12. Tailoring surface properties from nanotubes and anodic layers of titanium for biomedical applications

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Abstract

The following chapter gives an overview on the anodic layers and nanotubes produced with plasma electrolytic oxidation. An introduction into the mechanisms involved in producing these nanofilms, such as the required processing parameters including voltage, current and time are discussed. In addition to an examination into the relation and the requirements for a good interface between the implant using these nanofilms and the bone, we also investigate and discuss the available commercial implants employing nanofilms. Commercial applications have enormous potential and are an area of interest for future work. Finally, we discuss the mechanical properties and the improvements obtained on these nanofilms by the scientific community.

Keywords: Plasma electrolytic oxidation, titanium, oxide film, microstructure, growth characteristics,

List of Contents

12.1. Introduction

In the last decades there has been a considerable improvement in both quality of life population and life expenctancy [1,2]. The increase in longevity contrasts with increasing numbers of traumatic accidents with resultant life changing injuries. The use of biomaterials for bone repair, fracture fixation, dental implants and orthopedic prostheses have been widely used to alleviate the effects of these traumas. The improvement of life quality is allied to the technological advances and new surgical techniques. The development of materials able to mimic the human tissues is still in progress [3], therefore metallic prosthesis are the replacements most commonly used for routine bone surgeries [4,5].

There is ongoing progress in the techniques of characterisation and development of novel materials to repair hard tissues, since the surfaces of these materials are generally bioinert. These characteristics are important because there are many situations where the surface of the biocompatible material must be bioinert, such as orthopedic bone screws. In this case there is a formation of a fibrous tissue that isolates the material from the biological environment [1,4].

In more difficult settings, these metals can be used as partial or total bone replacement where it is necessary that the surface must be bioactive, as it must induce bone growth and connect with living tissues through chemical and/or biological bonds to promote osseointegration between the implant and living tissue [6]. Surface treatments are used to improve these surfaces, making them bioactive [4,7] and is necessary that this interface is free of inflammatory processes with formation of fibrous encapsulating tissues. Eventually, if the osseointegration of the implant is interrupted, it will result in loss of the primary stability of the material causing the implant to loosen [1].

Implants undergoing cyclic stressing are subjected to stress shielding, a phenomenon responsible for bone resorption, loosening, and eventually replacement surgeries. The mechanical compatibility of the synthetic material and the bone are essential to avoid stress shielding which can be attained by matching the Young's Modulus. Hence, alloys containing β stabilizers elements are being studied and the addition of elements Nb,Ta,V, Mo, Mg, Cr, to Ti decreases these alloys´elastic modulus to values as lower as 40 GPa, which is much closer to the range of values for bones (10-40 GPa) than pure metals (typically >100 GPa) [8,9], although the microstructure of these alloys depends on the %wt [4–6].

Among the various techniques of surface modification, anodic oxidation is an effective electrochemical method that has been successfully used in surface treatment of implants in order to promote the bone integration of biomaterials. This technique allows the production of oxides films on the surface of transition metal and its alloys, such as Ti, Ta, Zr, Nb, TiNb, TiNbTa, TiNbTaZr [4,7,10,11]. The surface modification is essential to promote the bone integration of biomaterials [4,5,10] and with this technique, one can obtain compact, porous and roughnened oxides or nanotubes structures. However, the morphology of these surfaces will depend on the voltage applied, with low voltages resultings in compact oxides and as the voltages (V) increases, it is possible to obtain sparking during the oxidation process (V value depends on the electrolyte) leading to anodic films being more rough and porous. When this occurs, the process is known as Plasma Electrolytic Oxidation (PEO) or Micro Arc Oxidation (MAO). If fluoride ions are introduced into the electrolyte, nanostructured and self-organized surfaces are obtained because these fluorine ions attacks the oxide surface giving rise to the nanotubular structure [12].

Ti and its alloys are the metals most used as dental (grade 2 Ti) and orthopedic (Ti-6Al-4V) implant materials due to their mechanical properties, suitable for the substitution of hard tissue, excellent corrosion resistance and biocompatibility conferred by the natural oxide film. However, bone growth is a slow process onto metallic implants without superficial treatments when compared to healing times required for implants. One method to decrease the time for healing is a fast osseointegration between the metallic implant and the bone tissue. Thus, it is necessary to use surface modification techniques to improve the biological activity of these materials and to promote bone integration [4,7,10].

Biocompatibility of titanium is closely related to the properties of oxide surface layers in terms of its structure, morphology and composition [7,13]. The surface of Ti when is exposed to air it is rapidly coated with a thin layer, in the order of tens nanometers, of amorphous titanium oxide which has shown to have important values of corrosion resistance [4]. This layer also has been shown to be essential for an inert body response since it forms an interface layer between biological systems and implants [7]. In addition, it also acts as a barrier preventing metal ions from the interior of being released into the biological medium, and prevents corrosion of the metal [4,7]. This low tendency to corrode, is necessary in order to avoid ions to be released into the biological medium and it guarantees stability for the implant.

The success of osseointegration process between the implant and bone tissue depends on surface chemical composition, porosity, surface topography, surface energy, wettability and mechanical compatibility [13].

Surface chemical composition is a determinant for bioactivity. Anodic films rich in Ca and P elements produced by anodizing process may be more effective due to formation of calcium phosphates after being implanted in the human body [14]. On titanium treated surfaces, it was observed that presence of Ti-OH functional groups are directly related to formation of apatite [15,16].

Porous interfaces increases the fixation through bone growth towards the coating which forms a mechanical bond. Results *in vivo* have shown that pores interfaces influences the vascular formation on mesenchymal cell proliferation and the osteogenesis process [7]. Interconnected pores are important characteristic for blood circulation, as it increases the osteocondution and for the exchange of extracellular liquids [7,17,18].

The surface topography significantly influences cellular orientation, adhesion, proliferation and differentiation of osteoblasts [1,19]; such topography is defined by surface orientation and roughness, which is characterized by successive peaks and valleys [20]. Additionally, the most commonly used parameter for implant surfaces is R_a (arithmetic or average roughness) [21,22].

The surface energy can be measured from contact angle of this surface with a drop of liquids with different viscosities such as water [23], which is related to the chemical composition and surface geometry [18,22]. Hydrophilic surfaces exhibit better responses from the biological environment [18,22] as it can: enhance the wettability with blood; disseminate and bind fibrin proteins and matrix; induce a greater differentiation of osteoblasts; increase osteoconductivity [24,25]; aid in the adsorption of proteins [24]; improve initial bone apposition and bone/implant contact [26]; facilitate the fixation of the cells and accelerate the healing of tissues especially soon after the surgical placement of the implant [27].

