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Titanium and Titanium Alloys as Biomaterials

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1. Introduction

Bone and its several associated elements – cartilage, connective tissue, vascular elements and nervous components – act as a functional organ. They provide support and protection for soft tissues and act together with skeletal muscles to make body movements possible. Bones are relatively rigid structures and their shapes are closely related to their functions. Bone metabolism is mainly controlled by the endocrine, immune and neurovascular systems, and its metabolism and response to internal and external stimulations are still under assessment [1].

Long bones of the skeletal system are prone to injury, and internal or external fixation is a part of their treatment. Joint replacement is another major intervention where the bone is expected to host biomaterials. Response of the bone to biomaterial intervenes with the regeneration process. Materials implanted into the bone will, nevertheless, cause local and systemic biological responses even if they are known to be inert. Host responses with joint replacement and fixation materials will initiate an adaptive and reactive process [2].

The field of biomaterials is on a continuous increase due to the high demand of an aging population as well as the increasing average weight of people. Biomaterials are artificial or natural materials that are used to restore or replace the loss or failure of a biological structure to recover its form and function in order to improve the quality and longevity of human life. Biomaterials are used in different parts of the human body as artificial valves in the heart, stents in blood vessels, replacement implants in shoulders, knees, hips, elbows, ears and dental structures [3] [4] [5]. They are also employed as cardiac simulators and for urinary and digestive tract reconstructions. Among all of them, the highest number of implants is for spinal, hip and knee replacements. It is estimated that by the end of 2030, the number of total hip replacements will rise by 174% (572,000 procedures) and total knee arthroplasties are projected to grow by 673% from the present rate (3.48 million procedures) [6]. This is due to the fact that human joints suffer from degenerative diseases such as osteoarthritis (inflammation in the

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bone joints), osteoporosis (weakening of the bones) and trauma leading to pain or loss in function. The degenerative diseases lead to degradation of the mechanical properties of the bone due to excessive loading or absence of normal biological self-healing process. Artificial biomaterials are the solutions to these problems and the surgical implantation of these artificial biomaterials of suitable shapes help restore the function of the otherwise functionally compromised structures. However, not only the replacement surgeries have increased, simultaneously the revision surgery of hip and knee implants have also increased. These revision surgeries which cause pain for the patient are very expensive and also their success rate is rather small. The target of present researches is developing implants that can serve for much longer period or until lifetime without failure or revision surgery [7]. Thus, development of appropriate material with high longevity, superior corrosion resistance in body environment, excellent combination of high strength and low Young´s modulus, high fatigue and wear resistance, high ductibility, excellent biocompatibility and be without citotoxicity is highly essential [8] [9].

In general, metallic biomaterials are used for load bearing applications and must have sufficient fatigue strength to endure the rigors of daily activity. Ceramic biomaterials are generally used for their hardness and wear resistance for applications such as articulating surfaces in joints and in teeth as well as bone bonding surfaces in implants. Polymeric materials are usually used for their flexibility and stability, but have also been used for low friction articulating surfaces. Titanium is becoming one of the most promising engineering materials and the interest in the application of titanium alloys to mechanical and tribological components is growing rapidly in the biomedical field [10], due to their excellent properties.

This chapter is focused on the use of titanium and its alloys as biomaterials from a tribological point of view. The main limitation of these materials is their poor tribological behavior characterized by high friction coefficient and severe adhesive wear. A number of different surface modification techniques have been recently applied to titanium alloys in order to improve their tribological performance as well as osseointegration. This chapter includes the most recent developments carried out in the field of surface treatments on titanium with very promising results.

2. Biomaterial properties

The main property required of a biomaterial is that it does not illicit an adverse reaction when placed into services, that means to be a biocompatible material. As well, good mechanical properties, osseointegration, high corrosion resistance and excellent wear resistance are required.

2.1. Biocompatibility

The materials used as implants are expected to be highly non toxic and should not cause any inflammatory or allergic reactions in the human body. The success of the biomaterials is mainly dependent on the reaction of the human body to the implant, and this measures the biocompatibility of a material [11]. The two main factors that influence the biocompatibility of a material are the host response induced by the material and the materials degradation in the body environment (Figure 1). According to the tissue reaction phenomena, the biocompatibility of orthopedic implant materials was classified into three categories by Heimke [12], such as "biotolerant", showing distant osteogenesis (bone formation with indirect contact to the material); "bioinert", showing contact osteogenesis (bone formation with direct contact to the material), and "bioactive", showing bonding osteogenesis (bone formation with chemical or biological bonding to the material).

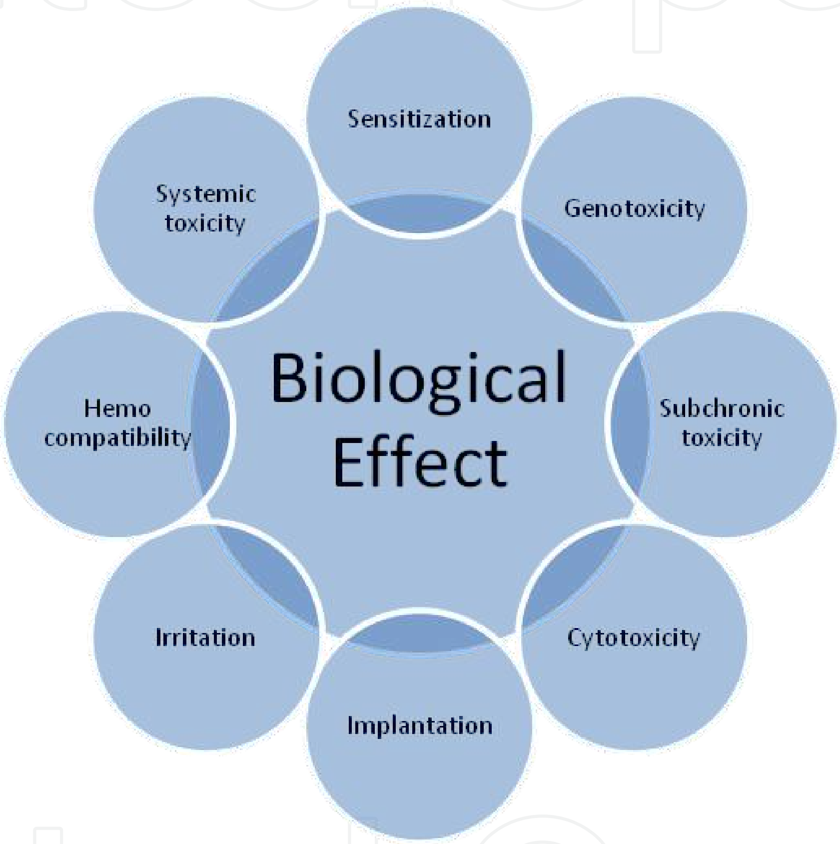

Figure 1. Biological effects of a biomaterial

When implants are exposed to human tissues and fluids, several reactions take place between the host and the implant material and these reactions dictate the acceptability of these materials by our system. The issues with regard to biocompatibility are (1) thrombosis, which involves blood coagulation and adhesion of blood platelets to biomaterial surface, and (2) the fibrous tissue encapsulation of biomaterials that are implanted in soft tissues.

