BIOACTIVE FILMS ON TITANIUM SURFACE OBTAINED BY ANODIC OXIDATION IN SULPHURIC AND PHOSPHORIC ACID

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Abstract. *The anodic oxidation technique has been used with success to became titanium surface bioactive. The literature reported that anodized surface presented good response concerning to bioactivity tests in vitro and in vivo. A great variety of electrolytes has been used with ion incorporation on the anodic film in many cases. This characteristic is very important to surface that will be used in human body when the osseointegration is necessary. This surface also must present good mechanical property because there are situations where the implant is submitted to load and the ensemble bone/implant must give an adequate response. However hardness and elastic modulus measurements on the anodic films are not found frequently due to their surface characteristics (roughness and porosity) that difficult the mechanical tests. So, the aim of this work was to increase the natural titanium oxide on the commercial pure titanium using anodic oxidation technique and characterize the morphology and mechanical properties of these new surfaces. The material used in this work was commercially pure titanium sheets (20x10x1) mm^3. The samples were abraded with silicon carbide paper grade 300 and 400. Anodic oxidation was carried out under potentiostac mode at room temperature using 1M H_2SO_4 (180V/60s) and 1M H_3PO_4 (200V/60s) electrolytes and a rectangular titanium plate as counter electrode. The morphology and structural changes were evaluated by scanning electron microscopy and X-ray diffraction techniques, respectively. The relation between hardness and reduced elastic modulus (P/S^2) was analyzed using a nanoindenter and the model proposed by Oliver and Pharr. It was observed that both oxidized surface present pores. It was observed that the anodic film produced with phosphoric acid showed an appearance of pores formed on the relatively flat ground oxide surface, while the surface obtained with sulphuric acid presents smaller pores and a rougher surface than another one. Concerning to nanoindentation results the analysis of P/S^2 showed that the elastic modulus of phosphoric acid is smalller than that obtained with sulphuric acid.*

Keywords*: titanium, anodic oxidation, hardness, elastic modulus*

1. INTRODUCTION

From the origins of medicine man has substituted, partly or all, living tissue using the most diverse materials. However only in the last 60 years there has been a significant progress in the field of the engineering of materials (Brånemark *et al*, 1977).

Artificial materials implanted in bone are usually encapsulated through fibrous tissue which isolates them from direct contact with the bone matrix, resulting in the absence of chemical or biological connection in the tissue/material. In other situations some materials can just contact physically with bone matrix, which also limits the use of them when the objective is bone-repair. Among the materials that present such characteristics are stainless steel AISI 316L, titanium, the alloys of Co-Cr-Mo and polyethylene, which are considered bioinerts (Kokubo *et al*. 2004).

Hench and Shirtliff (2003) showed that bone can bond spontaneously with some ceramics, without it being fiber encapsulated, as in the case of metals. These ceramics or all materials that present similar characteristics are known as bioactive, and they are capable of promoting the bone and implant bonding, inducing a specific biological answer in an interface with living tissue. As examples of these materials are bioglass, glass-ceramic and calcium phosphate.

The metallic materials do not link directly to the bone tissue; therefore they are usually covered with another type of material, for instance, hydroxyapatite. This type of surface treatment can improve the ability of the material in bonding directly to the living tissue that is, turning it bioactive (Santos Jr. *et al*., 2007, Yang *et al.*, 2004, Chen *et al*., 2009).

Among the metallic materials titanium and its alloys have been used in the confection of biomedical components, mainly in the orthopedic and dentistry area, due to excellent mechanical properties, biocompatibility, resistance to corrosion, chemical stability in a physiologic atmosphere and elastic modulus closer to bone elastic modulus, when compared with stainless steel and Co-Cr-Mo alloys. The existence of an oxide layer formed naturally on the surface is responsible for the excellent biocompatibility and resistance to corrosion of the titanium and its alloys (Sul *et al.*, 2003).

Several superficial treatments have been performed on the metallic titanium to become its surface bioactive (Santos Jr. *et al*., 2007, Velten *et al.* , 2002 , Feng *et al*., 1999 , Liu *et al*., 2004). When in contact with bone tissue, the bioactive surface forms an active biological apatite on it, and they bond to the tissue through this layer. This is the principal interaction mechanism between a bioactive artificial material and the bone tissue (Kokubo, 1991). When this happens, a strong chemical bond is initiated between the bone mineral and the apatite surface formed on the bioactive material, reducing the interface energy between them (Kokubo *et al*., 2004).