Mechanical compatibility influences the recovery of damaged bone due to applied mechanical stress, also, the absence of mechanical stress can cause atrophy and bone resorption. Modulus of elasticity E of the Ti-6Al-4V alloy (110 Gpa) is lower than others metals used for this application but it is still higher than the bone tissue (10-40 Gpa). If these values differ significantly in the relationship between the implant and the bone, the transfer of tension between them will not be homogeneous. A low value in the modulus of elasticity can result in a better distribution of stresses between the bone and the implant, thus avoiding its loss [6].

12.1.1 Films formation by electrochemical process

12.1.1.1 Anodic Oxidation and Plasma Electrolitc Oxidation (PEO)

Anodic oxidation can be performed in an electrochemical cell (fig. 1) with two electrodes (titanium anode, platinum or titanium cathode), under galvanostatic (constant current density) or potentiostatic mode (potential constant) [5,28,29]. Oxidation and reduction reactions occur in the anode when a current or constant voltage is applied, establishing an electric field that guides the diffusion of ions present in the electrolyte, and leading to the formation of an oxide film on the surface of the anode. The main chemical reactions that occur during titanium anodization are [28,29]:

$$Ti \leftrightarrow Ti^{2+} + 2e^{-} \quad (1)$$

$$2H_2O \leftrightarrow 2O^{2-} + 4H^{+} \quad (2)$$

$$2H_2O \leftrightarrow O_2\,(gas) + 4H^{+} + 4e^{-} \quad (3)$$

$$Ti^{2} + 2O^{2-} \leftrightarrow TiO_2 + 2e^{-} \quad (4)$$

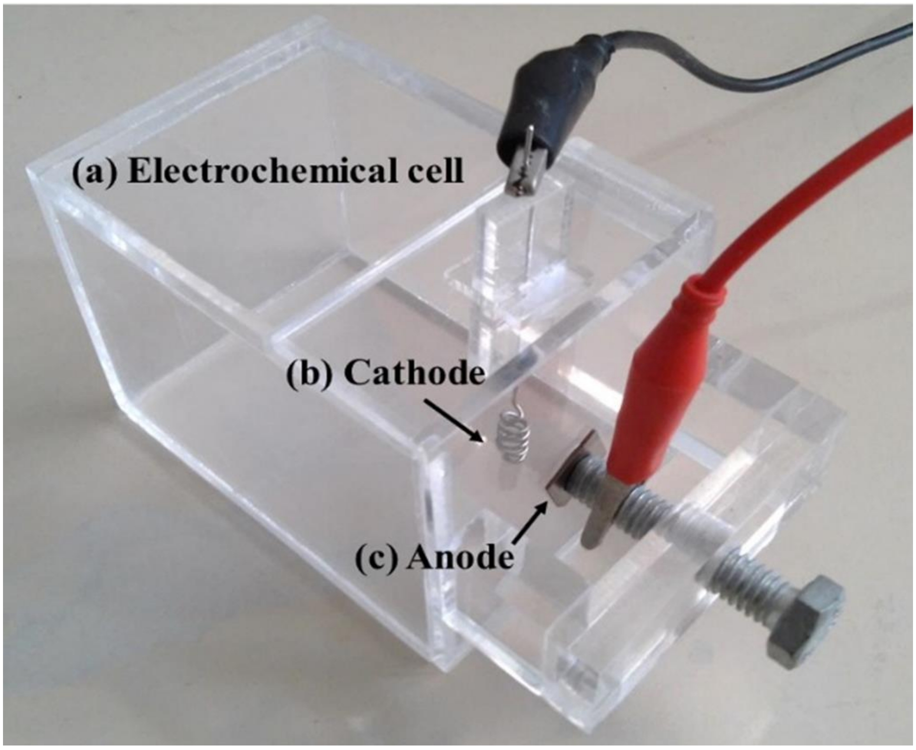

Figure 1. Photo of the anodizing apparatus: (a) Electrochemical cell, (b) Cathode and (c) Anode.

Anodic titanium oxides have high resistivity with respect to electrolyte and metallic substrate, thus the current/voltage drop occurs mainly through the oxide film. Since the electric field is sufficiently high to conduct ions through the oxide, with a current in free flow, the oxide will continue to increase, creating a thicker layer [29]. In this case, the thickness – d – of oxide layer is almost linearly dependent on the voltage U applied following the relation $d = \alpha U$, where α is a constant, which is usually within the range of 1.5 – 3.0 nm V^{-1} [29]. It has been reported that at 80 V and 100 V, using H_3PO_4 and H_2SO_4 electrolyte, anode oxide films are relatively thin and generally non-porous [30].

In conventional anodizing, with increasing voltage, if it exceeds the threshold of dielectric rupture potential of oxide barrier, a discharge phenomenon occurs. This phenomenon is an intermediate process between conventional anodizing and high energy plasma coating in a controlled gas pressure chamber without an aqueous solution [31].

Discharge phenomenon in electrolytic process was described first in the 1880s and further developed in the 1930s [32–34]. Despite the technology's relative old age, the treatment has a wide range of technological applications mainly due to the ability in modulate superficial characteristics like hardness, elastic modulus, wettability, porosity, roughness, chemical composition, crystallinity, corrosion resistance, and tribological behavior [35–37]. Others features are the process speed, ease of application, low safety hazard, relative geometrical independence of the sample surface, and incorporation of positive and negative ions into the oxide formed over the anode, even when using DC current [38,39].

The discharge phenomenon in an electrolyte is known as a Plasma Electrolytic Oxidation (PEO) or Micro-Arc Oxidation (MAO), however, this technique is also referred to as anode spark electrolysis, anodic oxidation under spark discharge, microplasma anodizing, anode spark electrolysis, anodic spark deposition, and anodic discharge anodizing [31].

There are different ways to perform PEO by modifying only the electrical source parameters. The PEO may be conducted using DC or AC mode, electric current or voltage ramps, in one-step or two-step and the simplest PEO configuration uses two electrodes immersed in an electrolyte and DC source with the possibility to apply the oxidation in Potentiostatic or Galvanostatic mode.

Plasma Electrolytic Oxidation (PEO) consists of an electrolysis process, similar to anodizing with the formation of sparks or electric discharges [11]. Under relatively low voltages, the anodizing phenomenon can be equated by Faraday's Law. When the applied voltage exceeds the dielectric rupture limit of the oxide, it will behave like a conductor which lead the process to the release gas and sparks could be generated [7,28,29], which contributes to the formation of a porous morphology film.