2.2. Mechanical properties

The most important mechanical properties that help to decide the type of material are hardness, tensile strength, Young´s modulus and elongation. An implant fracture due to a mechanical failure is related to a biomechanical incompatibility. For this reason, it is expected that the material employed to replace the bone has similar mechanical properties to that of bone. The bone Young´s modulus varies in a range of 4 to 30 GPa depending on the type of the bone and the direction of measurement [13] [14].

2.3. Osseointegration

The inability of an implant surface to integrate with the adjacent bone and other tissues due to micromotions, results in implant loosening [15]. Osseointegration (capacity for joining with bone and other tissue) is another important aspect of the use of metallic alloys in bone applications (Figure 2). A good integration of implant with the bone is essential to ensure the safety and efficacy of the implant over its useful life. It has been shown in previous studies [16], that enhancement of the bone response to implant surfaces can be achieved by increasing the roughness or by other surface treatments [17]. Although the precise molecular mechanisms are not well understood, it is clear that the chemical and physical properties of the surface play a major role in the implant – surface interactions through modulation of cell behavior, growth factor production and osteogenic gene expression [18] [19] [20].

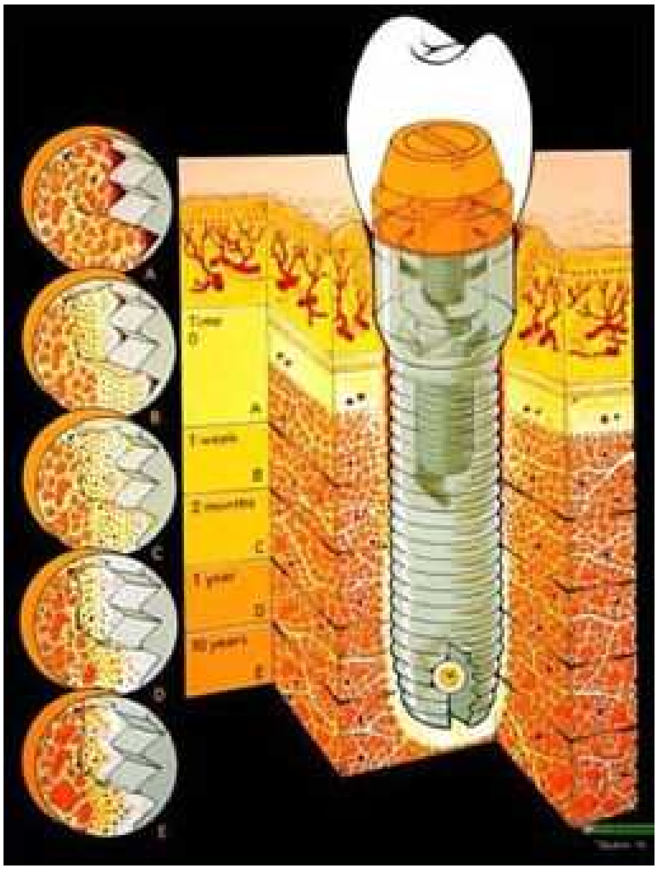

Figure 2. Schematic drawing of the principles of osseointegration [21]

Furthermore, it is known that even if initial implant stability is achieved, the bone may retreat from or be isolated from the implant because of different reasons or situations listed below:

1. Reaction of the implant with a foreign body as debris from implant component degradation or wear, or to toxic emissions from the implant [22]

2. Damage or lesion to the bone through mechanical trauma surgery

3. Imposition of abnormal or unphysiological conditions on the bone, such as fluid pressures or motion against implant components

4. Alteration to the mechanical signals encouraging bone densification; strain reductions or stress-shielding of replaced or adjacent bone.

2.4. High corrosion resistance

All metallic implants electrochemically corrode to some extent. This is disadvantageous for two main reasons: (1) the process of degradation reduces the structural integrity and (2) degradation products may react unfavorably with the host. Metallic implant degradation results from both electrochemical dissolution and wear, but most frequently occurs through a synergistic combination of the two [23] [24]. Electrochemical corrosion process includes both generalized dissolution uniformly affecting the entire surface and localized areas of a component.

Metal implant corrosion is controlled by (1) the extent of the thermodynamic driving forces which cause corrosion (oxidation/reduction reactions) and (2) physical barriers which limit the kinetics of corrosion. In practice these two parameters that mediate the corrosion of orthopedic biomaterials can be broken down into a number of variables: geometric variables (e.g., taper geometry in modular component hip prostheses), metallurgical variables (e.g., surface microstructure, oxide structure and composition), mechanical variables (e.g., stress and/or relative motion) and solution variables (e.g., pH, solution proteins and enzymes) [25].

The corrosion resistance of a surgically implanted alloy is an essential characteristic since the metal alloys are in contact with a very aggressive media such as the body fluid due to the presence of chloride ions and proteins. In the corrosion process, the metallic components of the alloy are oxidized to their ionic forms and dissolved oxygen is reduced to hydroxide ions.

The corrosion characteristics of an alloy are greatly influenced by the passive film formed on the surface of the alloy and the presence of the alloying elements.

2.5. Wear resistance

Wear always occurs in the articulation of artificial joints as a result of the mixed lubrication regime. The movement of an artificial hip joint produces billions of microscopic particles that are rubbed off cutting motions. These particles are trapped inside the tissues of the joint capsule and may lead to unwanted foreign body reactions. Histocytes and giant cells phagocytose and "digest" the released particles and form granulomas or granuloma-like tissues. At the boundary layer between the implant and bone, these interfere with the transformation process of the bone leading to osteolysis. Hence, the materials used to make the femoral head and cup play a significant role in the device performance. Since the advent of endoprosthetics, attempts have been made to reduce wear by using a variety of different combinations of materials and surface treatments.

Nowadays, the materials used for biomedical applications are mainly metallic materials such as 316L stainless steel, cobalt chromium alloys (CoCrMo), titanium-based alloys (Ti-6Al-4V) and miscellaneous others (including tantalum, gold, dental amalgams and other “specialty” metals). Titanium alloys are fast emerging as the first choice for majority of applications due to the combination of their outstanding characteristics such as high strength, low density, high immunity to corrosion, complete inertness to body environment, enhanced compatibility, low Young´s modulus and high capacity to join with bone or other tissues. Their lower Young´s modulus, superior biocompatibility and better corrosion resistance in comparison with conventional stainless steels and cobalt-based alloys, make them an ideal choice for bio-applications [26]. Because of the mentioned desirable properties, titanium and titanium alloys are widely used as hard tissue replacements in artificial bones, joints and dental implants.

3. Titanium and titanium alloys

The elemental metal titanium was first discovered in England by William Gregor in 1790, but in 1795 Klaproth gave it the name of titanium. Combination of low density, high strength to weight ratio, good biocompatibility and improved corrosion resistance with good plasticity and mechanical properties determines the application of titanium and its alloys in such industries as aviation, automotive, power and shipbuilding industries or architecture as well as medicine and sports equipment.

