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Advanced Surface Treatments on Titanium and Titanium Alloys Focused on Electrochemical and Physical Technologies for Biomedical Applications

Elena Fuentes, Sofia Alves, Ainara López-Ortega, Lucía Mendizabal and Virginia Sáenz de Viteri

Abstract

Titanium and its alloys are becoming very promising materials in biomedicine due to their excellent properties. However, their poor tribological behavior characterized by high friction coefficient and severe adhesive wear is their main limitation. Surface modification technologies based on electrochemical and physical techniques have been successfully employed to improve the tribological performance and osseointegration of Titanium materials, ensuring an effective protection against both wear and corrosion. For instance, anodizing and plasma electrolytic oxidation (PEO) are two electrochemical techniques that allow the growth of an oxide film of high hardness and good adhesion. The formation of these oxide films in electrolytes with bioactive elements has been reported to enhance cell functionalities and improve the tribocorrosion performance of Titanium surfaces considerably. Similarly, physical vapor deposition (PVD) technologies such as cathodic arc evaporation (CAE) and magnetron sputtering (MS) are commonly used today for the growth of protective hard coatings on different Titanium components in the biomedical field. Diamond-like-carbon (DLC) and transition metal nitride (MeN_x) and carbide (MeC_x) protective films grown by PVD have proven to be excellent candidates to enhance Titanium and Titanium alloys performance and durability, owing to their excellent adhesion, high hardness, low friction coefficient and enhanced wear and corrosion resistance.

Keywords: Titanium, Titanium alloys, surface treatments, anodizing, plasma electrolytic oxidation, physical vapor deposition, osseointegration

1. Introduction

Biomaterials are of great importance in medicine because of their ability to treat, improve, or replace damaged tissues, organs of body functions. Apart from ceramics, polymers, and composites, metallic materials rank distinguished in the field of biomaterials. Titanium (Ti) is considered the most biocompatible of all metals

because of its superior resistance to corrosion from bodily fluids, bio-inertness, capacity for osseointegration, and high fatigue limit. Titanium develops a very strong passivating oxide layer which forms naturally in the presence of oxygen on its surface. This protective oxide film, with a thickness of 3–10 nm [1] is strongly adhered, insoluble, and chemically impermeable, preventing reactions between the metal and the surrounding environment.

Titanium was first used in surgery in the 1950s and in dentistry a decade earlier. Recently, Titanium-based materials are attracting much interest as implantable materials because of their superior corrosion resistance, better mechanical properties such as remarkably high specific strength, low elastic modulus, and excellent biocompatibility compared to other competing biomaterials like stainless steel, Co-Cr alloys and nitinol alloys. They are now extensively and routinely accepted by medical professionals as the material of choice for prosthetics, internal fixation, inner body devices and instrumentation.

Ti6Al4V is the most commonly used Titanium alloy in orthopedic applications, for knee and hip prosthesis bone screws, and plates. It is as strong as steel and twice as strong as aluminum, but it is 45% lighter than steel and only 60% heavier than aluminum. This alloy is widely used as hard-tissue replacements in artificial bones and joints because of their outstanding characteristics such as high strength, low density, immunity to corrosion, complete inertness to body environment, enhanced compatibility, relatively low Young's Modulus and high capacity to join with bone or other tissues. However, the most important limitation of this and other Titanium alloys is their poor tribological behavior characterized by a high friction coefficient, and a low wear resistance, suffering from a severe adhesive wear [2].

Research and development on Titanium's medical applications are concentrated on new alloys, production technologies and surface treatments that improve biocompatibility and prevent fretting fatigue. Nowadays, the relatively poor tribological properties and possible corrosion problems of orthopedic devices made of Titanium alloys have led to the development of suitable surface treatments to effectively increase near-surface strength, improving the hardness and abrasive/adhesive wear resistance, thereby reducing the friction coefficient as well as avoiding or reducing the transference of ions from the surface or bulk material to the surrounding tissue, and improving biocide capacity and osseointegration of implants. Some surface treatment methods prone to be applied to achieve these objectives could be mechanical, chemical, electrochemical and physical methods. Mechanical methods such as machining, grinding, polishing and blasting produce specific surface topographies to improve adhesion in bonding. Chemical methods include acidic or alkaline treatments, hydrogen peroxide treatment and sol-gel, whose main objective is to improve biocompatibility, bioactivity or bone conductivity as well as chemical vapor deposition (CVD) for improving wear and corrosion resistance and blood compatibility, and biochemical techniques for inducing specific cell and tissue responses. Electrochemical methods include anodic oxidation, cathodic deposition and plasma electrolytic oxidation for improving corrosion resistance, biocompatibility, bioactivity or osseointegration. Physical methods involve thermal spray, physical vapor deposition (PVD), ion implantation/deposition and glow discharge plasma treatments for improving mainly wear and corrosion resistance.

In this chapter, two very promising surface modification methods, electrochemical and physical techniques, have been considered to develop highly corrosion- and wear-resistant and totally biocompatible coatings with improved osseointegration properties that extend the performance of Titanium alloys-based systems, several times beyond its natural capacity.

Electrochemical techniques such as anodizing and plasma electrolytic oxidation (PEO) have been employed to synthesize well-controlled ceramic-like oxide

TiO₂ films with improved features. Both techniques are simple, cheap and effective electrolytic passivation processes used to increase the thickness of the natural oxide layer on the surface of Titanium-based materials parts. In both techniques, a biocompatible and corrosion resistant oxide layer of high hardness and good adhesion is generated on the surface of the alloy. In anodizing, the part to be treated forms the anode electrode of an electrolytic cell. A direct current is passed through the part to be anodized while submerged in a water-based electrolyte. The water breaks down, liberating oxygen at the surface of the part, which then combines with the Titanium to form the thick Titanium oxide layer. Thickness is determined by the level of electrical current and the process duration applied. In PEO method, the layers are formed by polarizing the Titanium-based part to the dielectric breakdown voltage in a suitable electrolyte. A wide range of polarization conditions are available for formation of the coatings, including DC (direct current) and AC (alternating current), with control of the current, voltage or power supplied to the cell. The main differences between anodizing and PEO techniques rely on the lower voltage that is used for anodizing with no discharges/plasma generation during the process, and higher thickness in case of PEO. Despite the similarities between both, the lower voltage applied during anodizing significantly influences the properties of the anodic film grown during the process in what regards morphology, topography, chemistry and crystalline structure. The formation of Titanium oxides by anodizing in electrolytes composed of bioactive elements, has been reported as a very promising method either to enhance cell functionalities or to improve the tribocorrosion performance of Titanium surfaces. The ceramic oxide layers generated by PEO technique are characterized by a high corrosion and wear resistance. The oxide layers generated by PEO on Titanium alloys have been observed to have a suitable topography for cellular proliferation, and improve the wear-corrosion response of the substrate considerably.

As well, physical vapor deposition (PVD) technologies are commonly used today for the growth of protective hard coatings on different Titanium components in the biomedical field. Among them, cathodic arc evaporation (CAE) and magnetron sputtering (MS) techniques are the most popular ones. Diamond-like-carbon (DLC) and transition metal nitride (MeN_x) and carbide (MeC_x) protective films grown by PVD techniques have proven to be excellent candidates to enhance Titanium and Titanium alloys performance and durability in biomedical applications, owing to their excellent adhesion, high hardness, low friction coefficient and enhanced wear and corrosion resistance in body fluids. Besides this, PVD process parameters can be tuned to develop biomedical protective coatings with tailored properties. Particularly, Ti-C-N, Ti-C-N + Ag, Ti-DLC, (Ti,Zr)CN, TaN and TaN-Ag films performance to enhance Titanium and Titanium alloys features is described in this chapter, but the number of possible PVD coating materials (including completely different characteristics) is huge and continuously increases.

2. Problematics related to Titanium alloys in biomedical implants

A successful clinical implantation depends on the initial primary stability provided by the distribution of bone tissue around the implant, its quality and its amount. The integration of the implant in the bone is affected by several factors [1, 3–9]. The implant material, the design characteristics of the implant and its surface features, the implant loading conditions, the surgical technique employed, or the microbial adhesion and colonization are some examples. Also, the state of the host, i.e., the quantity and quality of the bone, and the mismatch of the mechanical properties of the bone and the implant are of great importance. Finally, the release of

the wear particles of metal ions from the implant during implantation is a key issue concerning the durability of the implants. In this context, wear, corrosion, and their synergistic interaction is a concerning issue to deal with, once it might influence the durability and clinical success of biomedical implants, and this chapter provides a brief insight into these phenomena and their detrimental effects.

2.1 Wear

One common degradation mechanism of orthopedical materials is wear. The integration of the implant in the bone tissue involves a relative movement between both surfaces. Furthermore, once the implant has been placed, the loads generated by the daily activity of the human body will result on micromovements on the implant/bone interface (fretting) [7, 10, 11]. One of the principal drawbacks of Titanium alloys relay on their low fretting-fatigue resistance and their poor tribological properties because of their low hardness [12–14] and the poor mechanical integrity of the TiO_2 passive film formed on their surface [15, 16]. Titanium-based alloys are characterized by a high coefficient of friction and severe wear either against themselves or other materials [2, 17]. 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. This implies the liberation of metallic particles or wear debris from the implant material into the surrounding tissues that results in an inflammation and gives rise to the bone resorption (osteolysis), which ultimately leads to loosening of the implant and hence the implant has to be replaced by a new one.