The Fig.2 exhibits Niobium (Nb), Titanium commercially pure, grade 2, (2cpTi), and Ti20%(wt)Nb alloy that were oxidized by PEO during 60s using electrolytes containing phosphoric acid (1 mol.l^{-1} H_3PO_4), under 350 V for Nb, 250 V for Ti and Ti20Nb alloy. For Nb condition it was added hydrogen peroxide H_2O_2 (80% vol. 1 mol. L^{-1} H_3PO_4 + 20% vol. H_2O_2).

The dielectric rupture, during the formation of anodic film, produces high temperatures and pressures in the electric discharge channels over the anode, resulting in electrolyte thermolysis and incorporation of ions presented in solution during the formation of film structure [11]. One of the main characteristics is a formation of luminescent gas that is attributed to electrolyte vaporization near the electrode (in this case anode) due to the Joule effect, combined with the electric voltage in electrolytic cell.

The dielectric rupture, can contribute to the crystalline transformation of the anodic films [11,28]. In general, when low voltage is applied, anodic oxide film is amorphous [11,28] and as the voltage increases, the oxide structure changes from an amorphous to a crystalline structure [40]. However, films grown on pure Ti at galvanostatic mode, exhibit a degree of crystallinity at low applied potentials (10-20 V) [30]. Additionally, the crystallization sites inside the films can be associated to presence of anions of acid residues in the film [30].

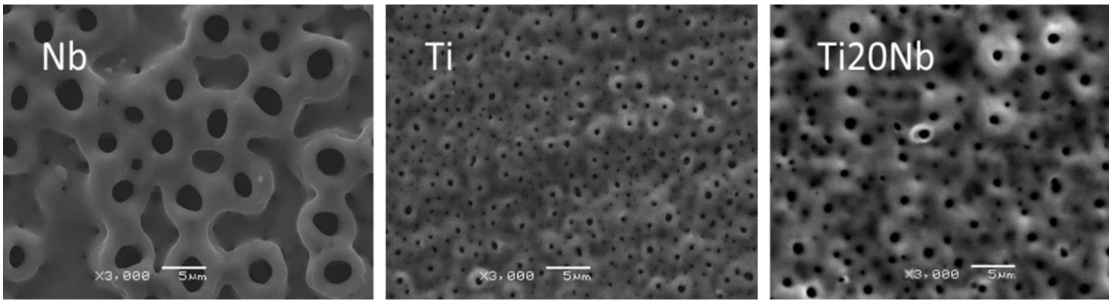

Figure 2. SEM images of oxide coatings grown on Nb with 80% vol. 1 mol. L^{-1} H_3PO_4 + 20% vol. H_2O_2 electrolyte under 350 V/60s, cp2-Ti and Ti-20Nb with 1 mol. L^{-1} H_3PO_4 under 250 V/60s.

The electrochemical parameters of anodic oxidation significantly affects growth behavior, chemical and structural properties of the films. Such parameters includes the electrolyte solution, concentration, temperature, electrical parameters, anodizing time and stirring speed of the solution [7,29]. In general, it is accepted that growth behavior of anodic oxide film is characterized by electrochemical dynamics between the oxide film formation capacity and oxide dissolution rate determined by the nature of the electrolyte [29,40].

By optimizing experimental conditions of oxidation by electrolytic plasma it allows the production of porous crystalline films with good adhesion to the substrate, high hardness and with thicknesses up to 100 μm [5,7,28,36,38]. For anodic films obtained on Ti6Al4V, the KOH and Na_2WO_4 additions in aluminate-based electrolytes smooths the surface and reduces porosity of these films, improving the tribological properties [41].

12.1.2 Nanotube arrays

Many types of process have been used to prepare nanotube arrays, such as anodizing, sol-gel chemistry, polymerization and hydrothermal [10,42]. The anodization is the most effective method to obtain nanotubes arrays as it can grow self-organized nanotubes, and when a fluoride-based electrolyte is used, their dimensions can be controlled [43,44].

The anodization technique allows growth of nanotubes on transition metals (Ti, Al, Zr, Hf, Nb, Ta, W) and its alloys [7]. Fig.3 shows a typical nanotube morphology via top-view and cross-section grown on Nb, Ti and Ti-40Nb alloy [45].

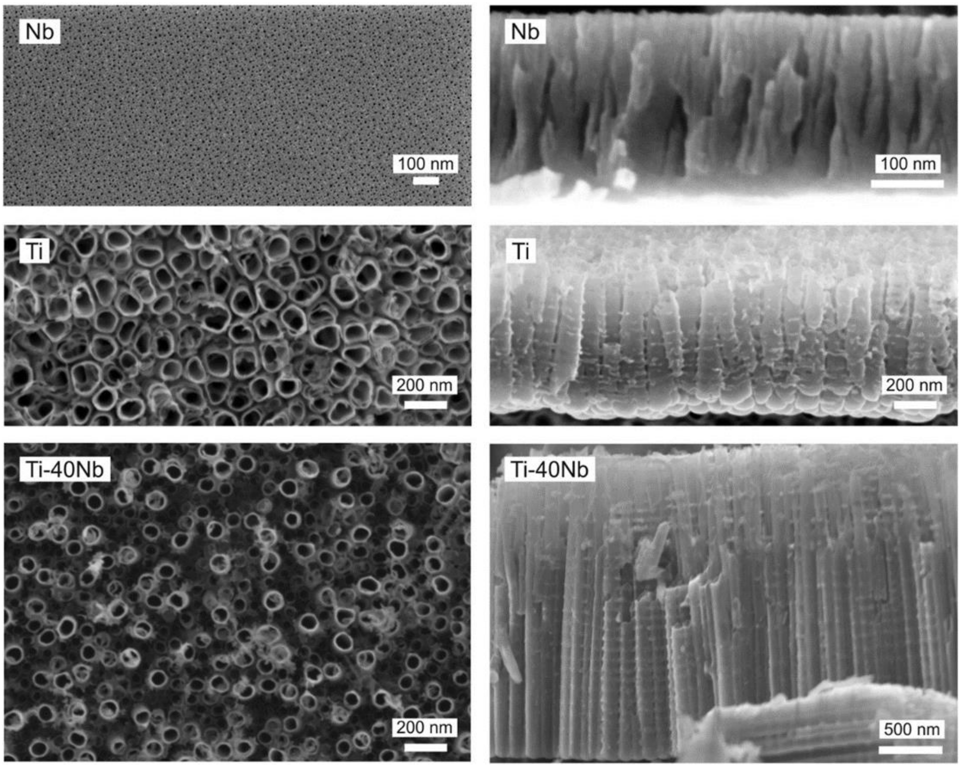

Figure 3. SEM images of oxide coatings grown on Nb, cp2-Ti and Ti-40Nb at 20 V in 1M H3PO4 with 0.16 M HF solution: *left column* - top view after 2 hours anodization and *right column* – cross-sectional view after 4 hours anodization. Reproduced with permission from Gebert, A., Eigel, D., Gostin, P.F., Hoffmann, V., Uhlemann, M., Helth, A., Pilz, S., Schmidt, R., Calin, M., Göttlicher, M., Rohnke, M., Janek, J., 2016. Oxidation treatments of beta-type Ti-40Nb for biomedical use. Surf. Coatings Technol. 302, 88–99. ©2016, Elsevier [45].