Increased use of titanium and its alloys as biomaterials comes from their superior biocompatibility and excellent corrosion resistance because of the thin surface oxide layer, and good mechanical properties, as a certain elastic modulus and low density that make that these metals present a mechanical behaviour close to those of bones. Light, strong and totally biocompatible, titanium is one of the few materials that naturally match the requirements for implantation in the human body. Among all titanium and its alloys, the mainly used materials in biomedical field are the commercially pure titanium (cp Ti, grade 2) and Ti-6Al-4V (grade 5) alloy. They are widely used as hard tissue replacements in artificial bones, joints and dental implants. As a hard tissue replacement, the low elastic modulus of titanium and its alloys is generally viewed as a biomechanical advantage because the smaller elastic modulus can result in smaller stress shielding.

Other property that makes titanium and its alloys the most promising biomaterials for implants is that titanium-based materials in general rely on the formation of an extremely thin, adherent, protective titanium oxide film. The presence of this oxide film that forms spontaneously in the passivation or repassivation process is a major criterion for the excellent biocompatibility and corrosion resistance of titanium and its alloys.

Concerning the medical applications of these materials, the use of cp (commercially pure) Titanium is more limited to the dental implants because of its limited mechanical properties.

In cases where good mechanical characteristics are required as in hip implants, knee implants, bone screws, and plates, Ti-6Al-4V alloy is being used [27] [28]. One of the most common applications of titanium alloys is artificial hip joints that consist of an articulating bearing (femoral head and cup) and stem [24], where metallic cup and hip stem components are made of titanium. As well, they are also often used in knee joint replacements, which consist of a femoral and tibial component made of titanium and a polyethylene articulating surface.

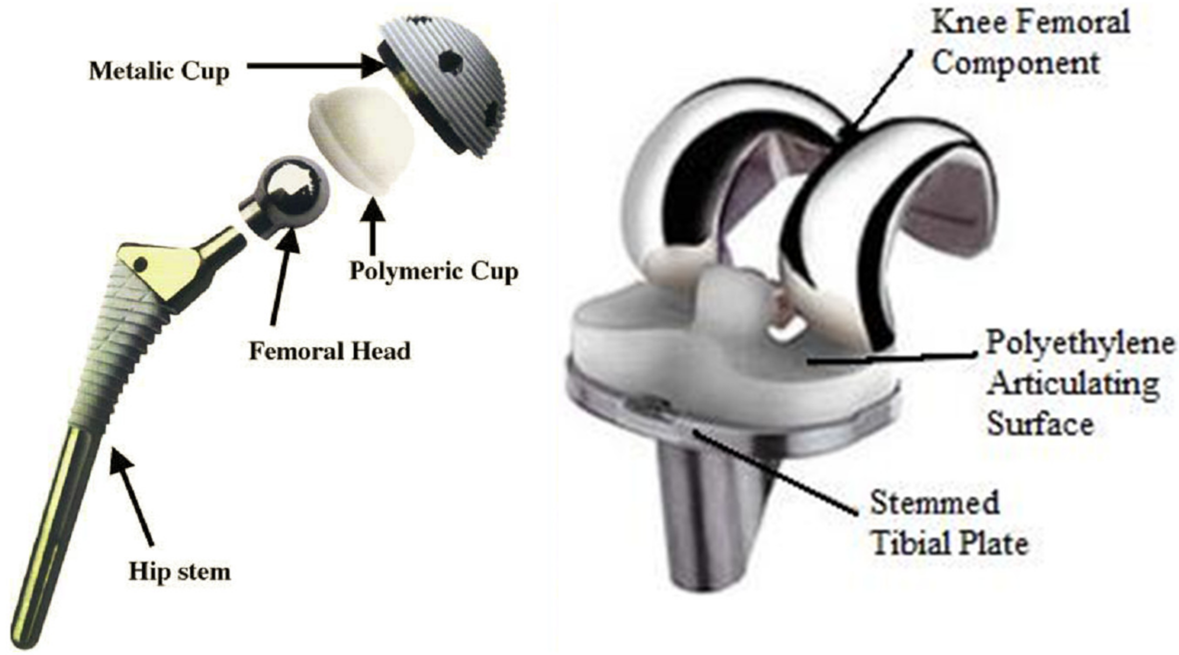

Figure 3. Schematic diagram of artificial hip joint (left) and knee implant [29] (right)

3.1. Wear problems in titanium and titanium alloys

The fundamental drawback of titanium and its alloys which limits wider use of these materials include their poor fretting fatigue resistance and poor tribological properties [30] [31], because of its low hardness [32]. Their poor tribological behavior is characterized by high coefficient of friction, severe adhesive wear with a strong tendency to seizing and low abrasion resistance [33]. Titanium tends to undergo severe wear when it is rubbed between itself or between other materials. Titanium has tendency for moving or sliding parts to gall and eventually seize. This causes a more intensive wear as a result of creation of adhesion couplings and mechanical instability of passive layer of oxides, particularly in presence of third bodies (Figure 4). Owing to this effect, in cases of total joint replacements made of titanium head and polymer cup, the 10%-20% of joints needs to be replaced within 15-20 years and the aseptic loosening accounts for approximately 80% of the revisions [34]. The reason for the failure of the implants is due to the high friction coefficient of these materials that can lead to the release of wear debris from the implant into the bloodstream that results in an inflammation of the surrounding tissue and gives rise to the bone resorption (osteolysis) [35] [36], which ultimately leads to loosening of the implant and hence the implant has to be replaced by a new one.

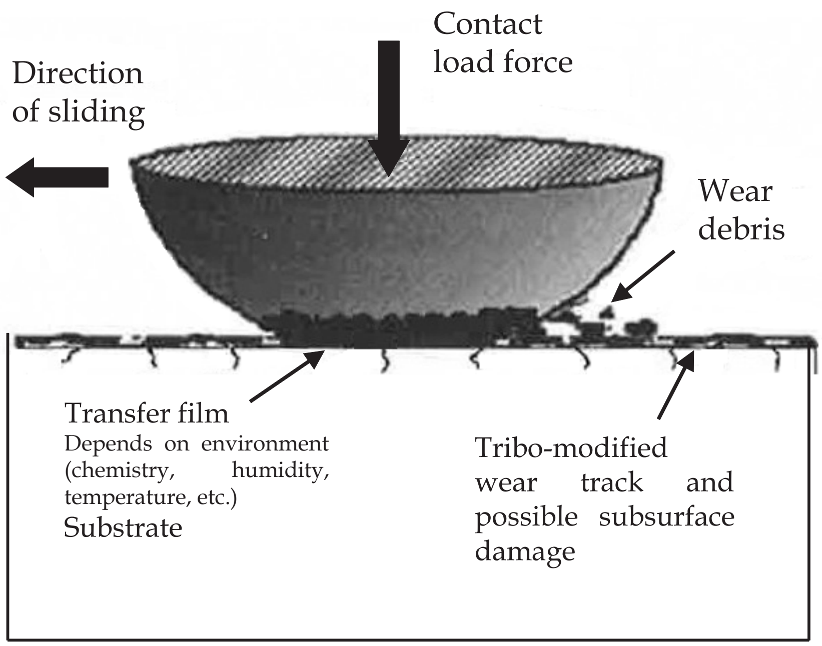

Figure 4. Schematic representation of a sliding tribological coating with the presence of third bodies [37]

3.2. Corrosion behaviour of titanium and titanium alloys

All metals and alloys are subjected to corrosion when in contact with body fluid as the body environment is very aggressive owing to the presence of chloride ions and proteins. A variety of chemical reactions occur on the surface of a surgically implanted alloy. The metallic components of the alloy are oxidized to their ionic forms and dissolved oxygen is reduced to hydroxide ions.