2.2 Corrosion

On the other hand, the human body comprises a highly corrosive environment, which might accelerate the degradation of metallic implants, regardless of their high corrosion resistance [18]. Corrosion is a degradation mechanism resulting from the electrochemical processes of oxidation and reduction taking place on a metal in a hostile electrolytic environment [19, 20]. The corrosion characteristics of implant alloys are influenced by the passive film that is formed on their surface [8]. This passive layer, of about 3–10 nm [1] and composed of TiO_2 , is the responsible for the adequate corrosion resistance of Titanium alloys, by acting as a physical barrier between the metal and the surrounding environment [21]. However, the presence of chloride ions (Cl^-) makes human fluids considerably aggressive. Due to the small size of these ions, they can penetrate through the passive film and break down this protective layer by inducing localized corrosion [9, 22]. The corrosion of Titanium alloys has been found to be influenced by several factors, either accelerating or inhibiting their degradation. Some examples are the pH levels [23], the presence of proteins [24], the presence of bacterial colonies [25], or human cells [26], among others. Corrosion of biomedical implants would lead to the liberation and accumulation of metallic ions and corrosion products [10, 17, 27].

2.3 Tribocorrosion

Since implants are simultaneously subjected to wear and corrosion solicitations, the degradation mechanism expected is a combination of both phenomena [28, 29]. When wear and corrosion take place simultaneously, the process is known as tribocorrosion [20, 30, 31]. Tribocorrosion involves a complex synergism between wear and corrosion, since the material loss when both processes take place together

is higher than when they occur alone [10, 32–36]. This synergism is schematically represented in **Figure 1**. When the passive layer generated on the surface of the alloy is destroyed and removed (depassivation), fresh material is exposed to the electrolyte where corrosion reaction take place (wear-accelerated corrosion). On the other hand, the wear debris generated can oxidize and accumulate in the tribological contact increasing the wear extent (corrosion enhanced wear). The material degradation by tribocorrosion depends on different variables, such as the properties of the materials involved in the systems (composition, microstructure, roughness, mechanical properties...), the electrochemical parameters (composition of the corrosive media, pH, conductivity, temperature...), and the mechanical parameters (load, frequency of the contact, vibrations...).

All in all, the release of metallic ions and corrosion products coming from both wear and corrosion and their interaction will enhance the likelihood of biological complications. This can result in peri-implant inflammatory reactions and aseptic osteolysis leading to the loss of the implant [16, 37, 38]. Therefore, tribocorrosion is one significant clinical issue that can compromise the osseointegration process as well as the further mechanical integrity and the biomechanical stability of the implant [21, 39, 40].

2.4 Infection

Certain microorganisms can grow in layers, forming biofilms on medical surfaces like implants. Biofilm-associated infections on implants are responsible for 15–25% of implant failures as biofilms are resistant to most of the conventional anti-microbial agents. So far, implant coatings with biocidal properties have been generated, which release silver ions or conventional antibiotics to inhibit biofilm formation. The need to resolve biofilm-associated infections is urgent to reduce the necessity for revision surgery. Besides, higher medical costs such infections lead to significant pain and distress in patients.

2.5 Challenges of Titanium in biomedicine

For all the aforementioned reasons, a primary goal on implantology research is the mitigation of wear and corrosion debris formation during the implantation. For this aim, the improvement of the wear-corrosion resistance of the implant material is a key factor. Functionalization of implant surfaces has been recognized as a promising approach to overcome current problematics [41]. In this context, the use of surface modification techniques that allow the modification of features such as

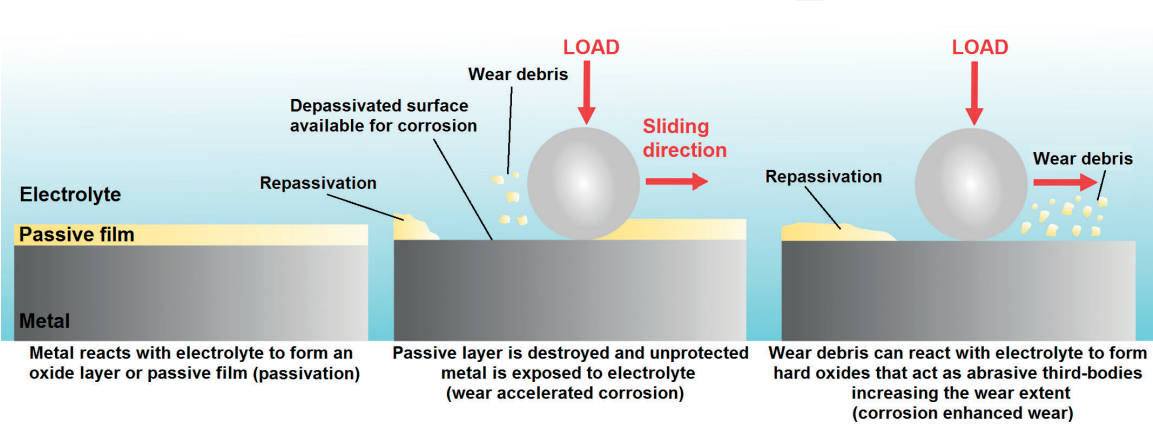


Figure 1.
Schematic representation of the synergism in tribocorrosion.

morphology, topography, structure, or chemistry has been gaining attention of the biomedical sector. In this sense, electrochemical techniques are simple, cheap and effective alternative methods used to improve the tribological and electrochemical properties of Titanium-based materials for biomedical applications, increasing their durability.

3. Electrochemical surface modification techniques

3.1 Introduction

Degradation of Titanium-based implant materials is feasible to occur *in vivo* conditions through corrosion and tribocorrosion processes, therefore being an issue of high clinical significance. One must be expected that the release of wear particles/corrosion products through tribocorrosion processes taking place during implantation, may seriously compromise the osseointegration process [41]. Degradation and inflammatory processes may also contribute to the loss of mechanical integrity, influencing the magnitude of micromovements at implant/bone interface, thus compromising the biomechanical stability of the implant as well as the long-term health of peri-implant tissues [39, 40, 42]. Wear debris resulting from tribocorrosion, besides trigger locally aggressive biological reactions at peri-implant tissues, can go into bloodstream and subsequently be disseminated into human organs, leading to adverse effects at a systemic level, and therefore presenting serious risks for human health [43]. To overcome these problems, surface treatments have been widely employed to Titanium and its alloys, among which anodic oxidation (anodizing) at low and high voltage processing conditions is found.

The high biocompatibility and corrosion resistance of Titanium and its alloys are associated with the ability of Titanium to spontaneously form a stable and adherent TiO_2 thin film on its surface, named as passive film, when exposed to oxidizing conditions [42]. The characteristics of this oxide film of around 3–10 nm thick [1], such as its morphology, topography and chemical composition play an important role on its osseointegration ability [44, 45]. Titanium oxide, i.e., Titania (TiO_2) can be found on three polymorphic forms: rutile, anatase, and brookite. Anatase and brookite can convert to rutile upon heating, achieving the unique properties of rutile at room temperature. Recently developed high voltage techniques allow the generation of oxide films composed of crystalline rutile/anatase phases [8], which play a crucial role on their tribocorrosion responses [46].

Among the many methods of Titanium surface modification, electrochemical techniques are simple, cheap and effective. While anodizing is an anodic electrochemical technique, electrophoretic and cathodic depositions are cathodic electrochemical techniques. By anodic oxidation it is possible to obtain oxide films with the desired roughness, porosity and chemical composition. This technique once employed at high voltages can improve the crystallinity of the oxide. Also, it allows the doping of the coating with the bath constituents and the incorporation of these elements can improve the properties of the film. Electrophoretic deposition may use hydroxyapatite (HAP) powders dispersed in a suitable solvent at a specific pH. Under these operating conditions these particles acquire positive charge and coatings are obtained on the cathodic Titanium by applying an external electric field. These coatings require a post-sintering treatment to improve their properties. Cathodic deposition is another type of electrochemical method where HAP is formed *in situ* from an electrolyte containing calcium and phosphate ions. It is also possible to alter the structure and/or chemistry of the obtained deposit. Nano-grained HAP has higher

surface energy and greater biological activity and therefore emphasis is being laid to produce these coatings by cathodic deposition [47].

As abovementioned, electrochemical techniques such as anodizing and plasma electrolytic oxidation (PEO) have been employed to synthesize ceramic-like oxide films with improved features. These treatments have been claimed to enhance the tribocorrosion behavior of Titanium-based materials, as well as their osseointegration by the incorporation of certain chemical elements into the oxide composition (e.g., calcium, phosphorus, zinc, etc.). In this section, anodizing and PEO processes are described, and some interesting findings on their tribocorrosion and biological performances are reported.

3.2 Anodizing

3.2.1 Definition and influence of anodizing parameters on anodic oxide film features

Anodizing has attracted considerable attention as a simple and fast electrochemical method to modify Titanium surface features, by promoting the growth of an oxide film on its surface [37, 48, 49]. Conventional anodizing process relies on the application of a predetermined current or voltage between Titanium material (anode) and an unreactive/inert material (cathode, e.g., platinum and graphite), previously immersed in a conductive solution. When polarized, a flux of electrons is generated between both materials, and the oxide film is grown on Titanium surface through oxidation reactions, along with field-driven ion diffusion [50–52].