Formation mechanism of nanotubes is similar to anodic films since the electrochemical cell is the same [42]. Normally, the anodization process to grow nanotube arrays is usually carried out by applying a potential step (or ramp) at a constant voltage (1–30 V) in aqueous electrolyte or in non-aqueous electrolytes (5–150 V) containing approximately 0.05m–0.5m (0.1–1 wt %) of fluoride ions (and usually some background ion species) [44].

The process of nanotubes formation occurs in accordance to reactions and stages illustrated in Fig.4 [46]. The three steps (Fig. 4 c-e) can be monitored by a typical curve of current vs time obtained during the anodizing process [42,46], corresponding to stage I-III of fig. 5, respectively. At the stage I of anodization (Fig.5), a rapid decrease in the current due to formation of a compact oxide layer is observed. At stage II, the current rises to a maximum value owing to process of pores nucleation. Finally at stage III, the current attains a constant value and at the oxide/electrolyte interface, the rate of oxide formation and dissolution are equal; allowing the formation of nanotube arrays [44,47].

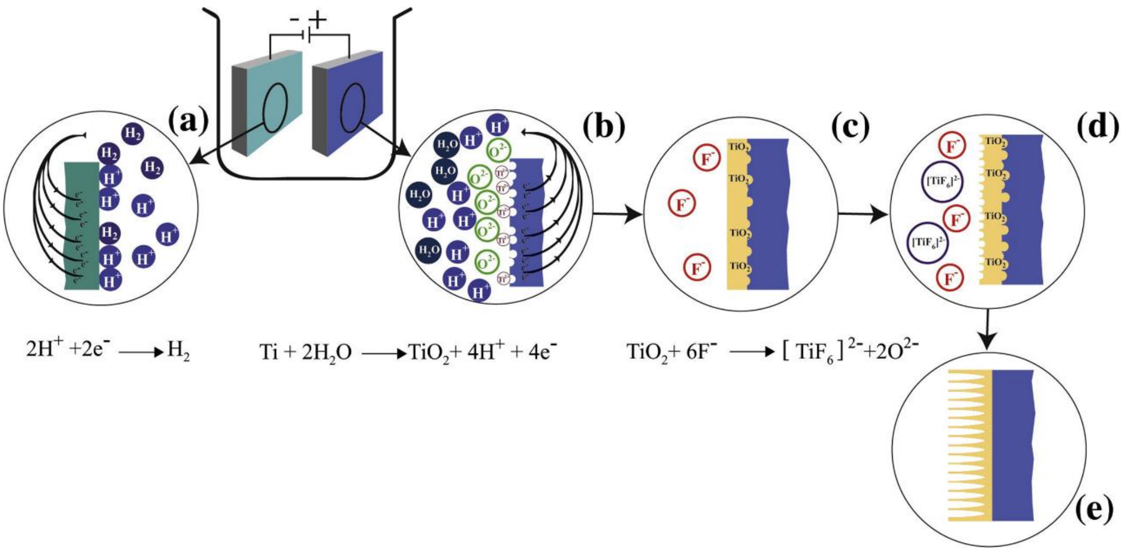

Figure 4. Growth of regular TiO_2 nanotubes: (a) cathodic reaction, (b) anodic reaction, (c) transition state of TiO_2 layer, (d) starting of nanotube formation and (e) titania nanotubes Reproduced with permission from Minagar S, Berndt CC, Wang J, Ivanova E, Wen C. A review of the application of anodization for the fabrication of nanotubes on metal implant surfaces. Acta Biomater 2012;8:2875–88. ©2012, Elsevier [43].

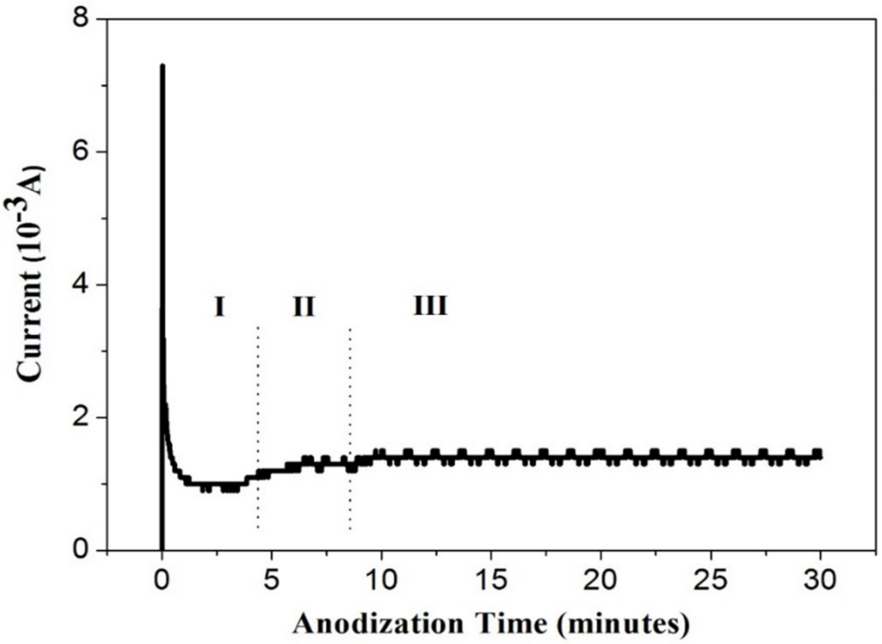

Figure 5. Typical current-time anodizing curve to titanium alloy sample; I, II and III are the different nanotubes growth process steps.

Various parameters can influence the physical properties and morphology of nanotubes. The most important are composition, pH and concentration of electrolyte, applied voltage, current density, temperature, and anodization time, which can be controlled by anodizing techniques [46–51]. Researchers have not only analyzed the characteristics of the nanotube arrays, but also demonstrated biocompatibility, bioactivity and bone cell/material interaction of nanotubes surfaces using *in-vitro* or *in-vivo* tests [48–53].

