral and simultaneous evaluation of this relationship [94].

The following describes the superficial modification techniques that have been used in this work:

2.3.2.1 Machined surface

The prosthetics and manufacturing technicians have to manage to mechanize the required components, automatically, with the lowest cost, in the shortest time and with the quality required by the client.

In the case of the prosthetic technician, and before solutions based on the manufacture by material removal, should apply these criteria on all types of machine tools and different

prostheses, implants and structures of zirconium, cobalt chromium, titanium, polymethyl methacrylate (PMMA) , wax, ceramics and lithium disilicate. For this, it has to use optimized machining techniques based on the use of 3-axis and 5-axis machine tools, and CAD / CAM applications with the implanted functionality required in dental machining operations. There are two different machining lines in dental laboratories:

1- Machining of soft materials (PMMA, wax, resins and pressed zirconium powder).

2- Machining of metallic structures (titanium and / or cobalt-chromium).

Said machining operations demand adapted machine tools with the following functional characteristics:

1- Small size to adapt to the space available in dental laboratories.

2- Machining of hard and brittle materials such as special glass and synthetic ceramics, as well as high-speed milling of demanding metals, such as titanium and cobalt chrome

3- Machining of complex geometries through flexible kinematic configurations and from 3 to 5 axes.

Conventional machining and sintering techniques do not achieve a reliable commitment to these demands. Conventional machining is limited in terms of machining time, tool size and simple geometries. The machining by EDM allows the machining of a wide range of shapes and sizes but is only suitable for use in conductive materials. In the case of sintering, the use of the laser causes a thermal modification of the surface that can have a negative impact on its final use, especially in applications that require high reliability. As for the advanced machining techniques , high-speed machining tools and ultrasonic machining are available. High speed machining is the most used technique for the manufacture of dental components in resistant materials such as Co-Cr, titanium, PMMA, wax and pressed zirconium alloys.

In the ultrasonic machining, there is no thermal, chemical and electrical influence, the physical properties of the piece are not altered and there are no changes in the chemical composition and the microstructure of the material. Ultrasonic machining is a viable alternative to generate complex geometries in advanced materials such as glass-ceramics, sintered zirconium, these can be machined quickly and accurately with machine tools with ultrasonic heads of 42,000 rpm and 30,000 pulses every second.

2.3.2.2 Acid treatments or etching

Acid treatments or etching by acid is aimed at the detachment of metal particles from the surfaces of the implant by immersing them in acidic sources. Acid treatment tends to leave areas of higher corrosion in the peaks and valleys of the grooves left by surface fabrication. The advantages of this method lie in the fact that from it is possible to control the degree of porosity of the surface, as well as to allow an adequate method for cleaning the unwanted impurities generated during the manufacture of the implant [67]. implementing this method for implant surfaces had increased the cell adhesion and bone formation, thus enhancing the osseointegration due to the increase of the bonding into the implant surface [68].

2.3.2.3 Sandblasting (BCP surface treatment)

Treatment with jet of particles also known as sandblasting, this type of treatment consists of blasting different materials with a durability greater than that of titanium, such as aluminum oxide, titanium oxide, silica and the hydroxyapatite and beta-tricalicium phosphate BCP, which is called by authors and companies as RBM (Resorbable Blast Media) treatment [66]. These particles generate a series of irregular depressions, which are called macro retentions. However, this method has a great disadvantage, since by which a homogeneous

surface cannot be produced [95].

2.3.2.4 Chemical mechanical polishing CMP

The term mechanical polishing is often used to describe the various final polishing procedures involving the use of special cloths, motions, products and suitable polishing abrasives. The rotational movements or vibratory movements are performed by hand or mechanically, or merely confined within the polishing area. For the reason of producing a non-contaminated Ti surface without reactive layers previous studies proposed the chemical mechanical polishing method to prepare clean Ti surfaces [69]. When this method was applied to Ti polishing, no elements responsible for causing contamination were detected [69]. In light of the result obtained, this method showed itself to be an effective surface treatment for Ti based implants to render it to be more biocompatible. In this scenario the developed 3D (CMP) of titanium dental implants was carried out to study the optimal 3D CMP that decreases the unwanted side-effects and toxicity in pursuance of the strict modern criteria for a contemporary therapeutic agent. Hence, in this present study, the 3-D CMP was evaluated in attempt to provide a unified set of features to control the Process Variables (Sample down pressure, Sample velocity, Pad velocity, Pad characteristics, Process time, Particle characteristics, Slurry, chemistry, Substrate characteristics). This paper focuses on topographical modification treatments and its effects from the biomechanical point of view. Four superficial modification techniques have been investigated: As is or machining, Blasting (BCP), Etched, and "3D CMP ". It should be mentioned that the CMP treatment have been developed in previous work to introduce an alternative technique to treat the titanium-based implants surface.

2.3.2.5 Coatings

Within the set of different materials used for endoprostheses, titanium is cataloged as the most versatile material, both in biomechanical and biocompatibility aspects. In relation to other materials, titanium shows advantageous conditions such as high ductility and tensile strength. Its Young's modulus (elasticity) is closest to the maxillary bone itself. In addition to all these characteristics, titanium has a high capacity for passivation and self re-passivation. Passivation is a self-generated oxide layer by the metal in contact with oxygen in the air. This passivation protects and masks the metal against the action of external agents. In stent and implantology, surface oxide of titanium serves precisely to the contrary effect, While the term "biocompatibility of titanium" is accepted for simplicity, it might be equally wise to speak of the "biocompatibility of titanium oxide". However titanium oxide itself lacks the biomechanical qualities of titanium. In this way we understand titanium in its different degrees of purity and alloys as the whole of its surface layer and its interior, which offers high biomechanical and biocompatibility qualities.

Since the discovery of titanium in the late eighteenth century has not stopped researching and improving its properties with alloys and chemical treatments, being the second half of the nineteenth century where titanium is incorporated with full right to the industry. In the 1950s the Soviet Union incorporated titanium into its military industry. During the cold war titanium was considered as a strategic material for the military industry. Currently the (American Society for Testing and Materials) recognizes up to 30 grades of titanium and alloys. Although probably there are more types of alloys not considered and developed in private or military industry.

The aim of the surface treatment of titanium for Bio-applications is:

- An increase in surface hardness and as a consequence an increase in resistance to moments of compression
- An increase in wear resistance
- An increase in corrosion resistance
- An increase in polarization resistance.
- A decrease in the coefficient of friction (Case of Titanium joints)
- Reduction of the release of titanium ions to the physiological medium. This reduction ranges between 40 and 80% depending on the type of treatment. As a consequence, there is a decrease in local irritations and metallosis.

There are multiple systems of surface modifications with different purposes. In addition, these techniques are often combined in order to achieve various objectives. In the case of titanium for dental implants, this type of treatment is carried out for the following purposes:

- Increase of contact surface with the implant by roughness.
- Increase in hardness and surface resistance.
- Incorporation of osteo-conducting elements.
- Increase of the external layer of titanium oxide in order to avoid the exit of electrons to the surface.

Elimination of polluting remains from other surface treatments (silica, alumina...) Some types of surfaces applied to titanium for dental implants:

- Electropolished surfaces
- Machined or machined surfaces
- TPS (titanium plasma-sprayed) surface
- Surface sandblasting with titanium oxide TiO_2
- Surface sandblasting with alumina ($Al2O_3$) with different grain types

- Surface sandblasting with alumina of different diameters (Al_2O_3) combined with acid etchings
- Machining combined with acid etchings
- SLA Surface sandblasting with titanium oxide TiO_2 and alumina (Al_2O_3) and acid etching.
- RBM (Resorbable Blast Media) - Bombardment of the surface with calcium derivatives and / or titanium oxide followed by acid marking.

To understand the coating of an implant, this will need a very purified deposition technique, in order to avoid the detachment of deposited layers. A large number of titanium implant coating techniques have been implemented using osteoconductive calcium phosphate bio-ceramic elements (with their variations and derivatives), titanium, magnesium alloys, austenitic surgical steels, alumina, zirconia, polymers and carbons. To do this, non-thermal, thermal and mixed methods are used. All these coatings are focused on a greater effectiveness of the implant result. Hydroxyapatite, an osteoconductive material formed by crystalline calcium phosphate, a compound very present in tooth enamel and in bones, is one of the most relevant osteoconductive materials in implant coating. At least 3 layers are used in the titanium coating. Any stress of the layer connected to the titanium superior to the moment of force, can lead to a delamination of the coating. These coatings can be carbon, glass, ceramic coatings, hydroxyapatite, bioactive calcium phosphate, TiO_2 coating and other coatings of Titanium derivatives.

Every day these types of superficial treatments are being improved with very marked objectives to improve the osteo-conductivity, the osseointegration, the duration of the implant and the comfort of the patient.

2.3.3 Interface cell-material

Characteristics of the tissue-material interface are of importance to define the functioning of a biomaterial or biomedical device. An interface is defined as the physical connection between two independent devices or systems, in this case the independent systems are the surface of the implant and the surrounding biological tissue. The study of various interfaces (implant-bone, implant-blood, implant-skin, etc.), as well as in vitro studies of cell adhesion and proliferation on different biomaterials, has shown that biological systems have the ability to recognize any detail a level molecular [96]. The recognition is programmed in the molecules and cells through the combination of its three-dimensional architecture, the chemical architecture and its dynamic properties. The physical-chemical properties of the surfaces that have been determined affect the cellular response: wettability (hydrophobicity or hydrophilicity of the surface), surface energy, roughness, texture, chemical composition , surface charge and morphology [97].

Surface energy is one of the most important surface factors in terms of cell adhesion and proliferation and, however, has less influence on cell orientation. In terms of cell orientation, factors such as texture, morphology and roughness play a more relevant role. However, cellular orientation, in turn, can affect cell differentiation [98] and the roughness itself can modify the correlation between surface energy and cell proliferation. General rules have yet to be established [99], since the cellular response depends on the cellular phenotype; fibroblasts, osteoblasts, etc., and also depends on the adsorption of proteins and their information on the surface [100].

These processes have been described by Kasemo et al . [77, 101], summarized in a series of events that occur when placing a biomaterial within the human body and are described below

taking into account the properties of the biofluids, the surface itself and the time scale:

1. The first bio-molecules that reach the surface are the water molecules (Figure 2-3 a), which occurs in nanoseconds. The water molecules adhere to the surface forming a mono-layer or a bi-layer, whose structure is different from that of liquid water.
2. Subsequently, the hydrated solutions present in the biological medium are incorporated (Figure 2-3 b), such as Na^+ and Cl^- forming the known double-layer whose extension depends on the electrostatic properties between the solution and the surface of the implant.
3. A short time later, proteins and other molecules approach the surface where they adsorb and / or de-sorb following the relative concentration in the solution, their size and the electrostatic properties established between the biomolecules and the water layer (Figure 2-3 c). In fact, biomolecules (including proteins) also have a surface hydration layer and it is this layer that interacts with water adsorbed on the surface. The thermodynamic equilibrium between the two interfacial layers determines the final configuration of the proteins. The adsorption-desorption processes are controlled by the Vroman effect [102], which relates the surface properties of the material (energy and surface charge) with the adsorbed protein layer (concentration, conformation and size). The layer of adsorbed proteins will be a mixture of different proteins in different conformation states whose composition depends largely on the surface properties of the implant, particularly the previous adsorption of the water molecules (Figure 2-3 d).

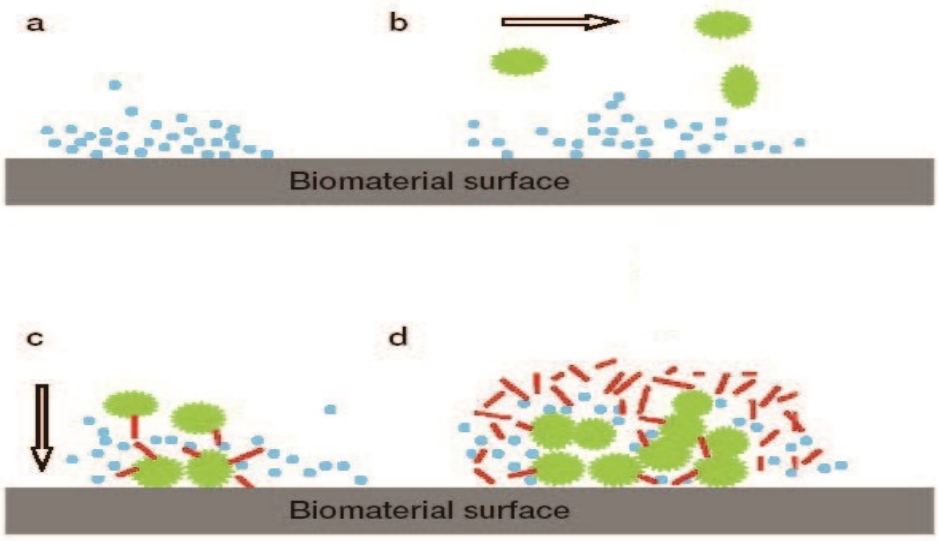


Figure 2-3 Sequences of events occurring when placing a biomaterial within the human body.

4. As the cells approach the surface, what they "observe" is a surface covered with a layer of proteins whose composition and conformation varies according to the superficial physico-chemical properties. Cells are much more complex (in structure and functions) and large (100 to 10,000 times larger) than proteins and interact with them through cell extensions, the cell membrane, and proteins and cell receptors. So, the implant-cell response will depend, in large part, on the type of proteins and their conformation. The result of this interaction may be the integration of the implant or the encapsulation of the latter in a fibrous layer. Two other factors that influence the cellular response against surface properties are ion release and topography [103]. The type of proteins and cells with which these biomaterial-body (host) interactions occur will depend on where the implant or device is placed, for example, the oral cavity, the urinary tract, the different tissues of the human body or the system. circulatory. The composition (proteins) of the layer or film that forms around the implant (Figure 2-3 *c*) depends on the surrounding

fluid at the implant site, which can be saliva, urine, tissue fluid, blood or serum and also from the surface physical-chemical properties, such as composition, hydrophobicity and charge.

2.3.3.1 Metal-Hard Tissue

In an "ideal" bone-implant interface, a different behavior would be expected; followed by the inflammatory reaction a reparative response is initiated between 2-3 days after the implant is placed. Then, the pluripotent cells from the bone marrow would differentiate into osteoblasts, forming a layer near the surface of the implant together with the fibroblasts [104]. The osteoblasts, fibroblasts and capillaries would penetrate the clot layer, replacing it and filling the space between the bone and the implant with an extracellular matrix rich in collagen, which would subsequently mineralize [105]. The mineralization process has been widely studied in order to find superficial properties that induce this process [106]. During mineralization, vesicles form in the matrix that confine the calcified material. So, the presence of vesicles on the biomaterial shortly after implantation is a good sign of primary acceptance of the material. Upon rupture of the vesicle membrane, apatite crystals form calcified structures. These continue to grow and mineralize until they reach and join the surface of the implant. In an optimal situation, the material would be covered by bone tissue and not by the fibrous layer. Bone tissue recovery would continue as well as during recovery from a bone fracture [107]. Changes in the local environment, such as acidity, with oxygen, electric charge, ionic concentration, enzymes, growth factors, etc. they have a strong effect on the differentiation and migration of stem cells; precursors of osteoblasts [108]. The adhesion of these pre-urinary cellsto the substrate together with the formation of the mineralized extracellular matrix (ECM) are essential for the differentiation

of osteoblasts. In these ideal biomaterials, there is a great abundance of osteoblasts, which is confirmed by studying the adhesion and proliferation of these cells on the surface [109]. Clinically, this process in bone-implant interface, instead of a fibrous capsule, was defined by Branemark as osseointegration [110], considering the formation of a mineralized interface microscopically (0.5 μ m). In optimal situations, such as what has been observed with titanium, the bone accepts the implant as part of its extracellular matrix (ECM), establishing a rigid bone-implant fixation progressively as load is applied to the implant [111]. The other metals for medical use, generally have a fibrous layer between the bone and the implant that makes them "almost-inert", but not osseointegratable, although with excellent mechanical properties to support loads. A contrary situation is observed with the bio-active glasses, which manage to form a chemical union between the implant and the bone, but whose mechanical properties are inferior to those of the metals [112].

Another cause of rejection of metallic implants is the consequence of the release of biologically active substances (metal ions) or of micro-particles worn from the surface [113, 114]. Even micro-particles of non-toxic materials can trigger an inflammatory response due to their size. These particles cause irritation of the phagocytic cells and activate them, thus initiating the production of inflammatory factors, which eventually leads to chronic inflammation, fibrosis, osteolysis and porosity in the bone. The wear particles prevent the formation of an interface between the prosthesis and the implant, which leads to the loss of the prosthesis. In addition, the wear of the metal surface increases its surface area and consequently the amount of metal ions released.

2.3.3.2 Metal-Blood interface

Another current application of metal biomaterials, including SS316L stainless steel,

nitinol, titanium and alloys, Co alloys, platinum-iridium alloys and Mg alloys, is in cardiovascular applications, particularly in the development of stents [115]. Stents are used to treat coronary artery disease (ACE). The most common cause of ACE is a disease called "atherosclerosis" that occurs when a waxy substance forms within the arteries that irrigate the heart. This substance, called "plaque", is composed of cholesterol, fatty compounds, calcium and a coagulating substance called "fibrin". As the plaque builds up, the artery narrows, making it harder for blood to flow to the heart. As the degree of obstruction increases, the flow of blood to the heart is reduced and angina may appear. Over time, the partial or totally blocked artery can cause a heart attack. Several medications can be used to relieve the pain of angina caused by ACE. However, because medications can not clear clogged arteries, a narrowed coronary artery requires surgery to reduce the risk of a heart attack. One option is to perform a percutaneous coronary intervention, such as balloon angioplasty or stent placement. The stent is a tubular metal mesh, whose function is to act as a support or frame to keep the blood vessel open. The stent, by keeping the vessel open, helps to improve blood flow to the heart muscle and reduce the pain of angina. However, a high percentage of patients are at risk of additional obstructions in the treated area, that is, the artery closes again, a process called "restenosis". Restenosis is influenced by the surface properties (surface energy, texture, surface potential and stability of the passive layer) of the cardiovascular implant, since these controls the formation of thrombi and hyperplasia or growth of the tissue or internal wall of the heart. The arteries. The high reactivity of the metals in the blood causes the adhesion of platelets and their aggregation, which initiates the thrombogenic processes, which even under medication are difficult to control. The superficial modifications of the stents try to avoid or minimize the thrombogenic properties of the metals [116].

In metal stents, the stability of the passive layer directly influences the biocompatibility of the material, since the surface acts as a barrier to the release of ions from the bulk material beneath the surface. Damage to endothelial cells caused by the release of low concentrations of metal ions is considered a potential toxic effect [16]. The stability of the passive layer is also key to maintaining the surface characteristics since it influences the surface energy giving it a certain hydrophilicity, and the surface charge since it prevents the release of electrons. Stents are used in applications to long term where its chemical stability is even more questionable, since corrosion processes can produce the release of a large variety of metal ions in variable oxidation states [117]. The corrosion induced by the fluids in the blood also causes a degradation of the mechanical properties, which can induce the total failure of the device, with lethal consequences. So, in this type of applications, the main factor that determines the functionality of the biomaterial is corrosion.

2.4 Corrosion behavior of titanium-based implants

Several studies have shown that the metal components of the alloys used in orthopedics can be toxic and dissolve in physiological fluids due to corrosion [118]. Each metal has its own intrinsic toxicity with the cells, but it is the corrosion that controls the existing concentration. So, the biocompatibility of metal alloys is determined by both the corrosion resistance and the toxicity of individual metals.

The corrosion of metals in aqueous solutions takes place via electrochemical mechanisms which are specific to each metal [38]. The more noble the metal, the lower its corrosion. However, the reactions that occur on the surface of the metal when it is in contact with the specific medium can radically modify its "nobility". After implantation, the metal is surrounded by serum ions, proteins and cells, which can locally modify the corrosion

resistance of the metal. In fact, the metal resistance measured in-vitro in non-physiological media may be totally different from the resistance measured in-vitro in physiological media and even more different from the in-vivo response [20].

After implantation, high concentrations of metal ions have been detected even in organs distant from the implant due to the fact that phagocytic cells circulate to metallic particles and metal oxides in the bloodstream [1].

There is a wide variety of factors that affect the corrosion of the metal, from surface factors of the implant, such as porosity or corrosion, to characteristics of the load distribution in the implant or the structure, composition and thickness of the passive layer of the metal, which in turn will depend on the processing of the metal and its surface properties. The corrosion resistance of metals and their alloys is mainly determined by the process of passivation of the surface. Passivation is the formation of a compact metal oxide layer that protects the metal and whose properties and structure vary according to the metal and are complex. During the corrosion process of the metal in the human body, which is highly saline in general, the metal ions are dissolved from the points at which the oxide layer is not fully formed through the formation of a metal complex. chloride, which dissolves in the physiological fluid. This limits the passivity of in a local way, a very small anodic zone is created surrounded by an extensive cathodic area and consequently local corrosion occurs in a rapid manner (pitting).

One way to avoid corrosion of metallic biomaterials is to form a passive layer or to coat the metal with a biocompatible protective layer, which would be different according to the specific application; orthopedic or cardiovascular.

2.4.1 Definition of in-vivo corrosion

Corrosion can be defined as the "destruction or deterioration of a material by the chemical or electrochemical reaction of a material with the environment that surrounds it and has as a consequence the release of ions in the environment". In general, thermo-corrosion is applied exclusively to metallic materials. Damage caused by physical means is not called corrosion, but erosion, abrasion or wear. In some cases the chemical attack is accompanied by mechanical effects, in which case it is often called corrosion - erosion, corrosion by cavitation, corrosion - fatigue, etc. According to the definition given by the American Society for Testing and Materials (ASTM), G15-93 standard [119], corrosion is "the chemical or electrochemical reaction between a material, usually a metal, and its environment, which produces a deterioration of the material and its properties ".

2.4.2 Types of corrosion

The corrosion processes can be classified according to several criteria, but the most common is classification according to the mechanism of attack, since any corrosion process takes place through one of these two mechanisms:

TYPES OF CORROSIONS		
Kind	**characteristics**	**Examples**
Alveolar (Pitting)	- (concavities) are formed in the metal. - More severe form of metal corrosion, usually releasing toxic metal ions. - Usually begin in defects of the protective layer of oxidation that is placed on metals.	- Stainless steel and other iron alloys. - Titanium and its alloys and cobalt, chromium, molybdenum and carbon alloys (CoCrMoC) do not present this type of corrosion.
By cracks (Crevice)	- Occurs in "slits", spaces and contact areas between pieces, in joints or seals, inside cavities, cracks and seams. - It is produced in metals that usually resist alveolar corrosion. - They can be produced in interfaces between metal and organic tissue, in which microenvironments can be highly corrosive.	- Interface between the stem of the femoral component of a hip prosthesis and the bone. It has been observed that ionic gradients are capable of producing pH as low as 1.
Fatigue and stress cracks	- Surface imperfections such as cracks are formed. - Secondary to cyclical compressive loads or tension forces on the material.	- Interface between screws and metal plates. - Frequent in titanium alloys.
Galvanic	- Secondary to the electrochemical differences between two metals or metal alloys that are in an electrical conductive medium such as water (extracellular fluid, serum).	- Interface between screws and metal plates with different materials between them (ex: stainless steel, titanium alloys).

Fretting	- Secondary to micro-vibrations, usually in implants with moving parts. - It is exacerbated when different materials or alloys are in contact.	- Modular prostheses.
Polymer degradation	- Degradation of polymers product of oxidation, depolymerization, hydrolysis, among other causes.	- Degradation of the polyethylene of a prosthesis.

2.4.3 Methods of Passivation

Passivity is understood as the property that certain metals and alloys have of remaining practically inert in certain media in which, according to what has already been said when thermodynamics has been spoken, they should behave like active metals and therefore dissolve with high speeds through of electrochemical corrosion mechanisms.

A metal or alloy is considered passivable if, by increasing the corrosion potential towards more noble values (more oxidizing conditions), the rate of dissolution in a determined aggressive medium is lower than that registered at lower potentials. The phenomenon of passivation can be a consequence of two mechanisms:

a. The formation of a layer of oxidized products of very small thickness but compact, adherent and of very low porosity that practically isolates the metal from the medium. This is the most usual case, and that is what happens for example with titanium.

b. The presence of monatomic layers, usually oxygen, absorbed on the metal surface. This case is much less common.

Some metals, such as chromium, have the ability to simply passivate in contact with the atmosphere even though in these circumstances the corrosion potential is not very high.

When this metal is alloyed with others, it is able to transfer this behavior to the alloy and thus improve its resistance to corrosion. Once the initial passive layer has been formed, constituted by a layer of mono or diatomic oxide, the growth in thickness of the same is carried out fundamentally as a consequence of phenomena of ionic migration through it propitiated by the strong electric field generated between its ends , taking into account the difference in potential generated between the cation-rich metal-film interface (positively charged) and the anion-rich film-electrolyte interface (negatively charged), which can be close to 1V. The passivation phenomenon begins at a certain potential value, known as passivation potential (Ep), at which the maximum current value recorded is known as critical passivation current density (Icr). Before the system reaches the limit current of diffusion, there is a significant fall in the response in intensity up to a value known as residual passivation current density (Irp) caused by the appearance of the passive layer of oxidized products. The passive film remains stable in a range of potentials for which the intensity response does not vary, density of passivation (Ip). This range of potentials defines the zone of passivation, where the corrosion of the metal is negligible. But in certain situations, which depend on the composition of the passive layer at those high potential values and the environment in which the metallic material is found, it may happen that increases in the intensity value begin to occur, and in more oxidizing conditions different oxidation products are formed that cease to be stable in the medium and become soluble, passing the metal from the passive zone to the trans-passive zone, in which corrosion becomes relevant again, similar to that corresponding to the active zone . In situations where the passive layer is degraded in a localized manner, a sharp increase in current density will be recorded at the pitting potential. When the material is susceptible to suffer this type of localized corrosion, the tracing of a cyclic potentiodynamic curve allows to determine characteristic parameters of the re-passivation

capacity that the material presents, such as the re-passivation current density ($Irep$). And the potential for re-passivation ($Erep$). This last parameter allows establishing the potential below which the passivity of the material is perfect (no new bites are initiated and those that may exist are reviewed).

2.4.4 Corrosion of metallic implants in oral cavity

The human body acts as an aggressive medium with a predisposition to produce corrosion in the metals of implanted medical devices (orthopedic prostheses and dental implants). Under normal conditions, the extracellular fluids of the human body can be considered as an aqueous solution of oxygen and various salts such as NaCl, MgCl2, KCl, glucose, etc. It is, therefore, an electrolytic medium that contains chloride ions and conducts electrons, which facilitates the occurrence of electrochemical corrosion phenomena. The normal PH of body fluids is almost neutral and ranges between PH 7.2 and 7.4. This value drops to PH 5.2 (acid) in the places where a wound is produced, and in hematoma can reach PH 4, as happens after the surgical procedure of implant placement. In contrast, in cases of infection, the PH rises to alkaline values. In places where corrosion occurs, the medium becomes acid by means of corrosive products, favoring this process even more. In the oral environment, in this case, electrochemical corrosion processes (wet corrosion) take place, since it is constantly bathed in saliva. Human saliva consists mainly of water (99%) in which the remaining 1% formed by mineral salts such as sodium, potassium, chloride, bicarbonate and phosphate ions, and some proteins with enzymatic functions dissolve, acting as a weak electrolyte. in the oral environment. The electrochemical properties of saliva depend on the concentration of its components, the PH (which varies from 5.2 to 7.8), the surface tension, and the buffering capacity. These variables are those that will control the processes of

corrosion. The characteristics that determine how and why dental materials corrode are [120]:

1. The oxidation-reduction reactions.
2. The processes of passivation or formation of a passive oxide layer in the metal surface.
3. Physical factors that prevent corrosion from taking place.

The oral cavity is constantly subjected to variable loads during chewing and swallowing and bathed in saliva. Saliva varies its composition and PH from person to person and even in the same individual at different times. In addition, due to its salinity it tends to be highly corrosive with the less noble metals. The mouth is therefore an environment hostile and the materials used for restoration require adequate resistance to mechanical stress and corrosion, which can lead to roughness of the surface, weakening of the restoration, and release of ions to the oral environment. The release of the elements resulting from corrosion can produce discoloration of adjacent soft tissues Figure 2-4 and allergic reactions such as oral edema, stomatitis, gingivitis, and extra-orally perioral manifestations and eczematous eruptions in susceptible patients. The pathogenic mechanism of wound healing is modulated by the specific metal ions released by corrosion [65].

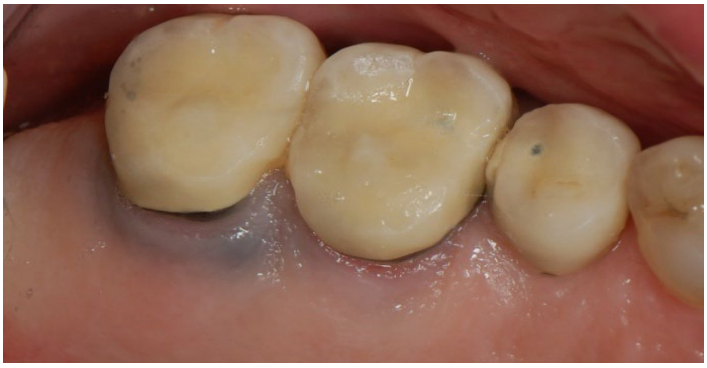


Figure 2-4 . Discoloration of the mucosa around a metallic implant that has suffered corrosion [65].

2.4.5 Ion-Releasing

The biocompatibility of metal alloys is related to certain parameters such as the quality and quantity of several elements released in certain clinical conditions, as they can cause adverse effects in humans, in addition to varying characteristics, properties and conduct of alloy [121]. Such ion release is of interest, mainly, as a potential source of allergens in hypersensitivity reactions [122]. Sometimes, the metal ions are released as a result of the process of corrosion of the materials, penetrating both hard and soft tissues, causing local and/or general symptoms [123]. The corrosion and the release of ions are two related processes that are sometimes not sufficiently well differentiated in the scientific literature. Both are related to the degradation of the materials but from different points of view. While the corrosion is an electrochemical process, in the release of Ions act a set of processes. The release of metal ions depends on factors belonging to the alloys, as well as external factors: type of alloy, quality and treatment of the material, surface area of the exposed alloy, polishing procedure, electrolytic composition, biomechanical conditions related to the load, among others. It also depends on the characteristics of the individual, specifically bodily fluids, because their physical properties, such as temperature, quantity and composition, are influenced by variables such as PH [124].

Corrosion products have been shown to be cytotoxic In vitro And yet its application In vivo it doesn't seem to generate cytotoxicity problems. On the other hand, both nickel, chromium and cobalt, present in these alloys, are potential elements Allergic, causing hypersensitivity reactions [125]. The concern over the long-term effects of CoCr steel and alloy corrosion products led to the use of titanium and its Ti6Al4V alloy as biomaterials due to its excellent corrosion resistance. After several years of using the Ti6Al4V as a material

for the manufacture of prostheses, they began to observe some cases of aseptic loosening. In addition, it was observed the presence of ions titanium, aluminum and vanadium in tissues adjacent to prostheses not loosened [126], being their levels much higher in the case of prostheses loosened [127]. It has also been detected the presence of ions titanium and aluminum in patients with Ti6Al4Vcon prostheses symptoms of local inflammation after 1-6 years of implantation [127]. In Vivo It has been shown that aluminum is deposited in the bone matrix instead of calcium slowing down the calcification of the bone [128] and has been associated a Brain diseases such as Alzheimer's [129]. In the case of vanadium, studies In vitro they have shown a high cytotoxicity on the part of this element [130].

A reduction in the release of metal ions would be beneficial as it could lengthen the average life of the implant. Treatments designed to generate a layer of oxide on the surface that can modulate the release of ions from the implant. The four methods of surface treatment were tested, and it was considered of interest to analyze the effect of these treatments on the behavior against the release of ions of Ti-based dental implants.

2.5 Mechanical Performance requirements of Dental Implants

Despite the high success rates of dental implants, failures and errors still occur depending on mechanical or biological problems, as a consequence of the lack of planning, the failure to observe correct principles in the sequence of the surgical and prosthetic stages or still lack of maintenance of the treatments carried out. The success rates should include, in addition to the information related to the stability of the fixations; information on bone stability around the implants, absence of symptoms or infection of peri-implant tissues, among others [131].

The biological failures could be considered whenever there is insufficient host to

establish or maintain osseointegration, which can be considered as an early failure, because this phenomenon cannot be maintained, when the implant is subjected to functional loads, it is considered as late failure [132]. Biological failures occur when osseointegration is not maintained after implant installation or when it is not maintained over the years.

It is essential to prevent the failure of the implants through proper planning that facilitates the establishment of osseointegration and preserves the same that has already been achieved [100].