Most metals and alloys that resist well against corrosion are in the passive state. Metals in the passive state (passive metals) have a thin oxide layer (TiO_2 in case of titanium) on their surface, the passive film, which separates the metal from its environment [38]. Typically, the thickness of passive films formed on these metals is about 3-10 nm [39] and they consist of metal oxides (ceramic films). The natural oxide is amorphous and stoichiometrically defective. It is known that the protective and stable oxides on titanium surfaces (TiO_2) are able to provide favorable osseointegration. The stability of the oxide depends strongly on the composition structure and thickness of the film [40].

Because of the presence of an oxide film, the dissolution rate of a passive metal at a given potential is much lower than that of an active metal. It depends mostly on the properties of the passive film and its solubility in the environment. These films which form spontaneously on the surface of the metal prevent further transport of metallic ions and/or electrons across the film. To be effective barriers, the films must be compact and fully cover the metal surface; they must have an atomic structure that limits the migration of ions and/or electrons across the metal oxide–solution interface; and they must be able to remain on the surface of these alloys even with mechanical stressing or abrasion, expected with orthopedic devices [25].

The relatively poor tribological properties and possible corrosion problems have led to the development of surface treatments to effectively increase near-surface strength, improving the hardness and abrasive wear resistance thereby reducing the coefficient of friction as well as avoiding or reducing the transference of ions from the surface or bulk material to the surrounding tissue.

3.3. Osseointegration of titanium and titanium alloys

When an implant is surgically placed within bone there are numerous biological, physical, chemical, thermal and other factors functioning that determine whether or not osseointegration will occur.

Titanium and its alloys have been widely used for dental and orthopedic implants under load-bearing conditions because of their good biocompatibility coupled with high strength and fracture toughness. Despite reports of direct bonding to bone, they do not form a chemical bond with bone tissue. For the last decade, various coatings have been attempted to provide titanium and its alloys with bond-bonding ability, which spontaneously bond to living bone. Hydroxyapatite plasma spray coatings are widely used in cementless hip replacement surgery, but the hydroxyapatite coating, although exhibiting a very good biocompatibility, presents some disadvantages including delamination of the coating layer from the substrate, difficulties in controlling the composition of the coating layer and degradation of the coating layer itself, which can release debris becoming a source of third body wear [41].

A strong and durable bone to implant connection can be achieved by the formation of a stable bone tissue at the bone-implant interface by proper implant surface treatments, as can be electrochemical deposition, dipping and physical vapor deposition techniques [42].

3.4. Surface treatments of titanium and titanium alloys

Surface engineering can play a significant role in extending the performance of orthopedic devices made of titanium several times beyond its natural capability.

The main objectives of surface treatments mainly consist of the improvement of the tribological behaviour, corrosion resistance and osseointegration of the implant. There are coatings for enhanced wear and corrosion resistance by improving the surface hardness of the material that can be applied by different surface modifications techniques such as surface oxidation, physical deposition methods like ion implantation and plasma spray coatings, as well as thermo-chemical surface treatments such as nitriding, carburizing and boriding [43] [44].

Great efforts have been devoted to thickening and stabilizing surface oxides on titanium to achieve desired biological responses. The biological response to titanium depends on the surface chemical composition, and the ability of titanium oxides to absorb molecules and incorporate elements. Surface topography plays a fundamental role in regulating cell behavior, e.g. the shape, orientation and adhesion of cells.

One possible alternative to solve tribological problems and which is going to explain more detail consists of protecting the alloy surface by means of biocompatible Diamond-Like Carbon

(DLC) coatings. "Diamond-Like Carbon" is a generic term referring to amorphous carbon films, deposited by either Physical Vapor Deposition (PVD) or Plasma-Enhanced Chemical Vapor Deposition (PECVD). DLC coatings basically consist of a mixture of diamond (sp^3) and graphite (sp^2). The relative amounts of these two phases will determine much of the coating properties. They are thus metastable and mostly amorphous, "crystalline" clusters being too small or too defective to reach graphite or diamond structures. Both the mechanical and the tribological properties of DLC coatings have been studied for about 30 years, and several different types of DLC coatings can currently be found. DLC films are attractive biomedical materials due to their relatively high hardness, low friction coefficient, owing to the solid lubricant because of its graphite and amorphous carbon contents [31], good chemical stability and excellent bio and hemocompatibility [45] [44] [46] [47]. Cells are seen to grow well on these films coated on titanium and other materials without any cytotoxicity and inflammation.

Oxidation remains the most popular technique for the surface modification of Ti alloys; these oxide layers on titanium are commonly produced by either heat treatment [48] [49] [50] or electrolytic anodizing [51]. Thermal oxidation results in the formation of a 15-30 μm thick titanium dioxide layer of the rutile phase. However, due to their long-term high temperature action, thermal diffusion processes can also lead to the formation of a diffusion sub-layer consisting of an oxygen solid solution in α-Ti, and development of phase segregation and coalescence which may cause substrate embrittlement and worsened mechanical and/or corrosion performance.

Conventional anodic oxidation, which is carried out in various solutions providing passivation of the titanium surface, generates thin films of amorphous hydrated oxide or crystalline TiO_2 in the anatase form [52]. These films exhibit poor corrosion resistance in some reducing acids and halide solutions, while rutile generally possesses much better protective properties. However, recent developments in high voltage anodizing allow the production of crystalline rutile/anatase films at near to ambient temperature [53]. By anodic oxidation, elements such as Ca and P can be imported into the surface oxide on titanium and the micro-topography can be varied through regulating electrolyte and electrochemical conditions. The presence of Ca-ions has been reported to be advantageous to cell growth, and in vivo data show implant surfaces containing both Ca and P enhance bone apposition on the implant surface.

Furthermore, there are alternative methods to improve the biocompatibility such as biocompatible chemicals [54] and materials such as ceramics for coating. In some studies, titanium surfaces were modified using phosphoric acid in an "in vitro" study to improve the biocompatibility of dental implants. Results indicated that pretreatment of the implant with phosphoric acid caused no citotoxicity to the osteoblasts [55]. Micro arc oxidation method in phosphoric acid on titanium implants provided chemical bonding sites for calcium ions during mineralization [56].

Moreover, there have been developed coatings for high osseointegration. Hydroxyapatite (HA) coating is a proven method to improve the implants´ mechanical bonding [57] [58], biocompatibility and improve the osseointegration. The higher the degree of osseointegration, the higher is the mechanical stability and the probability of implant loosening becomes smaller. The process of osseointegration depends upon the surface properties such as surface chemis-

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try, surface topography, surface roughness and mainly the surface energy. TiO_2, calcium phosphate, titania/hydroxiapatite composite and silica coating by the sol-gel method can be applied on the surface of the titanium and titanium alloys. Plasma Electrolytic Oxidation (PEO) or Micro-Arc Oxidation (MAO) technique is used for the synthesize TiO_2 layer. This technique is based on the modification of the growing anodic film by arc micro-discharges, which are initiated at potentials above the breakdown voltage of the growing oxide film and move rapidly across the anode surface. This technology provides a solution by transforming the surface into a dense layer of ceramic which not only prevents galling but also provides excellent dielectric insulation for contact metals, helping to protect them against aggressive galvanic corrosion. PEO process transforms the surface of titanium alloys into a complex ceramic matrix by passing a pulsed, bi-polar electrical current in a specific wave formation through a bath of low concentration aqueous solution. A plasma discharge is formed on the surface of the substrate, transforming it into a thin, protective layer of titanium oxide, without subjecting the substrate itself to damaging thermal exposure.

