EFFECT OF HOLLOW CATHODE DISCHARGE PARAMETERS ON THE OXIDATION OF PLASMA-TREATED TITANIUM SURFACES

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Abstract. *The osseointegration of Ti implants is significantly affected by their surface composition and topography. Recent studies have revealed that the growth of oxide surface layers potentially improve the wettability of implants with respect to physiological fluids thereby reducing the osseointegration time. The objective of the present study was to evaluate the effect of hollow-cathode plasma oxidation parameters on the surface properties of titanium pellets, aiming at the application of this novel technology to commercially available implants. The composition and morphology of the oxide layer as well as their effect on the contact angle between substrate and a synthetic organic fluid were mainly evaluated. Titanium pellets were plasma oxidized between 400 and 500°C using the hollow cathode configuration. The partial pressure of oxygen was adjusted between 2 and 20% and the total pressure set to values ranging from 2.2 to 4.0 mbar. The results suggested that the temperature range investigated was adequate for the oxidation of Ti between 2.2 and 2.6 mbar. The partial pressure of oxygen should remain between 2 and 10%. For the latter value, decreasing the pressure and increasing temperature improved wetting. For partial pressure values between 2 and 5%, several combinations of temperature and total pressure resulted in superior wetting. Optimized results were obtained oxidizing Ti at 500°C setting the pressure and partial pressure of oxygen to 2.2 mbar and 10%, or alternatively, 2.6 mbar and 2% oxygen, respectively.*

Keywords: *Osseointegration, dental implants, titanium, plasma oxidation, hollow cathode.*

1. Introduction

The successful integration of dental implants into bone tissue, also known as osseointegration, depends on the nature of the implant material as well as its topography. Commercially pure titanium (Ti cp) has been widely used in implant manufacture as a result of a combination of superior physical, chemical, mechanical and biological properties. In particular, the outstanding biocompatibility of Ti is intimately related to its passivation characteristic. The surface oxide layer that coats every Ti part works as a protective corrosion barrier against body fluids also preventing the release of ionic species to the environment (Branemark, 1985). In addition, it plays an important role as substrate in the proteic reactions involved in cell adhesion to the implant and consequently, in the osseointegration process (Albrektson, 1994). The design of dental implants must be chosen to allow its initial interlocking in the bone structure, whereas the microstructure and morphology (i.e., roughness and texture) determine the growth rate of bone tissue onto the surface of implants (Amarante, 2001). Extensive and rapid osseointegration can be achieved in Ti implants surfaces modified to improve texture, responsible for cell imbrication and surface energy, responsible for molecular adsorption and wetting (Brunnet, 1988, Baier, 1988, Sacher, 1998, Albrektsson, 1990 and Lampin, 1997). Rough oxidized Ti surfaces have depicted improved wetting compared to plain metallic ones, which potentially shortens the osseointegration period of the implant, grating the mechanical ability necessary to withstand mastication forces (Smith, 1991).

Different surface treatment techniques have been studied to improve the properties of Ti implants, especially those regarding osseointegration. In this scenario, plasma surface oxidation is a novel approach that has shown promising results, producing surface layers characterized by chemical composition, thickness and roughness compatible with the superior biological response required for fast osseointegration (Guerra, 2001; Kasemo, 1988 and Silva, 2002). Implants treated in lab scale have depicted significant improvements in wettability to physiological fluids upon the adjustment of just a few plasma process parameters, which include atmosphere, pressure, and cathode configuration. By confining the plasma discharge to a small area, the sputtering rate can be increased without affecting the characteristic energy of individual ions. This effect can be achieved using the so called hollow cathode configuration. In this set-up, the sample is shielded by two cathodically polarized surfaces, confining the charged species to a small region nearby the sample (Morgner, 1998 and Rossnagel, 1989). In such complex and hostile environment, the surface of materials is exposed to the impingement of electrons, ions, atoms, molecules and energetic radicals, responsible for a myriad of effects that can result in microstructural and topographical modifications (Dugdale, 1977; Benda, 1999; Silva, 2002 and Guerra, 2001).