Among surface treatment, anodic oxidation has been highlighted due to some advantages such as easily an oxide film deposited well adhered on titanium surface through an electrochemical process, porous and roughouss films can be formed by applying high voltage to produce dielectric breakdown. The parameters that affect the characteristics of the oxides are the electrolyte solution (type, concentration, pH and temperature), electrical conditions (potenciostatic and galvanostatic mode), anodization time and stirring speed (Sul *et al.*, 2003, Diamond and Pedeferri , 2006).

Yang *et al.*, (2004) oxidized titanium commercially pure (cp-Ti) in H_2SO_4 electrolyte with different voltages and observed that an increase in both the applied voltage (90V, 155V and 180V) and electrolyte concentrations (0,5M – 3M) leads to an increase in porosity and pore size on the oxidized surface due to the phenomenon of dielectric breakdown (105V). They also verified the presence of anatase and rutile crystal structures on the anodic film and the film obtained with 90V was formed only anatase phase and that obtained with 180V, only rutile. The heat treatment at 600^oC/1h after the anodic oxidation results in a predominance of rutile phase. They observed (Yang *et al.*, 2004) that all the samples submitted to heat treatment formed an apatite layer on the titania film when soaked during 3 days in simulated body fluid (SBF) while the apatite layer was not observed after 6 days in surfaces oxidized with voltage of 90V without heat treatment. Chen *et al*., (2009) observed the same influence of the voltage in porosity and pore size of the oxidized films, by using 1M H_3PO_4 as an electrolyte. The films anodized with 100V were very thin and those obtained with 200V and 300V, became more porous with bigger pores size. After oxidation process the anatase phase was observed only to surface oxidized with 300V. Cui *et al.,* (2009) evaluated the structural changes on the titania film obtained with four electrolyte: sulphuric acid, phosphoric acid, acetic acid and sodium sulfate under different voltages. Films anodized in sulfuric acid consisted of anatase and rutile phases and with the increase of the voltage only rutile phase was observed while those anodized in phosphoric acid and acetic acid electrolyte were amorphous. The anodic film obtained with sodium sulphate electrolyte was composed with only rutile. After bioactivity tests in vitro using SBF they verified the nucleation of the apatite layer on the anodic films obtained with sulphuric acid and sodium sulphate after 6 days and nothing on the surface obtained with phosphoric acid. So, the literature has been shown the role of the anatase and rutile phases present on the oxidized surface on the improvement of these surfaces bioactivity (Yang *et al*., 2004 , Cui *et al*., 2009).

Another important parameter that must be considered concerning to biomaterials is the elastic modulus. It is an important property that should be taken in account to materials designed for hard tissue replacement. Irregular stress transfer at the interface bone-implant, or stress concentration in a few points at the interface, can leave to an early implant failure and bone loss. This could be avoided using materials with reduced elastic modulus, preferentially near to the bone modulus. Ti anodic films are an attempt to create a gradient of elastic modulus from titanium substrate to bone. Artificial materials developed to replace hard tissues must possess low modulus to minimize bone resorption (Long *et al.*, 1998). Using instrumented indentation technique it is possible to determinate the hardness and elastic modulus (E) of the oxidized surface (Oliver and Pharr, 1992, Mante *et al.*, 1999). So, the objective of this work was to modify cp-Ti surface using the anodic oxidation technique and evaluate the morphological, structural and mechanical properties of this new surface.

2. EXPERIMENTAL

It was used a sheet of commercially pure titanium (cp-Ti), grade 2 with thickness of 1 mm. Samples of cp-Ti, with dimensions (20x10x1) mm, were abraded with silicon carbides sandpaper 300 and 400, washed in acetone, iso-propyl alcohol and distilled water during thirty minutes in each solution, dried during 24 hours in an oven at 40^oC. The anodic oxidation was carried out by potentiostatic mode and room temperature. A titanium plate was used as counter eletctrode. One group of the samples was oxidized with 1M sulphuric acid at 180V/60s and another group was oxidized with 1M phosphoric acid at 200V/60s. After then the oxidized surface were submitted to heat treatment at 600^oC/1h.