In relation to mechanical failures, various factors have been suggested as possible causes for failure in dental implants, such as: inadequate adaptation of the prosthetic structure, occlusal misalignments, design of prosthetic structures, location of implants, diameter of implants, etcetera [133].

Dental implants can present from small complications to their total loss. This definition involves biological complications (bleeding, gingival hyperplasia, purulent exudate, deep pockets, bone resorption, etc.) and mechanical complications (including loosening and / or screw fractures, implant fractures, and coating materials such as resins and ceramics). However, some authors consider cases of fractures of prosthesis connection screws as complications and not as failures, since such phenomena have conditions of reversibility and can be corrected in most cases [134].

Through the literature, it was possible to confirm that the failure rates in dental implant restorations are increasing, perhaps due to a process of validation of more criteria that describe such failures [135].

2.5.1 Mechanobiology of maxilla bones

Study the interaction between mechanical signals and biological processes that they produce in cells and tissues. Mechanical loading plays a crucial role in the growth, adaptation, regeneration and bioengineering of living tissues [136]. Van der Meulen described skeletal mechanobiology as "the science that studies mechanical forces that modulate the morphology and structural adaptation of skeletal tissues [137].

2.5.2 Immediate loading Conditions of endosseous implants

In the studies on immediate loading of implants, several factors have been identified on which the therapeutic success depends, which can be divided into 4 categories:

2.5.2.1 Implant macro-design, micro-design

Regarding the design of the implants, there is agreement in affirming that those with a conical shape provide greater mechanical retention and, therefore, better primary stability than cylindrical implants. Therefore, those are more suitable for immediate loading than the latter. If a rough surface is added to a threaded design, an increase in the bone-implant connection and an increase in the shear strength are combined with the aforementioned characteristics. One of the factors that is currently being investigated is the micro-design of the implant and how its surface and the modification in the thread designs can improve primary stability [138], accelerate osseointegration and thus reduce loading times. When the implant is inserted into the bone bed, that bone undergoes constant remodeling due to external stress. If the received load is optimal, the bone surrounding the implant will produce bone tissue, however, under external adverse stresses, micro-fractures of the alveolar bone may occur, which may induce bone resorption [139], sometimes resulting in severe bone loss and

in last instance failure of the implant. In order to reduce these adverse stimuli and favor the transmission of favorable forces towards the bone around the implant, the threads of the implant must be manufactured in such a way as to increase the superficial contact with the bone, improving the diffusion of stress and primary stability. These thread forms that provide better primary stability, especially in situations where we are going to perform immediate loading are those that present a right-angle profile. Likewise, studies have shown that to dissipate the tension peaks inside the bone, the depth of the thread is more important than the width of the bone, and that the realization of micro-treatments at the neck of the implant can improve the formation of bone and the distribution of tension for implants inserted in cancellous bone under immediate load [140].

2.5.2.2 Primary stability

The functional load of an implant requires its immobility, so that the stability of the implant is the most important factor of those that condition the therapeutic success at the time of establishing the load. Implant micromovements greater than 100 or 150 μm during the healing period induce the differentiation of mesenchymal cells from the bone-implant interface into fibroblasts instead of osteoblasts, which causes a fibrous encapsulation instead of osseointegration of the fixation, in the same way that occurs in unstable bone fractures. Therefore, if an implant is placed in spongy bone of low density and with poor initial stability, it must be loaded in a delayed manner, when once osseointegrated it obtains the stability it lacked at the time of installation. However, when there is initial stability, you can choose to perform immediate or deferred loading [138]. This initial stability must be at least 30 Ncm according to the majority of authors [141].

In addition to bone quality, a scrupulous surgical technique is also a key factor in

achieving initial stability and osseointegration of the implants, since excessive surgical trauma and resulting thermal injury can result in osteonecrosis and subsequent fibrous encapsulation of the implant. implant. The temperature reached during the preparation of the implant bed depends on several factors, among which are:

- Cooling during milling, because if this is insufficient and a temperature higher than 47 ° C is reached for one-minute, thermal bone necrosis occurs;
- Load applied to the drill during the ostectomy. It has been reported that the increase in the load increases the temperature in the bone, while the simultaneous increase in speed and load allows a more efficient cut, without significant increase in temperature;
- Volume of the prepared bone, depth of the osteotomy, thickness of the cortical bone.

After the preparation of the bed with well sharpened, it is necessary to insert the fixation. Depending on the design of the same and the density of the recipient bone, the implants can be installed with or without pre-tapping. The relevance of this step is conditioned because if the resistance to insertion is large, the implant has to be placed exerting considerable pressure, which can cause the appearance of microfractures in the neighboring bone. These lesions heal following a well-known sequence of events and whose main steps follow the following sequence: angiogenesis, migration of osteoprogenitor cells, formation of an osteoid network, deposition of lamellar bone and, finally, secondary bone remodeling [142], however, ideally in high-density bones is to perform the tapping prior to the placement of the implant, since micro fractions that occur in the bone, although they can lead to osteogenesis can also do so to a proliferation of fibrous tissue and bone loss in the portion more coronal of the implant.

2.5.2.3 General condition of the patient (diseases that affect the tissue healing capacity)

The moment of load of the implants also depends on the ability of tissue healing, so that when it is impaired (osteoporosis, diabetes, hyperparathyroidism, smoking, radiotherapy, etc.), it is preferable to follow a deferred loading protocol, even considering, in some occasions, wait for a long healing time. Among the circumstances that interfere with bone quality and reparability, diabetes and osteoporosis are among the most frequent. Although osteoporosis is considered an implant risk situation, nothing in the literature supports this when patients are treated with adequate loading protocols.

2.5.2.4 Occlusal forces

Most studies on immediate loading exclude patients with masticatory parafunction. Balshi and Wolfinger [143], placed 130 implants in 10 patients, 40 of them loaded immediately and another 90 submerged and loaded differently. After 18 months of follow-up, the survival rates were 80% for the implants loaded immediately and 96% for those subjected to deferred loading. They also observed that 75% of the failures that occurred among the first occurred in bruxism patients [144]. Therefore, although bruxomania is an implant risk factor, under any circumstances, in the presence of it, it is preferable to subject implants at a deferred load [143]. It is also recommended, in bruxism patients, the rehabilitation of implant-supported prostheses by means of a dog guide, since the group function can provoke an excess of tension [145].

2.5.3 Fatigue of materials

Fatigue is a phenomenon by which the materials are broken under cyclic dynamic loads (repeated forces applied on the material) when subjected to loads inferior to the elastic

limit. It occurs in structures subjected to dynamic and fluctuating tensions, such as hip and knee prostheses or dental implants. It is particularly dangerous because It can happen by action of stresses far below the limit of tensile strength or the elastic limit [146]. It is the first cause of rupture (~ 90%) in the metallic biomaterials.

The fatigue test methods are very varied. They are differentiated by the character of change of tensions in time, the scheme of solicitation (flexion, Traction-compression, torsion) and the presence or absence of concentrators of tensions. Figure 2-5 shows a typical example of cycles of stresses, being a cycle the set of alternative values of the tensions in a period of their changes. In this case, the stress represented has cycles of traction (when it is positive) and of compression (when it is negative). Each cycle is characterized by several parameters:

The mean cycle stress is the average of the maximum and minimum stress in each cycle:

$$\sigma_m = \frac{\sigma_{max} + \sigma_{min}}{2}$$

The stress range is the difference between maximum and minimum stress:

$$\Delta\sigma = \sigma_{max} - \sigma_{min}$$

The stress amplitude is half the stress range and varies around the average value:

$$\sigma_a = \frac{\sigma_{max} - \sigma_{min}}{2} = \frac{\Delta\sigma}{2}$$

The quotient of tensions R is the quotient between the minimum and maximum amplitudes:

$$R = \frac{\sigma_{min}}{\sigma_{max}}$$

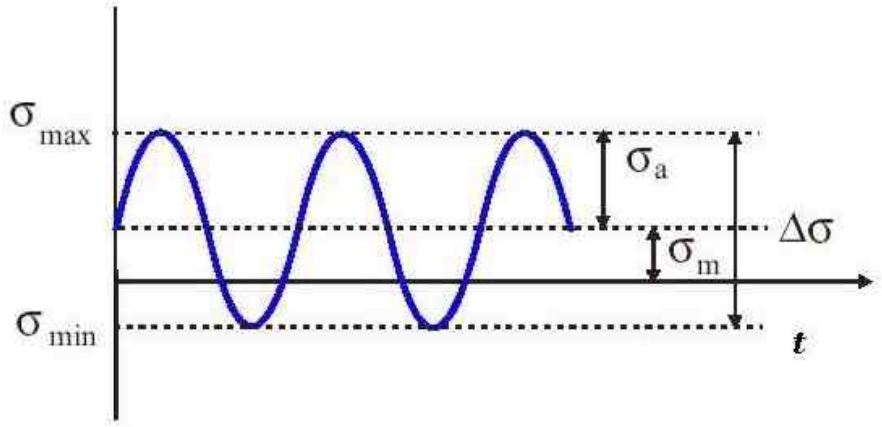


Figure 2-5 Typical example of cycles of stresses [147].

2.5.4 Influence of surface treatments on fatigue of materials

Since the fatigue cracks are formed in the surface layers of the samples, the state of these plays a crucial role. Fatigue cracks often appear near different stress concentrators, so attention is paid to the surface quality of test specimens. The most important stress concentrator is the incisions of the actual materials in the form of stripes, scratches, tiny cracks, etc. The sensitivity of the material to the incision in the fatigue tests, as well as in the static load conditions, is determined in the first place by its plasticity. The greater the plasticity, the greater the work of plastic deformation (even in the presence of a concentrator of tensions), the lower the speed of propagation of the crack and the greater the limit of fatigue. Thus, to obtain a high limit of fatigue, the structure of the surface layer must have the maximum possible resistance to deformation. This can be achieved by performing a chemical-thermal treatment, severe superficial deformation processes to harden the surface and/or fine-tune the grains, etc. [148]. However, it should be taken into account that the surface roughness and/or small furrows may occur on the surface of the workpiece in the latter. These marks limit the life to fatigue because they are small cracks, which are much

easier to increase. However, these processes create residual compression stresses, so that any external tensile tension is partially offset and reduced in magnitude by the residual compression stress. The net effect is that the probability of nucleation and/or propagation of the crack, and therefore of rupture by fatigue is reduced.

The processes of blasting, water a high pressure and "laser peening", in addition to generating surfaces with certain levels of roughness, usually generate plastic deformation and a hardening in the more superficial layer. This deformation induces residual compression stresses, so that an improvement in fatigue properties would come from increased hardness within the layer and residual compression stresses that originate in the process.

2.5.5 Fatigue of implants and connections

From the structural point of view, the fracture can be divided into two categories: (i) immediate fracture, which appears as a result of stress concentration points and (ii) fracture due to time-dependent mechanisms, such as corrosion or fatigue [149]. The most important causes of the immediate fracture are a poor choice of material, the appearance of stress concentration points due to inadequate machining or an incorrect manufacturing process and, finally, excessive use. As defined in the previous section, fatigue appears when cyclical loads intervene that modify the expected behavior of the material, causing its useful life to be reduced. Dental implants are subject to endless load cycles throughout the period in which they are placed in the mouth, mainly due to the loads that occur during chewing [150].

This situation of cyclic loads causes that the phenomenon of fatigue in dental implants is an area of interest for commercial manufacturers since, although the success rate is very high, some implants can fail due to rupture and / or fatigue. In order to evaluate the suitability

of the different designs of implants and components, fatigue tests are carried out defined by ISO 14801 (ISO14801 2007). This standard, entitled "Fatigue test for endosseous dental implants", specifies how endosseous implants should be tested individually. Figure 2-6 shows a universal testing machine in which it is possible to analyze dental implants according to ISO 14801 and the scheme of mounting the implant in said machine for further testing. According to the standard, a series of tests with different load levels must be carried out, increasing their value, applying five million cycles and repeating the test three times with each of said load values. The amount of time and money required for this type of testing is one of the reasons for applying fatigue life prediction models that help improve designs without the need for many trials [150].

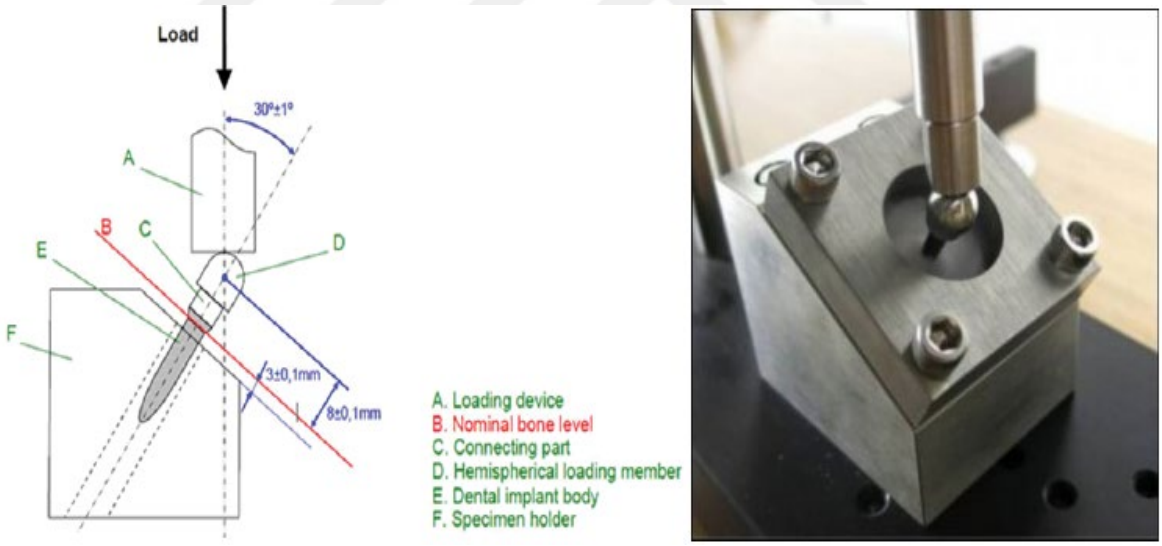


Figure 2-6 Universal testing machine in which it is possible to analyze dental implants according to ISO 14801 [151].

According to ISO 14801, fatigue tests should be carried out by applying cyclic loads at different levels to the lower limit of resistance level, below which the fatigue fracture is not expected to occur, presenting the results a load-cycle diagram [149]. In addition, the load

cycles that are applied on the implants and their implant-prosthetic connections represent the "worst working conditions", either creating excessive bending moments or imitating bone loss. The results obtained through this test, because it is performed under the worst possible scenario, cannot be used to predict the behavior in vivo or the life of the implant or prosthesis. Currently, different fatigue study procedures are used that try to estimate the life of a structure, in this case, of the implant system. This test is carried out to evaluate the number of cycles that the component supports until its fracture. The study structures are subjected to a constant amplitude of cyclic tension or deformation and the results are collected in the curve called S-N (stress vs. cycles) or Wöhler curve which, in addition, provide great information in the stages of initiation and propagation of cracks [152]. The interpretation of the results requires special attention due to its statistical nature. It is not strange to observe identical components that, under a same amplitude of load, they have extremely different behavior in terms of cycles. For this reason, and with the aim of obtaining results with a good level of confidence, it is necessary to repeat the mechanical tests with a large number of components [153]. In this sense, the ISO 14801 standard recommends paying special attention to the statistical nature of the phenomenon of fatigue. An important term of the S-N curve is the so-called "fatigue limit", or, what is the same, value below which the study component can be subjected to load cycles indefinitely without failure. This concept has been studied for years and has been applied to most materials. One of the main drawbacks of the phenomenon of fatigue in dental implants is that, unlike other processes in which it is possible to monitor crack growth and know how the component is, in the case of implants it is impossible to perform a visual inspection once it is in the mouth or X-ray inspections, which makes small cracks undetectable using conventional inspection techniques. This leads to the absence of techniques non-destructive that help early detection of possible implant failures [154]. The

fact that the cycles throughout the life of the implant are not constant and that, in addition, they can change the frequency and intensity of application, it is of great transcendence in implantology since this standard does not simulate real conditions of mastication or occlusal pathologies, reason why, as it has been commented previously, the results they cannot be extrapolated to in vivo behavior [155].

2.5.5.1 S-N curve "The Wohler curve"

The Curves S-N o Wohler curves are obtained through a series of tests where a specimen is subjected to cyclic tensions with a relatively large maximum amplitude (approximately 2/3 of the static tensile resistance) and cycles are counted to breakage. This procedure is repeated in other specimens a maximum decreasing amplitudes. The results are represented in a tension diagram, S, in front of the number N Cycles to the break, Figure 2-7, or in front of the logarithm of N, for each of the specimens. The values of S they are normally taken as tension amplitudes. At higher stresses, fewer cycles to breakage. In some iron alloys and titanium alloys, the curve S-N It is made horizontal for large values of N, ie, there is a limit tension, called fatigue limit, below which the fatigue break will not occur. Some non-ferrous alloys (aluminum, copper, magnesium, etc.) do not have a defined fatigue limit, given that the curve S-N continues to decline by increasing N.

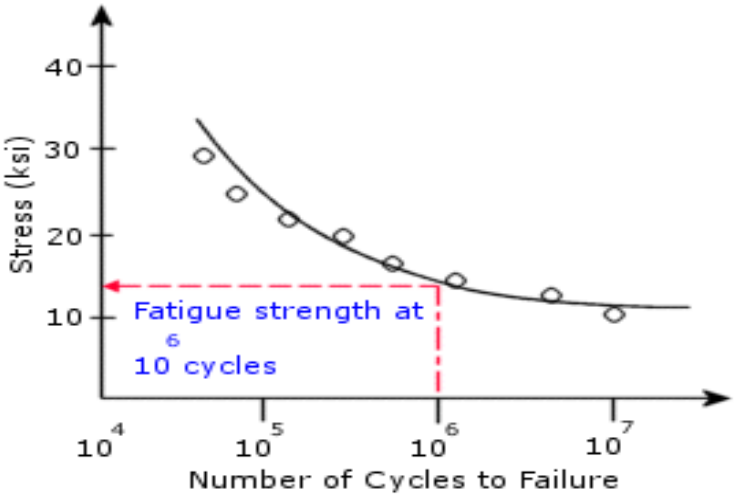


Figure 2-7 S-N Curve [156].

2.5.5.2 Break Nature by fatigue

As the number of cycles increases to a certain tension over the fatigue limit, the test specimen develops the following processes: 1) plastic deformation, 2) crack onset, 3) gradual growth of some of these and the predominant expansion of a Main crack, 4) fast and definitive break [157].

1- Plastic deformation:

The movement of the displacement and formation of the sliding lines under conditions of intermittent loads is observed under tensions lower than the limit of resistance to fatigue, which in turn is less than the elastic limit of the material. These slip deformations are similar to those obtained in the static case, so that the progress of these lines is the one that leads to break. The plastic deformation begins in the favorably oriented grains, near the concentrators of tensions [157].

The development of plastic deformation leads to hardening by cold deformation. This hardening can compensate and stop the glide advance.

2- Onset of fatigue cracks

Cracks that cause the breakage almost always gather on the surface at a point where there are stress concentrations (originated by design or finishes).

Cyclic loads can produce microscopic surface discontinuities from steps produced by sliding dislocations, which will act as concentrators of tension and, therefore, as places of nucleation of cracks.

1- Spread of fatigue cracks:

It can be defined in two stages:

a. In polycrystalline metals, once nucleated a crack, it spreads very slowly and along crystallographic planes of high shear tension; Cracks usually extend in few grains at this stage.

b. The spread speed of the crack increases and at this point stops growing in the axis of the applied effort to begin to grow in a perpendicular direction to this effort. The crack grows through a process of sharpening the tip because of the tension cycles.

2- Break

At the same time that the crack increases in width, the end advances by shearing continuous deformation until it reaches a critical dimension and the breakage occurs.

The region of a fracture surface that forms during the propagation stage (b) can be characterized by two types of marks, called Beach marks and stretch marks. Both indicate the position of the end of the crack at different times and have the appearance of concentric crests that expand from the points of initiation. The beach marks are macroscopic and can be seen at the naked eye, Figure 2-8.

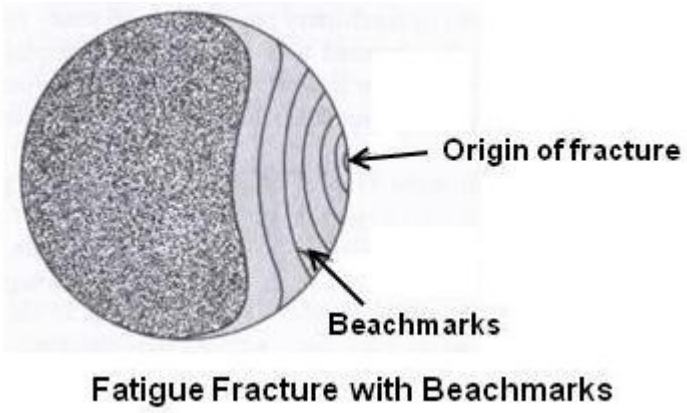


Figure 2-8 Typical fatigue fracture scheme [158].

2.5.5.3 The effect of Oral-like environment on fatigue performance in dental implants

Most dental implants used in dental rehabilitation to replace missing teeth are made of CP Ti or titanium alloys. Choosing those materials is related to its high biocompatibility, corrosion resistance, and high mechanical properties. The strong surface passivation layer that mainly consisted of TiO_2 make this material the optimum selection for the industry of bioimplants [159, 160]. The fracture failure in dental implants or its components are relatively uncommon complications. The determination of the related factors which are responsible for dental implant mechanical failure is consequently of high importance. The most reliable way to identify this problem is the use of SEM scanning electron microscope fractographic analysis of in vivo failed dental implants and implant parts. Shemtov et al. (2012) examined 32 fracture surfaces of intra-orally fractured implants. The analysis specified the failure as a combination of mechanical fatigue (detected by fatigue striations) along with the existence of biocorrosion products. It was concluded that the dental implants failed due to corrosion fatigue. Ansari et al. (2016) performed a fractographic analysis on 16 implants that fractured in vivo. Their analysis pointed out corrosion fatigue due to the presence within the oral cavity environment as the most likely mechanism for the implants'

fracture as well. The authors revealed that the implant's surfaces exposed to the oral aggressive environment as a result of bone regression, while the dynamic loading causes the collapse of the protective surface oxide layer. As a result, surface micro-cracks were generated, which increased by fatigue mechanisms consequently resulting in the implant's failure.

2.5.6 Vickers micro-hardness measurements

Hardness is a measure of the resistance of a material to permanent deformation. The hardness test is a very common method of inspection used to know the mechanical properties of a material due to the relationship between hardness and these properties. Compared to a tensile test, which measures resistance, modulus and elastic limit and elongation, the hardness measurement is a test of simple application and relatively non-destructive.

In the hardness test, a certain geometry indenter penetrates the surface of a sample when a known force is applied to it. The hardness, H, is evaluated from the magnitude of the plastic or permanent deformation observed on the material when the indenter is removed. The deformed surface is determined by measuring the penetration of the indenter or by directly measuring the area of the residual footprint on the surface of the material. The hardness is calculated according to the expression:

$$H = \frac{P}{A}$$

Where P is the normal force applied to the Indenter and A It's the surface area of the residual footprint.

2.5.7 Pull-out test

Mechanical anchorage is very important for the long-term surgical success of orthodontic treatment. Limited intraoral anchorage and implant acceptance problems related to extraoral appliances often lead to anchorage loss, which interferes orthodontic treatment. In the 1960s, Branemark et al came up with the use of titanium implants. years later, titanium implants have accomplished a more than 90% success rate. Dental implants are an effective and reliable treatment option for oral rehabilitation, and their use in reinforcing orthodontic anchorage has shown remarkable results. The aim of this part of this study is to evaluate the mechanical anchorage strengths of the used 3.3 mm in diameter mini-implants in terms of their vertical pullout strengths. The most common technique to evaluate the primary stability for dental implants is the pull-out test to determine the primary stability which is an indicator to guarantee of osseointegration figure 2-9.

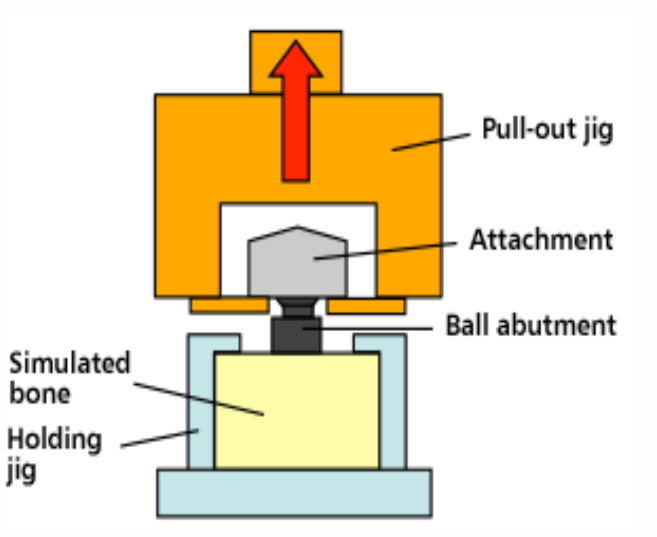


Figure 2-9 Pull-out test scheme [161].

2.5.8 Removal torque test

Osseointegration is fundamental in therapy with dental implants and depends on adequate biocompatibility, implant surface quality, surgical technique, adequate host status and conditions to obtain it [162]. The surface of the implant is a fundamental element to understand the interaction with the adjacent bone [24]. The increase in roughness and modifications in macro geometry and microgeometry allows to stabilize implants in the bone structure [163]. Some clinical challenges arise when there are defects that often accompany the installed implants, which could respond inadequately to the mechanical load and stability of the implant [163]. Under these conditions the use of bone grafts and biological membranes could contribute to improve the stability of the system. One of the ways to recognize the stability of the installed implant is through the removal torque that consists of performing the counter-torque on the installed implant in order to inform the degree of stability of the implant by breaking the implant-bone interface; this is based on the fact that there is an established relationship between removal torque and the level of osseointegration [164]. The objective of this research is to study the torque of removal of dental implants accompanied surface treatment type with biological membranes.

2.6 Conclusions

The degree of interaction between variables in dental implants is a challenge to random clinical trials that attempt to answer questions in a timely, unbiased, and cost-effective manner. Furthermore, the addition of complexity to the different scenarios is the various implant surface designs and the related bone response, the area of the implant, the bulk material implanted, the restoration, the fixation position. This chapter provided a critical

assessment of the most common mechanical testing methods used to characterize the dental implants. It attempts to provide an insight into the process of building an informed database of clinically relevant questions regarding pre-clinical evaluation of surface-related responses and mechanisms of failure. The mass production of dental implants with the same surface treatment without considering the patient special health condition and quality of life led to so many catastrophic failures, some of which can not be treated. CMP as proposed biomaterial surface treatment method can give different surface properties by changing one or more of the process variables to get different biological and biomechanical responses and more corrosion resistance surface without affecting the bulk material properties but even enhance them. Furthermore, this method is cheap compared with the other surface structuring methods. The treatment of biomaterial surfaces with 3-D CMP is a new and unprecedented method. Consequently, it is necessary to test the surface resulting from the new treatment in view of mechanical and chemical aspects. The biological response to the resulted surface is essential to assure the long-term clinical outcomes. All the tests included in this chapter are listed in the evaluation requirements of leading bioimplants companies.

CHAPTER III

3-D CMP ON TITANIUM IMPLANT SURFACES

3.1 Introduction

The CMP process uses an abrasive materials and PH adjusted colloidal slurries which consist of submicron size particles, contains corrosive chemicals together with a polishing pad attached to rotating ring. The rotational motion of the dynamic polishing head is adjusted to get different axes of motion. The main purpose of this combination is to remove material and any topographical irregularities. This kind of synthesis tends to form the very top film of the polished material by the interaction of the chemicals and the mechanical abrasion of the slurry submicron particles. Accordingly, and as a result of the above it was encouraging to use this novel method as an bioimplants surface treatment technique as compared to conventional surface treatment methods [165]. The surface quality and the required material removal rate that can be achieved through the unified set of features which controls the process variables are the fundamental reasons behind the adoption of CMP as a promising surface treatment method for metallic biomaterials. It has been clarified that it is possible to achieve the desired surface finish and the oxide film formation for which the biomaterial surface treatment is carried out. Hence it is possible to produce a specified surface finish designed for a certain surgical situation through the set of CMP process variables that includes (Sample down pressure, Sample velocity, Pad velocity, Pad characteristics, Process time, Particle characteristics, Slurry, chemistry, Substrate characteristics) . As compared to conventional surface treatment methods, CMP introduced itself as a good competitor for surface structuring in a controlled manner in terms of achieving desired biomechanical results

and stimulating the oxide film formation which protect the implant against corrosion.

In this chapter the results of the 3-D CMP process conducted by the in-lab developed setup using the SiO_2 slurry and H_2O_2 as an oxidizer on the 3-D titanium dental implants with the change of the process variables which includes (Sample down pressure, Sample velocity, Pad velocity, Pad characteristics, Process time, Particle characteristics, Slurry, chemistry, Substrate characteristics) are discussed in term of Material removal rate selectivity and its response to oxidizer concentration in correlation to the surface topography measured by High-accuracy Surftest SJ-400 Mitutoyo profilometer. Surface wettability analysis was conducted through the contact angle measurements. Furthermore, the effect of slurry chemicals (abrasive particles), effect of pad characteristics, effect of pad-sample relative velocity and the effect of oxidizer concentration on the produced surface were discussed in detail.

3.2 Experimental

3.2.1 Materials and methods

3-D CMP analyses were conducted on a machine shaped (baseline) titanium dental implants provided by Mode Medical company.

Silica slurry with an average particle size of 20 nm obtained from (NYACOL, Taiwan) with PH 3 was used for 3-D CMP. Hydrogen peroxide (Sigma Aldrich with purity %34.5–36.5ty) was utilized as an oxidizer during CMP experiments. The basic silica slurry containing H_2O_2 of 0.1 M and with (3%, 5%, and 10%) solids loading was used with adjusted PH using NAOH solution to get PH of 9 for the process stability. The 3-D CMP was performed using (metkon, Forcipol 1V) polishing machine with different speeds (50, 60, 70 and 80) rpm. In Figure 3-1c Each slurry prepared as mentioned above was dropped with 40

ml/min flow rate using (SEKO Solenoid dosing pump) on a Synthetic wool pad (Dekor 1056 20 cm Pure Wool) showed in Figure 3-1b. The sample holder is attached to a flexible shaft connected to an electrical motor and the speed controlled by rpm regulator, the test was carried out with different rpm (88, 260, 450, and 740) rpm. The polishing pad has been replaced with a new one after polishing some samples to keep it maintained at a certain roughness level for process performance stability. Moreover, it was taken into consideration the compressibility of the pad and the technique of slurry delivery. Figure 3-1 shows the setup developed in the lab to implement the 3-D CMP to the dental implants. In the 3-D CMP experiments of the 3D samples the downforce was kept constant however the angular speed of the pad and the sample were varied.

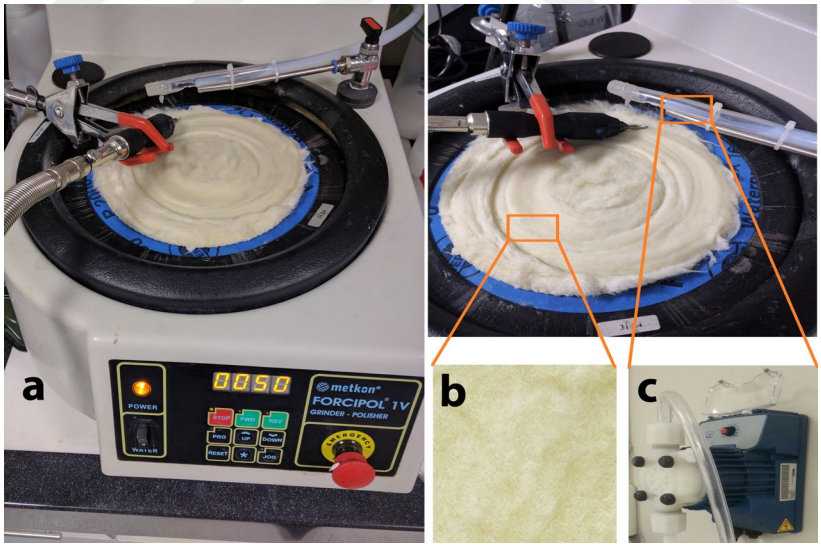


Figure 3-1 (a) The setup developed in the lab to implement the 3-D CMP on the dental implants, (b) Synthetic wool pad, (c) Solenoid dosing pump.