Several researchers have shown that the average tube diameter increases with increasing anodizing voltage [42,46,48–50]. This behavior occurred because the electric field strength across the oxide is determined by the applied anodization voltage, thus affecting migration of ions and consequently the dissolution rate of oxide layers [49,52]. As a result, the average internal tube diameter of nanotubes arrays is directly proportional to the applied voltage [49,52].

The effects of temperature and applied voltage on nanotubes grown on pure Ti are showed in Fig. 6 [48]. The electrolyte used was a non-aqueous solution containing ethylene glycol + 4 wt% H_3PO_4 + 0.25 wt% HF at range of voltages and temperatures of 60-120 V and 0°-30°C, respectively. When increasing the applied voltage, the diameter increases as well. However, at 30 °C the diameter was greater compared to 0 °C, this occurs due to a low temperature that decreases the ionic exchange in the electrolyte and at 0 °C the tube diameter had hexagonal shape, while at 30 °C a circular shape. These geometries were due the temperature effect, since at low temperature the role of fluorine ions etching becomes unnoticeable [48]. The nanotubes anodized at a 120 V and 0°C showed the better results for *in-vitro* tests, because the nanotube arrays showed the higher surface area exposed to SBF (Simulated Body Fluid).

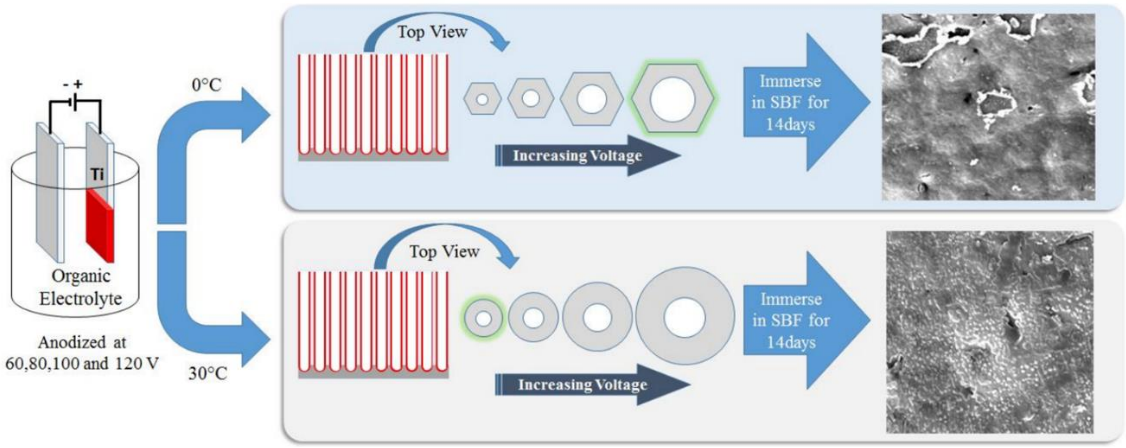

Figure 6. Effects of temperature (0 ^{0}C and 30 ^{0}C) and voltage (60 – 120 V) on diameter and *in-vitro* tests of nanotube arrays. Reproduced with permission from Nasirpouri F, Yousefi I, Moslehifard E, Khalil-Allafi J. Tuning surface morphology and crystallinity of anodic TiO2 nanotubes and their response to biomimetic bone growth for implant applications. Surf Coatings Technol 2017;315:163–71. ©2017, Elsevier [48].

The electrochemical process to obtain nanotubes or porous films have been shown to be efficient at improving the metals surfaces for biomedical applications. This knowledge regarding the experimental parameters of the electrochemical process are of significant interest, since the reactions of body fluids on to the implant surface depends on the surface properties.

12.2. Commercial applications

Surface treatments have been extensively proposed and developed for the dental and orthopedic applications of titanium devices [1,54]. Nanofilms are one of the most prominent class of surface modifications achieved through the use of several techniques aiming this area of application [55] between them, titanium oxide nanofilms are one of the most used in applications of commercially available medical devices.

Dental implants are generally intended to be used according to the osseointegration principle, which advocates a fusion between the implant and host bone. Surface modification techniques are often utilized to improve the osseointegration ability of titanium dental implants [54]; in these cases, osseointegration is highly desirable once these devices are permanent implants. The success of prosthetic devices strongly depends upon the implant stability and anchorage in bone and nanofilms obtained by anodic oxidation have been successively used to promote osseointegration of dental implants.

Busquim et al., [56] investigate the surface chemistry and crystal structure of a titanium oxide layer on a commercially micro-arc-oxidized dental implants. The surface chemistry and oxide crystal structure of machined dental implants and two types of commercially anodized titanium dental implants, Vulcano Actives® and TiUnite® (manufactured by Conexão Sistemas de Prótese (Brazil) and Nobel Biocare (Sweden), respectively). According to Busquim et al., [56], the implant anodized surfaces have the ability to promote osseointegration.

Liu et al., [57] compared the surface characteristics and cellular adhesion for several dental implants which are commercially available: 3i Nanotite® (4 × 10 mm, Biomet 3i, Palm Beach Gardens, FL), Astra OsseoSpeed® (3.1 × 11 mm, Astra Tech, Molndal, Sweden), Nobel Biocare TiUnite® (3.5 × 10 mm, Nobel Biocare, Goteborg, Sweden), and Straumann SLActive® (3.3 × 10 mm, Straumann, Waldenburg, Switzerland). Surface treatment technologies such as sand blasting, acid etching and anodic oxidation were employed by the manufacturers on the implants threads which should integrate with the host bone.

Gaintantzopoulou et al., [58], studied phases of the root surface of commercially available titanium dental implants, subjected to various surface treatments. Table 1 shows the commercially available implants tested by Gaintantzopoulou et al., [58]. According to Gaintantzopoulou et al., [58] titanium oxide anatase, rutile and amorphous phases may be present in commercially available dental implants. The anatase phase is more pronounced in implants submitted to anodic oxidation and can be accompanied with a rutile phase. Surfaces treatments such as double-etching, sandblasting sand and blast-acid etching are related with to the occurrence of rutile and/or amorphous phases. Thus, the identification of the TiO_2 phases in the surface layers of dental implants should be judged as mandatory by the manufacturers once variations in the biological activity of these polymorphs are possible.

In contrast to dental implants, orthopedic medical devices in many cases are not intended to osseointegrate, especially when plates and screws are used in the surgical internal fixation of fractured bones. Implants used in orthopedic trauma treatments generally are not permanent, they are used to provide stabilization of fracture focus during the time period necessary to the bone to heal; after that the plates and screws should be removed [6].