Among all the above mentioned surface treatments, Diamond-Like Carbon coating and Plasma Electrolytic Oxidation are the most promising ones applied on titanium surfaces. These two treatments are explained in more detail in the following sections.

3.4.1. Diamond-like carbon coatings

In some biomedical applications continuously sliding contact is required, subjecting the implant to aggressive situations. To achieve and maintain higher efficiency and durability under such increasingly more severe sliding conditions, protective and/or solid coatings are becoming prevalent.

These coatings can generally be divided in two broad categories [59] : "soft coatings", which are usually good for solid lubrication and exhibit low friction coefficients, and "hard coatings", which are usually good for protection against wear, and exhibit low wear rates and hence longer durability (Figure 5).

It would thus seem to be difficult to associate low friction and high wear resistance with all types of coating in most tribological contacts. Some trade-offs can be found in combining both hard and soft materials in composite or multilayer coatings, which require complex procedures and further optimization of the deposition process. Nevertheless, a diverse family of carbon-based materials seems to "naturally" combine the desired set of tribological properties, providing not only low friction but also high wear resistance. These materials are widely known as the diamond and Diamond-Like Carbon (DLC) coatings. They are usually harder than most metals and/or alloys, thus affording very high wear resistance and, at the same time, impressive friction coefficients generally in the range of 0.05-0.2 [60] [61] [62]. In some cases, friction values lower than 0.01 have been reported [63] [64], offering a sliding regime often referred to as "superlubricity". These exceptional tribological abilities explain the increasing success of Diamond-Like Carbon coatings over the years, both in industrial applications and in the laboratory. The exceptional tribological behavior of Diamond-Like Carbon films appears to be due to a unique combination of surface chemical, physical, and mechanical interactions at their sliding interfaces [65].

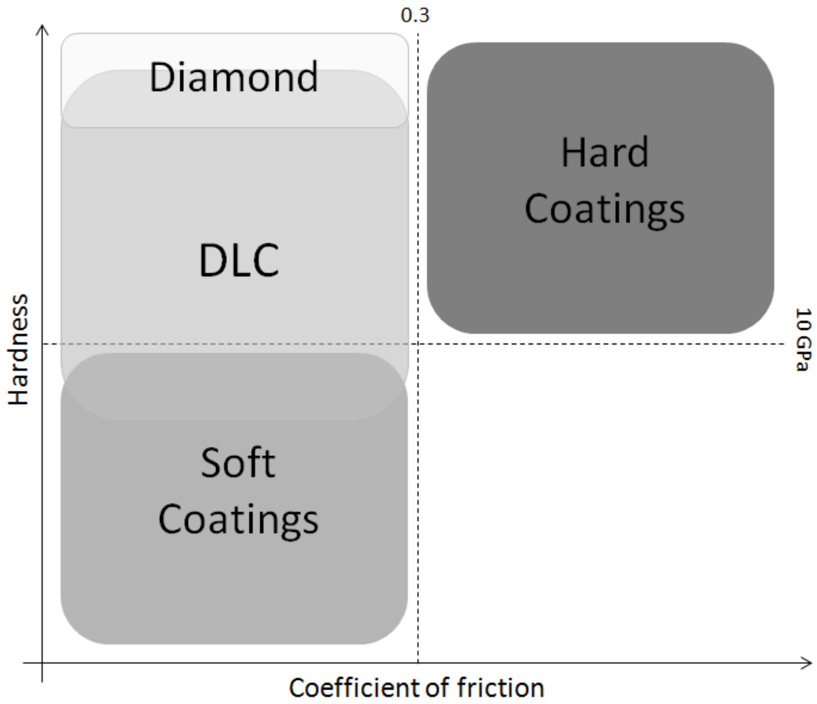

Figure 5. Classification of coatings with respect to hardness and coefficient of friction, highlighting the special case of carbon-based coatings

Since their initial discovery in the early 1950s, Diamond-Like Carbon coatings have attracted the most attention in recent years, mainly because they are cheap and easy to produce and offer exceptional properties for demanding engineering and medical applications. They can be used in invasive and implantable medical devices. These films are currently being evaluated for their durability and performance characteristics in certain biomedical implants including hip and knee joints and coronary stents.

Diamond-Like Carbon is the only coating that can provide both high hardness and low friction under dry sliding conditions. These films are metastable forms of carbon combining both sp2 and sp3 hybridizations, including hydrogen when a hydrocarbon precursor is used during deposition. The tribological behavior of Diamond-Like Carbon films requires a solid background on the chemical and structural nature of these films, which, in turn, depends on the deposition process and/or parameters. The chemical composition, such as the hydrogen and/or nitrogen content or the presence of other alloying elements, controls the mechanical and tribological properties of a sliding pair consisting of DLC on one or both sliding surfaces [66]. For example, DLC samples containing different concentrations of titanium (Figure 6) have also been examined "in vitro" to obtain a biocompatible surface that is hard, preventing abrasion and scratching [67].

It is well known that Diamond-Like Carbon films usually present smooth surfaces, except maybe in the case of films formed by unfiltered cathodic vacuum arc deposition (Figure 7). Roughness of the films on industrial surfaces will then be mainly controlled by the substrate roughness and can therefore be minimized.

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Figure 6. Scheme of titanium doped DLC coating. In this case, the first titanium layer was deposited in order to improve adhesion of DLC coating to the substrate and relax stress of the coating

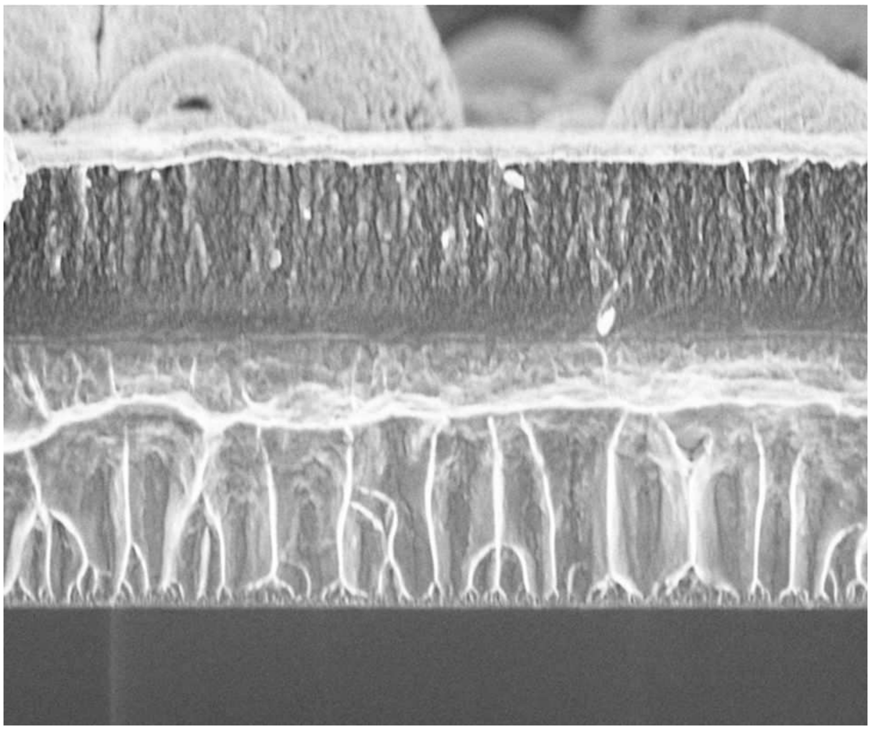


Figure 7. SEM (Scanning electron microscopy) micrograph of Ti-DLC coating deposited by physical vapour deposition technique using cathodic arc evaporation method