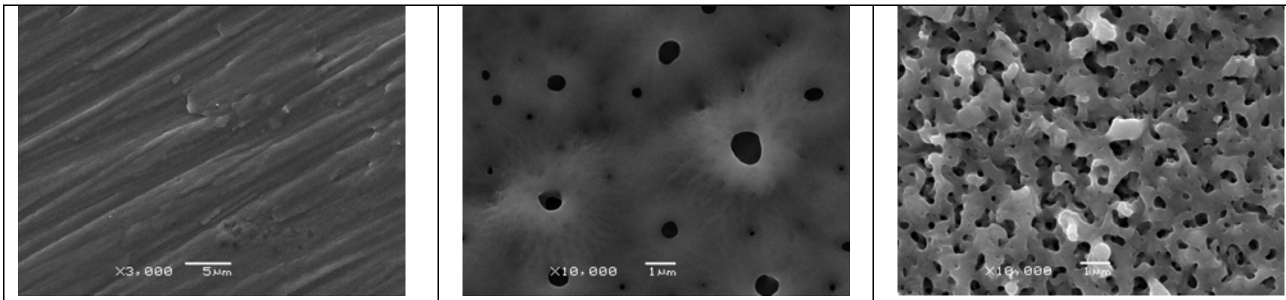
The morphology of the films was analyzed using a scanning electron microscope ZEISS DSM 940A working at 15kV with EDS system, and crystal structure of the anodic films was analyzed using an X-ray diffractometer Shimadzu XRD-7000, Bragg Brentano geometry, 40kV, 20mA and radiation Cu K_α.

The mechanical properties were measured using the instrumented indentation technique. It was measured the hardness and elastic modulus of anodic films, using MTS XP nanoindenter instrument with a Berkovich diamond indenter. Eight loading and unloading cycles were made with increasing loads until a maximum load of 400mN.

3. RESULTS AND DISCUSSION

The morphology of the samples used in this work is showed in fig. 1. It can observe the risks on the titanium (Ti) substrate due to abraded process (fig. 1a). After anodic oxidation process the new surfaces show a different morphology depending on the used electrolyte.

Firstly it can be observed the titanium oxide film obtained after anodic oxidation process is strongly dependent of the electrolyte. The titanium oxide film morphology is very different. Anodic films produced with phosphoric acid appear to be composed by round pores formed on the quite flat ground oxide surface while that produced obtained in sulphuric acid presents small pores on a roughous surface whose appearance is uniform. In both titania films the porous surface are resulting from dielectric breakdown. Spark-discharge occurs when the DC voltage is higher than 105V (Yang *et al.*, 2004). The pores size of the films showed in figure 1b are bigger than those showed in fig. 1c. X-ray diffraction results (XRD - fig. 2) showed that the anodic film obtained with H_2SO_4 is composed by anatase and rutile phase while those obtained in phosphoric acid is amorphous, being in accordance with others results (Yang *et al.*, 2004, Cui *et al.*, 2009). After heat treatment on the oxidized surface at 600°C/1h, it can observed the presence of small quantity of anatase and rutile on the anodic film obtained with phosphoric acid while the quantity of the anatase and rutile increased substantially on the another titania film.



(a)	(b)	(c)

Figure1: Scanning electron microscopy showing the morphology of the Ti surface: (a) abraded (b) oxidized with phosphoric acid (c) oxidized with sulphuric acid.

Some authors have been showed the role of the anatase and rutile phase on the enhancement of the bioactivity of the oxidized titanium surface (Yang *et al.*, 2004, Cui *et al.*, 2009). Yang *et al.*, (2004) verified that the titanium surface oxidized followed heat treatment showed an apatite layer when soaked in simulated body fluid (SBF) during 3 days, while the same sample without heat treatment took 6 days to form an apatite layer. So our results are an indicative that the oxidized surface in both electrolyte are bioactive being the anodic film with sulphuric acid plus bioactive than the other one. The next step is the evaluation the bioactivity of these surfaces using simulated body fluid.