Table 1. Commercially available implants. Reproduced with permission from Gaintantzopoulou M, Zinelis S, Silikas N, Eliades G. Micro-Raman spectroscopic analysis of TiO2 phases on the root surfaces of commercial dental implants. Dent Mater 2014;30:861–7. ©2014, Elsevier [58]

Product	Surface Treatment	Manufacturer
Allfit	Al_2O_3-blasted	Dr. Idhe Dental, Munich, Germany
Ice	Smooth machined	3i, Palm Beach Gardens, FL, USA
IMZ TPS	Titanium plasma-sprayed	Friedrichsfeld, Mannheim, Germany
Laser Lok	Tricalcium phosphate/hydroxyapatite-blasted	Biohorizons, Birmingham, AL, USA
PrimaConnex	Calcium phosphate-blasted	Lifecore Biomedical, Chaska, MN, USA
Ospol	Calcium-anodized	Ospol, Malmö, Sweden
Osseospeed TX	Titanium oxide blasted/fluoride-treated	Astra Tech, Mölndal, Sweden
Osseotite Full	Acid-etched (double)	3i, Palm Beach Gardens, FL, USA
Replace Select	Calcium phosphate-anodized	Nobel Biocare, Göteborg, Sweden
SLA	Al_2O_3-blasted/acid-etched	Institute Straumann, Basel, Switzerland
Trilobe	Al2O_3-blasted	Southern Implants, Irene, S. Africa

Orthopedic implant manufacturers have used anodized surface (TiO_2 nanofilms) to improve corrosion resistance and for identification purposes [59]. Titanium anodization produces surfaces with different colors due to interference phenomenon. Different colors have been used to identify differences in dimensions or other features in implants for a given application, e.g. orthopedics plates for bone fractures that possess right and left models. The different implant surface colors are used to avoid confusion by the surgeon during the implantation procedure allowing ease identification of implant models and dimensions.

Orthopedic permanent implants such as those used in hip and knee prosthesis; however, depends upon the osseointegration to achieve success in restore the articulation function. These medical devices can be manufactured to adapt better to bone using several methods such as meshing, texturing, and porous or bioactive coatings. Depending on the design strategy, these coatings either should be dissolved gradually or should provide a stable, non-dissolving interface for bone growth [60]. Commercially available implants for total hip arthroplasty typically have coatings applied using hydroxyapatite, calcium phosphate, and porous metal surface treatments. These approaches also have yielded good clinical results when premature delamination of the coatings is avoided by optimal adhesion to the implant [60,61].

Despite the clinical success of hydroxyapatite demonstrated after several years of patient follow-up [62], alternatives such as the use of nanofilms or the combination of different treatments have been proposed to obtain bioactive surfaces in total hip arthroplasty implants. As an example, Hall et al., [63] used hip arthroplasty femoral stems coated with Ti6Al4V beads that were treated by anodic oxidation for enhanced bioactivity. In vivo animal study was conducted and according to Hall et al., [63] treatment of titanium alloy using anodic oxidation had a marked effect on bone ingrowth and soft tissue in the porous coating of a functioning total hip replacement femoral stem. The surface treatment significantly increased the amount of bone ingrowth and enhanced implant integration with bone and marrow, decreasing fibrous tissue within the porous coating of the component.

According to Zhang et al., [64], the design of coatings for permanent orthopedic implants must satisfy several important criteria: firstly, the coating must be biocompatible and not trigger significant immune or foreign-body response; secondly, it must be osteoconductive; thirdly, the implant must also be osteoinductive. Furthermore, the coating must have sufficient mechanical stability when under physiological stresses and should have anti-microbial properties minimizing the risk of prosthetic infection. However, none of the commercially available prosthesis are able to satisfy all of the above criteria. In summary, there is enormous potential for new research and development of coatings and surface treatments for new dental and orthopedic medical.

12.3. Mechanical stability of anodic layers

Perhaps because of the complexity to obtain effective functional and novel coatings on materials used in medicine, authors can concentrate mainly on specific aspects of interest: bioinertness, bioactivity, drug delivery and, corrosion resistance. However, the compatibility must be satisfied as a whole, preserving or even improving other critical properties expected for coatings on biomaterials, as the thermal diffusivity [65], the absence of toxic elements to the living tissues [66] and much others. Our research group has developed a tradition to contrast two or more functionalities, searching for appropriate ratios among them, notably addressing to the *biocompatibility* and the *tribo-mechanical behavior* of layers and films produced on biomedical materials. The mechanical stability of a coating grown or deposited on a device is complementary to any other property it can exhibit. More than everything else, the functional coating must survive to the surgical procedure – it cannot be lost by screwing or shearing [67]; after that, it is expected to not release debris or detach prematurely form the surface [68], assuring the long-term use of the prosthesis in the body.

Analyses of residual stresses σ allow predicting a threshold layer thickness h to prevent spontaneous detachment [69]:

$$h = \frac{EG}{Z\sigma^2}. \tag{1}$$

In the equation (1), Z is a dimensionless constant, and $G = {(1-\nu^2)K_{IC}}/{E}$ is the released energy rate for a layer with elastic modulus E, Poisson´s ratio ν and stress intensity factor K_{IC}. However, we observed that such direct prediction is hardly effective for ceramic-like layers as those produced by PEO, because of its inherent porosity, allotropic transformations occurring in the film growth (which results in the material densification), and the pore settlement after cooling [70]. These statements are important since the estimated localized temperature during PEO is more than 600 ºC, attained during the electric breakdown regime (see section 12.1.1). As a result, PEO TiO_2 layers produced with H_2SO_4 electrolytes over Ti substrates detached spontaneously during growth when reached ~3 μm thick at 180 s anodization time, a much lower thickness than that predicted by the equation (1) - 45 μm. In non-detached coatings, the residual stresses in the interface substrate-coatings also dictated the surface performance under plastic deformation. In this particular case [70], optimum layer thickness versus adequate tribo-mechanical features (low elastic modulus, good scratch resistance) was attained with 60 s anodizing time. The coating presented *tensile* residual stresses in opposition to compressive residual stresses in the titanium substrate beneath. Since the substrate residual stresses varied from –30 MPa to –110 MPa in PEO processes carried out for 10-60 s, the critical load for detachment under severe scratching with acute tip could be increased 10-fold in the same anodizing time range.

Another matter of concern in coatings is the stress shielding in the implant-bone interface, previously discussed in the introduction section. The occurrence of such phenomenon at the implant site can permanently limit the stability and performance of a dental or bone prosthesis, eventually resulting in unexpected second surgeries and extra medical costs [9]. In spite of the low thickness of a layer or film as compared to the prosthesis dimensions, the surface is inwardly connected with living tissues, through which mechanical stresses are transferred from the body to the implant during the biomechanical activity of the patient. In the case of bone or dental implants, assuming a well-established osseointegration and negligible influence of micromotions, the lack of a matching elastic modulus can lead to the coating detachment either from the bone or from the implant bulk.