A frequently observed feature in tribological testing of Diamond-Like Carbon films is the formation of transfer layer. The formation of carbonous transfer layer on the sliding surface was observed to reduce the friction coefficient [68].

DLC coatings are usually applied by means of Cathodic Arc Evaporation Physical Vapor Deposition technology. An arc can be defined as a discharge of electricity between two electrodes. The arc evaporation process begins with the striking of a high current, low voltage arc on the surface of a cathode that gives rise to a small (usually a few microns wide) highly energetic emitting area known as a cathode spot. The localised temperature at the cathode spot is extremely high (around 15000 °C), which results in a high velocity (10 km/s) jet of vaporised cathode material, leaving a crater behind on the cathode surface.

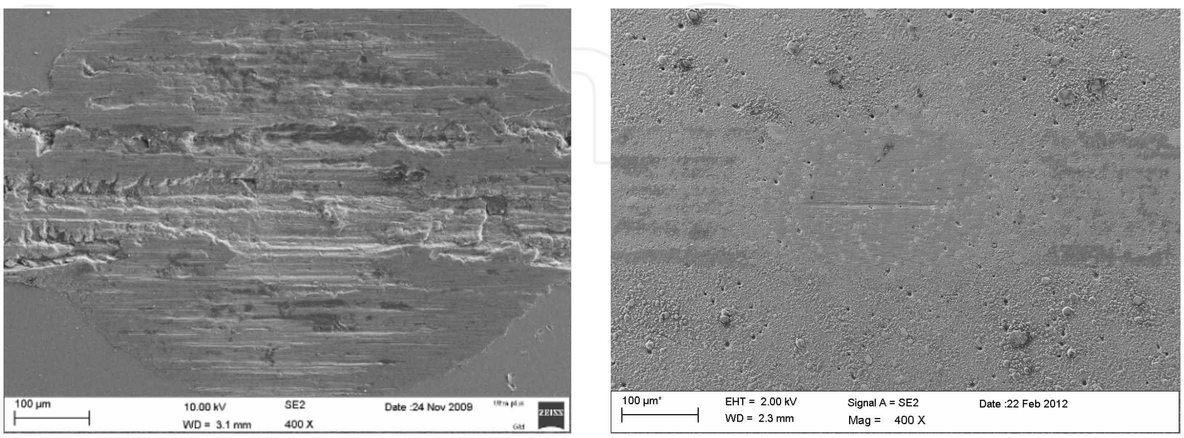
The plasma jet intensity is greatest normal to the surface of the cathode and contains a high level of ionization (30%-100%) multiply charged ions, neutral particles, clusters and macro-particles (droplets). The metal is evaporated by the arc in a single step, and ionized and accelerated within an electric field. Theoretically the arc is a self-sustaining discharge capable of sustaining large currents through electron emission from the cathode surface and the re-bombardment of the surface by positive ions under high vacuum conditions.

If a reactive gas is introduced during the evaporation process dissociation, ionization and excitation can occur during interaction with the ion flux and a compound film will be deposited. Without the influence of an applied magnetic field the cathode spot moves around randomly evaporating microscopic asperities and creating craters. However if the cathode spot stays at one of these evaporative points for too long it can eject a large amount of macro-particles or droplets as seen above. These droplets are detrimental to the performance of the coating as they are poorly adhered and can extend through the coating.

A recent tribological study carried out about the effect of deposition of Diamond-Like Carbon coatings on a substrate of Ti-6Al-4V for knee implants has confirmed that these types of coating improve the tribological response of substrate decreasing the coefficient of friction (μ) (Table 1) and reducing the wear of the surface (Figure 8) [69]. For this study fretting tests were performed using alumina balls as counter body, bovine serum as lubricant and a continuous temperature of 37 ºC, trying to simulate real environment.

Sample	**μ ± SD** (standard deviation)	**Disc Wear Scar, Maximum Depth (μm)**
Ti-6Al-4V	0.86 ± 0.08	10 ± 3
Ti-DLC	0.24 ± 0.01	Polishing Effect

Table 1. Friction coefficients values and ball and disc wear scars measurements



(a) (b)

Figure 8. SEM micrographs of the fretting tests wear scars. Ti-6Al-4V (left), Ti-DLC (right)

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3.4.2. Plasma electrolytic oxidation treatment

In biomedical application titanium is the most employed alloy due to its biocompatibility as an implant material, attributed to surface oxides spontaneously formed in air and/or physiological fluids [70]. Cellular behaviors, e.g. adhesion, morphologic change, functional alteration, proliferation and differentiation are greatly affected by surface properties, including composition, roughness, hydrophilicity, texture and morphology of the oxide on titanium [71] [72]. The natural oxide is thin (about 3–10nm in thickness [39]) amorphous and stoichiometrically defective. It is known that the protective and stable oxides on titanium surfaces are able to provide favorable osseointegration [73] [74]. The stability of the oxide depends strongly on the composition structure and thickness of the film [75].

On titanium and its alloys a thin oxide layer is formed naturally on the surface of titanium metal in exposure to air at room temperature [76] [77] [78]. Titania (TiO_2) exists in three polymorphic forms: rutile, anatase and brookite. Rutile, stable form of titania at ambient condition, possesses unique properties [79]. The metastable anatase and brookite phases convert to rutile upon heating. However, contact loads damage this thin native oxide film and cause galvanic and crevice corrosion as well as corrosion embrittlement. Moreover, the low wear resistance and high friction coefficient without applied protective coatings on the surface gravely limit its extensive applications. The most accepted technique for the surface modification of Ti alloys is oxidation. Anodizing produces anatase phase of titania that shows poor corrosion resistance in comparison with rutile phase. Recent developments in high voltage anodizing cause a crystalline rutile/anatase film at near to room temperature.