Preliminary results on the texturizing effect of hollow cathode plasma discharges revealed the possibility of adjusting processing parameters resulting in shorter osseointegration periods with the necessary reliability and reproducibility (Silva, 2002 and Guerra, 2001). The present study addressed the modification of Ti surfaces by depositing TiO_2 rough layers in hollow cathode plasma aiming at improved wetting and therefore reduced osseointegration time. The effect of the main parameters on wetting, chemical composition of the oxide layer and roughness of Ti surfaces were studied. The composition and morphology of the oxide layer as well as their effect on the contact angle between substrate and a physiological fluid were mainly evaluated. Titanium pellets were plasma oxidized between 400 and 500°C using the hollow cathode configuration. The partial pressure of oxygen was adjusted between 2 and 20% and the total pressure set to values ranging from 2.2 to 4.0 mbar.

2. Experimental Procedure

Commercially pure titanium rods (ϕ = 9 mm, L = 2 mm) that follow ASTM F67-89 specifications were cut into pellets, ground down using SiC paper and polished in alumina slurry. The average roughness of the polished surface, Ra, was 0.2 μm. The pellets were then rinsed in ultra-sound bath for 20 min using petroleum ether and 15 min in acetone, blow dried and placed in a stainless steel plasma chamber 400 mm in diameter and 400 mm in length. The hollow cathode consisted of a steel base and a stainless steel casing coated with a Ti sheet. The cathode was negatively polarized using a dc source whereas all other metallic parts of the chamber were grounded. A type-K thermocouple was inserted in the bottom of the sample holder to measure a reference temperature during oxidation. The internal pressure of the chamber was measured using a baratron capacitive gauge from Edwards Instruments (10^{-3} mbar full scale). A schematic representation of the plasma reactor chamber set-up is shown in Figure 1.

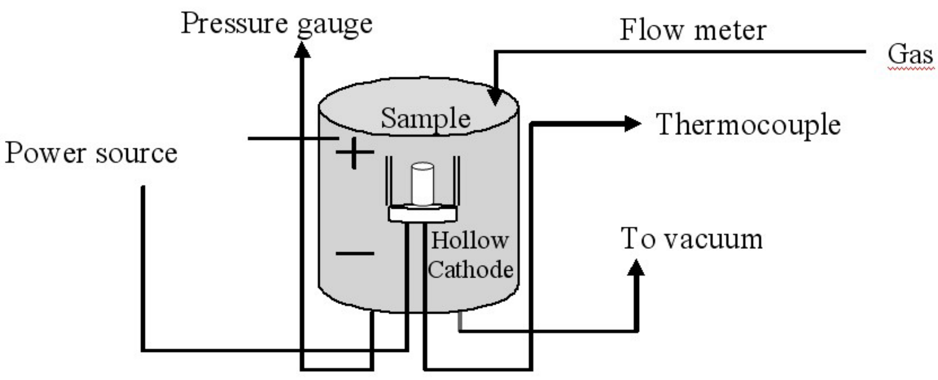


Figure 1. Schematic representation of plasma chamber set-up with Ti sample positioned on hollow cathode.

Preliminary tests were carried out to establish initial pressure and temperature conditions. The pressure range between 2.2 and 4.0 mbar was studied. Pressures below 1.5 mbar resulted in little or no growth of oxide coating layers whereas values above 5.0 mbar affected the homogeneity of the coating. Previous studies on plasma oxidation using planar cathode suggested that the temperature range between 400 and 500ºC should be studied. The chamber was initially pumped down to 10^{-3} mbar, purged with 99.9 % pure argon and pumped down again to 10^{-3} mbar. The discharge voltage was adjusted to 500 V under argon to establish a glowing discharge at approximately 180 to 284ºC. After 20 min, oxygen was introduced in the chamber along with argon, resulting in constant total flow of 50sccm until the working pressure was established. Different contents of oxygen were used, i.e., 2, 5, 10 and 20 vol.%. The samples were labeled according to the oxidation parameters, total pressure, temperature, and % oxygen (Table 1).

Table 1: Sample labeling and plasma oxidation parameters.