Our group has worked with PEO TiO_2 layers rich in Ca and P. These elements are incorporated to the oxide during the spark regime of the anodization, as discussed previously in Section 1.1.1, providing bioactive surfaces for dental and bone prosthesis. The process involves ion release in the material´s surrounding with subsequent calcium phosphate growth on its surface, and improved cellular response [71–73]. The good bioactivity was easily confirmed in our experiments through *in vitro* tests, carried out using a simulated body fluid with 14 days soaking time [74]. We first reported that these layers are featured by low elastic modulus values as compared to the titanium substrate, i.e., about 40 GPa in TiO_2 layers in contrast with ~130 GPa in the bulk titanium [75]. The results indicate that PEO modified surfaces presented conditions to be more mechanically compatible with the host bone, therefore facilitating the load transfer to the biomaterial. Of course, the aforementioned elastic modulus of the Ca-P containing TiO_2 layers are much lower from a dense TiO_2 bulk, ~200 GPa [76]. Such drastic reduction owes to the inherent porosity of layers anodically grown in the dielectric rupture regime, as depicted in Figure 2.

One matter of concern could be the real effectiveness of a mechanically biocompatible coating, with few micrometers thick, to minimize stress shielding effects with a material of a with higher elastic modulus than the host bone. In this case, one should consider that titanium and some Ti-alloys as Ti-6Al-4V present relatively low elastic modulus (~130 GPa) as compared to other typical metallic biomaterials, as stainless steel AISI 316 L (200 GPa) and CoCr (220 GPa) [76]. Moreover, Ti(Nb,Ta,Zr)-based alloys present even lower elastic modulus (< 100 GPa) [1]. By assuming mechanical compatibility as the only criterion, PEO TiO_2 layers could be adequate choices for Ti and Ti-based alloys, better than stiffer coatings as DLC or dense ceramic layers, with the additional advantage to present adequate conditions for the osseointegration. Moreover, PEO layers grown on low elastic modulus alloys presented similar features as those produced on commercially pure Ti, as discussed in section 12.1. However, besides adhesion and elastic modulus, the tribo-mechanical compatibility also involves the layer strength during loading, as seen further.

As discussed above, as well as in other ones presented in this section, elastic modulus were assessed through the instrumented indentation technique, a method where force and displacements of a tip loaded against the surface are controlled with nN and nm resolutions, respectively, as schematized in Figure 7. Typical indenters used present the Berkovich geometry, a three-sided pyramid made of diamond. This method, also known as nanoindentation, is the technique suitable to investigate thin films and a few micrometer-thick layers [77], which are not assessed by traditional methods designed for bulk materials, say, the tensile strength testing, since a thin coating represents only a tiny fraction of the whole centimeter-size specimen. In instrumented indentation, hardness and elastic modulus are obtained from the force-displacement curve (Figure 7.b), calculated by the well-established Oliver and Pharr analytical method [78]. Some limitations occur in applying the Oliver and Pharr method if the surface is rough [79], or if the material present some limited strain-hardening [78].

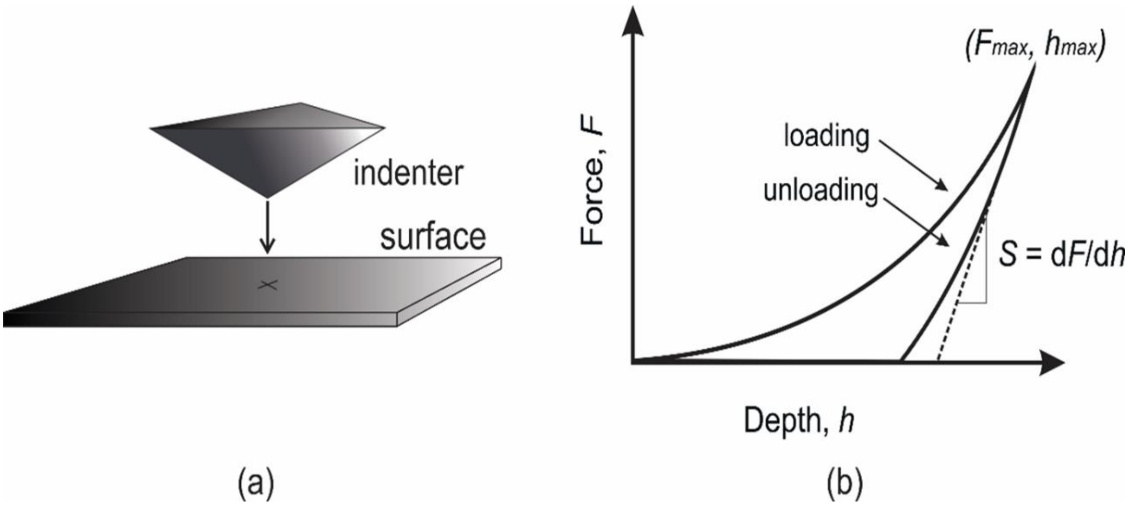

Figure 7. (a) Schematic representation of a Berkovich tip reaching a surface, in an indentation test. (b) A typical force versus depth curve, from which hardness and elastic modulus are calculated through the Oliver and Pharr method. The analysis demands the knowledge of maximum force and depth, the contact stiffness *S*, and tip geometric factors.

In addition, it is possible to determine the effective elastic modulus, by subtracting the substrate effects from the surface elastic response. The knowledge of a layer´s effective elastic modulus is important for design purposes. The obtained result correlates “only” to the PEO layer, instead of the layer + substrate (the composite). The Xu and Pharr proposition proved to be an efficient method for several types of PEO layers. It presents a solution for the effective elastic compliance $[(1-\nu)/\mu]$ of a layer over a half-space indented with a flat cylindrical punch, where μ and ν are the composite shear modulus and Poisson´s ratio, respectively. The adaptation of the method to provide elastic modulus *E* of a layer measured with a Berkovich tip demands some basic assumptions from the contact mechanics theory [80]. Figure 8 shows the elastic modulus profile measured on a PEO TiO_2 layer over a titanium substrate, and the corresponding effective elastic modulus profile of the layer, calculated with the Xu and Pharr method [81]. As values of the composite profile increased toward the titanium elastic modulus with the penetration depth, due to the increased depth to the layer thickness ratio, they were approximately constant in the substrate independent profile. We have been employed other analytical methods in biomaterial coatings, as the Doerner and Nix method [35] and the proposition by Hay and Crawford [82], also obtaining satisfactory results.