Attempts to improve surface properties of titanium and its alloys over the last few decades have led to development of Plasma Electrolytic Oxidation (PEO) technique by Kurze et al. [80] [81], which is a process to synthesize the ceramic-like oxide films at high voltages. This technique is based on the modification of the growing anodic film by spark/arc microdischarges in aqueous solutions (Figure 9), which are initiated at potentials above the breakdown voltage of the growing oxide film and move rapidly across the anode surface [53]. Since they rapidly develop and extinguish (within 10^{-4}-10^{-5} s), the discharges heat the metal substrate to less than 100-150 ºC. At the same time the local temperature and pressure inside the discharge channel can reach 10^{-3}-10^{-4} K and 10^{-2}-10^{-3} MPa, respectively, which is high enough to give rise to plasma thermo-chemical interactions between the substrate and the electrolyte. These interactions result in the formation of melt-quenched high-temperature oxides and complex compounds on the surface, composed of oxides of both the substrate material and electrolyte-borne modifying elements. The result is a porous oxide coating.

The PEO coating shows a significantly higher thickness (18 μm ± 4 μm) than PVD coatings and also a different morphology. The external part of the layer is porous (with pore diameter ranging from 3 to 8 μm) (Figure 10). The coating becomes increasingly compact on going towards the interface with the substrate. This kind of morphology leads to a relatively high surface roughness.

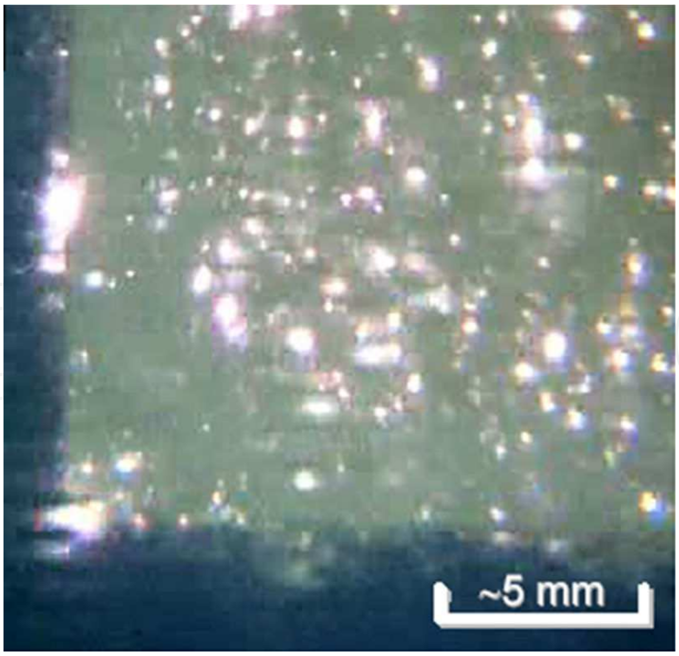

Figure 9. Photography of the arc micro-discharges in PEO process

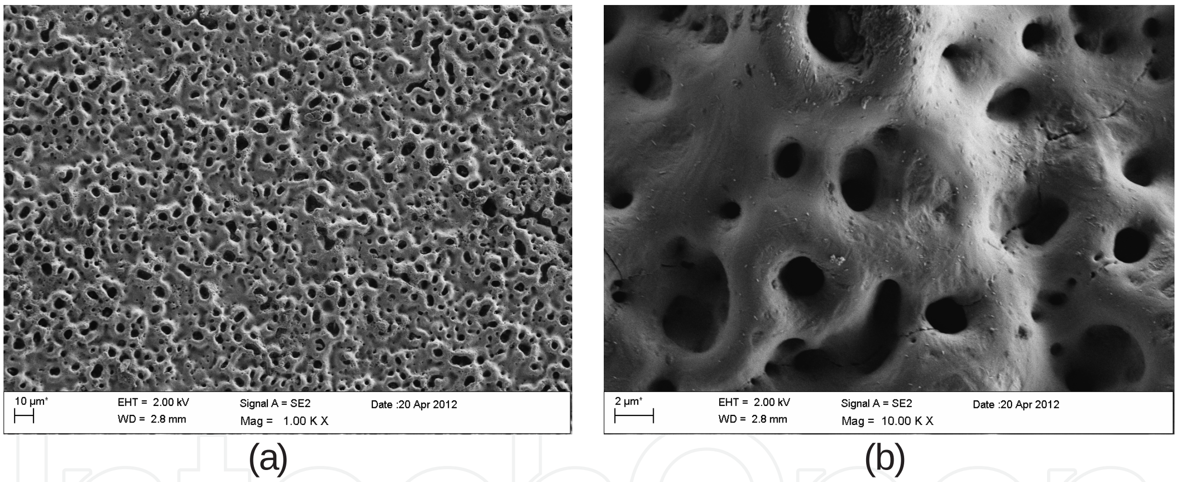

Figure 10. SEM micrographs of porosity of the external layer in PEO treatment. a) overview and b) detail

This method is characterized by the titanium surface, at near-to-ambient bulk temperature, into the high temperature titanium oxide (rutile) modified by other oxide constituents. Economic efficiency, ecological friendliness, corrosion resistance, high hardness, good wear resistance, and excellent bonding strength with the substrate are the other characteristics of this treatment [82] [83] [84].

The main conversion products formed by the PEO treatment are titanium oxides: rutile and anatase, typical anodic oxidation products of titanium. The structure and composition of anodic oxide films are known to be strongly dependent on film formation temperature and potential [85] [86]. In the case of PEO coatings, both the electrolyte composition and the current

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density regime have an influence on the phase composition and morphology of the anodic oxide layer [87]. A higher spark voltage causes a higher level of discharge energy, which provides a larger pore [88].

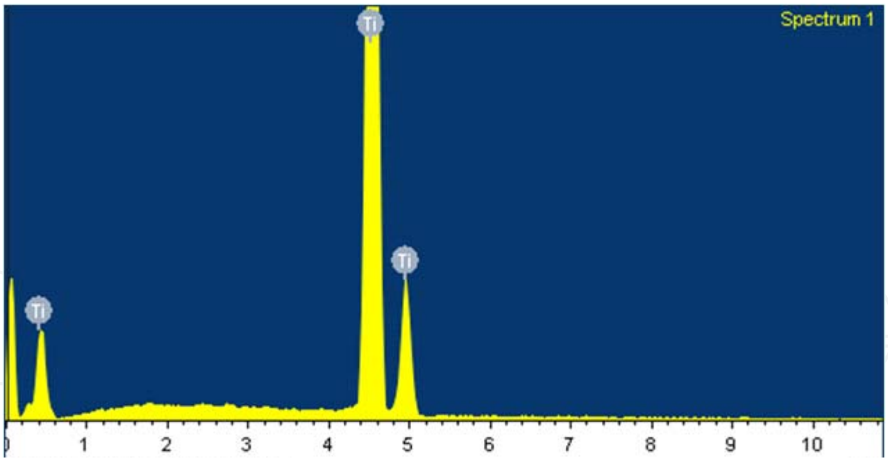
The influence of electrolyte characteristics on the phase composition of PEO films on titanium has previously been studied [89] [90]. It has been shown that surface layers composed of rutile, anatase, rutile/anatase, as well as oxides of electrolyte elements (e.g. Al_2O_3, MgO, WO_3), their hydroxides and complex oxides (e.g. Al_2TiO_5, $AlPO_4$, $CaWO_4$, $BaTiO_3$, $MnTiO_3$, etc.) can be produced.

Surfaces containing Ca and/or P induce osteoinduction of new bones and become bioactive. Ca and P ions can be incorporated into the layer, controlling the electrolyte employed during the electro oxidation process, and they further transform it into hydroxyapatite by a hydrothermal treatment [41].