The sample holder was attached to a flexible shaft connected to an electrical motor and the rotational speed was controlled by an rpm regulator. CMP tests were carried out at different rpm values (88, 260, 450, and 740 rpm). The polishing pad was replaced with a new

one after polishing a given set of samples to maintain a certain roughness level for process performance stability through standard compressibility of the pad providing efficient slurry delivery to the surface. Figure 3-1a shows the CMP set-up developed in the lab to implement the 3-D CMP onto the dental implants. In the 3-D CMP implementation on the 3-D samples, the downforce was maintained constant and only the angular velocities of the pad and the samples were varied.

Figure 3-2 illustrates the 3-D CMP process scheme designed in the lab. The CMP treated samples were characterized for surface topography (surface roughness), wettability and material removal rates as function of CMP input variables. The chemical mechanical polishing was run for 10 minutes in the presence of 0.1 M H_2O_2 at 3, 5, and 10wt% slurry solids loading.

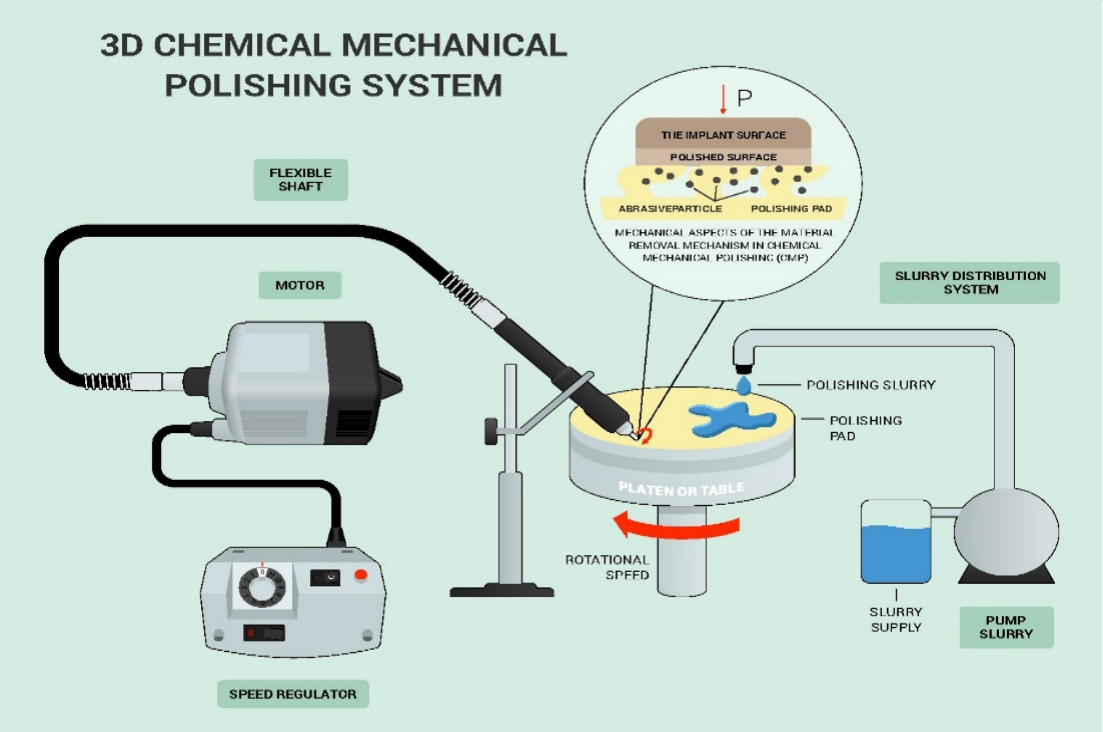


Figure 3-2 The 3-D CMP set-up configuration.

The material removal rates in CMP experiments were calculated by pre and post polish weighing the samples using Swiss Made ES125SM model precise scientific balance (five digits after the decimal point, 0.01 mg accuracy). In order to obtain the oxidizer concentration that gives the least material removal rate, solutions with seven different concentrations were tested (i.e. 0M, 0.001M, 0.01M, 0.075M, 0.1M, 0.3M & 0.5M). In addition, five samples were polished without adding the H_2O_2 to investigate the influence of the presence of oxidizer on material removal rate.

3.2.2 Evaluation of Process Variables

3.2.2.1 Sample down pressure

The down pressure can be applied to the sample to maintain that the biomaterial surface being processed can be adjusted to compensate for irregular topographies and do hybridization of the micro-grooved surface by the 3-D CMP treatment to diminish its dimensions for exhibiting a more homogenous state. In regular CMP processes the sample down pressure application is controlled using the computer interface.

Polishing pressure is applied on the sample and presses the sample surface on the pad, while the slurry is continually dosed at the sample/pad interface. With the combined action of the chemicals and the abrasive slurry particles, micro material removal of the sample surface is realized. Early study found that, the polishing process strongly depends on the contact pressure, and a thin slurry film and fluid pressure were formed at the wafer/pad interface Increasing the down force can increase the ratio of the positive pressure and the average fluid pressure significantly.

3.2.2.2 Sample velocity

The sample holder is able to rotate in a clockwise direction, and at different speeds of up to 740rpm. The carriers can be adjusted to move only with the polishing pad depending upon the required material removal rate. Different combinations will result in preferential material removal from the sample surface area.

3.2.2.3 Pad velocity

Continuously, it is necessary to consider the wear and compressibility factor for the polishing pad because these variables affect the removed material measurements, the amount of error can be quite high and unpredictable. According to the above, focusing on the pad speed to remove the material uniformity can be a miscalculated. That is, from the perspective of the end user, it is desirable to have a uniform final layer on the surface of the implant (this is not necessarily a result of uniform removal speed). The present developed setup applies different control of material removal speed during CMP processing to meet the desired surface requirements. It should be understood that the present invention can be implemented in several ways, including to meet the mentioned above needs.

3.2.2.4 Pad characteristics

Selecting the polishing pad fits the requirements of the developed experimental set up needs a particular understanding, since the polishing pad is responsible to transfer the mechanical force over to the surface to be polished, holding with its woolly nature the slurry chemicals and abrasive particles to do the job of removing the materials dissolved from the polished surface. Due to the nature and the technical characteristics of the developed experimental setup it was necessary to sufficiency of one type of polishing pad. Furthermore the chosen Synthetic wool pad is compatible to be inert with respect to the slurry chemicals

Figure 3-3. However, a relatively flexible pad is necessary to ensure that the precise threaded geometry of the implants will be polished during the CMP process.

Figure 3-3 Synthetic wool pad.

3.2.2.5 Slurry chemistry

One of the fundamentals of conventional CMP process is that the pad with presence and the help of chemicals is to do the action of cutting the higher-level characteristics with higher rate than that of lower characteristics to implement the polishing process. Thus, the colloidal silica-based basic slurry (incorporating SiO_2 abrasive particles,H_2O_2 as an oxidizer, and NaOH as a PH buffer) characterized here to show an excellent material removal effect and consequently a desired behavior of planarization.

The abrasive particles type is one of the most effective properties of the slurry used in CMP process. Hence, it provides the mechanical cutting action during the CMP process which results in material removal. The concentration of these cutting tools can effectively change the intensity of the mechanical polishing which considered as one of the factors determine the load applied per particle. In addition, the mechanical action also depends on the number of abrasive particles that will be in contact with the sample surface. Feed rate is

adjusted using the (SEKO Solenoid dosing pump) with 40 ml/min flow rate on a Synthetic wool pad.

Through varying of the slurry chemistry and constant feed rate of the chemicals mixture onto the polishing pad, the operator can produce the ideal conditions, or 'recipes' for successfully CMP process.

3.3 Results and Discussions

3.3.1 CMP performance evaluation

3.3.1.1 Material removal rate response for 3-D samples

a- The effect of H_2O_2 concentration on material removal rate

Figure 3-4 illustrates the CMP performances based on the material removal rate MRR measured for 3-D CMP with the developed process setup at a constant pad-sample rpm. For the purpose of detecting the optimal H_2O_2 concentration and obtain the minimum MRR, 7 different concentrations of the oxidizer were tested (i.e. 0, 0.001, 0.01, 0.1, 0.2, 0.3 & 0.5 M) together with (3, 5 and 10wt%) of slurry solids loading, 63 samples were tested by 3 samples for each test. It can be seen that the effects of slurry oxidizer concentration and slurry solids loading on the measured implant sample weight losses were very significant. The material removal rates decreased with the increasing oxidizer concentration to a point where the morphology of the oxide film changes and the surface is passivated that is controlled by the surface chemical activity. On the other hand, at higher slurry solids loading, MRR values tend to be higher as a result of increasing mechanical activity provided by the slurry particles acting as mechanical cutting tools on the chemically activated surface.

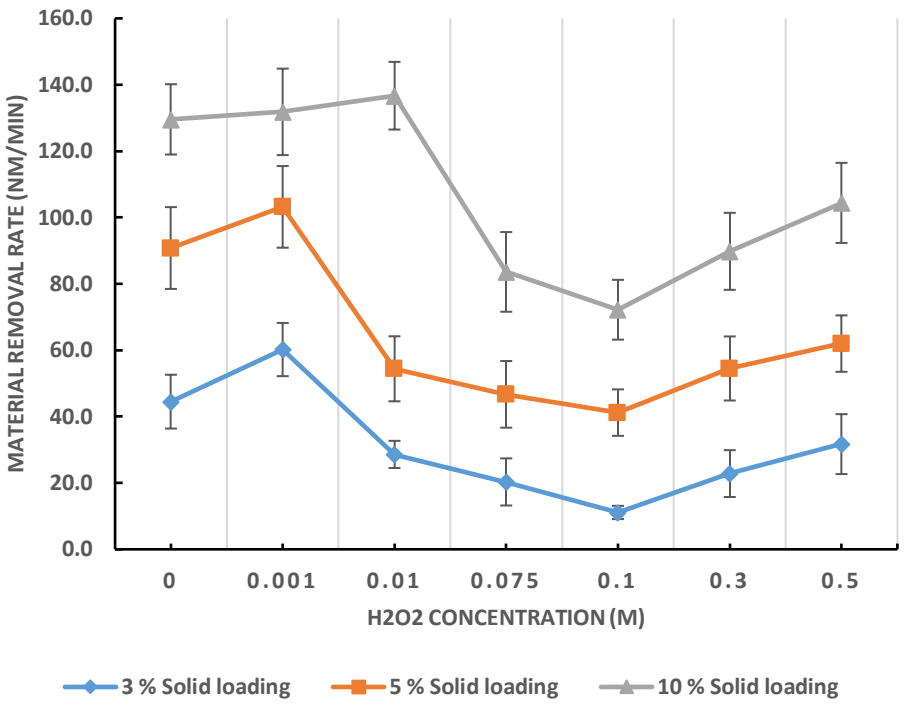


Figure 3-4 Material Removal Rates of Ti based Dental implants at different H_2O_2 concentrations and with (88,50) pad, Sample RPM.

Table 3-1 summarizes results of CMP MRR findings highlighting that the adequate H2O2 concentration for minimal MRR is 0.1 M for all solids loadings tested. The presence of oxidizer in the slurry solution helps passivate the titanium surface by converting Ti to TiO_2 [69, 166].

Table 3-1 Material Removal Rates MRR of Ti based Dental implants at different H_2O_2 concentrations and different solids loading and with (88,50) pad, Sample RPM.

Solids loading	**H_2O_2 concentration (M)**						
	Material Removal Rates MRR (nm/min)						
	0	0.001	0.01	0.075	0.1	0.3	0.5
3wt%	44.5	60.2	28.6	20.3	11.1	22.8	31.7
5wt%	90.8	103.2	54.4	46.7	41.2	54.5	62.0
10wt%	129.6	131.8	136.7	83.6	72.2	89.8	104.4

The passivating action assists the material removal action because the oxide is more brittle as compared to the titanium metal. Passivation also slows the removal rate due to the oxide layer acting as a etch stop layer preventing the chemicals from etching the titanium surface. Based on the results presented in Figure 3-5, it can be concluded that the surface passivation continues up to 0.1M oxidizer concentration that leads to a continuous reduction in the MRR values. Beyond this concentration, the addition of the H_2O_2 seems to result in a porous and unprotective oxide layer that tends to increase the MRR values as a result of combined mechanical removal with the continuing chemical etching on the metals surface. In the same approach it has been observed that the oxidizer concentration parameter gave the same response regardless of the material removal rate obtained. Figure 3-5 shows the material removal rate results for the CMP process with polymeric brush for 10 minutes as a result of slurry and oxidizer concentration.

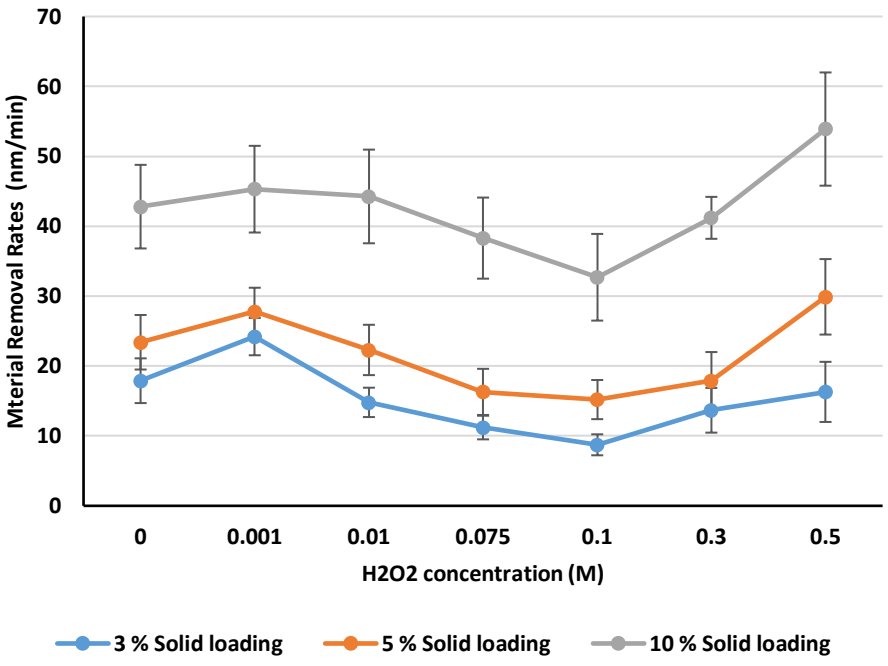


Figure 3-5 Mterial Removal Rates of Ti Implants at different H_2O_2 concentration (Polymeric brush).

The MRR response is listed in Table 3-2 which illustrates the lowest removal rate observes in 0.1M oxidizer concentration. The slurry chemistry can change the CMP mechanism more specifically at low H_2O_2 concentrations.

Table 3-2 Material Removal Rates MRR of Ti based Dental implants at different H2O2 concentrations and different solids loading (Polymeric brush).

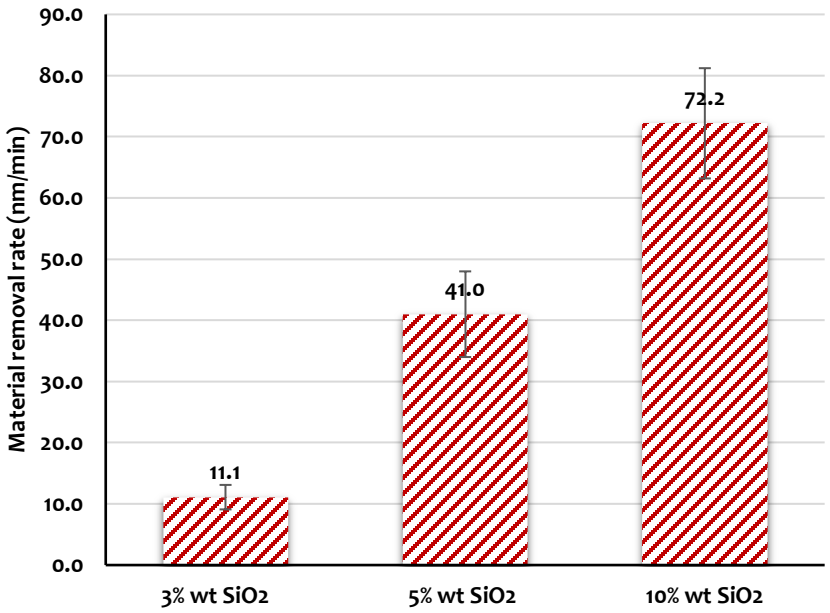
Solids loading	**H_2O_2 concentration (M)**						
	Material Removal Rates MRR (nm/min)						
	0	0.001	0.01	0.075	0.1	0.3	0.5
3wt%	17.9	24.2	14.8	11.2	8.7	13.7	16.3
5wt%	23.4	27.8	22.3	16.3	15.2	17.9	29.9
10wt%	42.8	45.3	44.3	38.3	32.7	41.2	53.9

MRR strongly dissolution-dependent. at high H_2O_2 concentrations, the protective oxide film rapidly forms on the surface an prevent heavy dissolution. in this case, the process is controlled by mechanical removal of titanium and subsequent dissolution . the slurry chemistry was found to strongly affect the formation of the passivation film on the titanium surface and thus change the friction force of the surface.

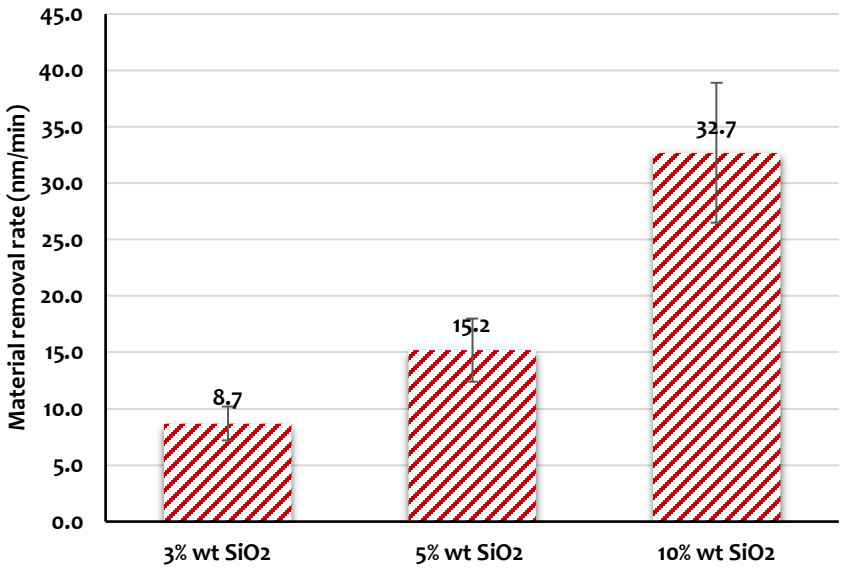
b- Effect of slurry chemicals (abrasive particles)

CMP process combines both mechanical and chemical actions, the abrasive material in a liquid medium is the embodiment of the mechanical action, and in addition to the abrasives, other additives typically have the 'chemical' action in the slurry, comprising a complexing agent, an oxidizing agent (here we have hydrogen peroxide), and it may contain corrosion inhibitors such as benzotriazole, detergents and surfactants. However, it can also be implemented with a fixed concentration of abrasives, which optionally can have a contoured surface. Thus, CMP process can be applied to any biomaterial comprising a

metallic layer. This kind of controlling the abrasives concentration can give a dominated material removal rate and very uniform surface roughness Grade (Ra). The main purpose of the original CMP process is reducing the layer deposited to the required thickness and flatness. The challenge here is to make an observation of the abrasives concentration to remove the material with accepted rate and leave surfaces with required roughness. The key issue for CMP process is the balance between the mechanical cutting by abrasion particles and the chemical reaction which consist the corrosive wet etching of the metal and metal oxidation & passivation. Different metal oxides have different degrees of water solubility and if the oxide is insoluble adherent and continuous, it can prevent the oxygen diffusion until the slurry particles mechanically abrade the surface layer. This enables topographic selectivity. The CMP evaluations was based on choosing a synthetic pad (Dekor 1056 20 cm Pure Wool) was used to provide smooth surface finish by using three different slurry concentrations of SiO2 abrasives. CMP experiments were conducted without oxidizer and in the presence of 0.1 M H_2O_2. Figure 3-6a shows the removal rate values, in which there are a significant difference for all the three slurry concentrations. The highest material removal rate (MRR) for the both 3-D CMP methods is recorded for the 10wt% SiO2 concentration as a result of increasing the percentage of the mechanical cutting tools. Additionally, the material removal rate values as can be seen from the Figure 3-6a and b is increasing proportionally with increasing the abrasives concentration for the fixed H_2O_2 concentration. Removal rate mechanism of the slurry in CMP treatment was observed to be affected by the percentage of the selected abrasive particles as they affect the mechanical abrasion. So, when the process or oxide film formation is fixed as the oxidizer concentration fixed, the role here comes to the amount of the abrasive material which if increased can give higher rate of abrasion.



(a)



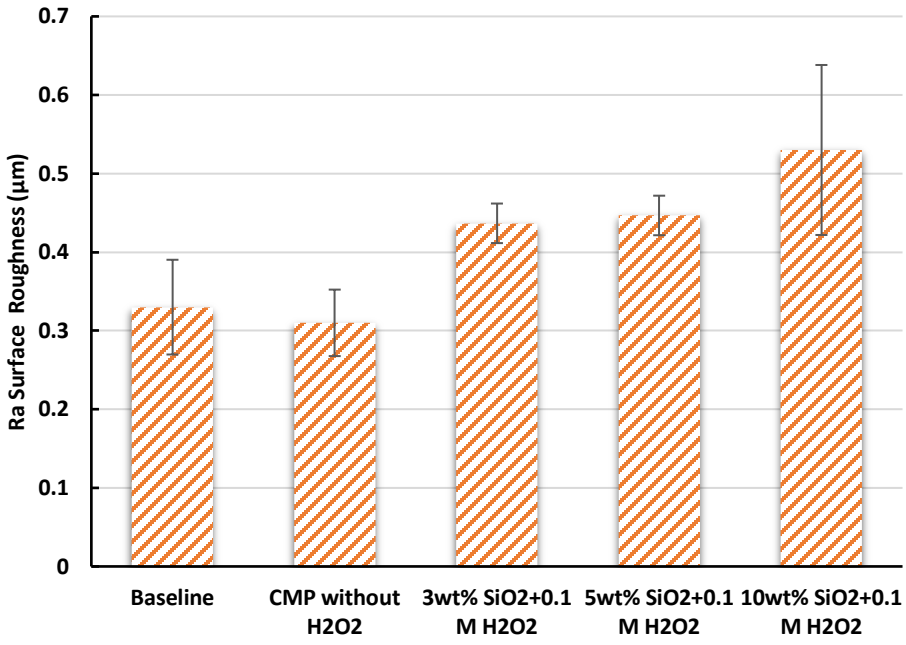
(b)

Figure 3-6 Material removal rate for (3-D CMP) with (a) setup 88,50 RPM (b) Polymeric brush.

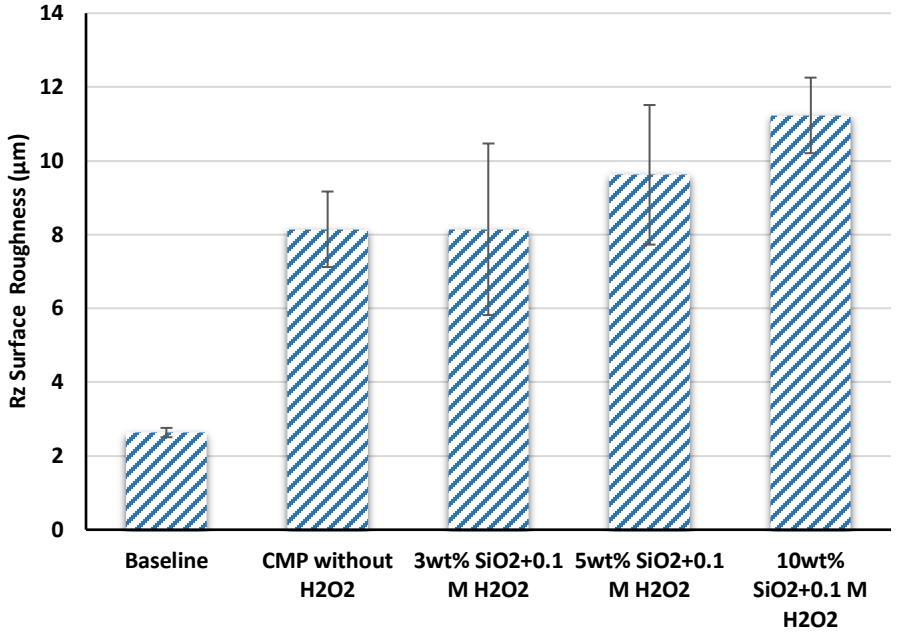
3.3.1.2 Effect of slurry solids loading on surface roughness

Since the surface roughness of an implant is a determining factor of its surface quality [167], the surface roughness measurements of the 3-D samples were performed by a High-accuracy Surftest SJ-400 Mitutoyo profilometer. Pre and post CMP surface treatment values of the surface roughness (Ra) were recorded as an average of three measurements taken on the 3-D samples. For the improvement of implant performance in accordance with literature findings, the main strategy followed was to obtain rough surfaces of Ti implants in a controlled manner by selecting the variables for the CMP process to give the desired surface topographical results [168].

The surface roughness values of the implants polished with the developed process setup are plotted in Figure 3-7a and b. It can be seen that as the slurry solid loading increased the surface roughness of the implants also gradually increased. The changes in topographic features have a significant influence on the series of biological events that lead to the acceptance of the implant by the host tissue [169], from the adsorption of proteins until the mineralization of the extracellular matrix of the bone tissue, going through the adhesion, proliferation and differentiation of both osteoblasts and osteoclasts. All these entail a greater speed in the healing processes and, therefore, a faster and biologically more effective osseointegration can be achieved [170].



(a)



(b)

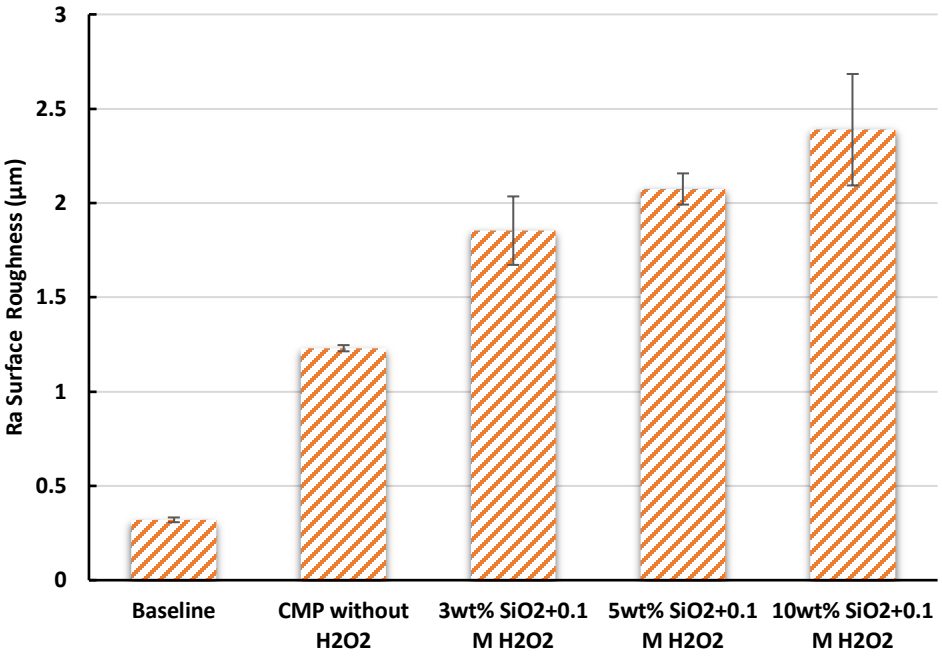
Figure 3-7 (a) Ra (b) Rz surface roughness post 3-D CMP (with wool pad) for different SiO_2 concentration.

The interdigitation of the bone tissue with appropriate surface topography effectively reduces the interfacial movement [171]. This factor promotes bone healing in direct contact with the implant and, consequently, improves its long-term fixation [172]. This allows the

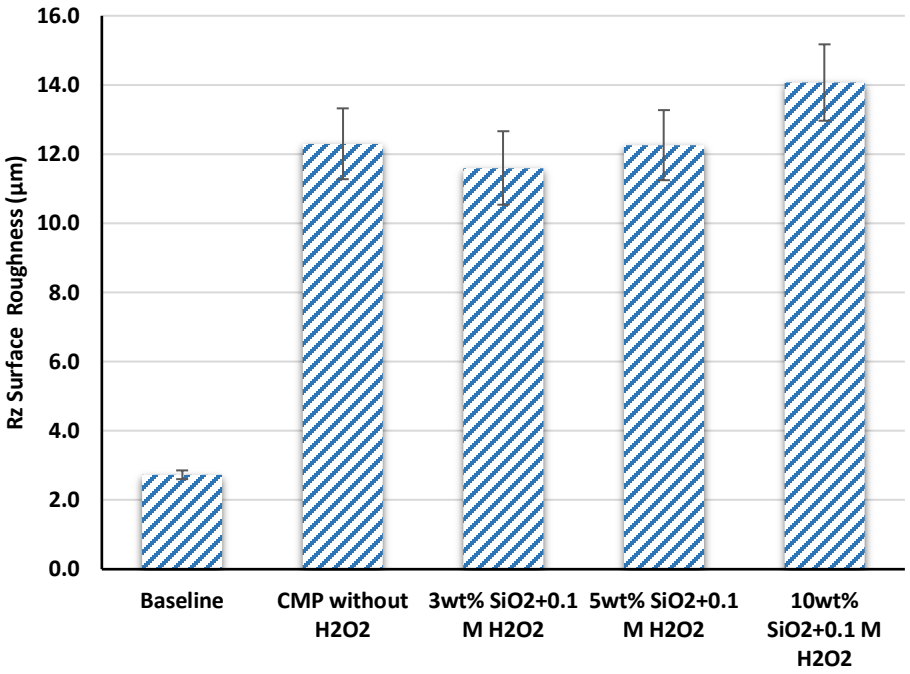
placement of shorter implants, meaning a more manageable implantation procedure is possible for a greater number of surgical situations. For the improvement of implant performance in accordance with the given trends of research, the main strategy followed has been to obtain rougher surfaces of Ti c.p. The preliminary clinical studies of Predecki et al. [173] obtained results that led to a large number of investigations on the relationship between the roughness and healing of the bone tissue. In the specific case of dental implants, an appreciable number of studies have already been carried out to characterize the surface roughness of implants and how they correlate with to the in vivo implant attachment responses [90, 174, 175]. In summary there are sufficient evidence to consider that roughness improves osseointegration, since:

1. reach osseointegration occurs more quickly,
2. show higher percentages of bone in direct contact with the implant, and
3. increase the resistance to loosening, since removal torques required are higher for extraction.

The same approach was used in CMP process with polymeric brush where the H_2O_2 concentration was evaluated.



(a)



(b)

Figure 3-8 (a) Ra (b) Rz surface roughness post 3-D CMP (polymeric brush) for different SiO_2 concentration.

Figure 3-8 gives the H_2O_2 concentration impact on surface roughness responses. As can be seen in the Figure 3-7 the same response was obtained from the CMP setup.

Terms such as contact angle or wettability and Rugophilia have been used to describe the interaction of cells and tissues with textured surfaces. The dental implants morphological properties should a dual role depending on the nature of the encirclement cells. Rugophilia literally means “rough-loving” like bone hard tissues. Whereas some type of cells like fibroblasts will accumulate on smooth surfaces [176].

Disadvantages of the Ra parameter:

- The value of Ra in a measurement module represents the average of the roughness, therefore a non-typical peak or valley in a surface will alter the value of the measurement, not faithfully representing the average value of the roughness.
- The value of Ra does not define the shape of the irregularity of a profile, that way we can have a value of Ra practically equal for surfaces with different finishing processes.

3.3.1.3 Surface wettability

As can we see in Figure 3-9 which summarize the contact angle measurements taken with DI water on titanium 3-D dental implants samples. The high contact angle resulted from baseline samples obtained by creating air bubbles between the micro-voids roughness of implants which is the leading cause of hydrophobicity and consequent lack of wettability. But with the roughness obtained from the baseline samples with 0.32 µm the high contact angle can be attributed to the porous structure of the oxide film formed on untreated baseline samples [177]. The CMP process implemented on the 5 baseline samples without the presence of the oxidizer addition removed the oxide layer and exposed the titanium-based

surface with an 66º contact angle which is less than the contact angle measured from the baseline samples. This declares the fact of removing the self-formed oxide layer from the titanium-based implant surface since the wettability response changed significantly. Furthermore, the high surface energy of the freshly exposed titanium-based implant atoms can also lead to higher interaction with water molecules which eventually leads to higher hydrophilicity and hence lower contact angle.