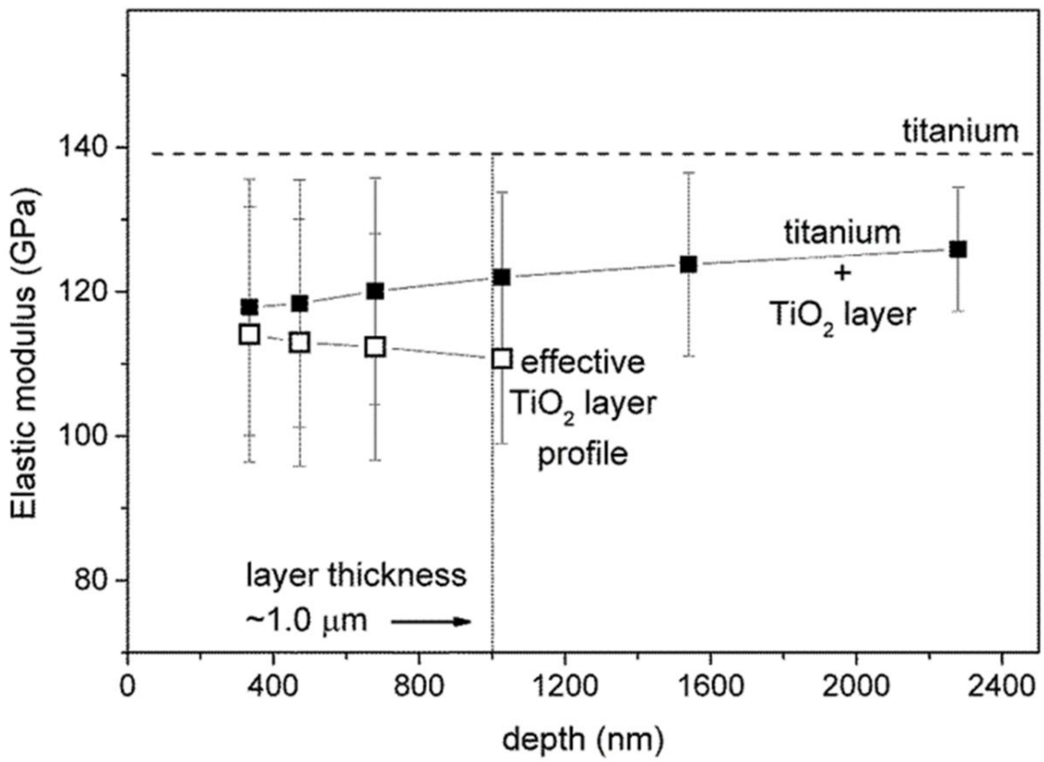

Figure 8. Elastic modulus from instrumented indentation, of a 1.0 μm thick TiO_2 layer produced on titanium by PEO, using H_2SO_4 electrolyte. Close symbols correspond to the layer + substrate profile, calculated directly with the Oliver and Pharr method. The

open symbols ascribe to the effective layer elastic modulus, independent from the substrate influence, inferred with the Xu and Pharr method. The dashed line indicates the substrate elastic modulus for comparison purposes.

In spite of the interesting elastic response disclosed by the CaP-containing TiO_2 layers, whose elastic modulus is close to the bone values, layers were rather fragile [75] under scratching and indentation tests. Improvements into the structure of these layers were investigated using various methods, with the focus in preserving the good bioactivity response of these Ca- P rich layers.

One of the methods proposed by our group was the heat treatment subsequent to PEO [83]. The wear rate of CaP-containing TiO_2 layers decreased one and two orders of magnitude after heat treatments in air at 400 ºC and 600 ºC, respectively, as compared to the only PEO sample, maintaining the integrity of the film at specific conditions. The enhanced wear strength was mainly due to the anatase to rutile alotropic transformation. However, such improvement was obtained with the expenses of elastic modulus, which increased from 40 GPa to ~140 GPa. On the other hand, these heat-treated layers presented very hydrophilic surfaces due to the production of vacancy sites favorable for chemical bonds of OH groups, leading to an increase in water adsorption.

Another method investigated to improve the tribo-mechanical response of PEO layers was the combination of two treatement techniques at the same surface, namely the use of shot blasting or plasma nitriding prior to PEO. In this configuration, instead of changing the layer properties by varying their crystalline structure, the modification of the substrate offers different conditions for the anodization process, at the same time that it provides a better load-bearing capacity to the layer under scratching or normal loading [84]. The shot blasting technique consists of blasting the surface with hard particles, such as alumina (Al_2O_3), which can be chemically stable and not harmful to the body [29]. The CaP-rich TiO_2 layers grown over titanium surfaces, previously shot blasted with alumina particles of 280 µm diameter, presented low values of elastic modulus, similar to those of layers formed on the raw titanium (~40 GPa). Moreover, the shot blasted + PEO layer maintained their integrity under nanoscratch tests, disclosing critical loads for detachment three times higher than that presented by the only PEO layer [84]. Thus, joined shot blast and anodic oxidation processes can lead to some of the requirements for the improved bioactivity on titanium surfaces. In a different approach [85], the plasma nitrided titanium surface was harder and stiffer than the substrate, consisting of a stratified case composed of nitride precipitates (TiN, Ti_2N) and nitrogen-expanded Ti matrix. PEO TiO_2 layers grown on these surfaces presented elastic modulus of ~75 GPa, with reduced brittleness under normal loading and scratch tests.

Although sodium hydroxide is relatively known for modification of surface on Ti in the alkali treatment, our group performed the use of sodium hydroxide as an electrolyte for PEO [80] exhibiting better mechanical properties compared to the conventional alkali treatment [85]. The combination of the shot blasting of the substrate follow by the PEO treatment using the sodium hydroxide as an electrolyte [86] improves the corrosion resistance when compared with the reference Ti (surface without treatments). Results of electrochemical measurements using the open-circuit potential (OCP) conditions showed that the protective effect to corrosion in the studied physiological environment increased in Ti and shot blasted Ti after the oxidation process, due to the oxide layer.

12.4. Conclusions

Ideal materials that can be a substitute for the use of orthopaedic applications are what drives the current research on titanium implants. The recent development on titanium surfaces assists in the biocompatibility, mechanical and chemical stability as well as the improvement in the healing process for targeted applications. Even though there has been considerable research on titanium surfaces, there are still need for improvement because of the specific properties of the bone and the wide use of commercial implants which will always need evolution in the regenerative process and compatibility of the body.

12.5. References

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