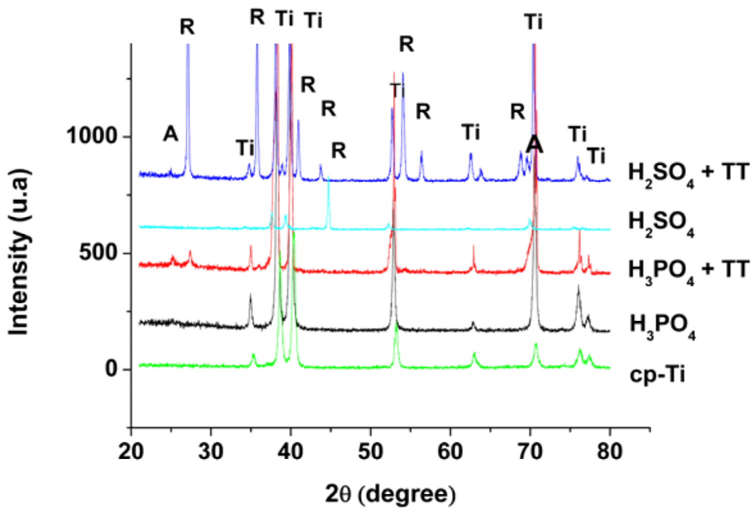
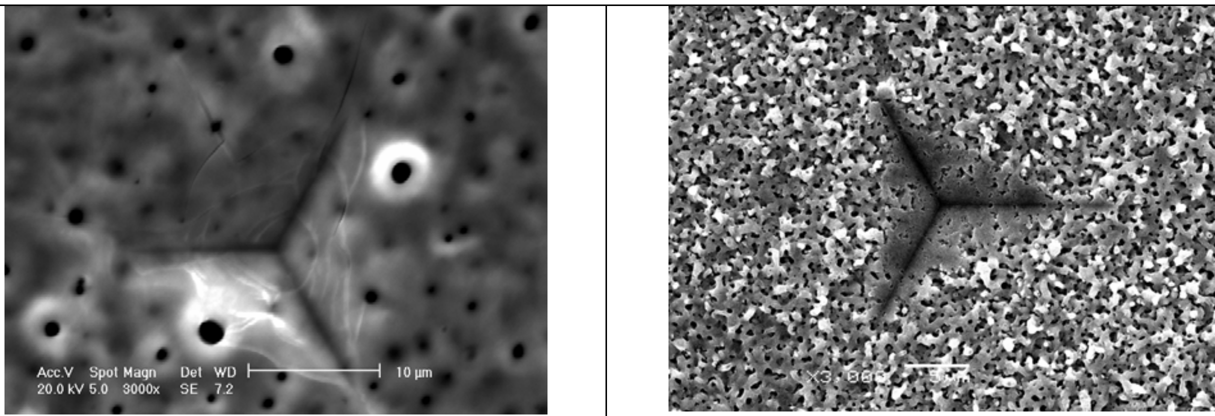


Figure2: XRD patterns of titanium surface and titanium oxidized surface. A = anatase, R = rutile, Ti = titanium, cp-Ti = commercially pure titanium, TT = heat treatment. Cu K_{α} radiation .

The results of the instrumented indentation tests are showed in fig. 3 and 4. Figure 3 shows the residual impressions left on titania film by indentations with Berkovich indenter with maximum load of 400mN on the films produced with 1.0M H_3PO_4 and 1.0M H_2SO_4 and fig. 4 shows the relation Load/Stiffness *versus* depth penetration for both anodic films. The Oliver and Pharr method was used to measure the hardness and elastic modulus profiles as a function of depth penetration (Oliver and Pharr, 1992). Analyzing fig. 3 it can verify qualitatively that the sizes of the indentations left on the TiO_2 surface are similar, that means that both films have similar hardness values.

The calculated hardness and elastic modulus show large dispersions, due to rugosity effects on the surface, so they are not shown here. Despite the differences in morphology of both anodic films the results indicate they have similar hardness dependence on depth displacement. For shallow depths, (surface until 250nm) the nano-hardness values of the oxide films are around 5GPa, greater than those for the polished cp-Ti substrate (Mante *et al.*, 1999 and Seo and Kurata, 2003). After 1.5 μm depth penetration, the nano-hardness approaches the value obtained for the polished cp-Ti, and it in good agreement with the literature (Mante *et al.*, 1999 and Seo and Kurata, 2003). Concerning to elastic modulus the results show an indicative the the $E_{suphuric}$ is bigger than $E_{phosporic}$ near the surface region and after 1500 nm the E values approach to $E_{titanium}$. We believe that these differences in H and E values are concerning to difference in pores size of the the titania film. Mante *et al.*, (1999) showed too that the nanoindentation technique is sensitive to changes in hardness due to oxidation of titanium surface. They verified that electrochemically polished policrystaline Ti has hardness about 2.2GPa. Seo and Kurata (2003) measured the hardness of anodized Ti under potentiostac mode with 5V and the polished Ti and found the values 2.3 GPa and 1.6 GPa, respectivelly. This difference showed that the TiO_2 film has a higher hardness than the polished Ti.