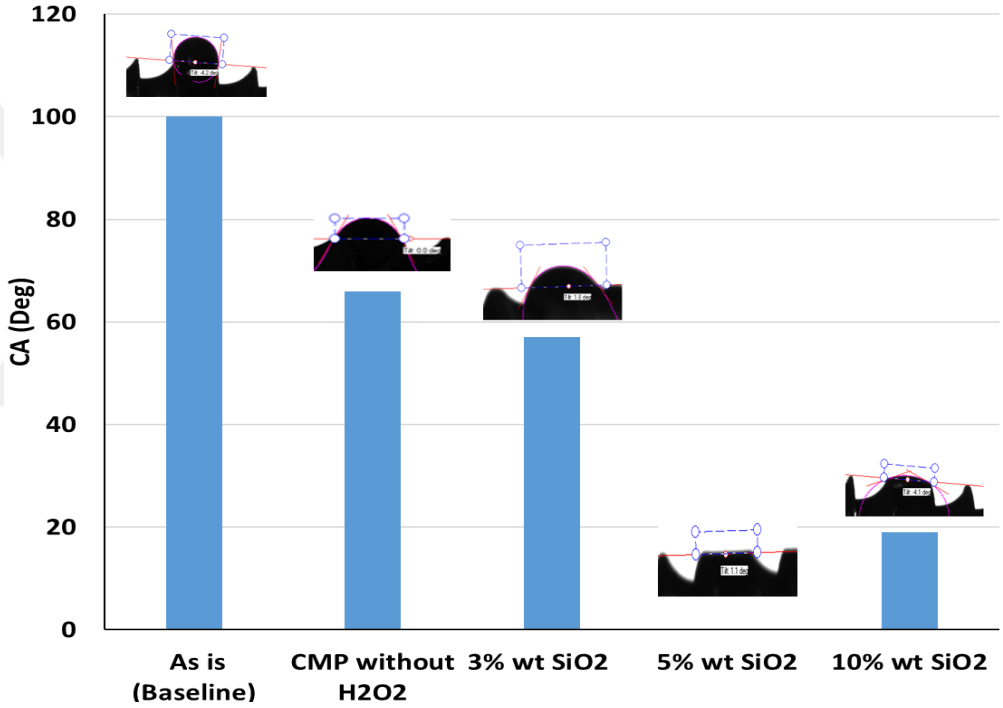


Figure 3-9 Results of the surface wettability of the baseline and CMP treated Ti-based implants.

However, the subsequent CMP treatments with the presence of the oxidizer and abrasive particles the effect of surface roughness on the contact angle measurements started to dominate. However, the alteration of two or more of the surface characteristics at the same time, in this case, surface roughness and chemistry, deliberately, can direct the assessment of

the functions of the parameters on the wettability behavior and the biological performance. The interaction of the surface of an implant with the blood is the first determining event in the regeneration of the peri implant tissues.

3.3.2 Effect of pad-sample velocity

In the Chemical Mechanical Polishing (CMP) process used for surface structuring, three contact regimes between the sample surface and the polishing pad may be proposed:

1- direct contact,

2- mixed or partial contact, and

3- hydroplaning.

An effective in-situ method for characterizing the sample/pad velocities and a systematic way of relating velocity values to the process parameters are investigated. In this work, the pressure on the sample carrier was kept constant. the sample/pad velocity and slurry concentration are specified and verified by experiments. Finally, a correlation amidst sample / pad velocity and the material removal rate (MRR) is established. Process optimization based on minimizing the material-removal is also suggested and discussed. The basic material removal mechanisms in CMP are not yet well understood. Long ago, Preston empirically found in glass polishing that the material removal rate (MRR) is proportional to the product of the applied pressure and the relative velocity [178]. Nevertheless, the experimental results show a consistent trend between the sample/pad velocity and the material removal rate MRR. For low sample/pad velocity values 88/50 rpm, the MRR results are between 11-70 nm/min dependent on both the slurry abrasion particles concentration and the relative sliding velocity. The relatively high MRR suggested a high friction coefficient in the low sample/pad velocity suggest that the sample/pad interface is

in the contact mode. After some point when the we doubled the sample/pad velocity by three times, the friction coefficient is no longer independent of pressure or velocity. The material removal rate MRR is no longer directly proportional to the sample/pad velocity as shown in Figure 3-10 and Table 3-3.

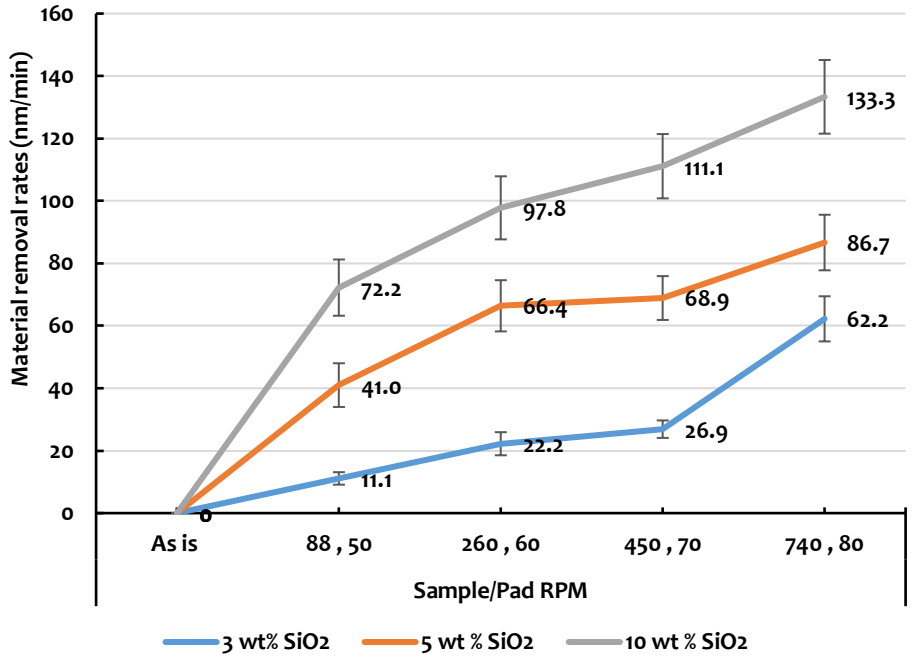


Figure 3-10 Removal Rates of Ti Implants at different sample/pad velocities.

Table 3-3 Removal Rates of Ti Implants at different sample/pad velocities.

MRR Sample/Pad RPM					
Solid loading	**As is**	**88/50**	**260/60**	**450/70**	**740/80**
3wt%	0	11.1	22.2	26.9	62.2
5wt %	0	41.0	66.4	68.9	86.7
10wt %	0	72.2	97.8	111.1	133.3

3.4 Summary

In this chapter the 3-D CMP process was examined as an alternative technique for surface structuring method of the titanium-based implant to produce a controlled surface roughness while simultaneously forming an oxide layer. The impact of the CMP process variables was evaluated by using a different SiO_2 based concentrations slurries with different oxidizer concentrations. Furthermore, to modulate and to verify the surface roughness, the other variables were tested and investigated. The evaluation of dependent 3-D CMP process variables used for surface structuring showed the optimal slurry and oxidizer synthesis that can give the desired Material removal rates, surface roughness and wettability. Furthermore, in the case of biomaterial application, putting the bioimplant in the human body environment requires a comprehensive study of the new host reaction to corrosion. So, in next chapter the systematic electrochemical evaluations also accomplished to give an assessment for the corrosion results. Finally, the application of the CMP on the 3-D dental implant surfaces also resulted in similar CMP responses as compared to the 3-D CMP with polymeric brush ”hand polishing” confirming that the CMP application can help enhance the surface properties of the titanium-based implants.

CHAPTER IV

MECHANICAL EVALUATIONS OF CMP TREATED DENTAL IMPLANTS

4.1 Introduction

In the last two decades, there has been a breakthrough both at the scientific and technological level related to dental implants, in such a way that it has become the most used therapy for the replacement of absent teeth, being the prosthesis rehabilitated with implants a predictable long-term treatment. The criteria for defining the success of implants have been changing over and over the years, and currently includes the absence of mobility, radio-lucidity around it, absence of Peri-implantitis with suppurative [179] and some authors add the absence of subjective complaints on the part of the patient [180]. Failure of dental implants may occur early or late, depending on whether it occurs before or after the occlusal load. Early failures have been defined as those occurring before the prosthetic phase and are usually caused by a lack of osteointegration. This alteration in bone healing after insertion of the implants produces a growth of fibrous tissue between the implant surface and the bone around it, resulting in an overgrowth of scar tissue extending from the portion Coronal of the implant towards the most apical, originating a fibrointegration of the implant. As a result of this fibrointegration, mobility and loss of implant fixation occur. Despite using implants with a solid scientific base, having an adequate clinical experience, using all the necessary measures to avoid cross-infection, and having a sufficient amount of soft and hard tissue, we can have a premature failure of Implant after insertion. The early failure rate varies from 0.7% to 3.8% [181]. The early failures of the implants are the most common, therefore it seems important to know the causes that produce them. Some clinical

studies have identified as risk factors for early implant loss age, implant length, tobacco, localization, bone quality, and systemic factors such as genetic predisposition and metabolism disorders [182]. More and more elderly patients requesting implant treatment to replace their absences, much has been discussed whether age constitutes a risk factor for early failure of implants. We know that osteointegration is not affected in elderly patients, although there has been postulated a lower blood supply and reduction of cellularity that could alter the apposition of bone, scarring of the bone and mucosa after insertion of implants, not It poses a problem in older patients [181]. As for gender, Chrcanovic et al. [183] claim that men are 1.255 times more likely to present failure early than women. The other factors that may influence the success or failure of dental implants which is related to the design the length and diameter of the implants, in this same review it is determined that the loss of narrow implants (diameter less than 3.5 mm) is more common than the standard diameter implants, and that although the short implants were more likely to failure the difference was not statistically significant, this increase in loss of these implants (short and narrow) can be due to that they are usually used in extreme situations where the amount of bone, space or bone volume is limited. The biomechanical evaluations for different surface treatments were performed by implementing three approaches; (i) implant pull-out test, (ii) removal torque test and (iii) the surface hardness measurements.

4.2 Experimental Approach

4.2.1 Chemical mechanical treatment of the implant's surfaces

CMP experiments were conducted with the The 3-D CMP was performed by using (metkon, Forcipol 1V) lapping tool carrying the polishing pad with different rotational

velocities of 50, 60, 70 and 80 rpm. CMP slurries with 3, 5 and 10wt% solids concentrations were flown at 40 ml/min flow rate by using a SEKO Solenoid dosing pump on a Synthetic wool polishing pad (Dekor 1056 20 cm Pure Wool) as mentioned previously. The selected polishing pad type, oxidizer concentration and the applied down-force were set by the suggested values of the design of experiment.

4.2.2 Evaluation of the responses

Three responses were evaluated after conducting the 3-D CMP treatment changing the process variables in order to access the optimal surface take into consideration the surface properties with a level of clinical interest, without compromising the bio-functionality and the release of ions from the materials. The surface-related mechanical properties and biomechanical responses were evaluated in terms of (i) microhardness, (ii) pull-out strength, (iii) removal torque values. Since CMP process has a mechanical impact, mechanical properties of the metal surfaces exposed to CMP may change during the treatment. In order to evaluate to mechanical properties of the samples which were exposed to CMP treatment, they were examined with Vickers hardness measurements as compared to the baseline sample. Future Tech, FM-300e Vickers hardness tester was utilized for the samples treated by the selected oxidizer and solids loading concentrations. Since the surface structuring through CMP affect the implant surface hardness simultaneously with the surface roughness, hardness measurements are critical to evaluate the implant's long-term mechanical integrity. Microhardness tests were conducted to provide a reference for comparison between the different surface 3-D CMP treatments. Using Vickers pyramidal tip indenter, a 1000 gm load was applied to previously surface treated samples of each of the 3-D surface treatments over a period of 10 s. Five indentations were made at different

locations on the sample surface. Pull-out test: Measurement of the maximum load required to pull out the fitted attachment. Handling of dental implants in applications for approval," pharmaceutical and Food Safety Bureau Notification 0713, No. 1, issued July 13, 2012. As worse case. In this test at first the synbones are used which are manufactured from toilored form of polyurethane foam consist of a cancellous inner core and a harder outer shell mimicking cortical bone which gives the feel of real bone and it has the same mechanical properties of natural bone.

The removal torque test is one of the reliable inspections that can give an indication about the primary stability of the dental implant after the surgical insertion. The removal torque values were conducted by changing the solids loading concentrations to obtain a unified process variables that gives greater roughness to the surface thus encouraging the osteoforming process by osteoblast cells.

4.3 Results and discussion

4.3.1 Mechanical Properties Evaluations for 3D Samples

4.3.1.1 Micro-hardness measurements

Vickers hardness measurement values taken on the 3-D CMP treated samples. Figure 4-1 shows higher hardness values as compared to untreated titanium-based sample. Indeed, 3-D CMP process has resulted in work hardening impact on the Titanium-based samples during the mechanical polishing process because of the mechanical action. furthermore, hardness findings revealed identical values even through different removal mechanism were active during the process. Despite of the usage of the same pad for all the 3-D CMP tests for design purposes, the solids loading gave the desired impact on the

titanium surface. The work hardening process was done by the solid particles, and it can be seen that the work hardened impact was more mechanically pronounced as the solids concentration increased.

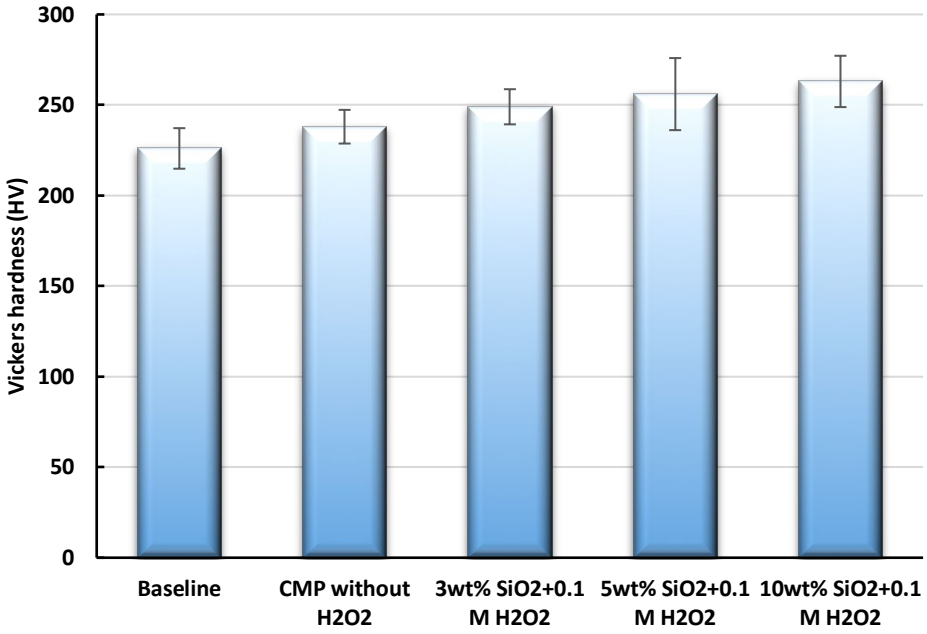


Figure 4-1 Vickers microhardness evaluation of 3-D CMP treated surfaces with different solids loading.

4.3.1.2 Pull-out test

Pull-out strength measurements were conducted on the 3-D CMP treated samples with different solids loading to compare the biomechanical response. The peak value of the bone-implant interface failure is considered as the pull-out strength which are illustrated in Figure 4-2. It can be seen that the solids loading effect is highly significant for the determination of the interface bonding degree. The highest pull-out strength is obtained with 10wt% of solids loading which can be interpreted by the fact that the pull-out strength is associated with the surface roughness. Despite the fact of the osseointegration process is correlating with the surface rugosity to a certain point after which it will become influential

on the mechanical success of the bio-implant. The high surface roughness means a high removal rate and hence severe plastic deformation rendered to the implant surface which in turn caused a stress concentration points.

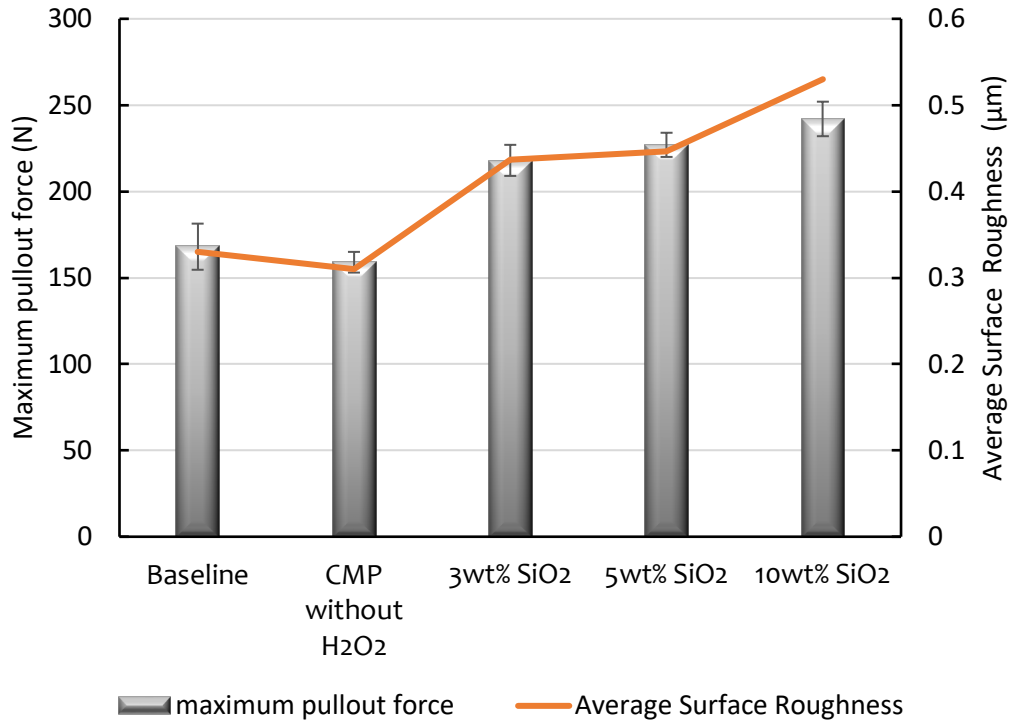


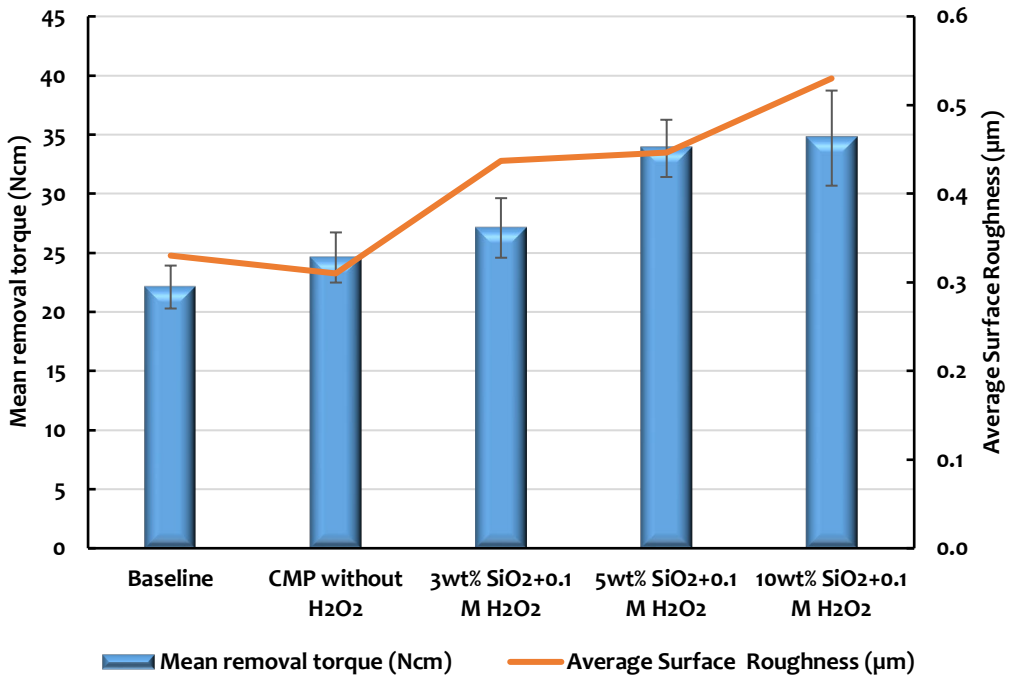
Figure 4-2 Pull-out strength results for Titanium based dental implants with different SiO_2 loadings.

The lowest value was observed on the samples treated with 3wt% of abrasive particles which is the lowest concentration used for 3-D CMP tests which gave a lowest average surface roughness Ra of 1.83 µm. In chapter 3 it has been noted that the implant primary stability is a substantial to determine the long-term success of the dentistry rehabilitation treatment.

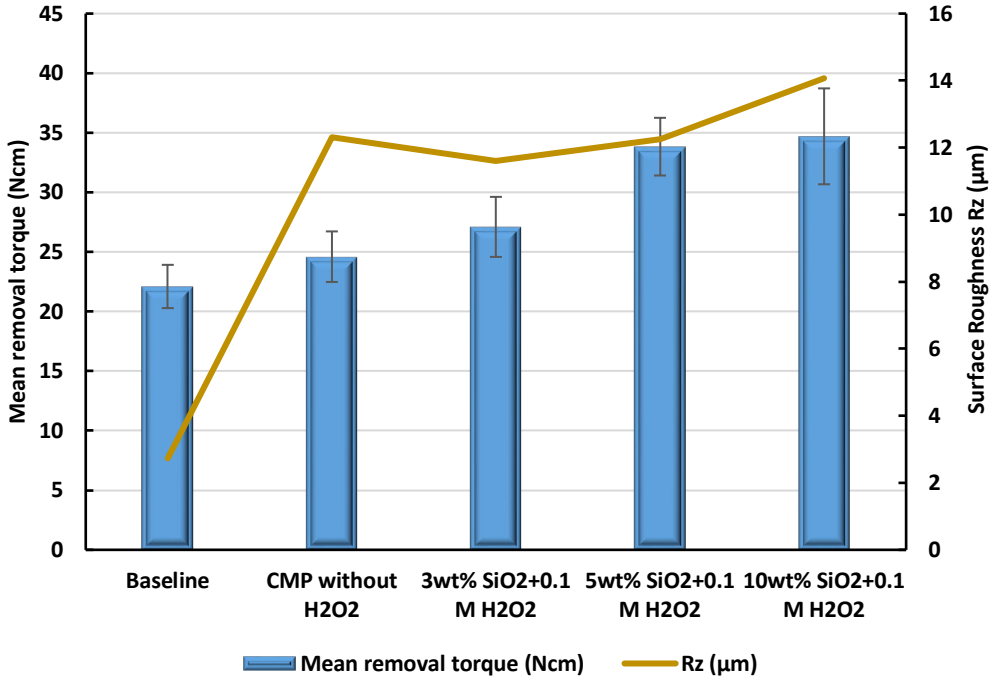
4.3.1.3 Removal torque test

Since short implants were used in this study it was one of the basics of this work is to produce an implant surface with optimal roughness to facilitate the use of shorter implants

for more surgical situations. Figure 4-3 shows the surface roughness influence on removal torque values in which the 3-D CMP treatment with different solids loading can increase the implant surface roughness values as the mechanical action alteration. The removal torque values were significantly altered by the change of the solids loading concentration. As mentioned in chapter three the surface roughness is one of the fundamental principles for ensuring the improved osseointegration of the current surfaces. The data indicate that CMP is a good alternative to commonly implemented implant surface treatments with optimum results comparable to those obtained by other surfaces and paving the way for possible clinical application in the context of early and immediate implant loading. The importance of the implant primary (mechanical) stability at different time points is to evaluate the long-term implant survival and successful clinical outcome. Therefore, the purpose of this test is to evaluate implant primary stability of pre-treated implants and to give an assessment to overall success rate of surface treated dental implants. A secure and successful bone-implant integration is positively associated with the accretion of the contact between the implant and the bone hard tissue stimulated by implant surface rugosity, allowing for faster bone-implant adhesion levels [184].



(a)



(b)

Figure 4-3 Mean Removal torque values for the 3-D CMP treated samples with 10 mm length with (a) average surface roughness and (b) Rz surface roughness values.

The removal torque test results which were in typical values, the peak of which was assumed to be the failure torque of the bone-implant interface. The length of the implant and the amount of bone-to-implant contact were the determinants for interface strength in cancellous bone. The results show that the longer implants with 10 mm height can give greater removal torque values due to the larger surface area of bone-to-implant contact.

4.3.1.4 Fatigue analysis

a. Specimens

The total number of tested samples is 19 dental implant under cyclic fatigue conditions. Figure 4-4 illustrates the sample provided by Mode Medical company.

Figure 4-4 the sample provided by Mode medical company.

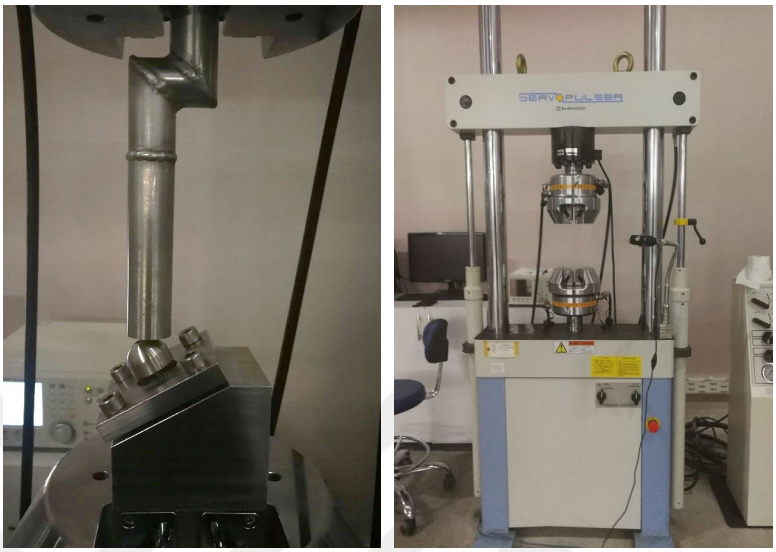
There are four groups of samples provided by Mr. Riaid Hadi Salih Alsaeedi and number of samples are shown in the following table 4-1:

Table 4-1 Groups and number of samples

Group	No. of Samples
Machined	7
CMP	4
BCP	4
Etched	4
Total	19

b. Testing fixture and machine

Testing conditions are determined based on ISO 14801:2007 Dynamic fatigue test for endosseous dental implants. The required test fixture was designed and manufactured according to the mentioned ISO. Samples were attached to the fixture as shown in Figure 4-5a. Tests were conducted using Shimadzu Servopulser Dynamic Testing Machine Figure 4-5b. Maximum capacity of the machine is 100 kN with ±50 mm stroke. The maximum frequency is determined loading conditions however overall maximum frequency is 50 Hz.



(a) (b)

Figure 4-5 (a) Test fixture attached to the testing machine and sample fixed (b) Dynamic Servopulser Testing Machine.

c. Test Method and Measurements

The tests comply with the provisions of the standard at all times ISO 14801: 2007. In this section we explain in a general way the methodology followed for the preparation of the samples and the performance of the fatigue tests, a more detailed description of the implant assembly in an anchoring device fixed can be seen in figure 4-6 .

Figure 4-6 Test fixture attached to the testing machine and sample fixed

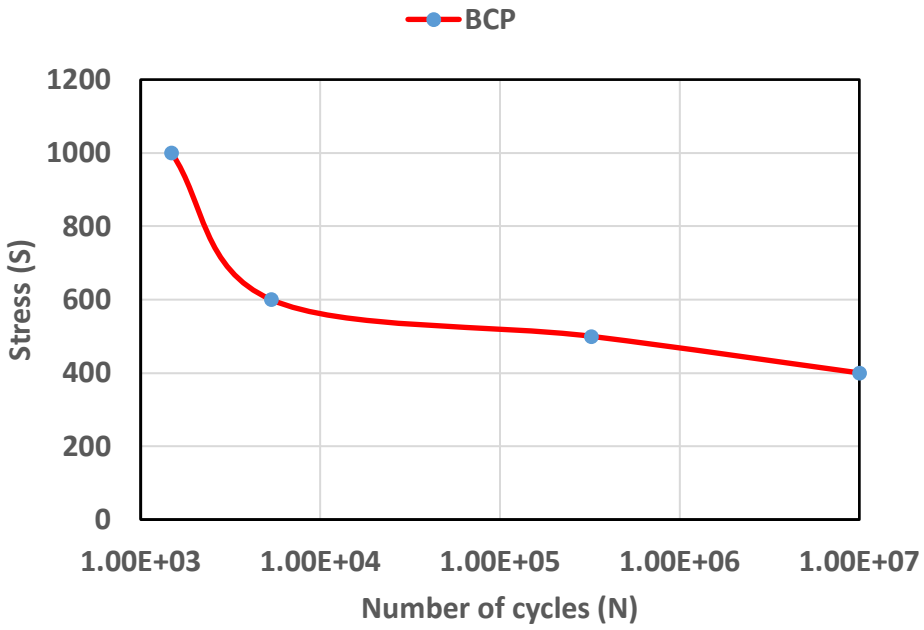
A system of collet has been used that places the sample in the correct test position. The implant is inserted in a collet fixture, that when compressed by the upper cover it deforms plastically, exerting a uniform tightening on the tested implant. All The components of the sample fixing system are made of steel. The collet chuck is made of Spring steel grade AISI 6150 and has an elastic module close to 190 GPa, higher value than the one that establishes at least the ISO standard 14801: 2007. This guarantees that the pressure of the collet on the sample does not plastically deform it. With this design of the fixture ensures that the load application angle is between 30º. For this, the support has been machined with a plane at 30º from the horizontal. This ensures that the implant will be fixed at 30º, with manufacturing tolerances. On the other hand, the positioning of the implant inside the collet, as well as the design and placement of the hemispherical load member is have been made in a way that ensures that the distance between the center of hemispherical member and the point of intersection of the implant axis and the face flat top of the cap (l, according to ISO 14801: 2007) it is within the tolerances allowed: 11 ± 0.5 mm. The load cycle curve is drawn to show the maximum load at which the endosseos dental implant system will withstand $5x10^6$ cycles.

d. Fatigue analysis results

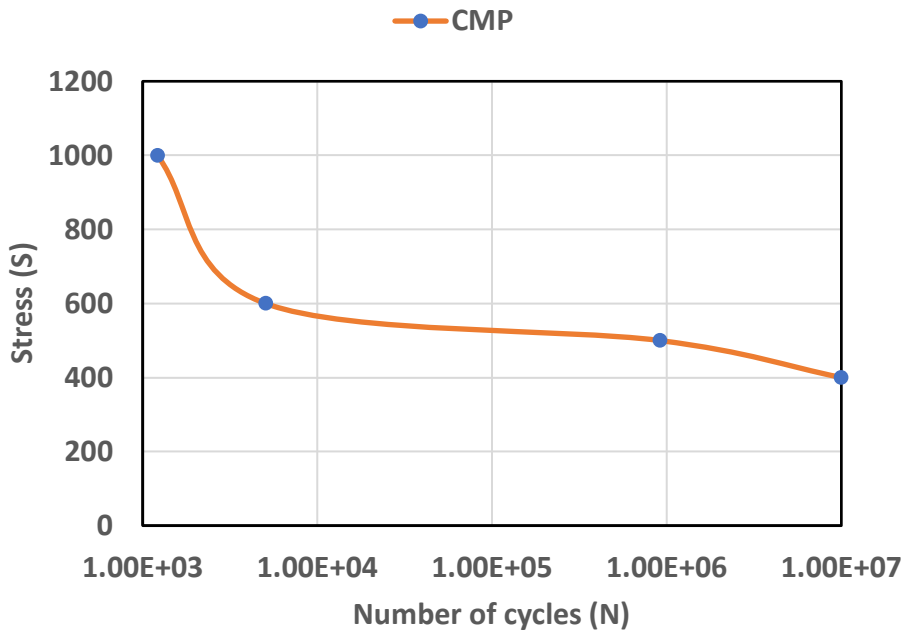
The load was applied via a rode of stainless steel. This test results showed that the mechanical properties offered by the dental implants referred for teeth has an excellent mechanical properties even in the worse conditions according to the standard ISO. The test of five million cycles is to replicate an oral environment and mastication function of about 15 years. Table 4-2 shows the fatigue life in cycles for the four surfaces included in this dissertation. The CMP treated dental implants resulted in the highest fatigue life 5 million cycles with load of 739 N. The fatigue life data also presented in the form of S-N curves plotted where the (S) is the stress against the number of cycles to failure (N). These data were very useful to give an indication about the fatigue life prediction for the pretreated dental implants Figure 4-7(a-d).

Table 4-2 Experimental fatigue life results for pretreated dental implants.