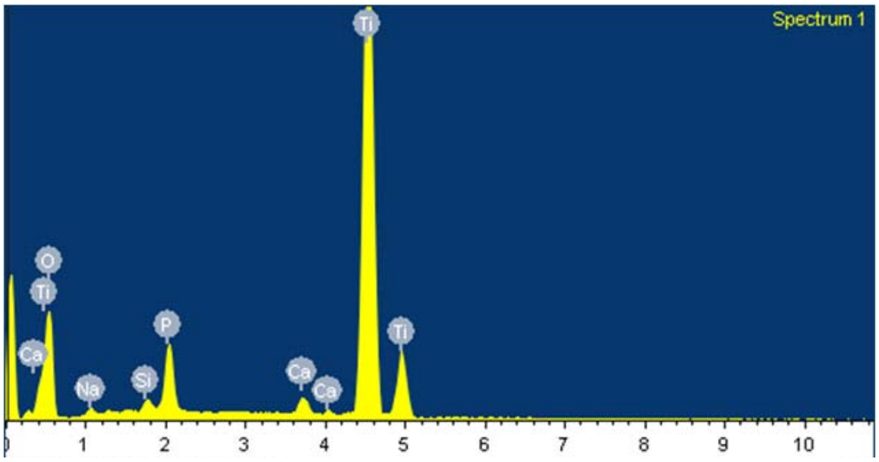
One technique that could show the effect of the electrolyte in the chemical composition of the coating could be the EDS (Energy Dispersive Spectroscopy) technique. In the following graphs a comparative study can be observed. The results of different samples, uncoated cp Ti, a coating obtained with a commercial electrolyte and a coating prepared in an aqueous electrolyte containing calcium phosphate and β-glycerophosphate, are showed in the following spectrums. The Ca- and P-containing titania coatings produced by PEO improve the bioactivity of the titanium-constructed orthopedic implant [91]. In Figure 11, in spectrum b) and c) can be observed the difference in the calcium quantity presented into the coating.

The biological response to titanium depends on the surface chemical composition and the ability of titanium oxides to absorb molecules and incorporate elements [92]. Surface topography plays a fundamental role in regulating cell behaviour, e.g. the shape, orientation and adhesion of cells [93] [94]. As a surface begins to contact with biological tissues, water molecules first reach the surface. Hence, surface wettability, initially, may play a major role in adsorption of proteins onto the surface, as well as cell adhesion. Cell adhesion is generally better on hydrophilic surfaces. It is known that changes in the physicochemical properties, which influence the hydrophilicity of Ti dioxide, will modulate the protein adsorption and further cell attachment [39]. By anodic oxidation, elements such as Ca and P can be imported into the surface oxide on titanium and the micro-topography can be varied through regulating electrolyte and electrochemical conditions. The presence of Ca-ions has been reported to be advantageous to cell growth, and "in vivo" data show implant surfaces containing both Ca and P enhance bone apposition on the implant surface.

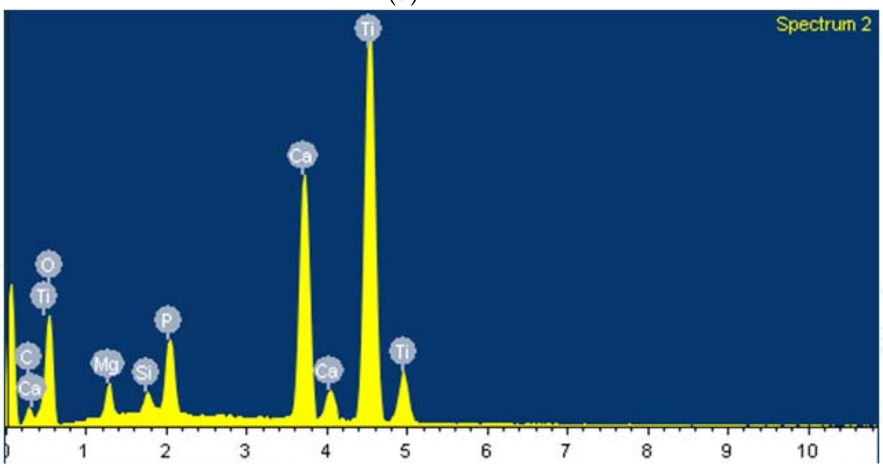
Some experiments carried out to study the tribological behaviour of the PEO-treated Ti-6Al-4V by means of dry sliding tests against PS (plasma sprayed) Al_2O_3–TiO_2 and compared with that of thin PVD coatings showed that the best tribological behavior, both in terms of low coefficient of friction and high wear resistance (i.e. low wear damage) was displayed by the PEO treated samples. The highest wear resistance was displayed by the PEO-treated samples, with negligible wear loss even under the highest applied load of 35 N. This good tribological behavior should be mainly related to the superior thickness of this coating that can better support the applied load.



(a)



(b)



(c)

Figure 11. a) Microchemical analysis of cp Ti, b) microchemical analysis of coating prepared with commercial electrolyte, c) microchemical analysis of coating prepared with calcium phosphate and β-glycerophosphate electrolyte.

The PEO treatment leads to a very good tribological behavior, significantly reducing both wear and friction of the Ti-6Al-4V alloy, even under high applied loads (up to 35 N). This good tribological behaviour should be mainly related to the superior thickness of this coating, which can better support the applied load. The main wear mechanism is micro-polishing and the coating thickness dictates its tribological life [95].

Last studies carried out have concluded that the PEO surface treatments enhance the biological response “in vitro”, promoting early osteoblast adhesion, and the osseointegrative properties “in vivo”, accelerating the primary osteogenic response, as they confirmed by the more extensive bone-implant contact reached after 2 weeks of study [94].

4. Conclusions

Titanium and its alloys are considered to be among the most promising engineering materials across a range of application sectors. Due to a unique combination of high strength-to-weight ratio, melting temperature and corrosion resistance, interest in the application of titanium alloys to mechanical and tribological components is growing rapidly in a wide range of industries, especially in biomedical field, also due to their excellent biocompatibility and good osseointegration. In such application, components made from Ti-alloys are often in tribological contact with different materials (metals, polymers or ceramics) and media, under stationary or dynamic loading and at various temperatures. These contact loads can cause damage of the thin native oxide film which passivates the titanium surface; and the metal can undergo intensive interactions with the counterface material and/or the surrounding environment. These interactions can generate various adverse effects on titanium components, such as high friction or even seizure (galvanic and crevice corrosion) as well as corrosion embrittlement, which lead to the premature failure of the implanted systems. The development of new specialized surface modification techniques for titanium and its alloys is therefore an increasingly critical requirement in order to control or prevent these effects and improve osseointegration, hence extending the lifetime of the implant.

Physical Vapour Deposition (PVD) technique allows develop Diamond-Like Carbon coatings that can be doped with different elements as titanium, tantalum, silver… which are biocompatible and increase the corrosion and wear resistance of the substrate, diminishing friction coefficient.

Plasma Electrolytic Oxidation (PEO) technique provides a possibility for the variation of composition and structure of the surface oxide film and attracts special interest for the corrosion protection and the optimization of friction and wear of titanium alloys as well as enhance the osseointegration.

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