The anodizing process is rather complex and depends on various parameters such as applied current density, concentration and composition of the electrolyte, the electrolyte temperature, duration of the process, the agitation speed of the solution during treatment and the cathode to anode surface area ratios [53]. Investigations have been carried out demonstrating that the features of Titanium oxide films generated by anodizing (e.g., morphology, topography, chemical composition and thickness) are strongly dependent on processing conditions, as below described in this section. In particular, over the last decades, many efforts have been done to develop nanoscale features on Titanium substrates to mimic the micro/nanostructures of natural bone and so, increase implants biocompatibility. In this field, anodizing technique is receiving a growing importance because of its convenience to create surfaces with biologically-inspired topographies with different chemical compositions according to the electrolyte used during the process [54–56].

Among various nanostructured materials, the decoration of Titanium-based surfaces with well-aligned TiO_2 nanotubes (NTs) has received special attention. Among the existing methods for TiO_2 NTs synthesis, anodizing has emerged as one of the most effective due to its versatility, easy operation, and commercial feasibility [52, 57, 58]. This technique is already widely used in industry to produce large-scale low-cost protective oxide coatings [52]. The anodizing process for NTs synthesis is commonly carried out by applying a constant voltage of 1–30 V in aqueous electrolytes, or 5–150 V in non-aqueous electrolytes, containing 0.1–1 wt.% fluoride ions (F^-) [51]. The anodizing setup for synthesis of TiO_2 NTs is illustrated in **Figure 2(a)**. The mechanisms of TiO_2 NTs growth by anodizing in a fluoride containing electrolyte, have been conventionally accepted as a result of a field assisted dissolution process consisting of three main stages: (1) the oxidation of Titanium metal involving Ti^{4+} ions formation/liberation; (2) the growth of an oxide film on Titanium surface, through recombination of Ti^{4+} and O^{2-} ions (provided by deprotonation of H_2O or OH^-) moving under the action of the electric field; (3) the local

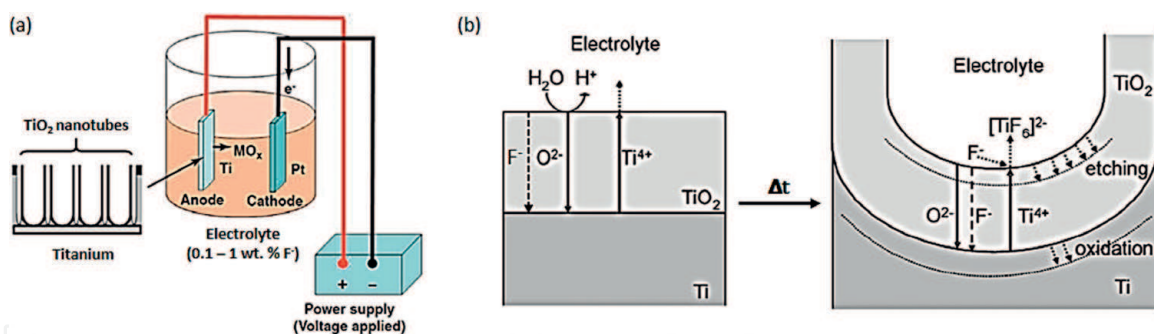


Figure 2.

(a) Anodizing setup for synthesis of TiO₂ NTs in a fluoride containing electrolyte. In (b) the mechanisms underlying nanotube growth evolution by anodizing are shown. Adapted from Refs. [51, 60, 61].

chemical dissolution of the growing oxide by fluoride ions and subsequently pore nucleation, with formation of water-soluble $[\text{TiF}_6]^{2-}$ species. This process assumes that nanotubes growth takes place through the balance established between the formation of the oxide film and its enhanced dissolution at the base of the pores/tubes, where the electric field is stronger, as schematically depicted in **Figure 2(b)** [50–52, 57, 59, 60].

The resulting features of TiO₂ NTs, namely morphology, chemistry, and length, may vary over a wide range according to the processing anodizing parameters, such as the applied voltage, duration, and electrolyte composition. As reviewed by Roy et al. [51], anodizing time and etching rate define tube length, while nanotube diameter is controlled linearly by the applied voltage. In general, thinner films are produced in acidic electrolytes as compared to neutral, mostly ascribed to the faster dissolution rate of the oxide in a lower pH solution [57]. Accordingly, Macak et al. [62] reported that by using a neutral NaF-based electrolyte, significantly thicker porous layers were obtained than in acidic solution. Furthermore, Shankar et al. [63] showed that by using non-aqueous organic electrolytes containing fluoride ions, such as ethylene glycol, highly ordered TiO₂ nanotube arrays up to 220 μm in length were grown, and depending on the anodic voltage, the inner pore diameters ranged from 20 to 150 nm. A remarkable advance has been reported by Han et al. [64], who fabricated TiO₂ nanotube arrays with enhanced self-ordering level by multistep anodic oxidation of Titanium in an organic electrolyte containing fluoride ions, and this methodology has been widely adopted for self-templating anodizing processes [65–67]. Generally, the structure of TiO₂ NTs grown by conventional anodizing is amorphous, however, it can become crystalline (e.g., anatase or a mixture of anatase and rutile) by thermal treatments at 280–800°C, for 2–3 h. Although this method is currently used to achieve enhanced surface bio-functionality, it is not standardized yet [51, 68].

3.2.2 Modification of Titanium and Titanium-alloys surface features by anodizing to improve the tribocorrosive and biological performances of osseointegrated implants

To achieve a good and fast osseointegration both the surface chemistry and topography of the implant material are of utmost importance. As abovementioned, various attempts have been made for the development of surfaces mimicking the hierarchical structure of bone which varies from micro- to nano-scale structures together with the inclusion of bioactive elements [69]. Zhao et al. [70, 71] observed that the conjunction of micro and nano-topographies on Titanium surfaces had a synergistic role on multiple cell functions, through the enhancement of multiple osteoblast functionalities, as compared to micro-textured surfaces. Furthermore,

micro/nano-textured surfaces showed enhanced ability to induce mesenchymal stem cells (MSCs) osteogenic differentiation. The benefit of a hierarchical micro/nano-topography on promoting MSCs adhesion was also demonstrated by Zhang et al. [72].

In particular, anodic nanotubular structures made out of TiO_2 have demonstrated unique morphological and physicochemical features with potential to stimulate implant-bone integration, either *in vitro* or *in vivo*, by modulating osteoblasts and human MSCs functions such as adhesion, proliferation, and differentiation [73–75], when compared to conventional Titanium surfaces. Furthermore, TiO_2 NTs have demonstrated ability, not only to control bone-forming cell functions, but also other types of cells that might have a major role in osseointegration process such as, osteoclasts, endothelial cells, and immune system cells (e.g., macrophages) [76, 77]. An additional exciting feature of TiO_2 NTs is their ability to prevent microbial adhesion and colonization, and therefore to avoid implant-related infections, which may end up in failure [78–80]. As demonstrated by Ercan et al. [80], Titanium surface features including chemistry, crystallinity, nanotube size, and hydrophilicity, significantly influence the responses of *S. epidermidis* and *S. aureus* pathogens. Several studies have reported that nanotube diameter besides influence the microbial adhesion and colonization, also modulate biological responses [81–83]. Furthermore, TiO_2 NTs display an improved corrosion resistance as compared to Titanium-based surfaces [84, 85]. Demetrescu et al. [55] studied the electrochemical behavior of TiO_2 NTs in Fusayama's artificial saliva (AS) and concluded that very low corrosion current densities were recorded for TiO_2 NTs due to a strong passive oxide film formation. Electrochemical impedance spectroscopy (EIS) results indicated that TiO_2 NTs consisted of a bi-layered oxide made up of an inner barrier layer associated to high impedance and responsible for corrosion protection, and a porous outer layer (NTs) of lower impedance.

An additional particularity of TiO_2 NTs is their potential to behave as a platform for drug-eluting and local delivery, due to their excellent controllable dimensions, surfaces chemistry and large surface-to-volume ratio. Easily by changing the nanotube diameter, wall thickness, and length, the kinetics of specific drugs can be adjustable to achieve stable and controlled release [86–88]. Bio-functionalization of TiO_2 NTs may be easily achieved by conventional techniques already used for surface modification of biomaterials. In this way, TiO_2 NTs may behave as effective bio-selective surfaces by incorporating different elements in its structure, hence inhibiting bacterial functions and concomitantly promoting osteoblast responses. Recently, Alves et al. [89] have also synthesized anodic TiO_2 NTs incorporating Ca- and P-based compounds, through a novel methodology that resembles on reverse polarization anodizing processes in an electrolyte composed of those bioactive species. Results showed that hydrophilic Ca/P-NTs improved osteoblast-like cells adhesion and proliferation, as compared to Titanium smooth surfaces. Furthermore, the corrosion resistance of these surfaces in AS was significantly improved, when compared to conventional NTs and Titanium surfaces. A step forward, aiming to address, simultaneously, the lack of tissue integration and infection problems, Alves et al. [90] incorporated Zn in TiO_2 NTs by anodizing of nanotubular structures in an electrolyte containing Ca, P and Zn elements. Results show that bio-functionalized TiO_2 nanotubular surfaces are biocompatible and modulated cell morphology. In particular, NTs enriched with Ca, P, and Zn, induced to significantly up-regulated levels of bone morphogenetic protein 2 (BMP-2) and osteopontin (OPN) genes of human MSCs, when compared to conventional NTs. TiO_2 nanotubular surfaces induced human MSCs to release a higher amount of vascular endothelial growth factor (VEGF), and showed the ability to impair *S. aureus* viability, therefore behaving as bio-selective surfaces.