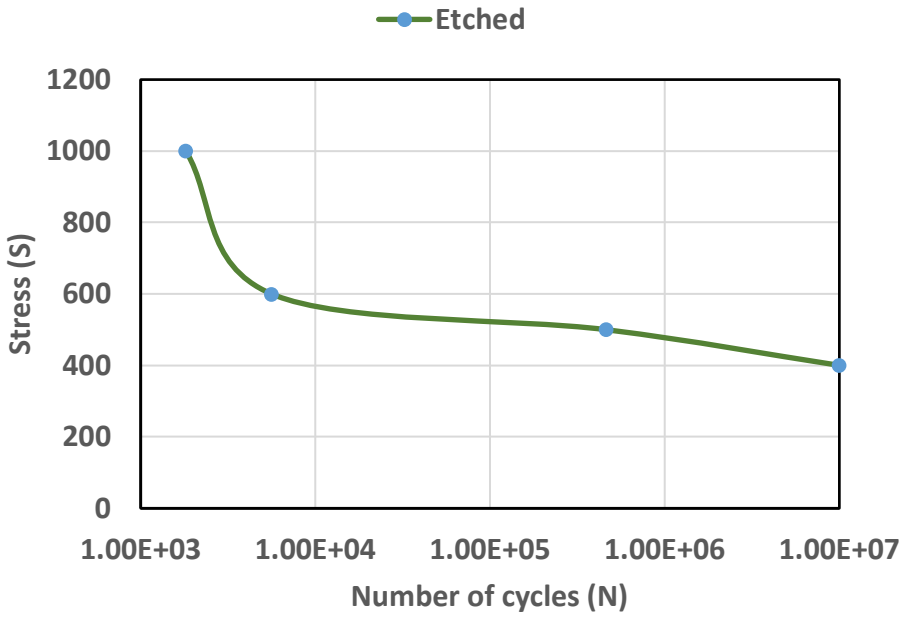
Maximum Load (N)	**Fatigue Life (cycle)**			
	BCP	**CMP**	**Etched**	**Machined**
350	1×10^7	1×10^7	1×10^7	1×10^7
400	1×10^7	1×10^7	1×10^7	1×10^7
500	3.2053×10^5	9.1271×10^5	4.6114×10^5	5.1984×10^5
600	5322	5046	5612	4868
1000	1486	1214	1815	1225


BCP
1200
1000
800
600
400
200
0
Stress (S)
1.00E+03
1.00E+04
1.00E+05
1.00E+06
1.00E+07
Number of cycles (N)

(a)


CMP
1200
1000
800
600
400
200
0
Stress (S)
1.00E+03
1.00E+04
1.00E+05
1.00E+06
1.00E+07
Number of cycles (N)

(b)



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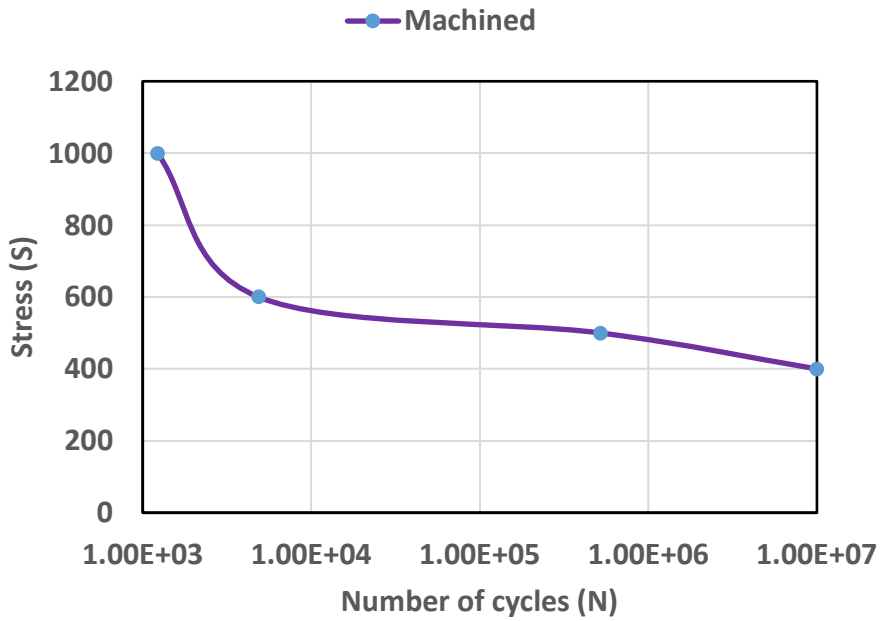


(d)

Figure 4-7 Comparison of fatigue life experimental data for the pretreated dental implants (a) BCP, (b) CMP, (c) Etched, (d) Machined samples.

There are factors that positively affect the fatigue behavior and others that adversely affect it. Grain refining, surface hardening and compressive stresses contribute to inhibiting

nucleation and / or propagation of fatigue cracks. However, roughness, scratch, etc., on the surface, act as stress concentrators favoring nucleation of cracks.

BCP blasting causes a sub-surface hardening, refinement of the microstructure and compressive residual stresses. However, the increase of surface roughness and the high mass fraction of embedded blasted particle fragments play a detrimental role decreasing fatigue resistance of titanium-based implants. On the contrary, the lower surface roughness makes the fatigue strength to increase in implants.

Fatigue crack initiation generally occurs on the surface of metal as a result of cyclic loading where the stresses are maximum at the surface. This is increased by absence of plasticity in failing metals. That is why (CRS) compressive residual stress field is developed using surface structuring methods such as sand blasting. In this kind of treatment, the metal surface is shot with high velocity particles in order to create a surface top layer of plastically compressed material up to a certain depth. The (CRS) Compressive residual stress works on two levels:

1. It reduces the amount of tensile stress on the surface of metal where the cracks normally initiate and propagate.
2. Sand blasting provides a plastically deformed surface layer up to a certain depth from the metal surface. Hence, cracks don't initiate in a plastic surfaces. consequently, the crack initiation points are moved below the surface where bending stresses are not at maximum value.

However, after long periods, the residual stresses are relaxed, and the microstructure is partially recovered, which contributes to the decrease of the fatigue resistance.

On the other hand, the 3-D CMP treatment for the dental implants and by which hybridizing the surface with nano-micro topography eliminated preferential crack initiation sites or stress concentration points associated with the uniform surface topography as a result increasing the fatigue life. The worst fatigue behavior is presented by the etched samples and is due to the higher roughness and this fact would be associated with the generation of superficial defects which affected the fatigue life behavior negatively.

Figure 4-8 shows two fractured external-connection implants after the fatigue test. In both, it is observed that the fracture occurs in the first thread of the implant, as confirmed by the finite element study described later.

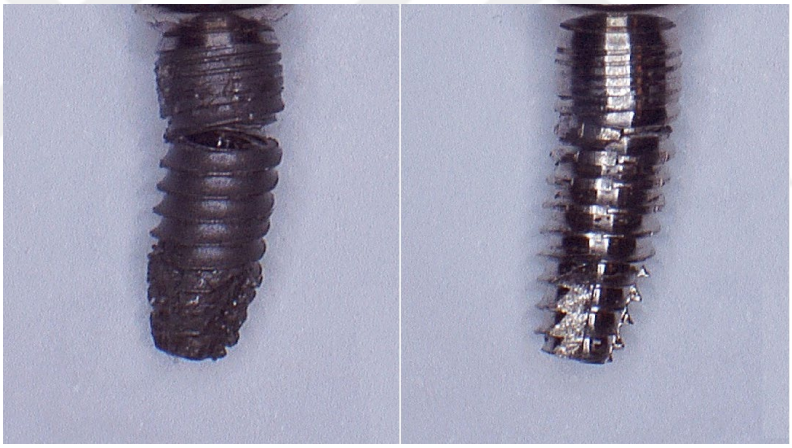


Figure 4-8 Images of two implants after the fatigue test.

4.3.1.5 Numerical fatigue test using finite element model

The break starts in small defects or stress concentration points. With each load cycle, an advance of the crack initiation occurs, so that the break occurs when the section does not support the static load. There is evidence that the initiation of the fatigue process requires local overcoming of the elastic limit (although macroscopically the stresses are lower than the elastic limit).

4.3.1.6 Factors that modify the limit of fatigue resistance

1- surface factor K_f

The samples used in the laboratory to identify the fatigue strength curve or endurance limit of a certain material have a standard size and surface finish that are closely monitored prior to the test. As discussed before, the initiation of microcracks is almost always linked with a free surface and, therefore, the surface condition of the location being reviewed plays a crucial role in assessing the modified fatigue strength. Figure 4-9 illustrates the determined surface factors associated with the ultimate tensile strength of titanium grade 4 used in manufacturing the tested dental implants.

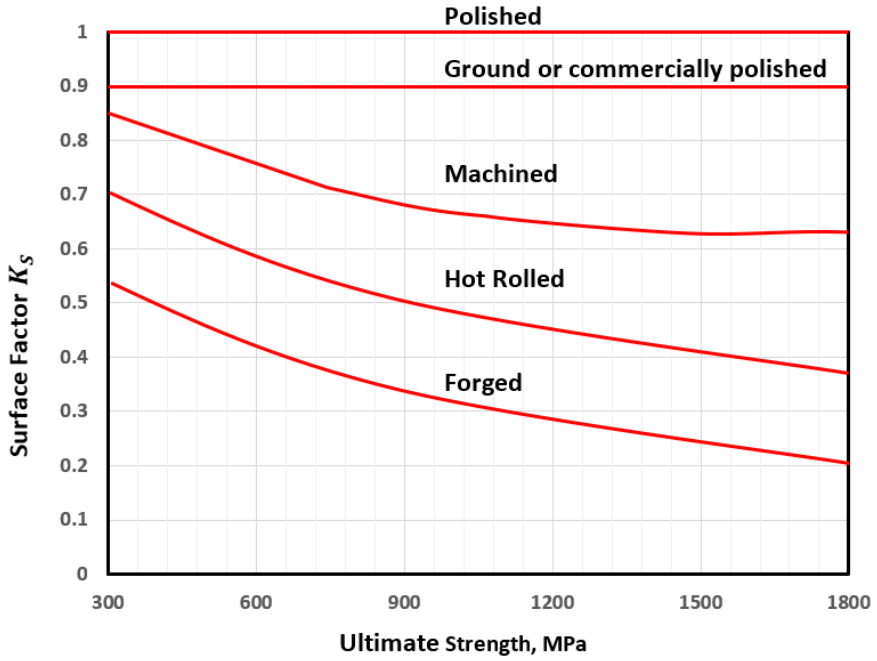


Figure 4-9 Surface factor associated with the ultimate tensile strength [185]

2- Load factor K_{load}

The strength values obtained from the S-N (Wohler plot) result from a reversed bending load as the specimen is rotated geometry.

- K_{load} = 1,0 When the loading is reversed bending
- K_{load} = 0,71 When the loading is reversed axial
- K_{load} = 0,6 when the loading is reversed torsional

3- Temperature factor K_{temp}

The temperature of the tested samples should be recorded because the lower and higher temperature for the tested material will associated to the material mechanical properties if it was different from those at which the mechanical properties of a material were obtained.

- K_{temp} =1,0 When the temperature is less than 450 C^{o}
- K_{temp} =1 - 5.8-3 (T-450 C^{o}) When the 450 C^{o} < t < 550 C^{o}

4- Size Factor K_{size}

The endurance limit of the samples have been noticed to change with their size. This is maybe related to the possibility of a high stress interacting with a critical defect within a certain size, i.e., when the size is bigger there is a higher possibility of failure. Therefore, when the size increases, the endurance decreases. For cylindrical samples of diameter, d, an accepted relation describes the specimen size effect on the fatigue endurance limit for the bending and torsion situations.

- K_{size}= 1 for d < 8 mm
- K_{size} = 1.2 for 8 mm < d < 250mm

The Modified fatigue endurance limit for, ferrous materials and titanium, is the endurance strength (S_e') determined from standardized test modified by a number of factors, which are also called fatigue modifying factors.

$S_e = (K_{surface} \times K_{size} \times K_{load} \times K_{temp}) S_e'$

$K_{surface}$

Surface treatment	$\boldsymbol{K_{surface}}$
CMP (commercially polished surface)	0.9-1
BCP	0.32
Etched	0.45
Machined	0.78

$K_{size} = 1.2\ (for\ 8\ mm < d < 250mm.)$

$K_{load} = 1\ (bending\ load)$

$K_{Temp} = 1\ (temperature\ between\ 20 - 50\ C^{\circ})$

Applying all these conditions for each case individually and put the value of extracted S_e in the engineering data in Ansys software will give the modified fatigue life according to the surface structuring method used.

4.3.1.7 approximate imitation of the fatigue test

a- Geometry

The geometry of the implants analyzed in this section was provided by the manufacturer, and it was necessary only to obtain the geometry of the bone Figure 4-10. To obtain the embedded material model of the fixture, the data used was for the rigid clamping

device with a modulus of elasticity higher than 3 GPa as described in the previous fatigue test section were carried out.

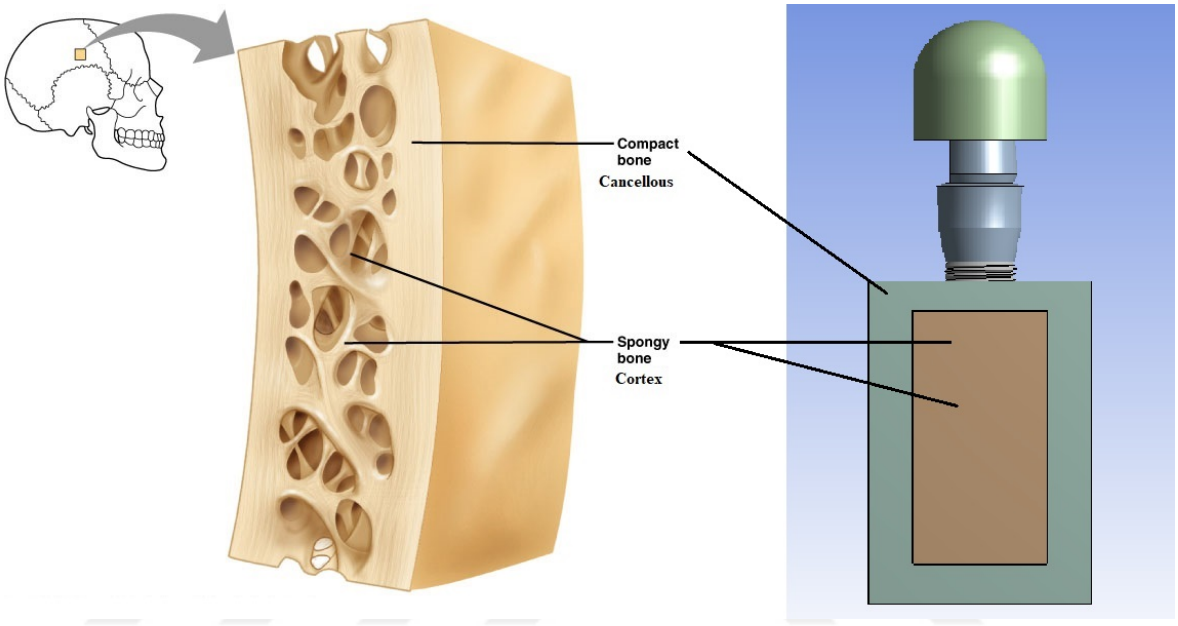


Figure 4-10 cross-section simulating cortical and cancellous bone.

b- External connection to the implants

This model was made in the commercial design software SolidWorks. Figure 4-11 shows the main geometry of the implant and the external connection part analyzed is this section.

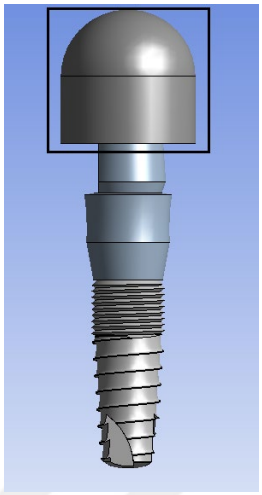


Figure 4-11 The implants and the external part connection.

c- Material properties

All materials have been considered as linear, elastic, isotropic and homogeneous. The elastic properties of the Crown (external connection) was taken as embedded material. The simulated bone was modeled as if it were cortical bone and the properties of the implant titanium were provided by the manufacturer. These elastic properties (Young's modulus and Poisson's coefficient) are summarized in table 4-3.

Table 4-3 Material Properties.

components	**Material**	**Elastic modulus (MPa)**	**Poisson's ratio**
Implant	Titanium	113000	0.34
abutment	Titanium	113000	0.34
Cortex	Palate	13700	0.26
Cancellous Bone Type II	Bone	1370	0.31
Hemisphere cup	steel	210	0.30

An important detail to consider when evaluating the behavior of any material is to know its limits, being the tension of break, an important property. In the case of cortical bone, the rupture stress described in the cortical bone is 170MPa for compression and 100MPa for tension [186].

d- Meshing

When the assembly of all components was obtained, it was transferred to the ANSYS Workbench finite element software, with which the structural static analysis described below was carried out. After the importation of the geometry, was carried out the mesh of the Assembly, which is represented in Figure 4-12, which is composed by 473254 nodes and 428084 elements.

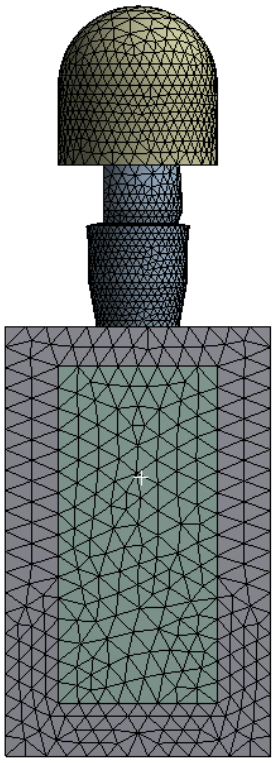


Figure 4-12 The components mesh needed for the simulation.

e- Contact and load conditions

The three-dimensional model was connected as detailed in Figure 4-13: All Degrees of freedom (displacement in the three directions of the space) of the bone are blocked. To

simulate an ideal osseointegration, the implant was rigidly adhered to the bone. The average applied load obtained in each case inclined 30º.

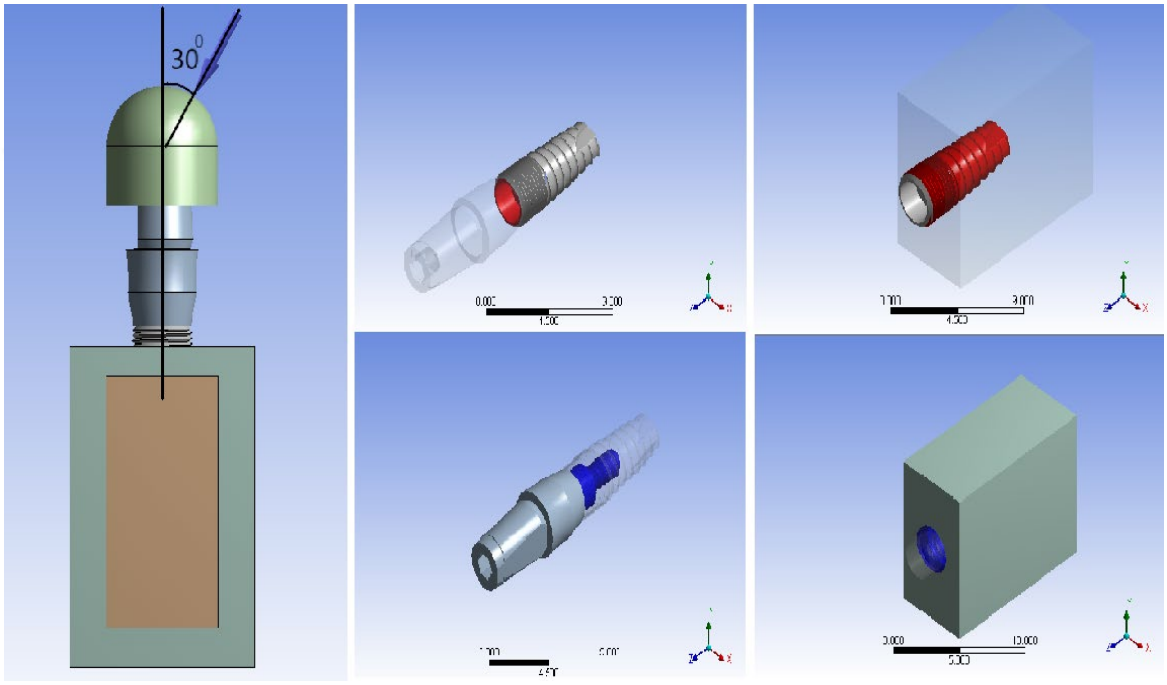


Figure 4-13 Outline of the contact conditions and the configuration of load used, the force applied with 30º according to the standard ISO.

f- Life expectancy in external connection implant

The deformation suffered by the implant and the crown during the fatigue test is affecting the fatigue life expected is shown in finite element model described in Figure 4-14.

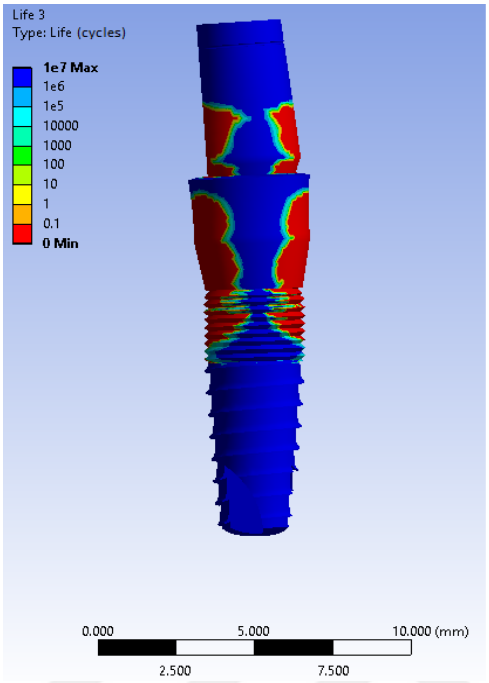


Figure 4-14 Life expectancy (in cycles) in external connection of the dental implant.

It is observed that the maximum deformations are obtained at the height of the insertion of the bone (3mm), which will lead to the tensions in that area are higher than the rest of the implant, with the consequent risk.

Figure 4-15 shows the distribution of stresses to which the implant is subjected under a static load of 1000 N.

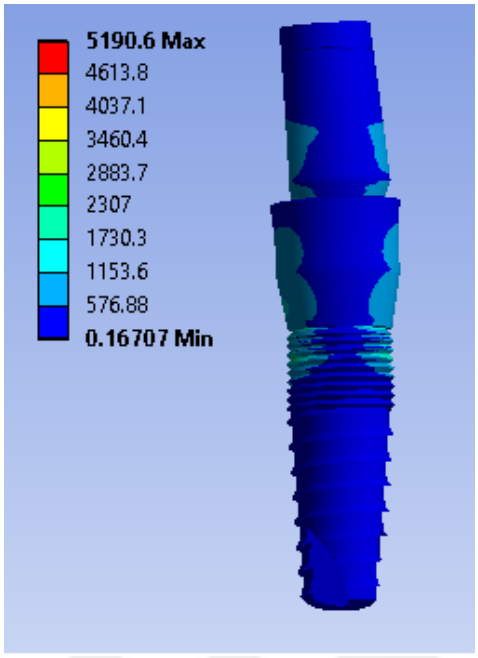


Figure 4-15 External connection implant stress von Mises under load of 1000N.

The maximum tensions correspond to the maximum deformations and, therefore, it will be the point where the fracture occurs, where appropriate. The maximum stress supported by the implant under these conditions is 2454.5 MPA, which proves to be a value clearly higher than the expected breaking stress in titanium (737MPa). In addition, these numerical results match those obtained in the fatigue tests and are described in table 4-4.

Table 4-4 Numerical fatigue life results for pretreated dental implants.

Maximum Load (N)	Fatigue Life (cycle)			
	BCP	CMP	Etched	Machined
350	1×10^{7}	1×10^{7}	1×10^{7}	1×10^{7}
400	1×10^{7}	1×10^{7}	1×10^{7}	1×10^{7}
500	3.8945×10^{5}	8.4218×10^{5}	4.8582×10^{5}	5.366×10^{5}
600	5079.7	5395.2	5568	5752.3
1000	1	1	1	1

g- Main tension and deformation in bone with external connection implant

After analyzing the stresses of the implant under the conditions of average fracture load, we proceed to the study of the biomechanical behavior of the cortical bone. The main difference between the titanium of the implant and the bone is that the latter is a brittle material, being understood as such that it requires very little deformation before breaking. In the case of brittle materials, it is not possible to obtain the stress of von Mises, which are valid for a ductile material, but must be calculated the maximum main stress. Another difference between the stress of von Mises and the maximum main stress is that the latter can take negative values depending on whether it works with tension or compression. This is why negative values appear in the legends of Figure 4-16 and 4-17.

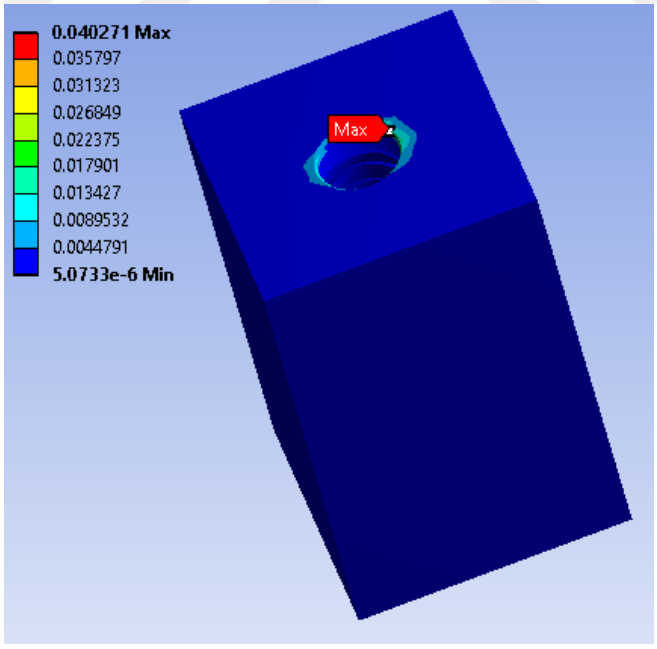


Figure 4-16 Maximum elastic core deformation in cortical bone.

As described above, the rupture tension of the cortical bone is 170MPa for compression and 100MPa for tension. In view of Figure 4-17, the compression zone would support 1977.8 MPa, a value clearly much higher than the limit supported by the material.

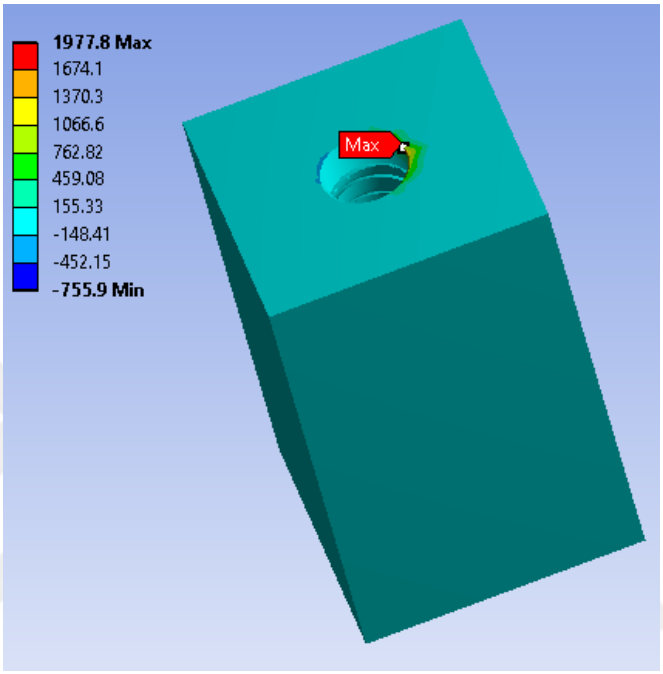


Figure 4-17 Maximum main stress on cortical bone.

4.3.1.8 Conclusions

In recent years the use of dental implants with different surface treatments has increased which led to an increase in the failure of these treatments due to fractures [187] not only due to biological factors but also to mechanical complications in the body of the implant , the implant fixture or its connections. Despite the high success rate of these treatments, a good knowledge of the biomechanical behavior of the implants is of particular interest when designing and avoiding mechanical failures. These mechanical failures are mainly due to fatigue caused by overloads or bone loss around the implant [149, 154].

Mechanical failures can be caused by the fatigue of the material, which can also be due to the physiological alterations of the patient, such as, for example, the parafunctional habits, being the bruxism the paradigm of this [144].

The conclusions reached in this part of the study are:

The process of certification of dental implants requires iterative mechanical tests table 6-5, which require the use of many implants (already manufactured), time and money.

Table 4-5 Iterative mechanical tests required to certify dental implants

Implant mechanical test	**Importance**
material tests such as physical testing (compression, tension and shear)	Testing the pre-clinical performance and biomechanical response
Pull-out test	evaluate the primary stability and the biological response to the implant
Removal torque test	Evaluate the hard tissue response
Microhardness test	Evaluate the implant surface in terms of scratch-ability
corrosion testing	Evaluate the surface of the implant in terms of survivability in oral like environment
Fatigue test	Give an estimation of fatigue life of the implant under the worse case
Corrosion fatigue test	To evaluate the fatigue life in real life environment

This model probabilistic avoids having to perform so many tests, being sufficient only when the manufacturer has achieved a design that meets the probability of failure desired. It is possible to predict the mechanical behavior that the implant will have before

placing it, and the dentist can be able to choose the one that is most suits to his patient in each particular case. The results obtained in the fracture compression test indicate that the maximum average load supported is 1000 N for the implants analyzed in diameter 4.1 mm, which is within the ranges accepted in the literature. When dental implants and their connections are subjected to physiological cyclic loads, with average loads under 400 N during 360,000 cycles, no cracks or fractures appear in them. Due to the random nature of fatigue in dental implants subjected to functional requirements, mechanical tests must be supplemented by random fatigue methods. The models analyzed by the finite element method confirm the previous conclusions and, therefore, constitutes a valid mathematical tool for the study of the mechanical behavior of the materials.

CHAPTER V

EFFECT OF 3-D CMP APPLICATION ON CORROSION PREVENTION

5.1 Introduction

The selection of the most suitable material for the fabrication of prosthetic structures on implants must be carried out taking into account their mechanical properties, their resistance to corrosion when combined with titanium and their biocompatibility. In this sense, noble alloys with a high gold content have shown an excellent resistance to corrosion thanks to the high thermodynamic stability of gold in the alloy, as reported by multiple studies, which has long been considered as the material of choice. choice for the manufacture of prostheses on implants. However, its high cost has led to the use of other alloys with different compositions, which have good mechanical properties and good cost-effectiveness, but its biocompatibility and resistance to corrosion are still a matter of controversy, since the combination of low corrosion resistance alloys with titanium can give rise to galvanic corrosion phenomena, even relating to the failure of the implant. The American Society for Testing and Materials includes in its standard ASTM G15-93 the definition of galvanic corrosion as the "acceleration of the corrosion of a metal due to electrical contact with another nobler metal or with a non-metallic conductor in an electrolyte of nature corrosive. " Galvanic corrosion means the destruction of the less noble metal, and thus, in implant-prosthesis systems, the release of ions into the medium could have adverse effects not only aesthetically (soft tissue pigmentation and discoloration of restorations), but also functional (reducing the resistance of the metal to fatigue) and with

greater importance possible biological effects derived from the dissolution of the components of the alloy, such as allergic reactions and possible bone destruction around the implants. Objective: The objective of the present study is to analyze the electrochemical behavior and Ions release in Hanks solution which a simulate fluids from the human body. The present surface treatments used for superficial mechanical treatment that is currently applied on commercially pure titanium dental implants (Ti cp) to increase its surface roughness, since this improves its fixation in the bone in the short and long term, as it has been demonstrated through various studies [67]. Likewise, in vitro studies have shown that cell differentiation and proliferation, and the production of bone matrix, are also positively influenced by the increase in surface roughness [67]. The optimum rugosity value has been studied to optimize the osteoblastic response and bone fixation, varying the roughness through the variation of the CMP process variables. The CMP treatment is considered as a good competitor against the treatment of the current choice which is BCP blasting treatment. Shot blasting consists of projecting particles of high hardness at high speed on the surface of the implant, the continuous beating of which is responsible for the plastic deformation of the surface, which remains rough. In addition, the treatment is adequate because it eliminates possible defects in the machining of the piece, cleans the surface of possible contaminants, and can increase the life to fatigue and resistance to corrosion under tension of the implant. But the blasting treatment presents a possible drawback derived from the chemical nature of the particles used to be projected against the surface of the metal to be treated, since due to the high energy in the impact, some of them are broken and remain embedded in the implant surface, even after cleaning, passivation and sterilization [188]. This fact can cause some of these particles to detach and pass to the surrounding tissues, hindering the mineralization adequate bone or stimulating adhesion and cellular

differentiation [188], depending on the nature of the particles. In addition, these particles can have an influence on other properties of the implant, among which its resistance to corrosion is noteworthy. The adhesion of the projection material on the surface causes physicochemical heterogeneity in the same, which, obviously, can be a clear conditioning factor in the response to the corrosive conditions to which an implant is subjected in the physiological medium. In the other hand the developed lab-setup for the 3-D CMP can give the desirable roughness to ensure the osseointegration without placing the bioimplant surface at the risk of sever plastic deformation and not to contaminate the bioimplant surface.