Sample Label	Temperature (°C)	Pressure (mbar)	% O_2
P2,2t400%2	400	2,2	2
P2,2t400%5	400	2,2	5
P2,2t400%10	400	2,2	10
P2,6t400%2	400	2,6	2
P2,6t400%5	400	2,6	5
P2,6t400%10	400	2,6	10
P2,6t400%20	400	2,6	20
P4t400%10	400	4,0	10
P2,2t500%2	500	2,2	2
P2,2t500%5	500	2,2	5
P2,2t500%10	500	2,2	10
P2,6t500%2	500	2,6	2
P2,6t500%5	500	2,6	5
P2,6t500%10	500	2,6	10
P2,6t500%20	500	2,6	20
P4t500%10	500	4,0	10

Wetting, roughness, visual aspect, texture and chemical composition of the oxidized surfaces were characterized. The wetting angle was established from sessile drop tests performed both on bare and oxidized pellets. The samples were stored in surgical paper to the moment of the test. They were handled using sterilized Ti tweezers to prevent surface contamination. Using a digital micropippete, a drop of Euro-Colins physiological solution containing 3.57% glucose, 70% glycerin and dye was placed on top of the Ti pellet. The volume of the drop was 0.25ml. The wetting angle (Figure 2) was estimated from digital pictures taken immediately and after 60s.

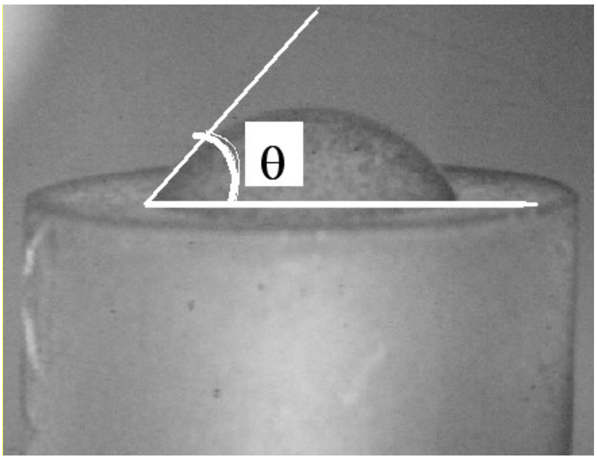


Figure 2. Wetting angle of physiological liquid onto Ti pellet measured from digital pictures.

The roughness parameter, Ra, for both bare and texturized surfaces were evaluated using a Robson Taylor Surtronic 3 equipment. The cut-off was set to 0.25 µm. Measurements were carried out in three different directions at angles of approximately 120º. Changes in color and detaching of the oxidized layer upon ultrasound cleaning were visually evaluated. Texturing was observed under a Philips XL 30 ESEM scanning electronic microscope using cross-sectionally cut samples, which were polished and etched to reveal surface details. Finally, the composition of crystalline phases present on the surface of Ti samples was analyzed by X ray diffraction using a Shimadzu diffractometer. Cu Kα radiation was used to scan the angular range $20° \leq 2\theta \leq 80°$ at 0.02˚ steps. The holding time per step was set to 1.5 s.

3. Results and Discussion

Initially, the adhesion of the oxide layers onto Ti substrates was indirectly inferred by submitting plasma-treated pellets to ultrasonic bath. Samples depicting peeled-out were ruled out since the characteristics observed would have no practical reliability whatsoever for implant purposes. Samples plasma oxidized in atmosphere containing 20 vol.% oxygen partially peeled-off, as shown in Figure 3. All other oxidizing conditions resulted in adherent layers according to this selection approach.