The growth of TiO₂ NTs on Titanium surfaces has demonstrated potential to reduce stress shielding effect, in accordance with their mechanical properties determined by nanoindentation. An elastic modulus of 4 – 43 GPa has been determined for TiO₂ nanotubular structures [91–93], which is much closer to that of natural bone (i.e., 0.02 – 30 GPa) [94–96] when compared to Titanium (i.e., 143 ± 23 GPa) [27, 97]. The mechanical behavior of TiO₂ NTs was studied by Xu et al. [93] by nanoindentation. In summary, the authors observed that TiO₂ NTs break as long as the indentation depth increases, interacting with neighboring NTs and causing them to bend and fracture, with formation of smaller fragments that become gradually compacted, resulting in densification. Furthermore, Crawford et al. [91], observed that TiO₂ NTs inelastically deform by tube crushing in the immediate vicinity of the indenter tip, accompanied by local densification. However, these studies provide very limited information to predict the *in vivo* degradation mechanisms that TiO₂ NTs undergo, when submitted to tribocorrosive actions. To emphasize the importance of this knowledge, it has been reported that nanotubular films are prone to peeling off from the Titanium substrate due to poor adhesion between them [98–100]. Therefore, tribocorrosion studies become of fundamental importance, not only because of the high probability of adhesion failure of the nanotubular systems, but also because of their high clinical relevance, since implant degradation *in vivo* can seriously compromise osseointegration or even its long-term stability. In the attempt to construct effective nanotubular systems based on an integrated and multidisciplinary approach that addresses the development of tribocorrosion resistant implant surfaces with potential to avoid infection, and simultaneously, promote osseointegration, Alves and co-workers have recently reported, for the first time, important findings on the tribocorrosion field [101, 102].

Alves et al. [101] studied the tribo-electrochemical behavior of bio-functionalized TiO₂ NTs in AS, providing a first insight on their degradation mechanisms under reciprocating sliding conditions. Titanium surfaces decorated with TiO₂ NTs of 50–90 nm diameter were bio-functionalized by anodizing in an electrolyte containing Ca, P and Zn. The results showed that the tribo-electrochemical behavior of TiO₂ NTs was significantly improved after bio-functionalization treatments, which was correlated with their improved adhesion strength to the Titanium substrate, granted by the formation of a nano-thick oxide film at the interface region. The authors found out that after conventional anodizing process used for NTs growth, there was the formation of a non-continuous interface characterized by a hollow space between the nanotubular film and the Titanium substrate. After bio-functionalization treatments by reverse polarization anodizing, remarkable changes were observed at the Ti/TiO₂ NTs interface region, due to the formation of a nano-thick oxide film (230–250 nm) during the second step anodizing process, which appeared to improve NTs adhesion to Titanium [103], as depicted in **Figure 3**. The adhesion properties and degradation mechanisms of TiO₂ NTs were investigated by tribo-electrochemical tests carried out in AS under single and multiple sliding actions, to better mimic real *in vivo* conditions that dental implants might be exposed to in real life [101, 102]. From these studies the poor adhesion of conventional TiO₂ NTs was undoubtedly confirmed, and bio-functionalization came out as a very promising approach to overcome it. Besides the more active electrochemical state, conventional TiO₂ NTs suffered catastrophic destruction right after 100–300 s sliding actions accompanied by significantly higher wear volume loss as compared to bio-functionalized NTs, either when submitted to single or multiple sliding actions in AS. The improved tribo-electrochemical behavior after bio-functionalization was correlated with the significantly higher adhesion strength of the NTs to the substrate, granted by the nano-thick interfacial film formed by anodizing.

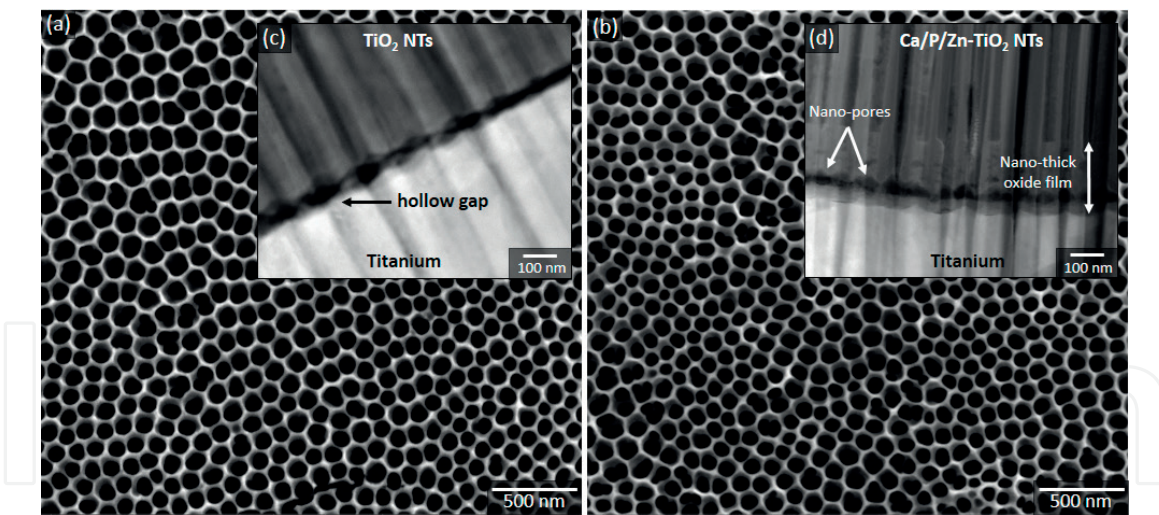


Figure 3. SEM micrographs of (a) NTs and (b) NT-Ca/P/Zn surfaces. Dark-field STEM micrographs at the interface of (c) NTs and (d) NT-Ca/P/Zn nanotubular films. In (c) the inset arrow shows the hollow gap between Titanium substrate and NT film while in (d) shows the nano porosity at the interface as well as the nano-thick oxide film grown during bio-functionalization (230–250 nm) [102].

The high adhesion strength was correlated with the higher hardness measured for these films, which consequently enhanced their mechanical wear resistance. From these studies a first insight on the main degradation mechanisms of TiO₂ NTs was proposed that relies on tube smashing and densification, along with delamination and detachment of the tubes, through cracks formation and propagation from the surface to subsurface regions of the film [101].

An additional important outcome from the study performed by Alves et al. [102], is the ability of TiO₂ NTs to induce the formation of a protective P-rich tribo-film with lubricating properties during tribo-electrochemical solicitations. This film may help to explain the open circuit potential (OCP) evolution during sliding, both for conventional and bio-functionalized NTs, as well as the high electrochemical stability observed in both cases when submitted to multiple sliding actions. Beyond the improved electrochemical properties, the formation of this tribo-film is believed to synergistically improve the wear resistance ability of TiO₂ NTs. Conventional NTs showed similar degradation by mechanical wear after sliding tests carried out for 300 and 1800 s, and furthermore, this trend was kept after two-cycle sliding periods undertaken for 1800 s each. As concerns bio-functionalized NTs, a trend of a gradual degradation was observed for sliding tests carried out for 300 and 1800 s, and no significant differences were registered when two-cycle sliding tests were carried out. These results highlight the ability of NTs to withstand multiple cycles of mechanical solicitations, and suggest that the degradation induced by mechanical wear in the beginning of sliding actions, dictate their long-term degradation. This ability of nanotubular films to avoid further mechanical degradation as long mechanical solicitations take place, is believed to be strongly related with the formation of the compact P-rich tribo-film, which grants both protection against corrosion and wear [101, 102].

In summary, anodizing has emerged as a very promising technique to modify the surface features of Titanium-based materials at a micron- to nano-scale level, providing them key functionalities for osseointegrated implant applications. Easily, by varying processing parameters such as the applied anodic voltage, process duration and electrolyte composition, surfaces with different designs may be fabricated through the growth of oxide films with different morphological/topographical and chemical features, which in turns modulate biological and bacterial responses, as well as their corrosion and tribocorrosion performances.