The potentiostatic and potentiodynamic studies allow to assess the corrosion behavior of metallic materials and the passivation behavior, subjecting them to a variable electrical potential in a physiological fluid at room temperature. The recording of electric current that circulates through the sample by varying the potential to which it is submitted, allows obtaining information on the resistance of the passivation layer of the material, the repassivation of the same, as well as its resistance to localized corrosion ("Pitting") and other aspects derived from its electrochemical behavior.

5.2 Electrochemical analysis on samples treated at various CMP conditions

5.2.1 Potentiostatic (current vs. time) scans

The excellent practical resistance to corrosion shown by titanium and its alloys is one of the main reasons for its use as biomaterials [20]. From the sixties, almost any type of implant or prosthesis made with stainless steel or chrome-cobalt alloys was redesigned with titanium or Ti6Al4V with great success. Much of the excellence of titanium as a

biomaterial is due to the passivation layer that forms on its surface, which protects it from electrochemical attack on the human body. This layer is composed of amorphous titanium oxides, from Ti_2O to TiO_2, with a variable thickness between 0.5 and 10 nm depending on the treatment, the surface finish, the medium, etc. [58]. The passivation layer forms naturally after a few milliseconds of titanium contact with a medium with oxygen present, although it can also be produced and made thicker by chemical and electrochemical treatments [189]. The passivation layer of titanium provides high electrochemical stability, as shown by the comparison of its potential-time curves with those of stainless steel or nickel base alloys. The stability of the titanium potential curve shows the electrochemical stability of the passivation layer, compared to the instability presented by other materials used as biomaterials.

The period of the potentiostatic scan was set to 1100 seconds with an input potential of 0 V vs. Eref (the real value shown during the test were ~ 90–100 μV which was negligible and assumed to be zero).

All the samples were dipped in DI water in the beginning of the experiments and the measurements were started. After a few seconds, different concentrations of H_2O_2 were added according to the desired molarity in the solution. Solutions with 7 different concentrations were tested (i.e. 0M, 0.001M, 0.01M, 0.1M, 0.2M, 0.3M & 0.5M). The total volume of the solutions was 150 ml in each case.

5.2.2 Potentiodynamic Scans

Cyclic potentiodynamic polarization curves of the studied materials were obtained following the ASTM G5 standard. This test realized by imposing an electric potential variable between the sample studied and the electrode of reference, which generates the

passage of a current between the sample and the counter-electrode. The imposition of the electrical potential, as well as the measurement of the circulating current, were carried out by means of a potentiostat Gamry 1000 Interface, Potentiodynamic scans were performed on the 3-D Ti surface treated implant samples in DI water at PH 6.5. The scans were collected at a range from -5V to 6V with a scan rate of 10mV/s and a step of 1mV for each point. Tafel data were calculated for each scan, which I_{corr} and E_{corr} were used to calculate the corrosion rate by the software. These tests allow to determine the corrosion potential and intensity, by extrapolation of the Tafel slopes from the obtained curves. They also allow you to determine the pitting potential, if exists, and the stability of the passivation layer, by studying the hysteresis of the cyclic curve obtained.

5.2.3 Ion release test

5.2.3.1 IN vitro analytical quantification by ICP-MS

To carry out the ion release test, Ti6Al4V titanium cylindrical bars and BCP dental implant were used, which were subjected to the processes under study. The cylindrical bars were subjected to etching and 3-D CMP and the third were used as it is “baseline”.

According to the standard ISO 16428:2005 [190] Hanks solution was used (With sodium bicarbonate, liquid, sterile-filtered, suitable for cell culture). This solution was used to simulate the effect of physiological fluids (blood serum). Each type of sample was prepared by cleaning process in the laboratory, following its internal protocol for Biocompatibility tests:

- Introduction of samples in 30% nitric acid for 30 minutes and subsequent rinsing with abundant water.

• Sonication for 10 minutes in a 10% aqueous solution of antiseptic and posterior rinse With plenty of water. The samples were placed in a horizontal position in 50 ML polypropylene tubes.

• Sonication for 10 minutes in acetone at 70% and Rinse back with distilled water.

• Sonication durante10 minutes in ethanol at 80%.

• Immersion in deionized water for 24 hours at 50 º C and drying after 120 º C for 1 hour.

• Introduction in Desiccator for 1 hour until ambient temperature is reached.

• Introduction in a 20% citric acid solution to A temperature of 45 º C for 30 minutes, as a passivation treatment.

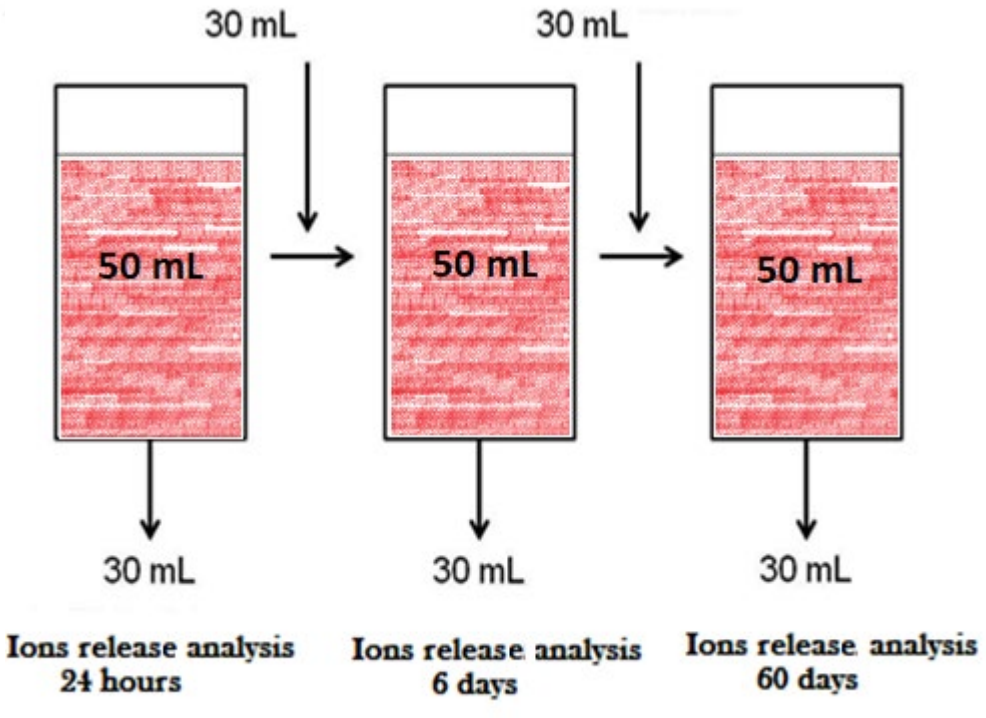


Figure 5-1 Outline of the Blood renewal simulation test.

Once the samples were ion release tested *In vitro* Figure 5-1:

- Each sample was introduced in 50 ML polypropylene tubes and 30 ML of the Hanks solution were added, leaving the entire surface in contact with the solution. The ratio between the solution volume and the surface area of the exposed sample was 10 ML cm^{-2}, as set out in ISO 8044:1999 [191].
- The samples were incubated in an atmosphere of room temperature for a total of 67 days.
- In order to simulate the blood renewal that occurs In vivo [192], 30 ML were extracted from the Hanks solution at 24 hours.

5.2.3.2 Ion-Releasing

To follow the evolution of ion release over time, two more extractions were made, one at 7 days of commencement of the test (or 6 days after the first extraction), and another at 67 days of commencement of the test (or 60 days of the second extraction). Resetting with 30 ML of new solution, as shown in the diagram in Figure 5-1.

The released ions were quantified using the mass Spectrometry technique (ICP-MS), which is based on the measurement of the ions generated by an inductive coupling plasma (ICP) in a tested sample and measured in a mass analyzer type Quadrupole. The reactions that take place in the plasma are produced by different mechanisms using for this technique the transfer of load between the ionized gas and the sample.

A Perkin Elmer, Model ELAN 6000, which shown in Figure 5-2. The instrumental parameters used are collected in table 5-1. A multi-elemental working solution with a concentration of 1 mg/L was prepared by successive dilutions of the Mono elemental certified solutions of 1000 mg L from Al, Cr, Fe, Mn, Mo, Ni, Si, Ti, V and Zr. Each of the

patterns was prepared in a final solution of ringer at 0.2%, which were added 50 M g/L of Rh, in and Y solution, as internal patterns to correct the instrumental drift and possible matrix effects.

Figure 5-2 Mass spectrometry equipment with ICP ionization source.

The three replicates of each sample type were analyzed below. The elements analyzed were Al, Cr, Fe, Mn, Mo, NOR, Si, Ti, V that correspond to the materials in study and Al, Si and Zr that are part of the particles with which the surface is shot. To obtain the Plasmogeno gas, argon was used with a richness of more than 99.999%.

Table 5-1 ICP-MS operating and instrumental conditions.

Parameter	Value
Instrument	
Nebulization Chamber	Cyclonical, No Baffle, SCP SCIENCE
Sample Extraction Cone	Nickel, orifice diameter 0.75 mm
Cone of Skimmer	Nickel, diameter orifice 1mm
Parameters of the Plasma	
Radio frequency generator	40 MHz
Power incident	1300 in
Argon plasma flow	15 L min^{-1}
Argon Nebulizer Flow	1.05 L min^{-1}
Argon Auxiliary Flow	1 L min^{-1}
Sample input Flow	1 mL min^{-1}
Inside diameter of torch nozzle	2,0 mm
Setting the mass spectrometer	
Measuring system	“Peak Hopping”
Resolution	High
Integration time	600 ms
Timeout	100 ms
Number of readings per replica	1
Number of replicas	6

Each doped sample was analyzed in six separate trials, estimating the accuracy as the percentage difference between the observed concentration and the expected value (% SD). The accuracy is expressed as the percentage of the coefficient of variation (% CV). Acceptance criteria for accuracy and accuracy according to ICH (1996) were adopted with the criterion that % SD and % CV averages should not exceed 15% of expected values.

5.3 Results and discussion

5.3.1 Potentiostatic Scans and Film Growth on Titanium Surface

Figures (5-3 - 5-9) illustrate the current vs. time relationships of the potentiostatic scans on Ti-based implant surfaces in the presence of H_2O_2, where each curve represents the response of 5 samples at a selected concentration. It can be seen that increasing the concentration of H_2O_2 in the solution increases the passivation of the surface, which is interpreted through the decrease in the measured current value (Im) as a function of time until it reaches a steady state. At this stable region, it is believed that the oxide film has grown continuously to completely passivate (in the case of a "pore free" surface oxide film) or limit current conductivity (in the case of a "porous film") on the surface. For both Ti-based implant surfaces, the current values continue to drop as the oxidizer concentration increases. Comparing the figures, Ti shows lower passivation current values with low oxidizer concentration. Titanium oxide (Titania) has a better surface coverage in higher oxidizer concentrations. In general, the higher oxide growth rates are attained with higher solution molarity of the oxidizer [193]. The slopes in the Figures (5-3 - 5-9) also show that a faster passivation mechanism is happening on the Ti surface, which can also be attributed to the self-passivation ability, continuous and pore free structure of the TiO_2 film with 0.1 M oxidizer. Therefore, oxide layer provides an excellent resistance to corrosion as indicated by the low-level electrical conductivity. This is very important in CMP as it enables the topographic selectivity.

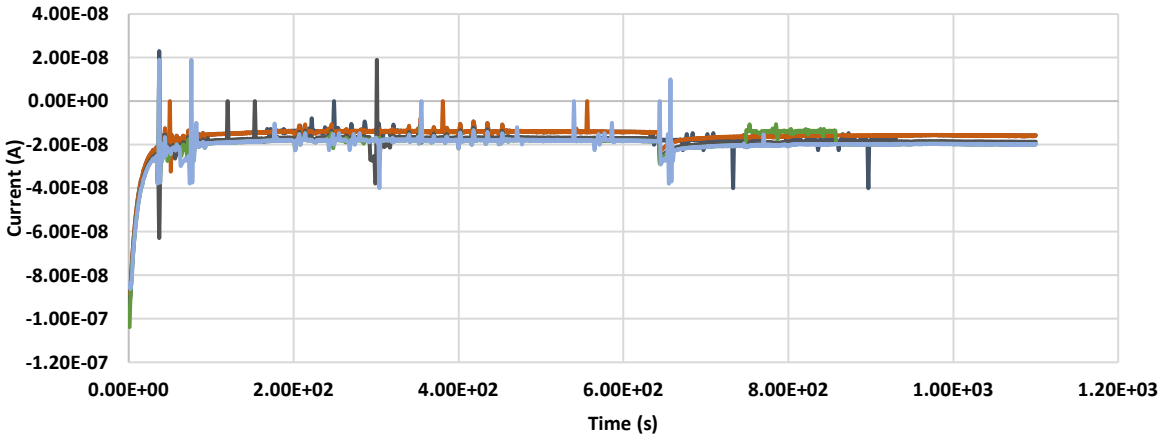


Figure 5-3 Potentiostatic test for five Ti implants treated by 3-D CMP with 0M H_2O_2.

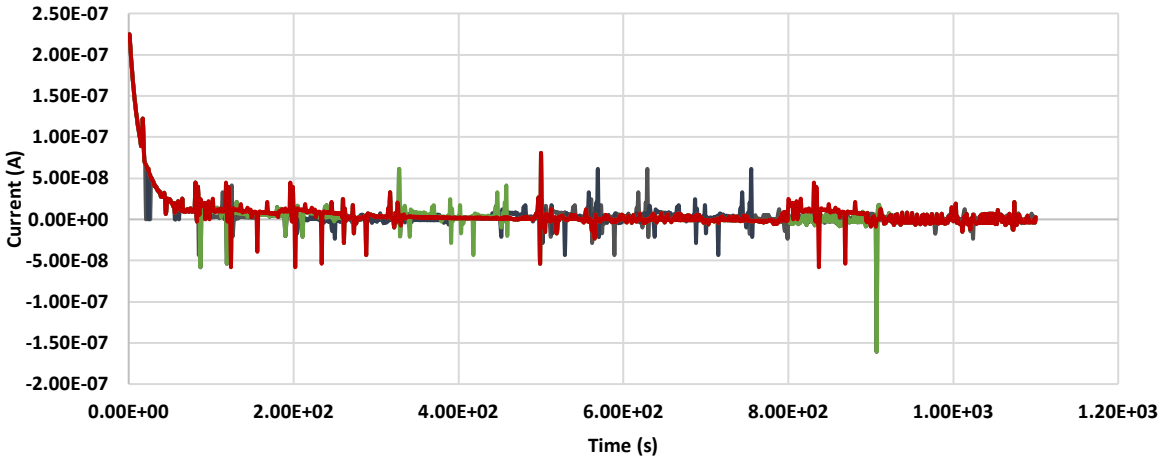


Figure 5-4 Potentiostatic test for five Ti implant treated by 3-D CMP with 0.001M H_2O_2.

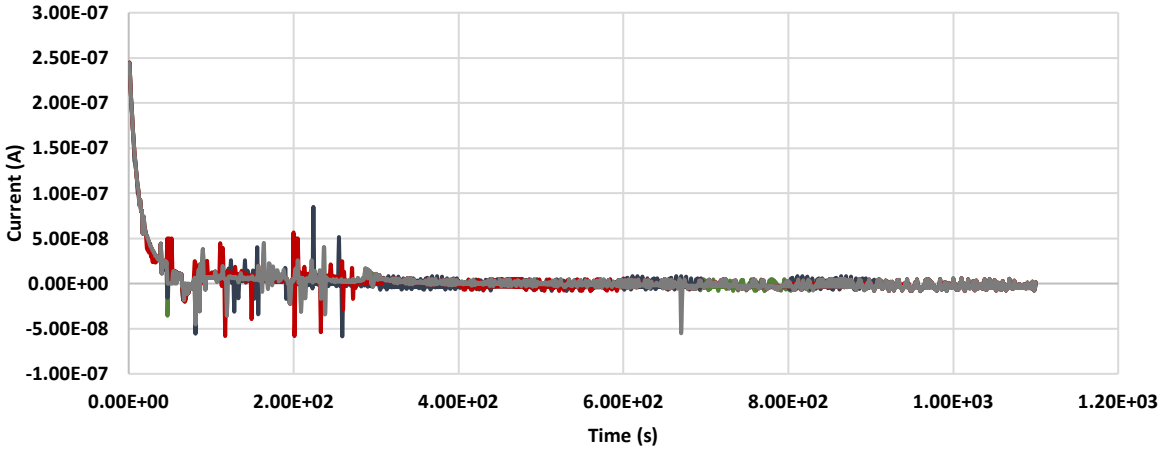


Figure 5-5 Potentiostatic test for five Ti implant treated by 3-D CMP with 0.01M H_2O_2.

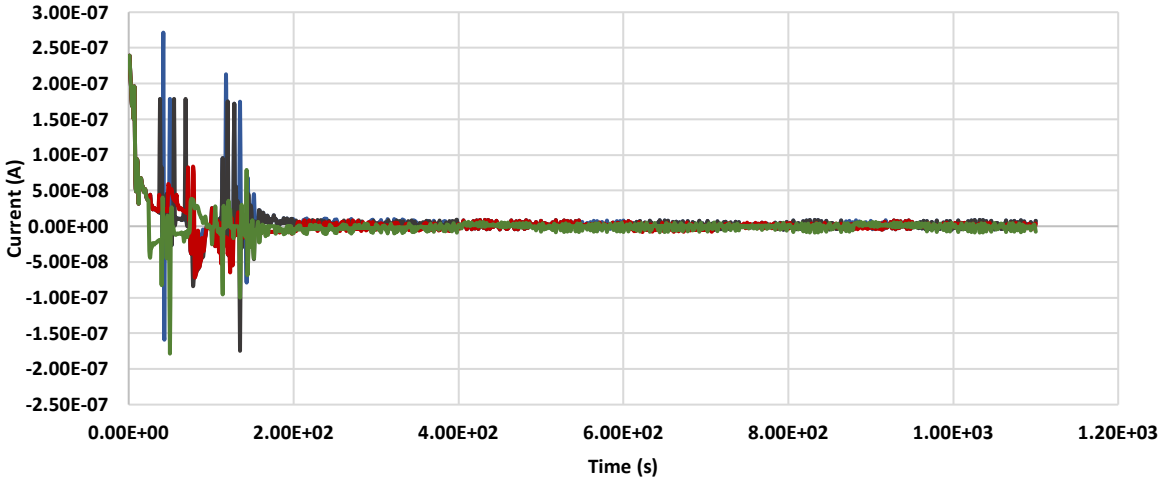


Figure 5-6 Potentiostatic test for five Ti implant treated by 3-D CMP with 0.1M H_2O_2.

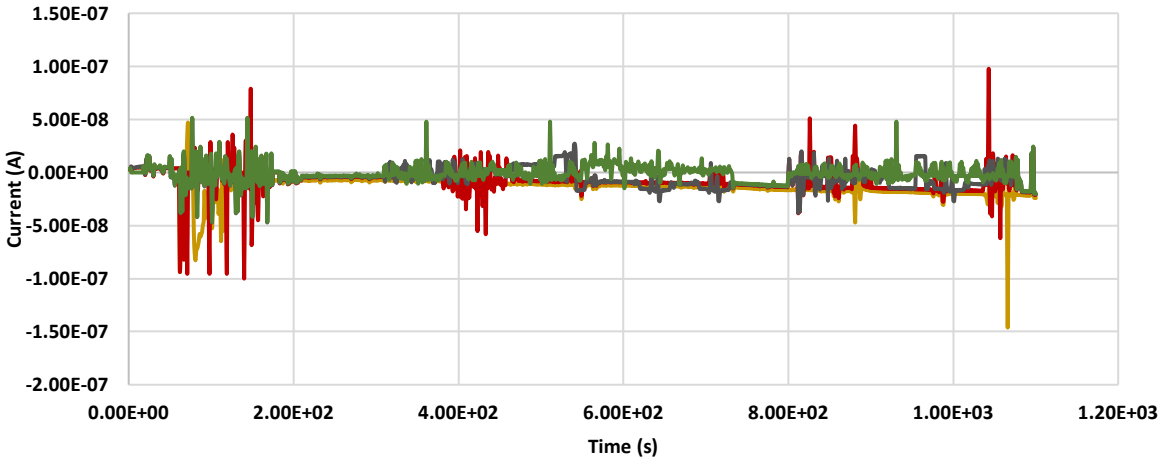


Figure 5-7 Potentiostatic test for five Ti implant treated by 3-D CMP with 0.2 M H_2O_2.

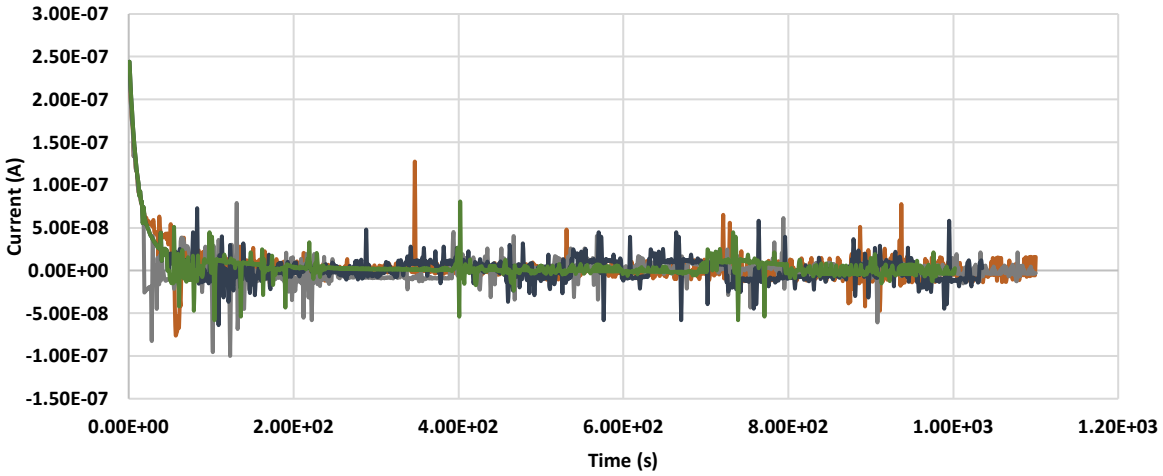


Figure 5-8 Potentiostatic test for five Ti implant treated by 3-D CMP with 0.3 M H_2O_2.

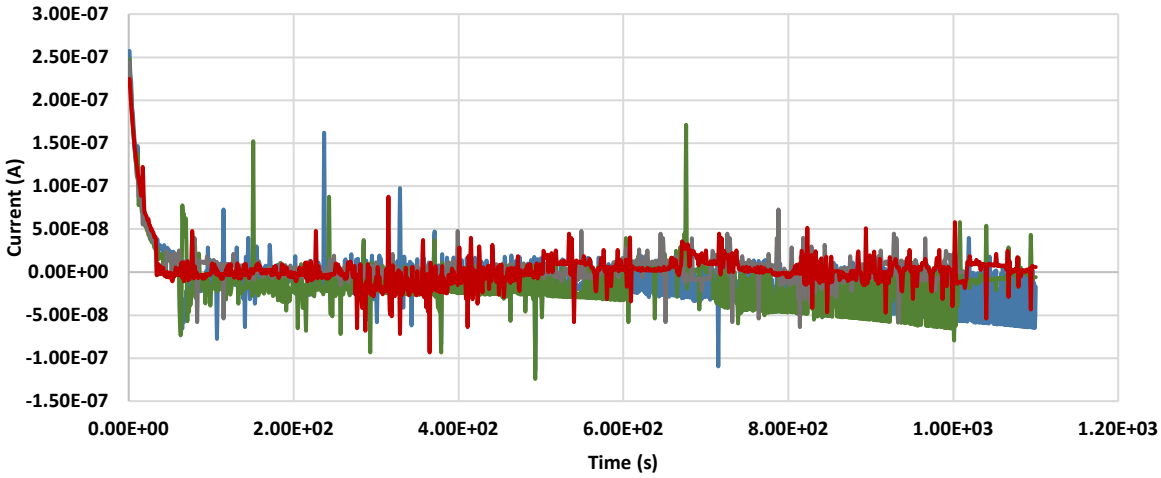
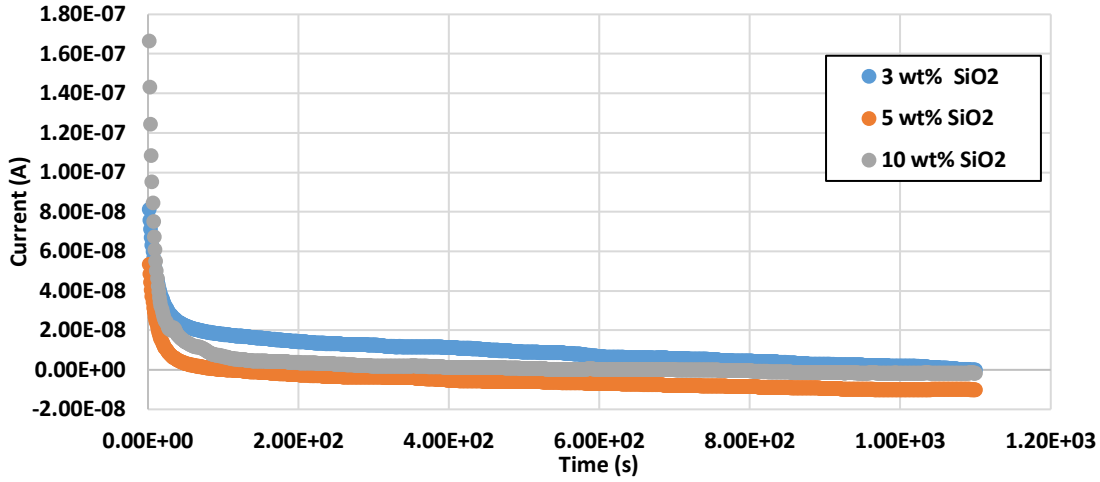
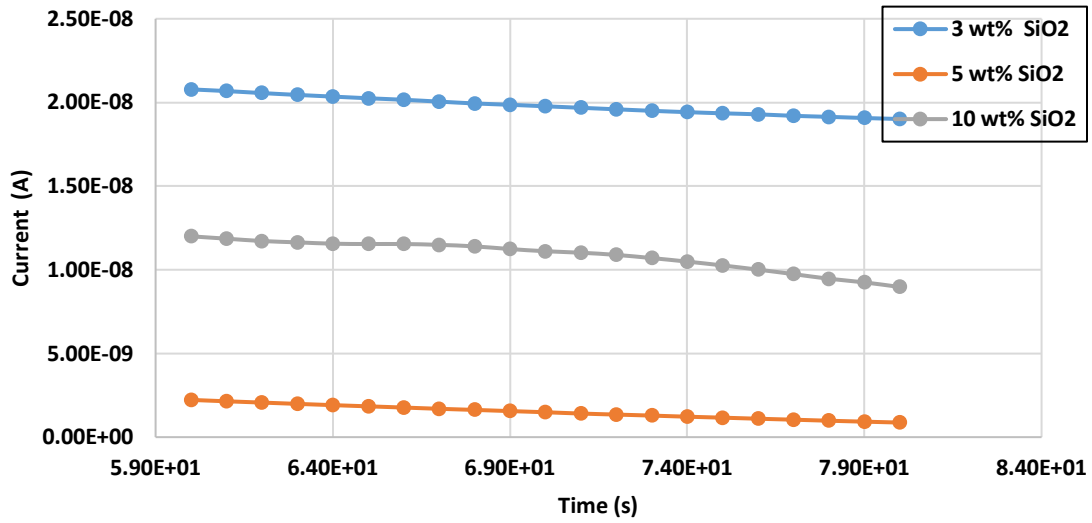


Figure 5-9 Potentiostatic test for five Ti implant treated by 3-D CMP with 0.5M H_2O_2.

Regarding the solid loading concentration effect, Figure 5-10a shows the potentiostatic measurements in which initially all the samples have positive current values with fixed oxidizer concentration of 0.1 M H_2O_2. The aim of this test is to determine the desired SiO_2 concentration that can reduce the time to reach stability. in figure 5-10b it can be seen that implementing the 3-D CMP with %5 solids loading gives the fastest and highest passivation on the Dental Implant surface. The Dental Implants surface passivation behavior from time 600 sec to 800 sec shows that the %5 solids loading can give the highest decrease in current within 200 sec.



(a)



(b)

Figure 5-10 **(a)** Potentiostatic test for Ti implant treated by 3-D CMP with 0.1M H_2O_2 and different solids loading **(b)** The Dental Implants surface passivation behavior from time 600 sec to 800 sec.

5.3.2 Effects of P-B (Pilling–Bedworth ratio)

Pilling-Bedworth (P-B ratio), in metal corrosion, is the ratio of the primary cell size of a metal oxide to the size of the primary cell of the conforming metal (from which the oxide is resulted). Based on P-B ratio, it can be said if the metal is likely to passivate in dry air by forming a protective oxide layer.

In this work with 0.1M H_2O_2 concentration the P-B ratio was kept in the range between 1-2 where the oxide coating provides a protecting effect against further surface oxidation. While in lower oxidizer concentrations the P-B ratio is less than 1 where the oxide coating layer created is too thin, likely broken and provides porous and no protective effect. Finally, in higher oxidizer concentrations > 0.1M the P-B ratio exceeded the value of 2 where the oxide coating layer chips off and cracks which provides no protective effect as shown in Figure 5-11.

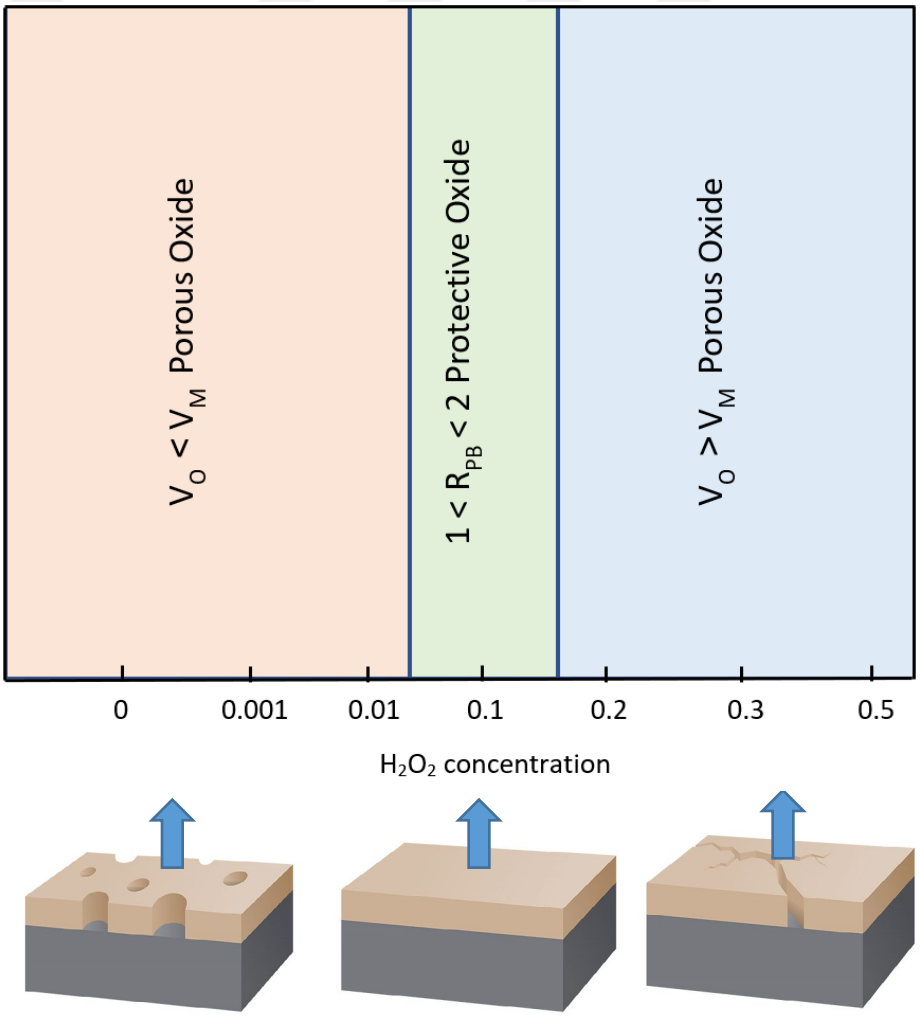


Figure 5-11 Oxidizer concentration effect on P-B ratio.