Wetting experiments indicated that after 60 s the contact angle between physiological liquid and Ti oxidized substrates varied from 27° to 58º, whereas the value obtained from bare substrates was ~ 64º (Figure 4). Therefore, all plasma parameters used improved the wettability of Ti with respect to the physiological liquid by the deposition of a surface oxide layer. In particular, experimental conditions resulting in contact angles lower than 45° were considered adequate for the selection of samples for further characterization. Although bone deposition takes place both on rough and smooth Ti surfaces, roughness is an important aspect to improve wetting (Smith, 1991) and increase tissue deposition rates (Lowenberg, 1987 and Misch, 2000). The best values of contact angle were obtained from samples oxidized in different conditions, including p2.2t500%10, p2.2t400%2, p2.6t400%5, p2.6t400%10, p2.6t500%5, p2.6t500%2 and p2.2t400%5. Samples oxidized under 4.0 mbar were abandoned. Therefore further characterization took into account samples plasma treated under 2.2 and 2.6 mbar with oxygen vol.% between 2 and 10%. The relationships between the different parameters involved in plasma treatment and the final properties of oxidized Ti samples are rather complex, since different combinations of pressure, temperature, and atmosphere may determine the experimental conditions necessary to produce stable Ti-O oxides and reasonable layer thicknesses to prevent peeling off due to embrittlement of the surface coating and failure by excessive mechanical stresses. Nevertheless, it could be established that vol.% O_2 = 10%, wetting can be improved by increasing the temperature and reducing the total pressure. For oxygen contents between 2 and 5 vol.%, different combinations of temperature and pressure result in low contact angles. Setting the total pressure to 4.0 mbar did not result in adequate wetting. That pressure was apparently too high to boost the hollow cathode effect, thus limiting the mechanisms taking place in surface modification of Titanium (Dugdale, 1977).

(a)P2.6t500%20 (b)P2.2t500%20

Figure 3. Oxide layer partially detached from Ti surfaces.

Results from the roughness tests (Figure 5) clearly indicated that plasma surface modification generally resulted in rougher surfaces compared to bare Ti pellets. The combination of low contact angles and improved roughness positively act towards cell adhesion and mechanical interlocking, thus improving osseointegration. Therefore, the number of combinations of experimental conditions was narrowed down to take into account these features. In these criteria, samples labeled p2.2t400%2, p2.2t500%10, p2.6t500%5, p2.6t500%2 and p2.6t400%5 depicted superior performance.

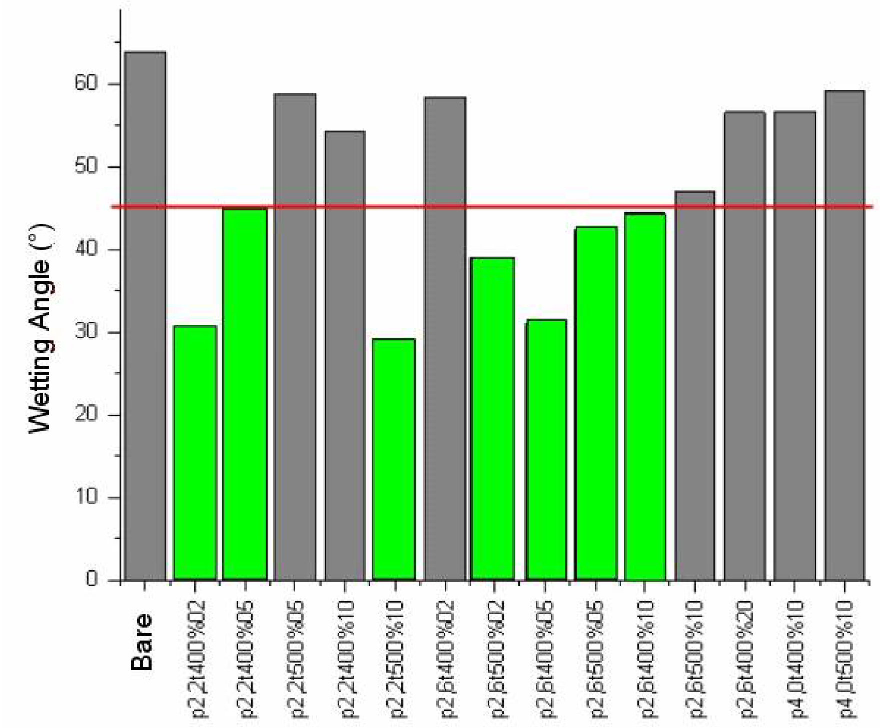


Figure 4. Wetting angle as a function of plasma oxidation parameters.