3.3 Plasma electrolytic oxidation (PEO)

3.3.1 Definition of the process and features of the anodic oxide films

Plasma electrolytic oxidation (PEO), also known as micro arc oxidation (MAO), is an electrochemical process of oxidation with which a ceramic oxide coating is generated on the surface of light alloys such as Titanium, Aluminum, or Magnesium (**Figure 4**). The oxide layers created with this process are characterized by a high hardness, adhesion and improved wear and corrosion resistances [104–108]. In this process, the samples are anodically polarized to high voltages exceeding the dielectric breakdown voltage, generating discrete short-living plasma micro-discharges on the surface [104–107]. The process is based on conventional anodizing, with similar configuration, but higher voltages (300–600 V) and current densities ($10\text{--}50\text{ A/dm}^2$) [109]. The high voltages facilitate the diffusion of oxygen ions through the discharge channels present in the oxide film to the substrate surface where they react to form the anodic film [110, 111]. Since the development and extinction of the micro-discharges takes place within microseconds ($10^{-4}\text{--}10^{-5}\text{ s}$), the substrate does not exceed $100\text{--}150^\circ\text{C}$ and thus is not subjected to thermal damage [2].

One difference between conventional or hard anodizing coatings and those obtained through PEO technique, is the thickness of the coating. Also, PEO is a high temperature process, which results in the formation of an oxide with a crystalline structure composed of rutile or anatase [112]. The improved wear resistance of the PEO generated layers is attributed to the presence of high temperature oxides and complex compounds, specially rutile, generated during the rapid melting by the micro-discharges and cooling in contact with the refrigerated electrolyte [2]. These oxide layers present excellent bonding adhesion to the substrate, and high hardness.

The PEO layer generated on Titanium alloys usually consists of two crystallographic phases, i.e., anatase and rutile. While anatase might present poor corrosion resistance against certain acids and halide solutions, rutile generally exhibits better protective properties [113]. Also, rutile has higher stability and mechanical properties than anatase, due to its higher hardness and denser morphology. For all these reasons, the presence of rutile in orthopedic implants is desired in order to improve tribological and corrosion properties of the Titanium alloys.

The microstructure of the PEO coating depends on the substrate material, the electrolyte composition and temperature, the dielectric breakdown, and the process parameters [106, 108, 110]. These coatings are characterized by a porous

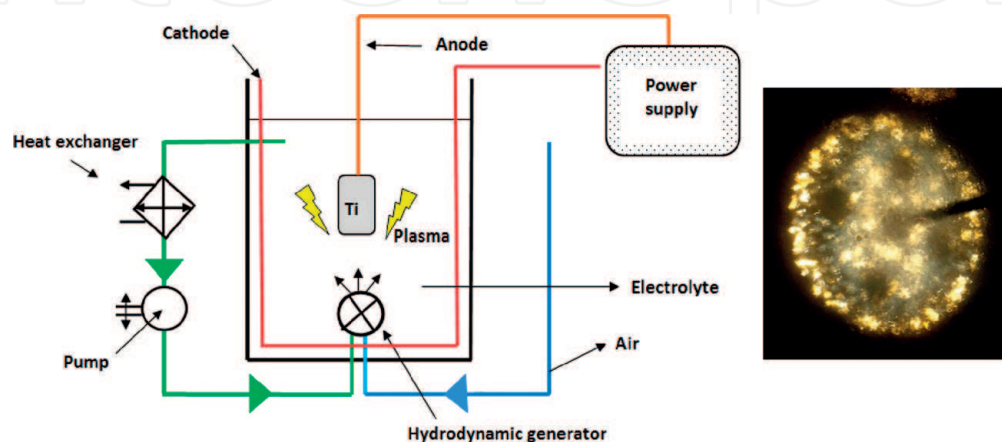


Figure 4. Schematic illustration of the Plasma Electrolytic Oxidation process and the plasma generated on the surface of a Titanium sample during the process.

microstructure resulting from the gas trapped into the material and the discharge channels created during the process. The higher discharge energy generated by larger spark voltages leads to larger pores in the anodic oxide layer [114]. The oxide layer generated by PEO technique usually consists of two or three layers of different porosity, i.e., an outer porous layer, an intermediate and a denser inner layer. The morphology of the intermediate and outer layers in terms of porosity, thickness, and composition can be tailored controlling the process parameters and the electrolyte composition. The pore diameter in the outer porous layer ranges from 3 to 8 μm in diameter, which results in a relatively high surface roughness [2]. The rough and porous surface of TiO_2 grown by PEO process makes these coatings appropriate for cell adhesion [115].

Furthermore, one of the main reasons for such a good osseointegration of Titanium alloys rely on the mechanical properties of the oxide layer. The elastic modulus of anodic Titanium oxide layers has been reported to be around 40 GPa, which is close to the values for human bones [97]. The low modulus of the oxide layer compared to those of Titanium alloys might be attributed to the porous morphology of this layer.

The use of alkaline electrolytes makes the PEO process sustainable and environmentally friendly. Furthermore, the chemical composition of the electrolyte can be accurately controlled and formulated, in order to control the composition of the resulting oxide layer. For instance, some previous studies on the generation of PEO coatings on Titanium alloys for biomedical implants have incorporated bioactive elements such as phosphorous and calcium on their composition to enhance their osseointegration and favor cell growth [113, 116, 117]. Also, the addition of other elements such as silver, copper, or fluoride to provide the coating with antibacterial ability has also been developed [113, 118–120].

Finally, the easy and rapid operation, and its ecological friendliness make the PEO process a promising technique for industrial applications related to surface modification of Titanium alloys. Furthermore, it is a versatile technique that can be used to coat samples and components of variable size and geometry [121, 122].

3.3.2 Enhancement of Titanium biomedical implants properties by PEO technique

Several investigations have already corroborated the improvement of the tribological properties of Titanium alloys, as well as osseointegration and bactericide properties achieved by means of the PEO technique. In this section, the findings of some studies are presented and briefly described.

The tribological performance of a Ti6Al4V alloy treated by PEO in dry abrasion conditions was investigated by Ceschini et al. [123]. They found the treatment to enhance the behavior of the alloy reducing both the wear extent and the friction coefficient, even under high applied loads up to 35 N. They ascribed this improvement to the high hardness and thickness of the coating, which could appropriately support the applied load protecting the substrate as long as there was a presence of the oxide layer.

The biological response *in vivo* of Titanium alloys treated by PEO technique was confirmed in a study carried out by Ravanetti et al. [124]. They observed the anodic oxide film to promote the early osteoblast adhesion, and the osseointegrative properties *in vivo*. The primary osteogenic response was accelerated during the extensive bone-implant contact after 2 weeks of study.

Alves et al. [125] developed anodic oxide layers on pure Titanium in an electrolyte composed of β -glycerophosphate (β -GP) and calcium acetate (CA). The Ca/P ratio in the resulting films was observed to increase for higher calcium acetate concentrations. In this study, they analyzed the influence of calcium acetate content

on the tribocorrosion behavior of the coatings in a sodium chloride solution. The results showed the crystallographic structure of the oxide layer to be affected by the calcium acetate concentration, presenting better tribocorrosion response for higher contents. This was the case of the films with higher Ca/P and rutile/anatase ratios.

Alves et al. [116] employed the PEO technique to develop anodic oxide films on a cp-Ti grade 2 used for dental implants. They evaluated the influence of process parameters on the coating properties, i.e., morphology, roughness, thickness, elemental composition, etc. The corrosion and tribocorrosion tests in artificial saliva (AS) revealed an improvement on the performance of the Titanium after the PEO treatment, in terms of higher corrosion and wear resistances. Also, they stated that the better response was obtained for the samples that were treated under higher current density, which possessed higher layer thickness. Alves et al. [117] continued the previous work by incorporating calcium and phosphorous into the TiO₂ layer of the cp-Ti grade 2 to enhance the osseointegration of the coating. For this aim, they modified the electrolyte composition, and compared the coatings achieved in two electrolytes with two process parameters. Similarly to that observed in the previous work [116], higher process currents and times led to larger pore sizes, and roughness. Also, the electrolyte composition and process time led to variations on the chemical composition and crystalline phases of the coating. The corrosion and tribocorrosion tests in AS revealed the sample with higher rutile/anatase ratio to possess the best performance, with increased mechanical and corrosion resistance. Finally, the cell-material interaction studies carried out with human osteosarcoma cells revealed an improvement on the cell viability/proliferation of the PEO coating compared to the substrate.

Ribeiro et al. [126] employed the PEO technique to develop an oxide layer composed of a mixture of anatase, rutile and amorphous phases. The coating consisted of an outermost nanometric amorphous oxide layer rich in Ca and P. They found this amorphous layer to improve the fibroblast viability and the metabolic activity, as well as the osteoblast adhesion. They observed the osteoblast adhesion to take place preferentially on the amorphous regions with higher Ca content. All the features observed in the layers containing both crystalline and amorphous phases showed a faster osteointegration than those with just crystalline phases.

Oliveira et al. [46] incorporated magnesium together with calcium and phosphorous in the structure of the anodic films, in an electrolyte containing β -GP, CA, and magnesium acetate (MA). They confirmed the addition of magnesium ions to enhance the formation of rutile in the crystalline structure, which also improved the tribocorrosion performance of the developed coating in simulated body fluids (SBF).