(a) (b)

Figure 3: Residual impressions left on titania film by an indentation with Berkovich indenter of an applied maximum load of 400mN: (a) oxidized with phosphoric acid (b) oxidized with sulphuric acid.

Another way to analyze these results is to take in account the relation between hardness and reduced elastic modulus. The indentation hardness and reduced modulus elastic of a material can be calculated by the following equation (Sahina *et al.*, 2008):

$$\frac{P}{S^2} = \frac{1}{\beta}\frac{\pi}{4}\frac{H}{E_r^2}$$

Where P is the applied load during at starting unloading during indentation, S is the contact stiffness calculated from derivative dP/dh (h is the displacement) at maximum load during unloading, β is a constant dependent of the indenter geometry, H is the hardness and E_r is the reduced elastic modulus.

The advantage in use this method is that the results are not affected by surface rugosity. The results showed in fig. 4 indicate that the relation P/S^2 are equal 0.000375 GPa^{-1} and 0.00018 GPa^{-1} to anodic film obtained with 1M H_3PO_4 and H_2SO_4.electrolytes, respectively. The bigger errors bars observed to phosphoric acid near the surface regions are probably due to pores size on the anodic film (fig. 1b and 1c).

For the same hardness it can observed that the relation P/S^2 is higher for the anodic film obtained with phosphoric acid than that obtained with sulphuric acid, near the surface. This result indicated that the mechanical properties of the anodic film obtained with phosphoric acid electrolyte are better compared to another surface. This value is also higher than that of cp-Ti. After 1750nm they have the same behavior and the values are around 0.000125 GPa^{-1} approaching that for titanium surface.

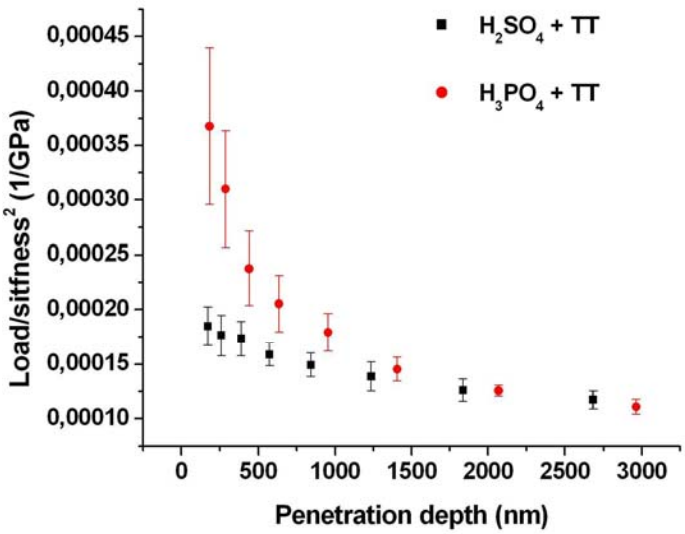


Figure 4: Load/Stifiness^2 against penetration depth of the TiO_2 anodic films produced with 1M H_3PO_4 and 1MH_2SO_4. electrolytes. TT = heat treatment.

Considering these results it is possible to conclude that the surface that presents bigger value to P/S^2 relation is the surface that was that oxidized with phosphoric acid. It means that in this case it was possible to obtain a surface with high H and low E values. Low E values are desirable once the elastic modulus of the implant must be near of the bone one to avoid bone resorption, and higher hardness indicates high resistance to contact during manipulation.

4. SUMMARY AND CONCLUSIONS

It was obtained titanium oxide films on the titanium substrate using anodic oxidation technique with two different electrolyte. The analysis of the films showed that:

1. The morphology of the anodic films depended on the used electrolyte. Phosphoric acid produced films with round and bigger pores than sulphuric acid.
2. Initially phosphoric acid titania films were amorphous while sulphuric acid anodic films presented the phases anatase and rutile. After heat treatment both films presented anatase and rutile phases.
3. The analysis of the relation between hardness and reduced elastic modulus showed that this relation (P/S^2)is higher for the anodic film obtained with phosphoric acid than that obtained with sulphuric acid, near the surface, indicating that the elastic modulus of the phosphoric acid film was smaller than that value obtained to sulphuric film.