5.3.3 Potentiodynamic Polarization and Corrosion Calculations

Figures 5-12 shows potentiodynamic polarization curves of Ti-based implant surfaces dipped into the H_2O_2 solutions at the selected concentrations. The anodic and cathodic portions of each curve correspond to the current conductivity through negative to positive potential sweep and between those is the region where passivation current corresponds to the lowest point along the x-axis.

Corrosion/passivation data are extracted by using the Tafel extrapolation plots whereI_{corr} is calculated through a series of steps involving Tafel constants βa and βc, respectively, to calculate the corrosion rate of the sample [194]:

$$I_{corr} = \frac{\beta a \beta c}{2.3(\beta a + \beta c)} \frac{\Delta I}{\Delta E}$$

The corrosion rate was calculated using the expression [195]

$$Corrosion\ Rate = \frac{0.13\ I_{corr.}(E.W.)}{Density}$$

The data are tabulated as given in Table 5-2.

Table 5-2 Tafel extrapolation data of Ti-based implants potentiodynamic curves.

Tafel plot variables	**0 M H_2O_2**	**0.001 M H_2O_2**	**0.01 M H_2O_2**	**0.1 M H_2O_2**	**0.2 M H_2O_2**	**0.3 M H_2O_2**	**0.5 M H_2O_2**
I_{corr} (µA)	13,00	9,200	9,580	4,21	25,60	9,870	10,40
E_{corr} (mV)	-236,0	-22,90	46,50	-284,0	67,60	122,0	2,050
Corrosion Rate (mpy)	5,203	3,687	3,839	1,930	10,27	3,954	4,185

The highest I_{corr} is realized at 0.2 M concentration, which complies with higher corrosion rate as illustrated. Higher corrosion rates could indicate higher removal rates and faster dissolution rates. Also, a high I_{corr} value, which also means a high corrosion current density. The lowest corrosion rate value is 1.930 mpy attained by the 0.1 M oxidizer concentration with I_{corr} of 4.21 μA and which is determinable to obtain the removal rate selectivity.

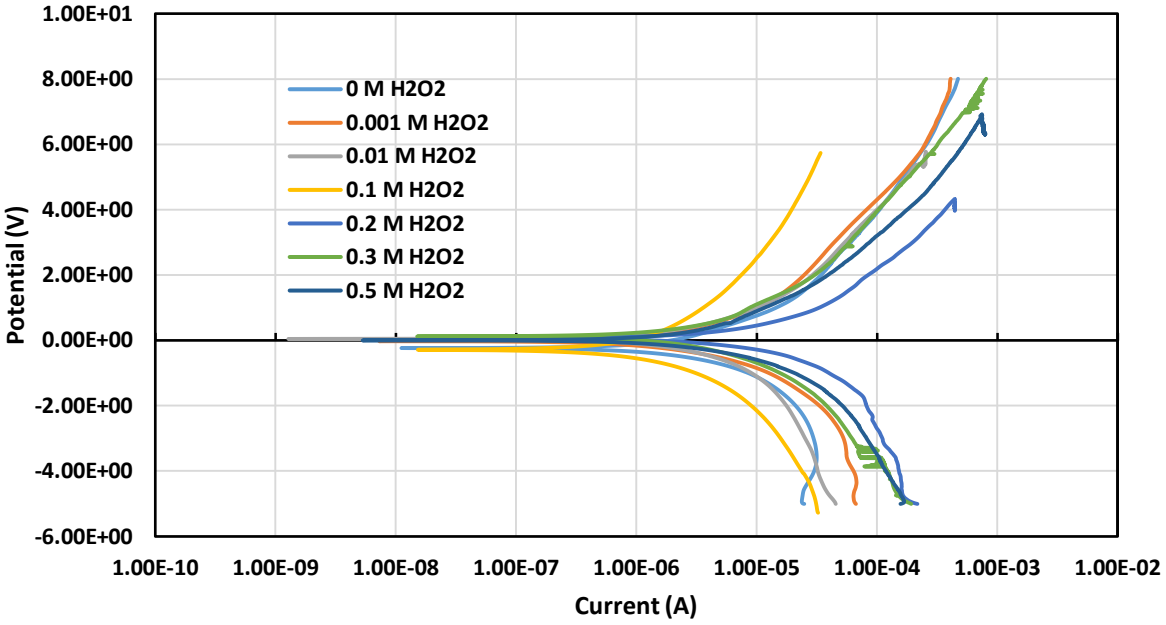


Figure 5-12 Potentiodynamic polarization curves of Ti-based implants in H_2O_2 solutions at different concentrations.

Potentiodynamic polarization was done according to the standard procedure that often used for laboratory corrosion testing shown in reference [196].

5.3.4 Ion release evaluation

5.3.4.1 Ion release in CMP treated samples

The concentration of the released ions of the CMP samples, is below the limits of detection Figure 5-13, which is attributed to the surface of the Ti6Al4V spontaneously formed a stable passive layer that acts as Barrier between the medium and the substrate [196] and gives the alloy a good corrosion resistance. The nature of this passive layer controls the release of metal ions and their associated effects [81]. Several authors [61, 159, 197] have shown that this film of oxide, of thickness between 0.5 and 10 nm [198], contains predominantly TiO_2 amorphous and small amounts of suboxides of TiO and Ti2O3 Near the metal-oxide interface, also detecting aluminum oxides (~ 26% in mass of Al) and vanadium (~ 1% in mass of V). This layer of passivation acts on the surface as a barrier against liberation of ions [81].

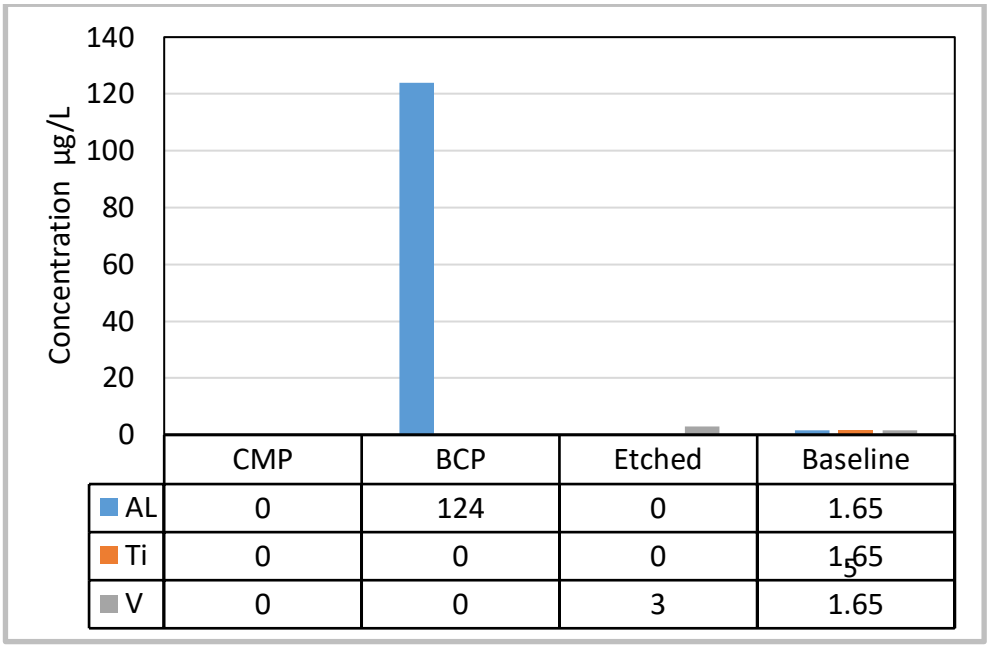


Figure 5-13 Ion release for CMP treated implants after 60 days.

However, in some special conditions such as: phase transformations induced by stress fields, texture formation and plastic deformation, it is possible to obtain a certain anomalous behavior. It is shown that the CMP treatment aimed at developing metastable, homogeneous and firmly adhered oxide layers on the surface of dental implants can modulate ion release.

This work has verified the absence of release of ions in CMP treated dental implants as a result of the development of a layer of oxide of greater thickness and stability that is generated spontaneously.

5.3.4.2 Ion release in BCP treated samples

Surface roughness increases with the severity of the process and, as a result, increases the area of the surface available for ion release. It is therefore to be expected that a rough surface facilitates such reactions. However, the solutions from the blasted samples were not detected titanium or vanadium ions, which may be related to the thickness, firm adherence and homogeneity of the oxide layer formed with the BCP treatment. On the other hand, the constituent ions of the high fraction of blasted particles that were embedded in the surface were detected. As mentioned above, this is particularly relevant in the case of aluminum, given its known toxic potential. The release occurs in quantities and velocities that, while small, must be taken into account by its known toxic potential, mutagenic and genotoxic, as well as carcinogenic [122]. Figure 5-13 after 60 days are detected 124 $\mu g\ L^{-1}$, which indicates a decrease in speed over time, being the average ion release a day of ~ 2 $\mu g\ L^{-1}\ Day^{-1}$. The absence of release of titanium ions in the BCP blasted samples, is in accordance with a work done by Okazaki and Col. [199], in which it studies the influence of PH in this alloy. It shows that the amount of titanium released at PH 4 and above is

attenuated sharply. In the present work the PH of the Hanks solution used oscillates between 6.4 and 6.5, which would explain that no ions are detected.

5.3.4.3 Ion release in Etching treated samples

Ti-based samples processed with etching only release a small amount of vanadium, (approximately 3 µg L-1, which half a day would be 0.05 µg L-1 Day-1) Figure 5-13. The rest of the ions are below the detection limits. Although below the detection limits established as dangerous. This small release could be related to increased roughness. Considering these results, it can be said that the processing with Etching could be an alternative to generate roughness of some special clinical interest without risk of releasing harmful elements.

5.3.4.4 Ion release in Machined samples

The concentration of all the ions of the Ti-based samples processed with machining is below the detection limits (5µg/L) Figure 5-13. This is due, on the one hand, that the roughness reached in the surfaces is much lower than in the samples treated with BCP particles or with etching and, on the other hand, that by the CMP treatment where a layer of titanium oxide (TiO_2) is generated.

5.4 Summary

Corrosion and ion release is particularly important when dealing with toxic (Al, V, Cr) or allergens (Ni) elements [200]. In vitro ion release from BCP blasted and etched samples increases in comparison with 3-D CMP samples. It is related to the increase of

surface roughness and embedded particles, which act as stress concentrators, allowing the ion release in simulated physiological solution. The effect is more pronounced when BCP blasting. The surface features have a high influence on the corrosion behavior due to surface structural inhomogeneities that would increase the density of pitting [201]. Moreover, the elements constituting the particles are also released, as the particles are in direct contact with the solution. When samples are 3-D CMP treated, the oxide layer formed on the surface plays a protective role against corrosion and ion release; however, some elements forming part of the oxide are easily released, since they are in direct contact with the solution. On the other hand, ions that are part of the particles are less released because the smaller particles are protected by the oxide layer. Despite the higher surface roughness generated by etching, the absence of embedded particles reduces the ions release by these samples. Machined samples also present decreased ion release, which is associated with the smaller roughness, absence of embedded particles, as well as with the formation of an oxide layer thicker than that generated with BCP, which are firmly attached.

CHAPTER VI

CHARACTERIZATION OF TITANIUM BASED DENTAL IMPLANTS TREATED WITH VARIOUS SURFACE STRUCTURING METHODS

6.1 Introduction

The surface quality of the dental implant depends on its physicochemical and topographic properties Table 6-1 [202]. Both are relevant in the biological behavior of Ti c.p.

Table 6-1 Properties and information necessary to describe the quality of the surface of an implant.

Property	Type of information
Chemical composition	Atomic composition Chemical state of the elements
Structure / Order Disorder	Crystallinity Inclusions Vacancies Grain limits
Morphology Texture Rugosity Shape	2D and 3D shape of the surface details Specific area Porosity
Surface energy	Wettability Adsorption Surface energy
Electric	Surface potential
Mechanics	Elasticity / plasticity Residual stresses

The particular importance of the fact that the first events that occur after implantation (contact with blood, adsorption of proteins and other biological molecules, cell adhesion, etc.) are due to the interaction between the biological environment and the surface of the

synthetic material. Likewise, the response of the biological reactions and the particular pathways that the cells and the living organism choose and, as a consequence, the sequence of events that lead to a better or worse osseointegration, depend to a large extent on a series of superficial properties. However, it is still not known in depth which one or more of these factors are the most clinically relevant; and how they influence the body's response. This is the reason why the main purpose of this Doctoral Thesis is the surface of Ti c.p., as well as the modifications that can be carried out in it through different treatments and processes. The properties of a surface that can potentially modify the biological behavior of the material are many and varied (Table 3). These properties allow us to define exhaustively the quality of the surface after the changes that are operated on it depending on the manufacturing processes or the time of exposure to the biological environment.

6.2 Physicochemical and topographic surfaces of titanium for use in implantology.

6.2.1 Physicochemical properties

Knowledge of the physicochemical properties of Ti c.p. It involves the exhaustive study of the properties of the titanium oxide layer that grows on it naturally and spontaneously, in contact with air and other media. This layer protects the metal against the uncontrolled increase of its oxidation, undesirable chemical and biological reactions, and corrosion. As a consequence, chemical and biological agents do not interact directly with the metal, but with this stable layer of oxide.

A series of different stoichiometries of titanium oxides can be identified on the surface of Ti c.p. (Ti_3O, Ti_2O, Ti_3O_2, TiO, Ti_2O_3, Ti_3O_5 and TiO_2) [203]. The most stable of

these is TiO_2, with titanium in its oxidation IV state.

From the analysis that of all these properties it can be concluded that [204]:

1. The highly protective nature of the oxide layer, which is generally only a few nanometers thick, is a consequence of its natural integrity and chemical stability over a wide range of PH's, electrolytes and body fluids.
2. The surface titanium oxide is quickly repassed after a local loss of passivation, as for example by the effect of mechanical wear.
3. The low solubility of the hydrated titanium oxides, together with the even lower tendency to form charged titanium compounds are very relevant aspects for the biocompatibility of titanium.
4. A certain physical-chemical similarity can be assumed between the clean surface of the titanium oxide and the water as a consequence of the extensive hydroxylation / hydration of the oxide and its moderate hydrophilicity. This involves a certain interaction of the surface with the shell of water that forms around biomolecules, such as proteins.
5. The dielectric constant of the oxide is similar to that of water. This fact causes, as it happens in the aqueous fluids, the reduction of the polarization effects and the shielding of electrostatic forces between charged particles.
6. The low surface electrical charge, due to the fact that the isoelectric point of the titanium oxide is only slightly below the physiological PH, is believed to reduce the risk of strong interactions between the surface of the titanium and the domains of proteins.
7. The "natural ability" to form calcium carbonate-phosphate layers on the surface of titanium oxide through specific processes of chemical exchange with the constituents of body fluids (blood, interstitial fluid), generates, after some time in vivo, the modification of the synthetic material / biological material interface, by forming a layer a few

nanometers thick.

6.2.2 Topographical properties

The surface topography (roughness and texture) can be considered the most important of the surface properties that influence the response of the organism to the presence of the implant. At least, it is the best known and studied, both in vitro and in vivo [167]. It is recognized that, for example, increase the roughness of Ti c.p. above the one obtained when being mechanized, the implant improves the osteoblastic response in vitro and the mechanical fixation in vivo. In fact, the surfaces of Ti implants c.p. commercial, in most cases, have surface topographies specially designed and manufactured according to the express knowledge that the topographic details, both micrometric and nanometric scale, is a relevant quality factor. The different superficial treatments whose object is to modify the topographic and physicochemical properties of Ti c.p. with the aim of being employed in the manufacture of dental implants. Therefore, it is very important, first, to determine and evaluate with rigor and precision the topographic characteristics of Ti c.p. in order to obtain reliable quantitative data and, in the second instance, to be able to optimize them with respect to their biological relevance. However, neither one nor the other has been put into practice in the past.

6.3 Experimental approach

6.3.1 Materials and methods

In the present work dental implants made of Titanium grade 5 (Ti-6Al-4V) have been investigated, which is widely used in biomedical applications such as orthopedic and dental implants. Titanium grade 5 has excellent tensile strength properties at room temperature,

excellent strength / weight ratio and a useful sliding resistance up to 300 ° C (570 ° F) Table 3-2. The resistance to breakage and crack propagation is excellent. Like most titanium alloys, Grade 5 has excellent corrosion resistance in most natural environments and in many industrial processing environments. Table 3-3 illustrates the Chemical composition of Ti6Al4V (in wt. %) dental implants.

Table 6-2 Chemical composition of Ti6Al4V (in wt. %) dental implants

Chemistry %	V	Al	Fe	O	C	N	H	Y	Ti	Remainder Each	Remainder Total
Min	3.5	5.5	--	--	--	--	--	--	--	--	--
Max	4.5	6.75	.3	.2	.08	.05	.015	.005	Balance	.1	.3

Table 6-3 Typical mechanical properties for well-processed Ti-6Al-4V alloy are shown below.

	Density g/cm3	Young's Modulus GPa	Poisson's Ratio	Yield Strength MPa (Tensile)	Ultimate Strength MPa (Tensile)	Hardness Rockwell C	Uniform Elongation %
Min	4.429	104	0.31	880	900	36 (Typical)	5
Max	4.512	113	0.37	920	950	--	18

All the materials were supplied by the implant manufacturing company MODE Medical in Istanbul, Turkey [205], in the form of dental implants 3.3 and 4.1 mm diameter and 8 and 10 mm length. The samples used in the tests of Ions release test were also supplied and mechanized by Mode Medical, in form of cylindrical bars and BCP dental implants respectively.

The 3-D dental implant sample showed in Figure 6-1a properly shaped by machining

before surface modification with different surface treatments. Silica slurry with an average particle size of 20 nm obtained from (NYACOL, Taiwan) with PH 3 was used for 3-D CMP. Hydrogen peroxide (Sigma Aldrich with purity 34.5–36.5 wt%) was utilized as an oxidizer during CMP experiments. The basic silica slurry containing H_2O_2 with different concentrations and with (5, 10, and 15 wt%) solids loading was used with adjusted PH using NAOH solution to get PH of 9 for the process stability. The 3-D CMP was performed using polymeric brush and pouring slurry prepared as mentioned above on the samples as they were polished with polymeric brush. Figure 6-1b the chemically etched samples were prepared by dipping in Hydrogen peroxide (%37 wt%) for 30 minutes Fig 1.c. The BCP surface treated samples were provided by the Mode Medical Company prepared by jetting calcium derivatives (Biphasic calcium phosphate) Figure 6-1d.

The Sol-gel coating with nano size TiO_2 technology was another applied method to the implants surface in order to evaluate nano-coating effect on the surface properties. Titanium dioxide nano film deposited using a sol-gel route according to the literature [206]. All chemicals used in the experiment obtained from Sigma-Aldrich .$TiOSO_4$ was used as precursor, 0.5M Ti source dissolved in 0.5M H_2O (DIW) and 20M Ethanol and mixed well under continuous stirring and PH adjusted wih HNO_3 (0.1M) as PH=1.23. Ti source undergo the hydrolysis reaction as given below;

$$TiOSO_4(s) + 2H_2O\ (aq) \rightarrow 2H^+(aq) + SO_4^-(aq) + TiO(OH)_2(s)$$

TiO_2 transparent solution was obtained according to hydrolysis reaction and implant samples dipped into this solution with Dip Coater tool (PTL-MMB01) was used for the TiO_2 nano film deposition. The abutments to be coated with the TiO_2 were lowered into the coating solution and then withdrawn at specific speed(140) and distance (100) range. The samples were dried in air using an oven combined with dip coater tool, at 200°C for 1 hour.

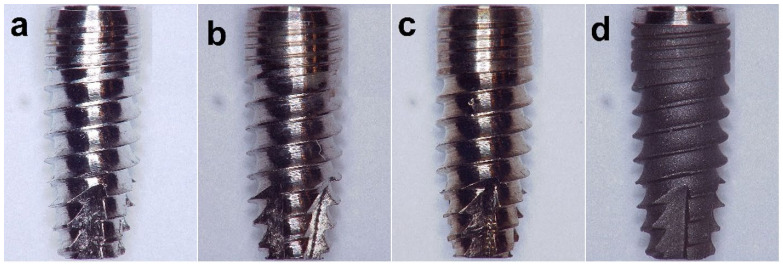


Figure 6-1 Micrograph of **(a)** Machine shaped, **(b)** CMP, **(c)** Etched, **(d)** BCP dental implant.

6.3.1.1 Sample Preparation

In current study mini-implants were used 8 mm in height which considered as a more manageable for more number of surgical situations. This fact generates the challenge of manufacturing implants with lower nominal surface, but capable of achieving satisfactory mechanical stability, on all in the long term. The samples were prepared by machining (used as baseline), BCP, chemical etching and chemical mechanical polishing. The baseline and BCP treated samples were provided by Mode Medical, Turkey. All the samples were cleaned in ultrasonic bath with ethanol for 10 minutes and rinsed with DI water then dried by blowing air before they were characterized.

6.4 Results and Discussions

6.4.1 Comparison of surface engineering methods.

6.4.1.1 Machined implants

Machining is one of the elementary methods to produce an implant surface with improved bone-implant response. The production of dental implants process simply involves the removal of unwanted material by machining with a cutting tool to remove undesirable parts from the sample to produce the predesigned CAD shape. and it is also called as the turning or milling process. After machining, manufactured implants are submitted to cleaning procedures to remove unwanted imperfections which considered as contamination. These techniques generally produce a surface with defects as can be seen in Figure 6-2, containing grooves, ridges and trace of the tool that is used for manufacturing. The presence of defects can cause elevated surface roughness that creates mechanical resistance through bone interlocking. Furthermore, these grooves may reduce the cell growth and can result in longer healing times after the implantation process [207]. This process enables relatively smooth surfaces with arithmetical mean roughness (Ra >0.2 μ). This value of surface roughness and surface free energy imped plaque formation on the surface of dental implants and its other components.

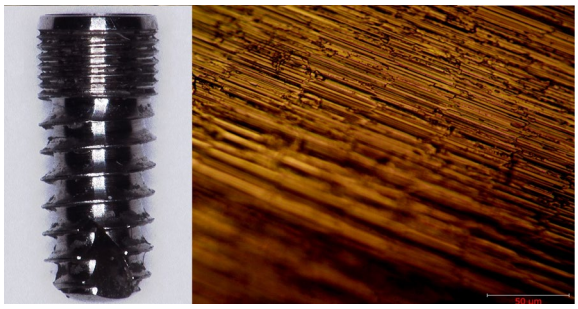


Figure 6-2 Microscopic images for baseline machined dental implant.

Implant material surface finish is qualified through surface roughness value as a factor as it affects the rate of osseointegration. Various roughness scales have been published with different measurement procedures for machined surfaces and optimal roughness for hard tissue implants is proposed to be in the range of 1-10 μm [207]. Literature showed that a turned surface roughness is around 0.96 μm with 8.6 μm average peak spacing. The baseline surfaces were competitive but revealed a drawback of slowing down of all the biological processes. On these bases dental implants which have average rough surfaces (Ra>0.2 μ) are recently widely used; they are most efficient from a biological point of view allowing a more rapid bone-implant adhesion and cell spreading. Besides these investigations, experimental results have demonstrated that for a better bone fixation of the implants an average surface roughness (Ra) around 1.5μm can be identified as a rough surface according to Wennerberg [208]. Machined titanium implants have been widely used for a long time and they perform successfully in clinical applications in the long-term. Nevertheless, this surface finishing method has not resulted in a good osteointegration for all the samples. Due to their lower resistance to removal torque, pull-out force, so machined dental implants are becoming less preferable and unavailable [209].

6.4.1.2 Acid etched implants

The other alternative method for surface structuring method is the chemical etching which involves the immersing of the implant into an acidic or basic solutions. Acid or basic solution corrodes the implant surface and forms micro pits and potholes with a certain form and these pits diameter ranging between 0.5 to 2 μm [210]. The chemicals that maybe used in acid etching includes various strong acids such as HCl, HF, HNO3 and H2SO4. The concentration of the chemicals used for this treatment defines the surface structure produced

by which, dipping time and the solution temperature. Depending on the resolution kinetics of the oxide film this process produced in optional removal of the protective oxide layer and may goes to remove some of the base material. The advantage of this treatment is it does not lead to any mechanical stresses on the material surface, if compared to the other surface structuring methods [211].

This method is applied in this study by dipping the dental implants in H_2O_2 solution for 30 minutes.

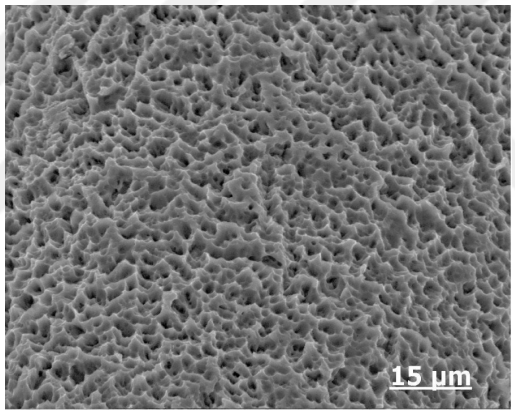


Figure 6-3 Acid etched Ti-based implant surface.

This method has an advantage of providing a rougher surface in micro-range which increases the osteogenic cells formation process on the implant surface [212]. In addition, the other advantage of etching surface treatment is creating a homogeneous surface roughness Figure 6-3.

Despite these optimizations, acid etching can induce hydrogen embrittlement of the titanium and decrease fatigue resistance through forming micro cracks on the material surface.

6.4.1.3 BCP implants

The processing of blasting the implants with calcium derivatives (Biphasic calcium phosphate) particles, whose characteristics are presented in Table 3-4, was carried out by the company Mode medical with its commercial team, making impact on the surfaces of the materials a stream of particles through air flow with a pressure of 350 kPa for approximately 1 minute.

Table 6-4 Biphasic calcium phosphate characteristics

Properties	
Chemical formula	$Ca_3(PO_4)_2$
Molar mass	310.18
Appearance	White amorphous powder
Density	3.14 g/cm^3
Melting point	Liquifies under high pressure at (1391 °C)
Solubility in water	0.002 g/100 g

Figure 6-4 shows the fully automated process is observed by doing the blasting in which the particles impact on the surface of a dental implant. Table 6-4 shows the Biphasic calcium phosphate general properties, which also called the RBM (Resorbable Blast Media) treatment [66].

Figure 6-4 The fully automated BCP blasting process [205].

The phase is necessary to be determined to its application in implants because it leads to a worse mechanical resistance and against corrosion if not controlled. In addition, their ferromagnetic behavior could promote the movement or detachment of the shot-blasted implant during magnetic resonance imaging (MRI) imaging.

6.4.1.4 CMP

It should be mentioned that the CMP treatment have been developed in previous work to introduce an alternative technique to treat the titanium-based implants surface. There are few studies devoted to quantifying the biomechanical properties behavior simultaneously with the topographic changes in surface of the metallic bioimplants, in addition to a lack of experimental techniques with simple and well defined procedures that can offer the Integral and simultaneous evaluation of this relationship [94].

Furthermore, the modifications in the superficial chemistry of a metallic substrate allow to improve its physical, chemical and biological properties. The techniques used for this purpose include surface treatments and the deposition of coatings. Surface treatments such as thermal oxidation, ionic implantation, anodizing or acid or alkaline treatments alter the surface composition of the material. With The purpose of improving its resistance to wear and corrosion as well as its biocompatibility [213]. For example, the thermal oxidation of Ti6Al4V alloy results in the formation of an oxide layer on its surface that decreases ion release and improves adhesion and proliferation of osteoblastic cells (bone forming cells) [214]. On the other hand, the treatments of anodization on this same alloy induce an increase in the activity alkaline phosphatase (enzyme indispensable for the formation of the bone) of the cells osteoblastic [213]. While these surface treatments lead to changes in the chemical composition of the substrate, the deposition of coatings allows to generate surface

compositions different from those of the base material without altering their mechanical properties Intrinsic and improving its resistance to wear or corrosion.

6.4.2 Topographic evaluation

The surface roughness values of the implants polished with the developed setup and the other surfaces are plotted in Figure 6-5. It can be observed that the surface treatment can significantly affect the surface topography and thus lead to altered tissue response. When analyzing the implants of the four groups of surfaces, the different aspects in the topography of the surfaces are observed due to the different treatments carried out on the implants.

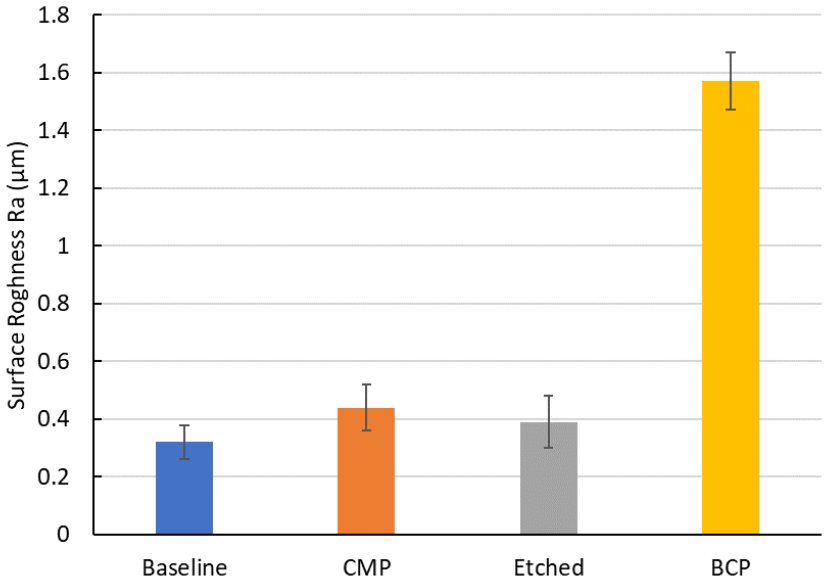


Figure 6-5 average surface roughness (Ra) for different surface treatments.

In the implants of group 1 (the Baseline) with 0.32 µm roughness which is an average value of roughness. According to some literature investigating the biofilm formation on different treated dental implants, the peri-implantitis complications are lower for machined samples between 3 groups or pre-treated implant systems [215].

In group 2 (the CMP group) implants it is possible to identify the degrees of roughness on

the surfaces of the implants, consequent to the treatment of titanium with CMP treatment; rugosity of 0.446 μm 'was observed. In this method, titanium dioxide layer is stimulated by using an oxidizer to promote the oxide film generating process.

Group 3 the treatment in this case by etching, it is possible to observe uniformity of the surface with 0.39 μm, regular and homogeneous pattern of the porosities is verified, without evidence of flat areas also observing the elimination of contaminants from the surface.

Finally, in last group (BCP samples) shows the highest roughness value with 1.57 μm. The BCP treatment reduces the effect of particle contamination on the tissue response. BCP is a mixture of HA (hydroxyapatite) and (beta tricalcium phosphate) presented in the form of abrasive particles, a rugged surface with high bio-compatibility. The treatment is carried out by means of subtractive sandblasting. This operation consists in jetting the BCP particles to the surface of the dental implant, thus creating micro-impaction. The changes in topographic features have a significant influence on the series of biological events that lead to the acceptance of the implant by the host tissue [169], from the adsorption of proteins until the mineralization of the extracellular matrix of the bone tissue, going through the adhesion, proliferation and differentiation of both osteoblasts and osteoclasts. All these entail a greater speed in the healing processes and, therefore, a faster and biologically more effective osseointegration can be achieved [170].

In the other hand, Figure 6-6 shows surface roughness measurements for the sol-gel coating surface treatment, it can be seen the effect of nano-silica sol content on the surface topographical structure by increasing average roughness values.

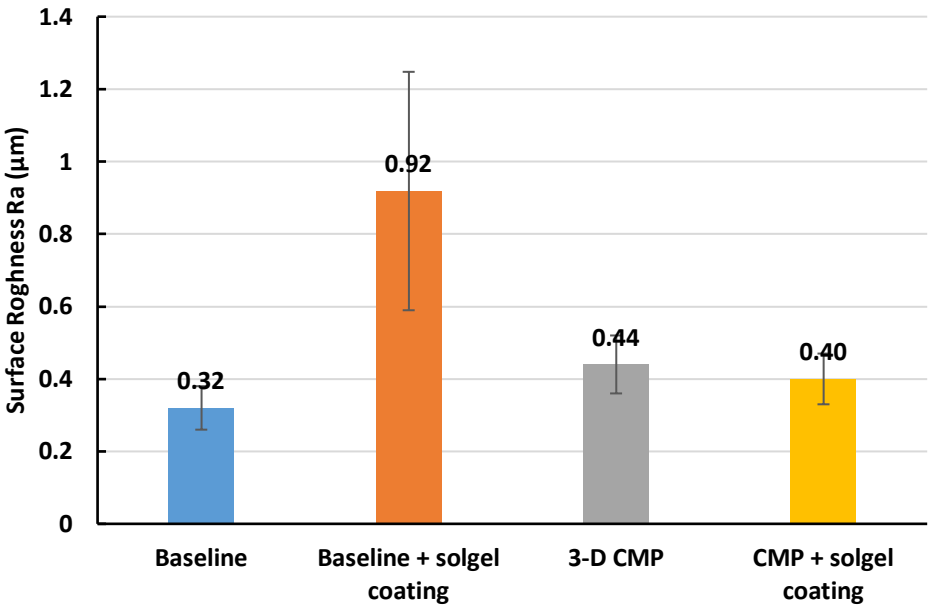


Figure 6-6 Surface roughness values after implementing the sol-gel coating.