SEM images were used to observe the texture of the oxidized surfaces (Figure 6). Samples plasma treated at low temperatures (400°C), i.e., p2.2t400%2 and p2.6t400%5, depicted limited texturizing effect (Figure 6c), probably as a result of the relatively low bombardment rate associated to thermal effects. Samples referred to as p2.6t500%2 and p2.2t500%10 (Figure 6a and b) revealed improved texture, so the corresponding treatment conditions could be selected for implant oxidation.

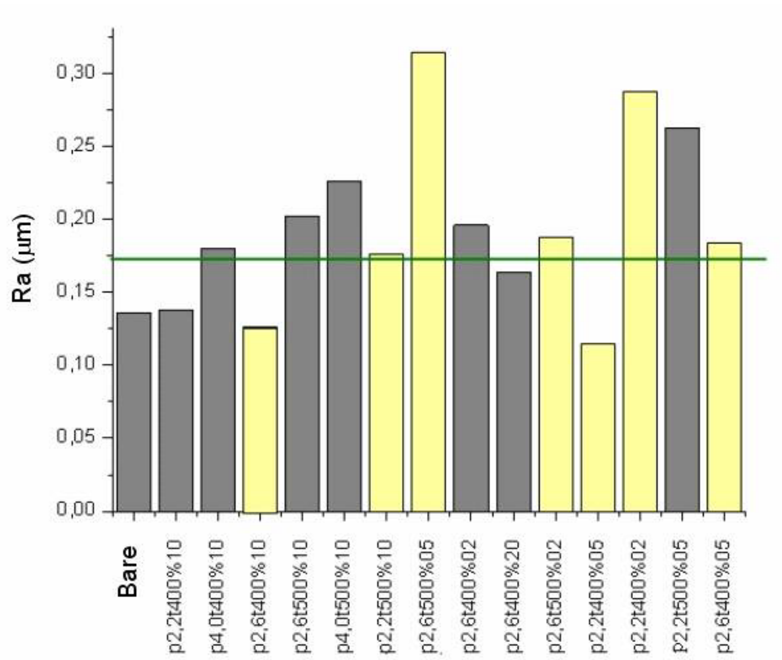
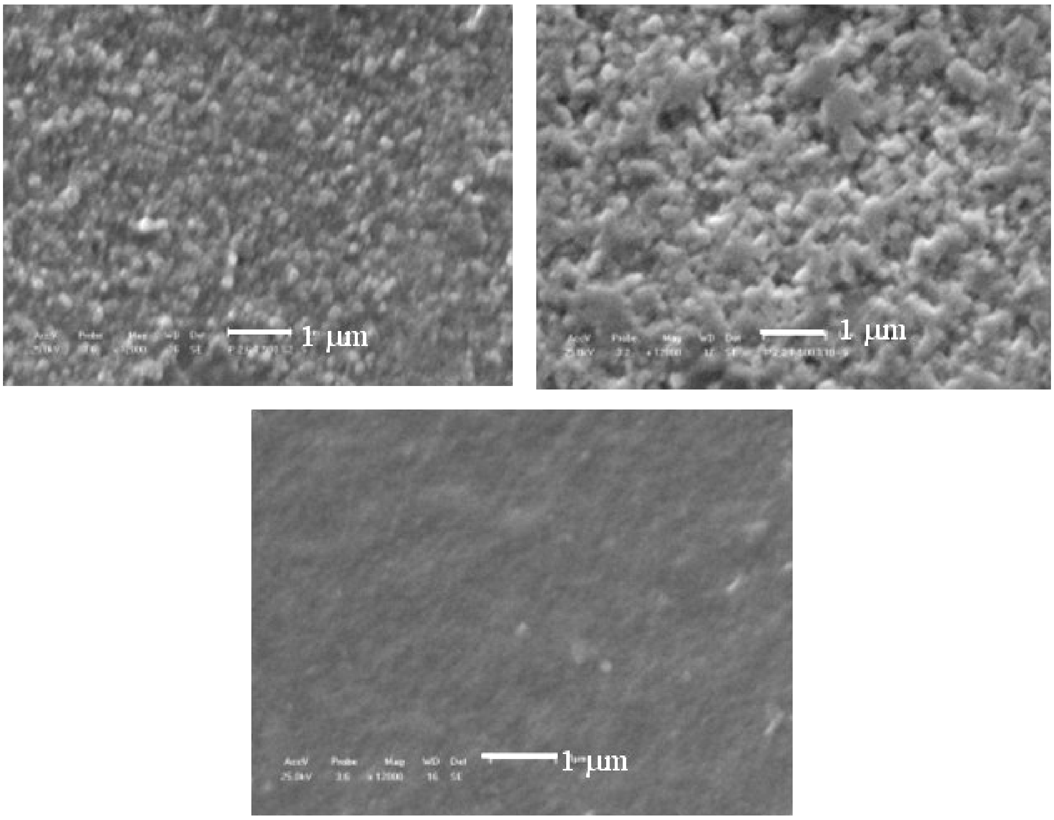