Saenz de Viteri et al. [112] developed TiO₂ coatings on Ti6Al4V biomedical alloy used in hip joint stem implants by PEO technique. Apart from Ca and P to generate suitable surface characteristic for cell adhesion and improve the osseointegration, they also incorporated iodine into the composition of the oxide layer to gain antibacterial properties. Iodine has been previously reported to be highly antibacterial, biocompatible and no cytotoxic [127]. However, due to the complexity of its manipulation at room temperature where it sublimates, no previous attempts in its use in PEO coatings has been found in literature. In this work, two process conditions were employed, 5 A/dm² for 19 min (PEO-1) and 15 A/dm² for 5 min (PEO-2). Similarly to previous results obtained by Alves et al. [116] and Alves et al. [117], the thickness of the coating increased and the pore size and density were higher with higher current density applied. However, the roughness of the oxide was not influenced by this parameter. A typical morphology of the topmost layer of the TiO₂ layer, showing high porosity adequate for cell proliferation is presented in the

Scanning Electron Microscopy (SEM) image of **Figure 5**. The Energy Dispersive Spectroscopy (EDS) and X-Ray Fluorescence (XRF) analysis performed on the samples confirmed the presence of phosphorous, calcium, and iodine in the coatings. Furthermore, the anatase/rutile ratio was quantified by X-Ray Diffraction (XRD), being 21/79 and 46/54 for the PEO-1 and PEO-2, respectively. On the other hand, the tribocorrosion tests in phosphate buffered solution (PBS) showed little influence of sliding on the electrochemical response of the coatings, compared to the Titanium substrate. The OCP lectures were more stable, especially for the PEO-1 coating (see **Figure 5**), and the corrosion resistance of the coatings was not affected after sliding. Finally, the antibacterial ability of Titanium against *S. epidermidis* was enhanced by the incorporation of iodine into the coatings.

Marques et al. [118] developed coatings with calcium, phosphorous, silicon, and silver on commercially pure Titanium (Cp-Ti) used in dental implants. The higher presence of rutile in the coatings with higher calcium concentration presented better corrosion properties in AS, also showing antibacterial and biocompatibility properties. They also observed little influence on the coatings performance with the incorporation of silicon and silver into its composition. Finally, the spreading and proliferation of human mesenchymal stem cells on the coatings was optimal, even in the presence of silver nanoparticles that were added to provide antibacterial properties.

Marques et al. [128] evaluated the tribocorrosion behavior of the oxide films containing P, Ca, Si, and Ag, developed in the previous work [118]. Coherently with the former results, the higher amount of Ca led to higher rutile crystalline phase formation on the coating, which was found to possess higher corrosion and tribocorrosion resistances. Also, this coating presented lower material loss, and no detriment was observed in the results with the incorporation of Ag nanoparticles into the coating.

More recently, Chen et al. [129] developed PEO coatings on a Ti-39Nb-6Zr alloy in a KOH solution. They evaluated the corrosion and wear performance of the coated alloy in PBS and studied the biocompatibility by osteoblast cells culturing. The corrosion and wear performance of the alloy was considerably improved after the treatment, showing higher corrosion resistance and lower material loss. The morphology of the oxide layer was found to be beneficial for protein adsorption, and the cell adhesion and osteoblast cell proliferation was also improved by the porous and rough surface.

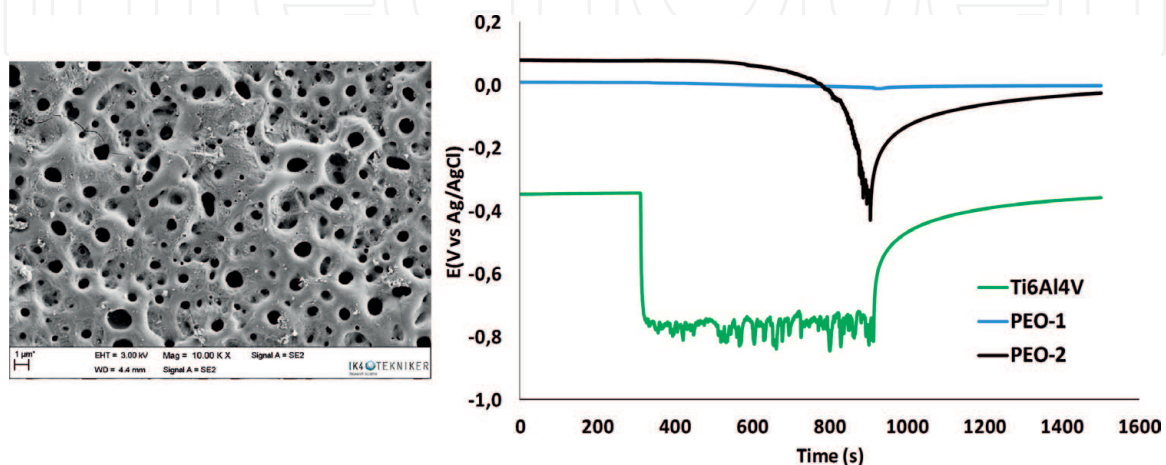


Figure 5. SEM micrograph of the TiO₂ coating generated by PEO technique on Ti6Al4V presenting adequate morphology for cell proliferation (left) and evolution of the OCP lecture before during and after tribocorrosion for the Ti6Al4V alloy and the two coatings generated by PEO technique [113].

Summarizing, PEO treatment has been found to be a promising surface modification technique for Titanium biomedical alloys. On the one hand, the surface morphology of the resulting TiO_2 layer presents adequate properties for cell proliferations. Furthermore, the electrolyte composition can be tailored modified to successfully incorporate several elements into the oxide composition, to improve different properties. Several researchers used Ca and P to enhance osseointegration, and I or Ag to provide the coating with antibacterial properties. Finally, the corrosion and tribocorrosion properties of Titanium alloys have been found to considerably improved in several biological fluids, e.g., SBF, PBS or AS. The higher enhancement of the TiO_2 layers has been confirmed to occur for greater rutile/anatase ratios.

4. Physical vapor deposition (PVD) technologies

4.1 Definition of PVD technology

Titanium and its alloys exhibit the highest biocompatibility, corrosion resistance, and specific strength (ratio of the tensile strength to density) among different biomaterials [130]. However, they exhibit poor wear resistance and high friction coefficients. Poor abrasive wear resistance results in the formation of wear debris at the implant area, inducing metal ion release, inflammation and pain. Besides this, human life expectancy is steadily growing up, which demands the development of new generation of implants with higher durability. In this sense, significant improvements can be obtained by the application of protective hard coatings by PVD techniques characterized by high hardness and toughness, low elasticity modulus, low friction coefficient and enhanced wear and corrosion resistance in body fluids along with good biocompatibility. PVD techniques are very versatile in terms of the selection of coating material since any type of inorganic material can be deposited.

Physical vapor deposition (PVD) technology refers to a variety of thin film deposition techniques where a solid material (target) is vaporized in high vacuum environment and then transported towards the substrate where it condenses to form a film [131, 132].

PVD processes takes place inside a vacuum chamber where the solid material is evaporated to form a plasma of atoms and molecules that are deposited on a wide range of substrates. As a process that transfers the coating material on a single atom or molecule level, it provides extremely pure and high-performance coatings compared with more conventional techniques. Besides, PVD is an eco-friendly technology in contrast to chemical and galvanic surface treatment methods. It is clean and dry, with no hazardous materials involved, and does not generate chemical waste or water pollution. A wide range of coating materials can be deposited by PVD technologies; including metals, alloys, semiconductors, and ceramics (nitrides, carbides, borides...).

PVD technologies can be divided into different categories regarding the mechanism to vaporize solid material: vacuum evaporation, cathodic arc evaporation, magnetron sputtering and pulsed laser deposition. Among them, cathodic arc evaporation (CAE) and magnetron sputtering (MS) are the most common and industrialized ones for the development of hard protective films.

Cathodic arc evaporation (CAE) is a low voltage, high current plasma discharge that takes place between two metallic electrodes inside a vacuum chamber [133, 134]. The arc discharge current is concentrated at the cathode surface, forming the cathode spots, which are characterized by extremely high current and power densities that

produce a localized phase transformation of the solid target (cathode material) to an almost fully ionized deposition plasma with high ion energies. The plasma expands rapidly into the vacuum towards the substrate to form a film. The high number of energetic ions generated in the CAE processes are the main advantage of this technique, which leads to the deposition of extremely dense (suppression of columnar growth) and well-adherent protective films compared with other PVD methods. However, CAE process produces also the so-called “macroparticles” along with the deposition plasma. Macroparticles (molten particles) range in size from less than 1 to about 10 μm in diameter, which adhere to the growing film causing defects, pinholes and rough surface coatings, representing an important disadvantage of CAE technique.

Magnetron sputtering technique relies on ejection (sputtering) of atoms from a solid source (target) by bombardment of gaseous ions from a plasma as shown in **Figure 6** [135–137]. Direct current magnetron sputtering (DCMS) is the basic sputtering process where a DC voltage is applied between the anode (chamber walls) and cathode (target) to ionize the sputtering gas (argon). The positively charged ions (Ar^+) are accelerated towards the cathode leading to an energetic bombardment against the target and ejecting target atoms by momentum transfer mechanism.

The main advantage of magnetron sputtering technology is that almost any material can be sputtered by simply introducing reactive gases such as nitrogen, oxygen or acetylene to form compound materials or by using a radio frequency (RF) power supply to sputtered insulating materials. Besides, there is no macroparticle generation during magnetron sputtering which leads to the development of smoother films compared with CAE technique. The principal drawback of DC magnetron sputtering is that only a small fraction of the sputtered atoms is ionized (<5%) which leads to the deposition of poor adhesion and low-density films characterized by columnar growth.