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6. REFERENCES

Brånemark, P.I., Hansson, B.O, Adell, R., Breine, U., Lindström, U., Hallén, O., Öman, A., 1977, "Osseointegrated implants in the treatment of the edentulous jaw. Experience from a 10-year period". Scand. J. Plast. Reconstr. Surg., Vol. 16, pp.7-127.

Chen, Z.X.; Takao, W.X.; Matsubara,T.; Ren,L.M., 2009. "Surface characteristics and *in vitro* biocompability of titanium anodized in a phosphoric acid solution at different voltages". Biomedical Materials, Vol. 4, 065003, pp.1-8.

Cui, X.; Kim, H.M.; Kawashita, M.; Wang, L.; Xiong, T.; Kokubo, T.; Nakamura, T, 2009. "Preparation of bioactive titania films on titanium metal via anodic oxidation". Dental Materials, Vol. 25, pp. 80-86.

Diamanti, M.V.; Pedeferri, M.P., 2007. "Effect of anodic oxidation parameters on the titanium oxides formation" Corrosion Science, Vol. 49, pp. 939-948.

Feng, Q. L.; Wang, H.; Cui, F. Z., Kim, T. N., 1999. "Controlled crystal growth of calcium phosphate on titanium surface by NaOH – treatment", Journal of Crystal Growth, Vol. 200, pp. 550-557.

Hench, L. L.; Shirtliff, V. J., 2003. "Bioactive materials for tissue engineering, regeneration and repair", Journal of Materials Science, Vol. 38, pp. 4697-4707.

Kokubo MT., 1991. "Bioactive glass-ceramics: properties and applications", Biomaterials, Vol. 12, pp 155-63.

Kokubo, T.; Kim, H.; Kawashita, M.; Nakamura, T.; 2004. "Bioactive metals: preparation and properties", Journal of Materials Science: Materials in Medicine, Vol.15, pp. 99-107.

Liu,X., Chu,P.K., Ding,C., 2004."Surface modification of titanium, titanium alloys, and related materials for biomedical applications", Mat. Science and Engineering, Vol. R47, pp. 49-121.

Long,M.; Rack, H.J., 1998. " Titanium alloys in total joint replacement-a materials science perspective". Biomaterials, Vol.19, pp. 1621 – 1639.

Mante F.K., Baran, , G.R. Lucas B, 1999. "Nanoindentation studies of titanium single crystals", Biomaterials, Vol. 20., pp. 1051-1055.

Oliver W.C.,. Pharr G.M, 1992. "An Improved Technique for Determining Hardness and Elastic Modulus Using Load and Displacement Sensing Indentation Experiments", *J. Mater. Res.* , Vol. 7, pp. 1564-1583.

Sahina, O., Uzun, O., Sopicka-Lizer, M., Gocmez, H., Kölemen, U., 2008. "Analysis of load-penetration depth data using Oliver-Pharr and Chen-Cheng methods of SiAlON-ZrO_2 ceramics", Journal of Physics D: Applied Physics, pp. 1-8.

Santos Jr, E., Kuromoto, N.K., Soares, G.A., 2007. "Mechanical properties of titania films used as biomaterials", Materials Chemistry and Physics., Vol.102, pp. 92-97.

Seo M. and Kurata Y., 2003. Nano-mechano-electrochemical properties of passive titanium surfaces evaluated by *in-situ* nano-indentation and nano-scratching", Electrochemica Acta, Vol. 48, pp. 3221-3228.

Sul, Y.T., Johansson, C.B., Petronis, S., Kroze, A., Jeong, Y., Wennerberg, A., Albrektsson, T., 2001. "The electrochemical oxide growth behaviour on titanium in acid and alkaline electrolytes", Medical Engineering & Physics, Vol. 23, pp. 329-346.

Velten,D., Biehl, V.F., Valeske, B., Possart, W., & Breme, J., 2002. "Preparation of TiO_2 layers on cp-Ti and Ti6Al4V by thermal and anodic oxidation and by sol-gel coating techniques and their characterization", Journal of Biomedical Materials Research, Vol. 59, pp.18-28.

Yang, B.; Uchida,M.; Kim,H.M.; Zhang,X., 2004. "Preparation of bioactive titanium metal via anodic oxidation treatment". Biomaterials, Vol. 25, pp. 1003-1010.