Implementing the sol-gel coating gives a new structure which called a hierarchical structure due which the max peak of the surface morphology will be increased Figure 6-7.

Figure 6-7 The surface roughness structures.

6.4.3 Wettability evaluations

Figure 6-8 summarizes the wettability behavior elucidated by the contact angle measurements taken with DI water droplets on the titanium-based implant samples with different surface treatments.

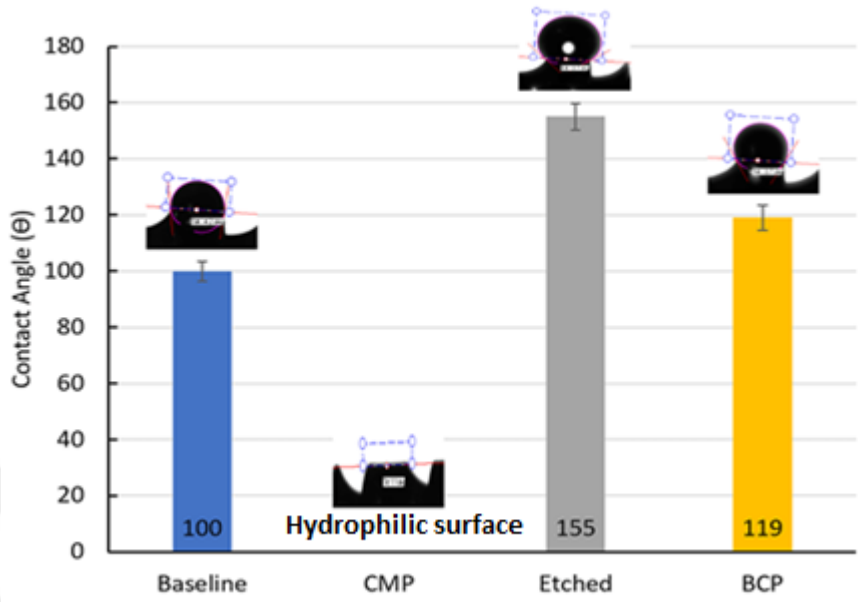


Figure 6-8 Surface wettability of the baseline and different surface treated Ti based implants.

The relatively high contact angle measured for the baseline samples, which was 100º is believed to be depending on both the surface topography and the chemical nature. According to the Cassie-Baxter model [216], when the water droplet stays on top of a solid texture with air trapped underneath, a hydrophobic behavior can be observed such as we observe with the machined samples. Since the surface topographic nature is irregular, it tends to trap air in between the water droplet and the implant surface. On the other hand, the sample treated with 3-D CMP resulted in full spreading of the water droplet. This is due to the fact that CMP treatment results in refreshed surface to be exposed to the water droplet with a greater number of dangling bonds making the surface become more hydrophilic with smoother interface. Implementing 3-D CMP with 5wt% slurry solids loading resulted in a more homogeneous wetting regime and facilitated the absorption of DI water on the implant surface. The contact angle is reported to be as low as super hydrophilic surface, although we know that this measurement is because of insufficiency of the optical measurement of contact

angle on threaded hydrophilic surfaces, on which the liquid spreads and the contact line cannot be recognized. On the other hand, the contact angle measured for different samples treated with BCP possessed higher contact angle of 119º. The micrograph given in Figure 6-1d shows the rough surface which is the main reason behind the higher hydrophobicity of the BCP. treated samples. Finally, chemical etched implants resulted in higher hydrophobicity with contact angle of 155º on the average. The enhanced hydrophobicity is believed to be caused by the presence of patterned morphology along with the low surface energy due to the longtime of etching (30 min dipping) in 37wt% H_2O_2 despite the increased surface roughness values. In order to take the microstructure of the implant into account for this evaluation, control experiments were conducted on Ti-based plate samples that had been treated respectively. Figure 6b illustrates the results obtained from the contact angle test on the Ti-based plate samples. The wettability behavior of the plates was identical to that of the pretreated dental implants. The slight difference in CA values was due to the planar and cylindrical-threaded liquid interfaces that were used for the plates and dental implants respectively [217].

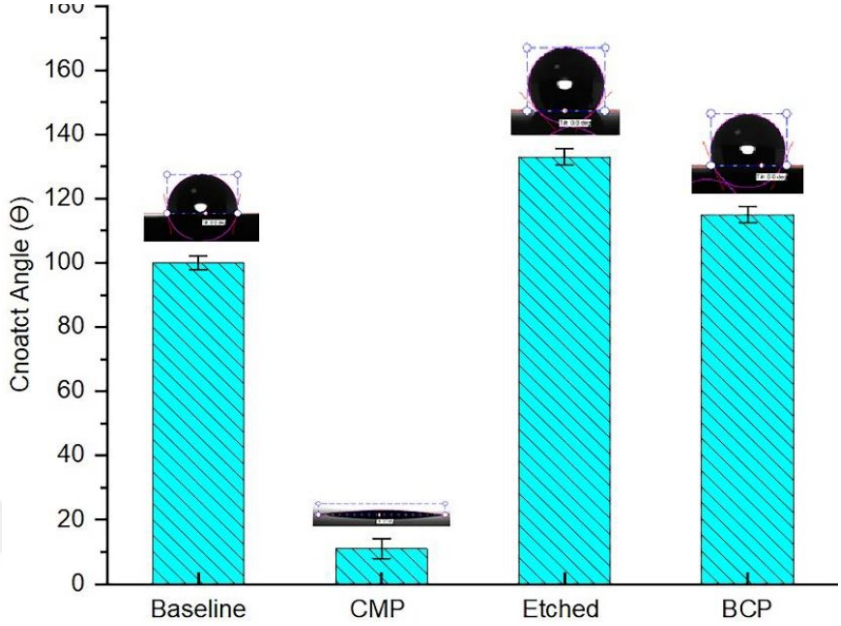


Figure 6-9 Surface wettability of the baseline and different surface treated Ti based plates.

Likewise, the sol-gel coating also evaluated in terms of surface wettability, by using same procedure was used to evaluate the other surfaces. Figure 6-10 illustrates the contact angle comparison between the baseline, baseline sol-gel coated, 3-D CMP and 3-D CMP coated surfaces, in which the topological rough surface generated by the colloid film produced a hydrophobic character with a contact of 115º due to the increase of the surface roughness trapping the air inside the surface grooves without penetrate them [218].

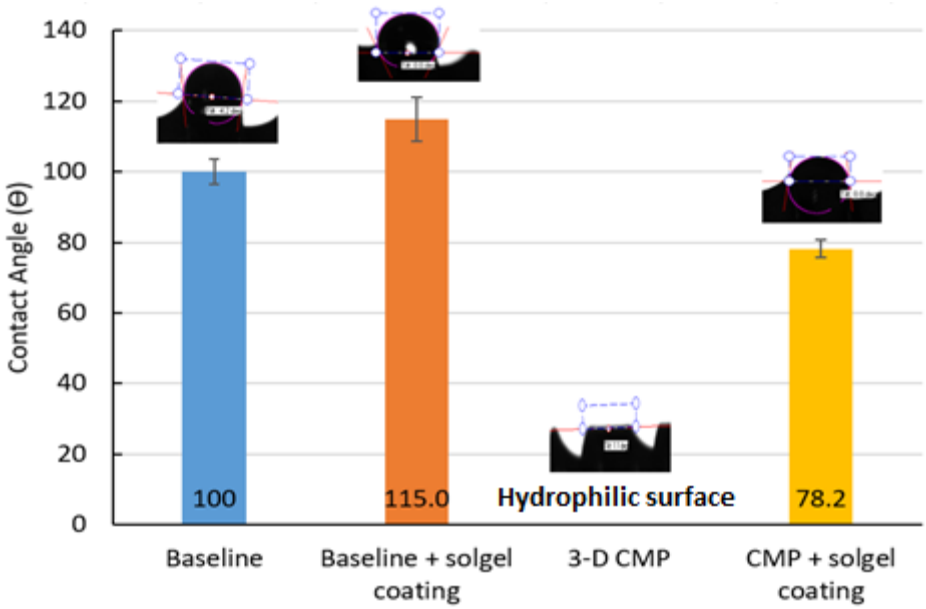


Figure 6-10 Contact angle measurements for sol-gel treated samples as compared to baseline and 3-D treated samples.

While a slight hydrophilicity with a contact angle of 78º is conducted from implementing the sol-gel coating on a 3-D CMP treated surface which indicates a change in chemical composition of the surface which is one of the dependent factors that affect on the surface wettability.

6.4.4 Potentiodynamic evaluation

Table 3-5 shows potentiodynamic polarization results of Ti based implants with the modified surfaces. Corrosion/passivation data are extracted by using the Tafel extrapolation plots where I_{corr} is calculated through a series of steps involving Tafel constants βa and βc, respectively, to calculate the corrosion rate of the sample [194]:

$$I_{corr} = \frac{\beta a \beta c}{2.3(\beta a + \beta c)} \frac{\Delta I}{\Delta E}$$

The corrosion rate was calculated using the expression [195]

$$Corrosion\ Rate = \frac{0.13\ I_{corr}.(E.W.)}{Density}$$

where E.W. = equivalent weight, I_{corr} = current density in μA/cm2, and density in g/cm3. The corrosion rates observed are in the order Etched > BCP > Machined > CMP. The highest I_{corr} is attained at Etched sample, which corresponds to a higher corrosion rate as illustrated. Higher corrosion rates could indicate higher dissolution rates. To prevent Peri-implantitis and irritation, the corrosion rate of a metallic implant should be less than 2.5×10^{-4} mm/year [219].

Table 6-5 Corrosion parameters for Potentiodynamic scan for the titanium-based samples with different surfaces.

	Baseline	**CMP**	**Etched**	**BCP**
Tafel plot variables	**Titanium implant Tafel data**			
I_{corr} (μA)	4,52	4,21	13,00	8.93
E_{corr} (mV)	-266,0	-284,0	-381,0	-212,0
Corrosion Rate (mpy)	2,068	1,930	5,933	4,089
Corrosion Rate (mm/y)	0.053	0.049	0.151	0.104

Furthermore, in biomedical applications, titanium is known to have good corrosion properties because of the stable, smooth and strongly adherent passive oxide film forming rapidly on the metal surface [69]. Since resistance to corrosion is directly proportional to the oxide layer formation, a strong passive film formation on the metal surface enhances resistance to corrosion. It follows from this that the worst situation is the prevention of passive layer formation for a biomedical metallic material. The concentration of the metal

ions released into the solution is related to the nature, composition and thickness of the metal oxides and adherence force to the alloy [117].

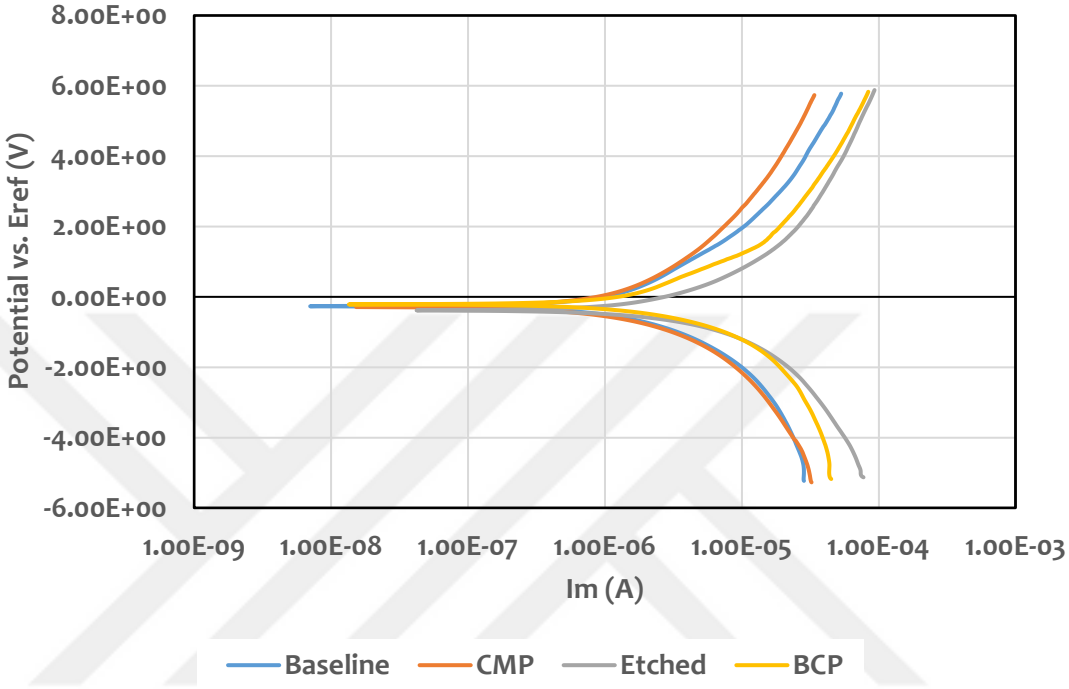


Figure 6-11 Potentiodynamic curves of Ti Implants with different surface treatments.

The increase in the thickness of the surface oxide layer is correlated with a greater corrosion resistance. A potentiodynamic test is commonly employed to measure a material's resistance to corrosion. This test determines the electrical potential at which a material begins to corrode. The measurement is called the pitting or breakdown potential. After passivation in the CMP treated implants have showed significantly higher breakdown potentials than those that were unpassivated surfaces Figure 6-11.

6.4.5 Mechanical Performance Evaluation

6.4.5.1 Microhardness test

The results of the microhardness testing of all four samples are shown in Figure 6-12.

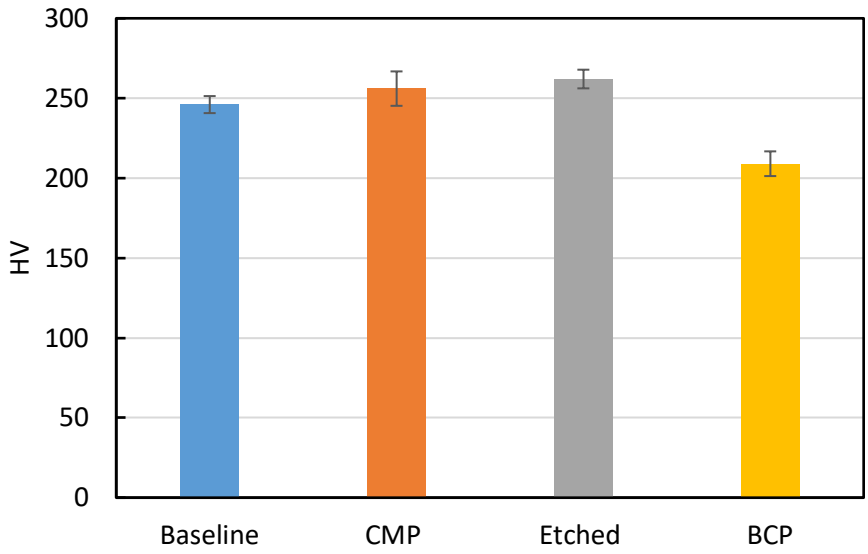


Figure 6-12 Vickers microhardness test results of the four treated samples.

Etched Ti based dental implant samples had a higher hardness than that of CMP treated samples (2.62 versus 2.56 GPa) and these samples had a higher hardness than that of BCP treated samples (2.09 GPa). For the BCP treated samples, it was necessary to place a 1000 gm of load in order to produce a wide enough indentation that would allow for accurate measurement of the diagonals as shown in Figure 6-13. Testing of a 280 HV baseline machined sample provided by the manufacturer of the microhardness testing equipment using the same test procedure and equations used to measure the hardness of the three test samples resulted in a measured hardness of 246 HV. Thus, the hardness measurements reported here are most likely within 0.12% less than their actual values.

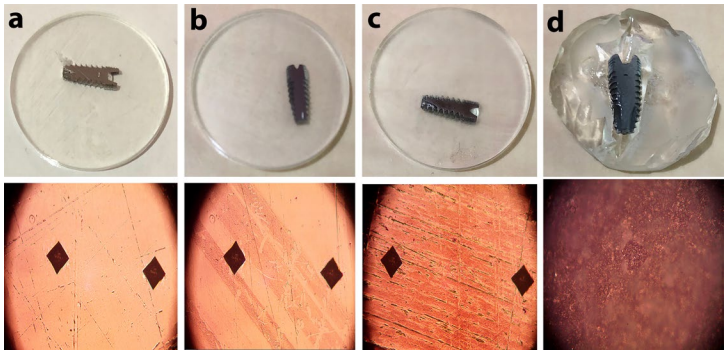


Figure 6-13 Vickers indentation (X50 magnification): (a) Baseline, (b) CMP, (c) Etched, (d) BCP samples.

6.4.5.2 Effect of surface topography on pull-out strength

The vertical pullout strength of each surface treatment was measured in five experiments Figure 6-14.

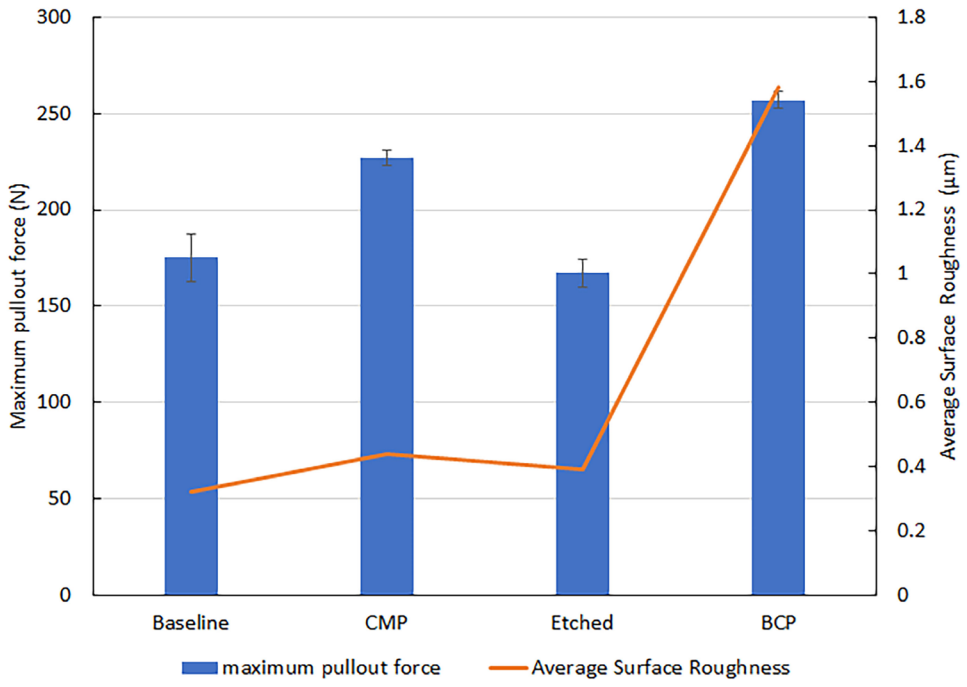


Figure 6-14 maximum pullout force for different surface treatments.

The BCP implants exhibited a greater vertical pullout strength of (257 N) than did the

CMP (226.8 N) and machined (175.32 N) implants. However, the etched implants were significantly lower than the other surfaces with (167 N). The extracted data demonstrate that relatively rougher implant surfaces have increased bone-to-implant contact tendency and require greater forces to break the bone-implant interface as compared to smoother surfaces. The aim of this test is to evaluate the treated surfaces and to determine if differences existed in the primary stability of implants with relatively smooth surfaces compared to implants having roughened ones.

According to the fact that the biological response of hard tissue cells (bone cells) is more effective with rough surfaces than smooth ones [3]. Z. Ozdemir et al. have observed that the best cell viability and attachment on CMP treated samples [69]. Consequently, this explains the high pull-out results obtained from the 5wt% solid loading CMP treated samples as shown in Figure 6-15 due to the high bone cells adhesion to the pretreated surface.

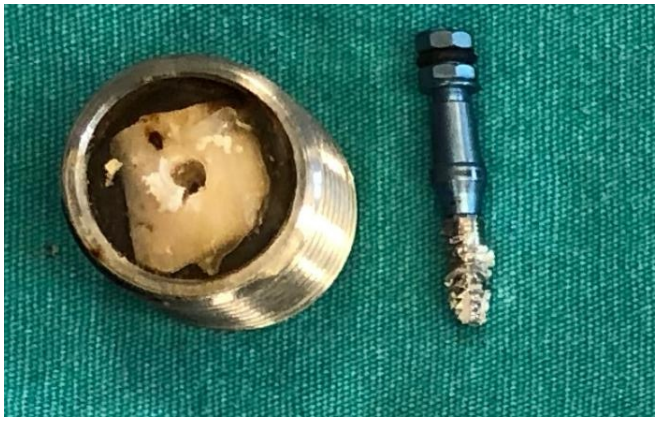


Figure 6-15 Bone cells viability and attachment to CMP treated samples.

With the presence of the great influence of the surface roughness on bone-forming process which has been demonstrated in previous studies, it was expected that the surface roughness will play the major role in determining the value of the pull-out force, but due to the significant difference between the two values of the average surface roughness of the

BCP and CMP treated surfaces it seems there is another factors should be taken into account when the subject comes to determine the implant mechanical anchorage. These factors include, bacteria attachment, the PH drop in bone-implant interface due to peri-implantitis, and the bioimplant surface wettability all these factors have a big impact on the biomechanical response. Thus, achieving the mechanical stability is a process linked to the existence of unified factors, including the surface mechanical and chemical properties, and the specific biological response.

6.4.5.3 Removal torque

The importance of the implant primary (mechanical) stability at different time points is to evaluate the long-term implant survival and successful clinical outcome. Therefore, the purpose of this test is to evaluate implant primary stability of pre-treated implants and to give an assessment to overall success rate of surface treated dental implants. A secure and successful bone-implant integration is positively associated with the accretion of the contact between the implant and the bone hard tissue stimulated by implant surface rugosity, allowing for faster bone-implant adhesion levels [184]. Figure 6-16 illustrates the removal torque test results which were in typical values, the peak of which was assumed to be the failure torque of the bone-implant interface. The length of the implant and the amount of bone-to-implant contact were the determinants for interface strength in cancellous bone. The results show that the longer implants with 10 mm height can give greater removal torque values due to the larger surface area of bone-to-implant contact.

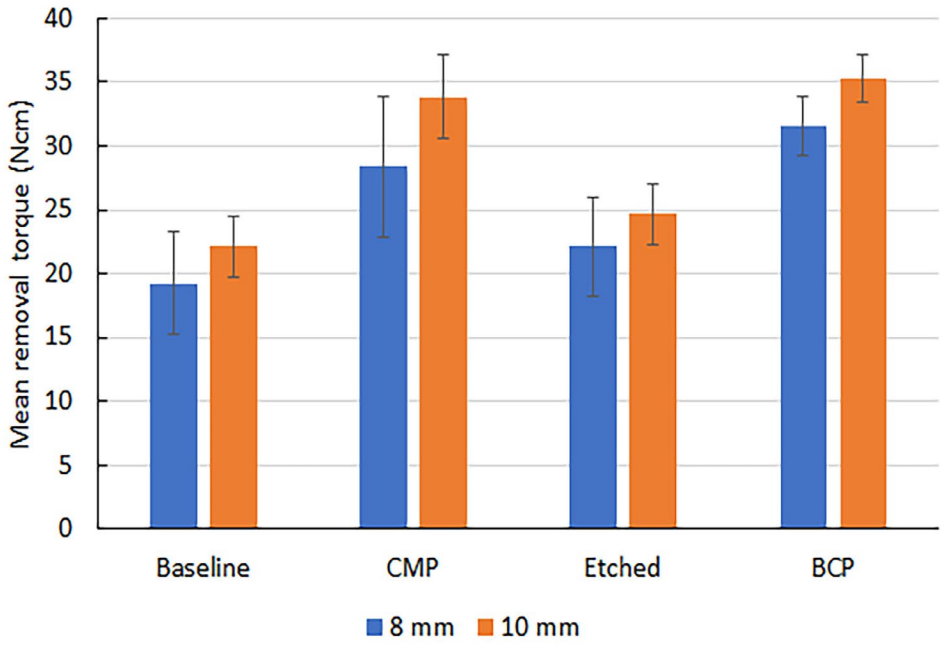


Figure 6-16 Comparative removal torque mean values between implants measuring 8 and 10 mm in length.

Figure 6-17 shows the surface roughness influence on removal torque values in which the CMP treatment increases the implant surface roughness as compared with machined surfaces and this being one of the fundamental principles for ensuring the improved osseointegration of the current surfaces.

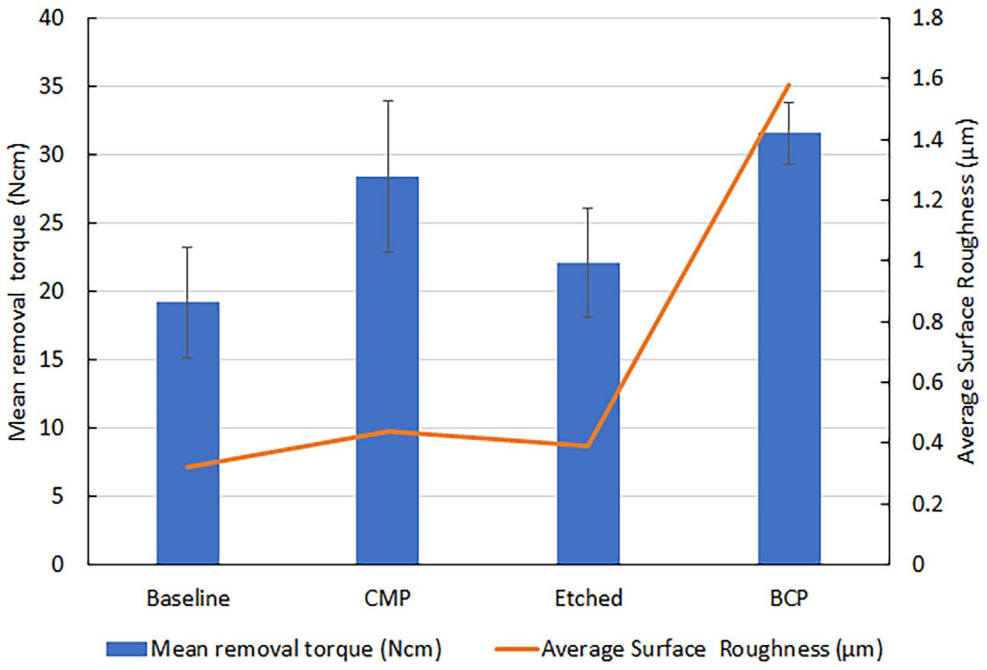


Figure 6-17 The mean removal torque values for different surface treatments.

The data indicate that CMP is a good alternative to commonly implemented implant surface treatments with optimum results comparable to those obtained by other surfaces and paving the way for possible clinical application in the context of early and immediate implant loading. Furthermore, and as described previously the high removal torque can be affected by the high adhesion behavior of the bone cells influenced by the surface chemical properties rather than the surface topography. In another words, we can conclude that the surface roughness is not the predominant factor that contribute in mechanical anchorage.

6.5 Conclusion

The aim of the presented study was to characterize the surface-related properties that are closely related to surface topography for the dental implants prepared by four different surface treatment techniques. Vickers microhardness, pull-out and removal torque tests were subjected to the machined, blastinized (BCP) and etched samples and these surfaces were

compared to the samples produced by the new 3-D CMP technique. Furthermore, the wettability, topographical and electrochemical characterization of the produced surfaces were performed for pre and post surface treatments. Microhardness, corrosion potential (E_{corr}) and corrosion current density (I_{corr}) of the produced surfaces were evaluated and the results obtained indicate that the application of the 3-D CMP improved the corrosion resistance of the implant surface, although the microhardness did not change significantly. The anchorage strengths were evaluated for the implants treated with the four different techniques in terms of their vertical pullout strengths and removal torque. The 3-D CMP treatment increased surface roughness as compared to the baseline machined and etched surfaces and this being one of the fundamental principles for ensuring the improved osseointegration of the implant surfaces. The obtained results showed an increase of bone-implant contact with the surface roughness increase. Identically the results showed that the surface roughness and wettability values of the 3-D CMP surface treatment enhanced with decrease in contact angle values which shows that there is an optimal level of surface roughness where a good wettability or hydrophilicity due to high surface energy and small contact angle (less than 90°) occurred. Implant surface properties are likely to be of specified connection to the chemical and biological response they elicit when implanted in the early healing stages after implantation. In this sense, CMP treatment technique is very interesting because it is able to modify only the outmost layer of the material which is exposed to body fluids, allowing for instance to change the way a surface will interact with the tissue and make sure that the bulk properties such as mechanical resistance will remain intact and, even more, become better. Furthermore, implementation of 3-D CMP with a certain percentage of oxidizer concentration gives the highest passivation on the Dental Implant surface, these results showed a significant improvement of the corrosion resistance of Ti based implants

that was related to the stimulation of a thin and very uniform Ti-based oxide layer. It is concluded that implementing the 3-D CMP treatment prescribed for titanium-based implants is to modify the oxide surface characteristics and therefore to improve their bio-corrosion responses. Finally the process of synthesis via sol-gel without sintering offers many advantages, all of them related to its low processing temperature [206], being able to better design its network and functionalizing it with biomolecules and drugs. The sol gel process without sintering is based on the hydrolysis and condensation of metal precursors. Silicon is commonly used, being able to form, networks of the Si-O-Si type with ramifications of functional groups. These materials are degradable, releasing ortho-silicic acid that induces osteoblastic proliferation, differentiation of the extracellular matrix, enzymatic activity and gene expression [220] inhibiting osteoclastogenesis [221] and favoring the formation of a biologically active layer of apatite hydroxycarbonate, mimetic to the cementing line synthesized physiologically in the process of bone remodeling, which favors cell adhesion and the formation of new bone on its surface.

CHAPTER VII

CONCLUSION AND SUGGESTIONS FOR FUTURE WORK

7.1 Conclusions

- CMP process has been shown as an alternative technique to induce microstructure or smoothness on the titanium-based implant surfaces.
- CMP also results in the growth of a self-protective oxide on the implant surface connected with surface alteration. It is suspected to be the reason for the corrosion prevention on the CMP performed samples in the presence of an oxidizer.
- Biocompatibility analyses conducted through wettability also showed a good hydrophilicity in dental implants associated with the increased surface roughness.
- The mechanical performance and biomechanical response for the 3-D CMP treated samples showed that the proposed method is a good competitor to the method of present choice which is the BCP method.

7.2 Suggestions for future work

This study reported some findings that can be expanded to cover several surface-related issues, which need to be taken into account to improve the Ti-based implant performance inside the human body. For the future investigation purposes this dissertation addressed the fundamentals of the CMP process to treat the 3-D bioimplants which were not possible to be treated with the CMP method normal setup that originally designed for the flat plates or 2-D surfaces. Consequently, several new invocations raised and needed to be answered.

The developed in lab setup is depending on several variables that determines the desired outcomes, among which the sample holder low pressure, yet the 3-D CMP setup is not suitable for the control the applied pressure on the given area. Therefore, the lab-scale setup needs to be designed to get a mechanism that give the ability to control the applies force efficiently. As a suggestion, a preliminary system with a semispherical platen with a inside concavity should be used to overcome the difficulty of polishing the cylindrical surface of the implant. this should be done with the presence of nano-microfiber pad with a special design of four layers (i) flexible nanofiber layer, (ii) fixation layer ,(iii) a grooved basal layer and (iv) sub-pad layer which can provide a unified desired properties to the surface being treated. The flexible non-fiber layer can assure the required slurry delivery limit to guarantee that the right amount of abrasives which are responsible of making the mechanical cutting action in the specified time. The grooves can keep the slurry in the required limit especially with the centrifugal action that can spread the slurry outside the pad. The other basal and sub layers can conform to the complicated shape design f the threaded- cylindrical shape of the implant.

The conducted biomechanical investigations and the determined results were carried out on animal hard tissues and synthetic bones, although these experiences can be adopted as a basis for adopting this method to treat the Ti-based bioimplants, it remains necessary to conduct experiments on animals in future work to see the in vivo response, which can give the clear results of how the organism responds to the CMP treated implant.

Furthermore, it is necessary to conduct the fatigue test in oral-like environment which can give a close results of how dental implants responds in aggressive environment of oral cavity.

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