In order to overcome this problem, high power pulsed magnetron sputtering (HPPMS) was developed in the 1990’s as a variation of conventional sputtering by simply changing the power supply used for the generation of plasma discharge

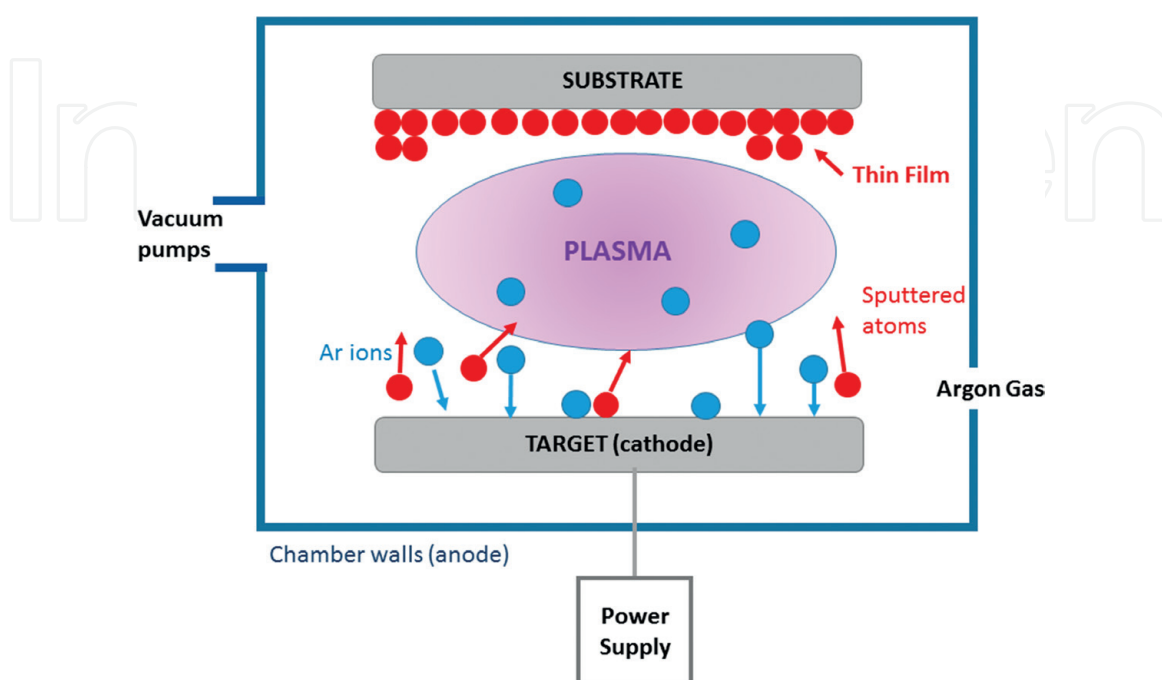


Figure 6.
 Schematic illustration of sputtering process.

[138–140]. During HPPMS discharge, the power is applied to the cathode in very short pulses of low duty cycle and frequency which prevents target overheating while increasing peak power density values up to several kW cm^{-2} (two orders of magnitude higher than during dcMS discharge). Such high peak power density values lead to the generation of ultra-dense plasmas, characterized by high ionization degree of sputtered particles. Consequently, thin film growth can be assisted by energetic ion flux bombardment from sputtered material, allowing the modification and densification of film microstructure and development of coatings characterized by excellent adhesion and extremely flat surface [141].

PVD coatings are therefore an excellent alternative to improve surface characteristics of Titanium and its alloys while increasing its durability. Protective biocompatible coatings with high hardness, smooth surface, high corrosion and wear resistance and low friction coefficient can be deposited by PVD techniques [142, 143]. Moreover, they can act as effective barriers to minimize ion release due to tribocorrosion. In addition, antibacterial agents such as silver and/or copper can be incorporated into the coating matrix to try to overcome bacteria colonization problem that occurs on implant devices. PVD process parameters such as pressure, reactive gas flows, power, current and voltage applied during discharge, process temperature...can be tuned to tailor the coating properties and develop an *ad-hoc* coating material for a specific application.

4.2 PVD coatings to improve Titanium and its alloys surface characteristics and performance

Protective coating materials applied by PVD techniques for Titanium and its alloys in biomedical applications generally fall into the following categories:

- diamond-like-carbon (DLC)
- transition metal carbides (MeC_x)
- transition metal nitrides (MeN_x)
- hydroxyapatite (HAP)

DLC is a carbon-based coating composed of diamond (sp^3) and graphite (sp^2) bonds that is commonly applied for the enhancement of Titanium and its alloys performance in biomedical applications [144, 145]. DLC coatings are excellent in both bio- and hemocompatibility, and exhibit very high corrosion resistance and chemical inertness. They can present superior hardness and toughness, besides very low friction coefficient and wear rates depending on the sp^3/sp^2 ratio. The ability to modify the DLC coating surface by doping and changing the compositional variation is an added advantage in improving the coating characteristics [146, 147].

Saenz de Viteri et al. [148] studied the performance of Ti-C-N films deposited on Ti6Al4V alloy by cathodic arc evaporation technique. Five Ti-C-N films were grown using metal Titanium as cathode material and evaporated under different nitrogen (N_2) and acetylene (C_2H_2) flows and arc currents in order to develop Ti-C-N films with different compositions. Tribological study was carried out on Ti6Al4V substrate and Ti-C-N coatings under fretting conditions in the solution of fetal bovine serum (FBS) with sodium azide and EDTA. All coatings reduced the friction coefficient of uncoated Ti6Al4V ($\mu = 0.8$) to values between 0.24 and 0.43 depending on Ti-C-N composition. All coatings could also reduce the wear shown by uncoated Titanium alloy. The coating deposited under lower C_2H_2 flow exhibited the best tribological

performance likely due to the higher sp^3/sp^2 fraction which provides the necessary hardness (10 GPa) and the nanocrystalline graphite (nc-G) and amorphous carbon (a-C) structure that confers the lowest friction coefficient and best wear resistance to the coating. Afterwards, Saenz de Viteri et al. [149] did also explore the deposition of silver (Ag) topcoat by magnetron sputtering on Ti-C-N surface to include the anti-bacterial property on the coating system. Bacterial adhesion tests showed that silver layer has broad-spectrum of anti-adherence activity. However, its low wear resistance makes the layer disappear during rubbing contact, and then their application should be limited to the avoidance of infection during the initial time of coating application.

Bayón et al. [150] investigated the influence of carbon content on the tribocorrosion performance of Titanium DLC (diamond-like-carbon) films deposited on Ti6Al4V alloy. Tribocorrosion analysis was carried out using a ball-on-disc set-up immersed in PBS (phosphate buffer solution) using an alumina ball as a counter-part. Three different deposition processes were accomplished in order to develop three different Ti_DLC coatings by varying some process parameters such as gas flows (nitrogen and acetylene) and arc intensity. DLC1 and DLC3 had same argon and nitrogen content but arc intensity of the process varied from 100 A in case of DLC1 to 75 A in case of DLC3. DLC2 had no nitrogen content on its structure. Corrosion response of uncoated Ti6Al4V and Ti_DLC coatings was very good before wear processes took place. However, high wear rates were measured on Ti6Al4V after tribocorrosion tests due to poor mechanical properties of this material. Ti_DLC films could considerably reduce the friction and wear of substrate material and there was no mechanical contribution to the total material loss due to tribocorrosion, demonstrating the excellent tribological properties of Ti_DLC. Noticeable differences were not detected between the three tested Ti_DLC films.

Braic et al. [151] analysed (Zr, Ti) CN hard coatings deposited by DC magnetron sputtering on Ti6Al4V alloy using Ti and Zr targets sputtered in Argon, nitrogen and methane atmosphere. They compared these films with ZrCN reference coatings. They correlated the composition and crystallographic phase of the films with their mechanical and corrosion properties and surface wettability and cell viability. Two coatings, with different non-metal/metal ratios $((C + N)/(Zr + Ti) \sim 1.1$ and $(C + N)/(Zr + Ti) \sim 2.6$) were deposited. Smaller grain size and smoother surface was observed for higher non-metal content coating. Contact angle measurements and corrosion tests demonstrated that the deposited coatings were hydrophobic and had improved corrosion resistance as compared with the Ti6Al4V substrate. The coating with higher non-metal/metal ratio exhibited the best performance and higher cell viability. The quaternary (Ti, Zr) CN films were found to have better characteristics than ZrCN reference films being better candidates to protect Ti6Al4V in orthopedic implants.

Transition metal nitrides (MeN_x) are generally used as protective hard coatings due to their high hardness and toughness, low elasticity modulus, enhance wear and corrosion resistance and excellent chemical stability. Among them, tantalum nitride (TaN) is particularly interesting for Titanium protection in biomedical applications owing to its outstanding biocompatibility. Tantalum metal is one of the most chemically inert and biocompatible material, showing an outstanding corrosion performance in many corrosive environments, even comparable to that of noble metals [152].

Mendizabal et al. [153] presented an investigation about TaN films deposited by HPPMS technique on pure Titanium (Ti-cp) grade 2 to be applied on biomedical implants. They investigated three different TaN films; i.e., monolayer TaN and two multilayer TaN films characterized by different bilayer periods were developed by alternatively switching two different HPPMS pulses within one overall deposition process. The microstructural analysis of the TaN films (**Figure 7**) revealed

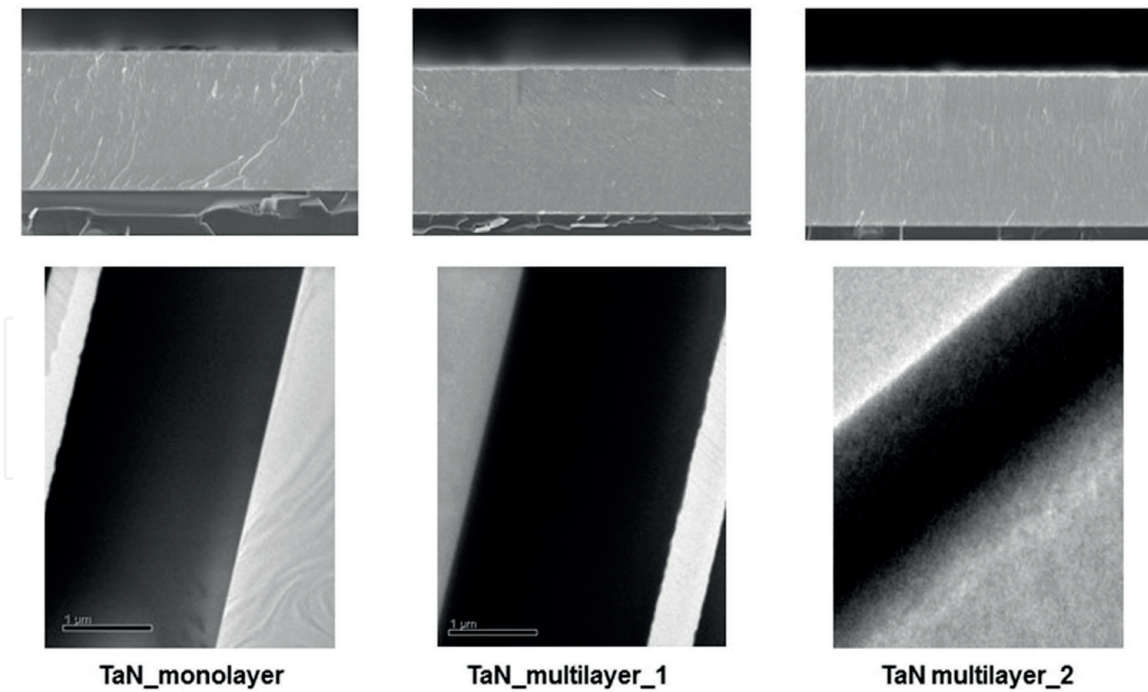


Figure 7.
Cross-sectional SEM and TEM micrographs of monolayer and multilayer TaN films [153].

extremely dense microstructures and suppression of columnar growth for all deposited samples confirming the importance of highly ionized plasmas developed during HPPMS discharges on the densification of the films.

Since the natural physiological environment contains not only inorganic species but also organic molecules such as serum proteins [154], Phosphate Buffered Solution (PBS) plus 1 g of albumin was chosen as experimental electrolyte to perform corrosion and tribocorrosion testing. The corrosion resistance of Ti-cp and TaN coatings before sliding was incredibly high ($\sim M\Omega$) and increased with time. TaN coatings exhibit similar electrochemical responses and slightly enhanced the Ti-cp resistance. The corrosion resistance of Ti-cp during sliding decreased up to 1 k Ω and TaN coatings exhibited one order of magnitude higher resistance values. The friction coefficient was reduced from 0.58 to 0.25 by all TaN coatings. The wear rate of Ti-cp was considerably reduced, and total material loss caused by tribocorrosion reduced up to 96% by best-performing TaN multilayer film.

Huang et al. [155] studied the incorporation of Ag on a TaN coating deposited on pure Titanium by co-sputtering of Ag and Ta targets in Ar/N₂ atmosphere in order to evaluate the antibacterial property of the system. They also investigated the biocompatibility of different TaN-Ag coatings grown with different Ag contents. The pure TaN showed a dense columnar structure with smooth surface and possessed the highest contact angle showing hydrophobic characteristics. The incorporation of Ag on the TaN matrix lowered the contact angle of the system. The TaN-Ag composite coatings with the highest Ag content (21.4 at.%) showed the most significant short-term antibacterial effect. All TaN_Ag films met the requirements in terms of cell viability independently from Ag content.

Hydroxyapatite (HAP) is the most common phase among calcium phosphate (CaP) ceramics studied for biomedical applications due to its similarity to natural bone and owing to their characteristics such as high biocompatibility, osteoconductivity, chemical stability at a neutral pH, and osseointegration [156]. HAP is, therefore, frequently considered as an adequate coating on Titanium orthopedic implants, which has been proven to promote and accelerate the osseointegration of an implant device into the body [157]. However, a major concern regarding

the application of HAP coatings is the low mechanical properties and high rate of decomposition of this material, which hinders its commercial application in high durability demanding devices. In order to overcome this problem, Vranceanu et al. [158] studied the addition of silicon carbide (SiC) into hydroxyapatite films deposited by RF-magnetron sputtering technique on Ti6Al4V for orthopedic applications. Previous results showed the improvement of wear and corrosion resistance of HAP films due to SiC incorporation in Titanium for dental implants [159, 160]. They studied the performance of base HAP and three HAP + SiC with different SiC contents by varying power applied to SiC sputtering target. They found that the SiC addition into the HAP matrix considerably improved the adhesion of the coating to the Ti6Al4V substrate and corrosion resistance compared to both base HAP film and uncoated Ti6Al4V. The biocompatibility tests demonstrated better cell proliferation and viability of all coatings compared with uncoated Ti6Al4V.

Summarizing, PVD technology is very versatile in terms of the available type of coating materials and properties that can be selected and tailored to enhance the performance and durability of Titanium and its alloys. Particularly,

- DLC and carbon-based films can strongly reduce the friction coefficient and wear rate of Titanium and its alloys in simulated body fluids.
- TaN films can considerably reduce the total material loss due to tribocorrosion observed for uncoated pure Titanium.
- The incorporation of silver into any of these coating matrixes can add the antibacterial property to the films without affecting their biocompatibility.
- Hydroxyapatite (HAP) films with enhanced adhesion and corrosion resistance due to SiC incorporation can be deposited by magnetron sputtering. Besides, HAP + SiC exhibited better cell proliferation and viability than uncoated Ti6Al4V.

The broad type of coating materials that can be deposited by PVD techniques, along with the possibility to tune their properties by fine adjustment of process parameters, presents these technologies as excellent candidates to enhance the durability of Titanium and its alloys for biomedical applications.

5. Conclusions

In summary, among the various electrochemical surface modification technologies nowadays available to enhance Titanium-based materials features for biomedical applications, anodizing and PEO techniques are among the most promising ones, for the following reasons:

- By varying processing parameters such as the process voltage, duration and electrolyte composition, surfaces with different designs may be fabricated by changing their topographical/morphological features, as well as their chemical composition.
- The electrolyte composition can be tailored to successfully incorporate several elements into the oxide film composition, to improve different properties. The enrichment of the oxide film structure with bioactive and antimicrobial

agents may induce to the production of new bio-selective functional surfaces for osseointegrated Titanium implants, by improving osseointegration and simultaneously avoiding infection.

- The growth of an oxide film on Titanium surfaces may improve considerably their corrosion and tribocorrosion properties in simulated body fluids, such as artificial saliva. In the case of PEO, which generally induces to the growth of an oxide film with a crystalline structure, the improved corrosion and tribocorrosion performances of TiO_2 films have been confirmed to occur for greater rutile/anatase ratios.

Furthermore, PVD technologies are very versatile and they are characterized for the development of well-adherent, hard, dense and high durability films. A broad range of coating materials can be grown by PVD, made of different compounds or in multilayer structures under low temperature deposition processes. Fine-tuning of process parameters enables the development of completely different surface features making possible the deposition of *ad-hoc* protective coatings. It must be highlighted:

- Very low friction coefficient and wear resistance carbon-based films are deposited by PVD techniques to protect Titanium from mechanical degradation;
- Transition metal nitride films with high corrosion and wear resistance are grown by PVD techniques, which considerably improve tribocorrosion performance of Titanium;
- The incorporation of silver into any of these coating matrixes can add the antibacterial property to the films without affecting their biocompatibility;
- Mechanical properties of hydroxyapatite films can be enhanced by SiC incorporation using PVD techniques, maintaining the excellent osseointegration of HAP while increasing its durability.

To conclude, this chapter is focused on promising electrochemical and physical technologies to modify the surface features of Titanium-based materials aiming to improve their functionalities for biomedical implant applications. In general, the implant surface requirements are defined based on its final application. Therefore, the most adequate technique for surface treatment must be selected considering the required surface features of the implant, namely topography, morphology, thickness, chemistry, hardness, as well as its response regarding corrosion and tribocorrosion processes. Based on this approach, implants with single or multiple functionalities may be designed, namely osseointegrable implants with antimicrobial properties, simultaneously displaying improved corrosion and tribocorrosion responses.

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