Figure 5. Highlighted combinations of improved wetting and roughness.

(a) (b)



(c)

Figure 6. SEM micrographs of oxidized Ti pellets. (a) p2.6t500%2, (b) p2.2t500%10 and (c) p2.2t400%2.

The color of titanium oxidized surfaces may vary according to the thickness of the oxide layer. Films thicker than 170 nm depict whitish hues, whereas surfaces between 70 and 170nm are predominantly blue (Fukuzuka, 1980). On the other hand, the concentration of oxygen in the coating affects the mechanical properties of the surface (Kasemo, 1983 and Edgerton, 1993) and, therefore, the strength and performance of the implant-bone system. Visual analyses were performed to assess the distribution of colors over the surface. Differences were observed between the central region and the periphery of some samples. The central area was taken as the characteristic color, since the main plasma reactions take place in that region. The color of the surface generally changed upon plasma oxidation. The metallic brightness was replaced by opaque shades of gray or blue. The final color was also determined by plasma processing parameters involved in establishing the intensity of ionic bombardment. Samples which depicted improved wetting upon plasma oxidation usually developed white or blue hues, except samples p2.6t500%2 which was predominantly dark gray (Figure 7b). It is also interesting to point out that sample p2.6t400%2, characterized by high contact angle (low wettability), was mainly yellowish. These results confirm statements and data published elsewhere which correlate thickness, color and wettability of oxidized titanium surfaces. Plasma oxidation eventually resulted in visual effects with the presence of concentric rings around the central area of the pellets (Figure 7a). This was probably a result of border effects, typical of plasma treatments and can be minimized either reducing the total pressure of the system (Figure 7c) or by using pulsed plasma.

X-ray diffraction analyses were carried out to identify the composition of the oxidized coating layers formed onto titanium pellets upon plasma in hollow cathode discharge. The composition of the oxide layers present also plays an important role in establishing the wetting behavior of the surface in contact with physiological fluids, since they determine the surface tension of the surface. An overall analyses of all oxidized samples revealed that mainly TiO and TiO_2 were formed. However, samples depicting best wetting properties and texture (p2.6t500%2 and p2.2t500%10) predominantly consisted of TiO_2. Contrary to other plasma process parameters analyzed herein, a direct relationship between improved wetting and the presence of TiO2 could be noticed. In summary, the ideal plasma process parameters resulting in optimal implant surface conditions to shorten the osseointegration period could be narrowed to total pressure between 2.2 and 2.6 mbar, oxygen vol.% between 2 and 10% and temperature between 400 and 500ºC. Plasma oxidation of titanium surfaces in hollow cathode discharge employing such parameters result in stable TiO_2 oxide coating layers with improved wetting and roughness. The best results were obtained for the following specific set of experimental conditions: p2.6t500%2 and p2.2t500%10. These results potentially imply in improved implant performance associated not only shorten osseointegration periods but also better distribution of stresses during mastication (Kasemo, 1983), and superior mechanical retention of the implant into living bone toissue (Kasemo, 1983; Ellingsen, 1998 and Misch, 2000).

(a) (b) (c)

Figure 7. (a) Rings typical of border effect and adequate visual aspect encountered on samples (b) p2.6t500%2 and (c) p2.2t500%10

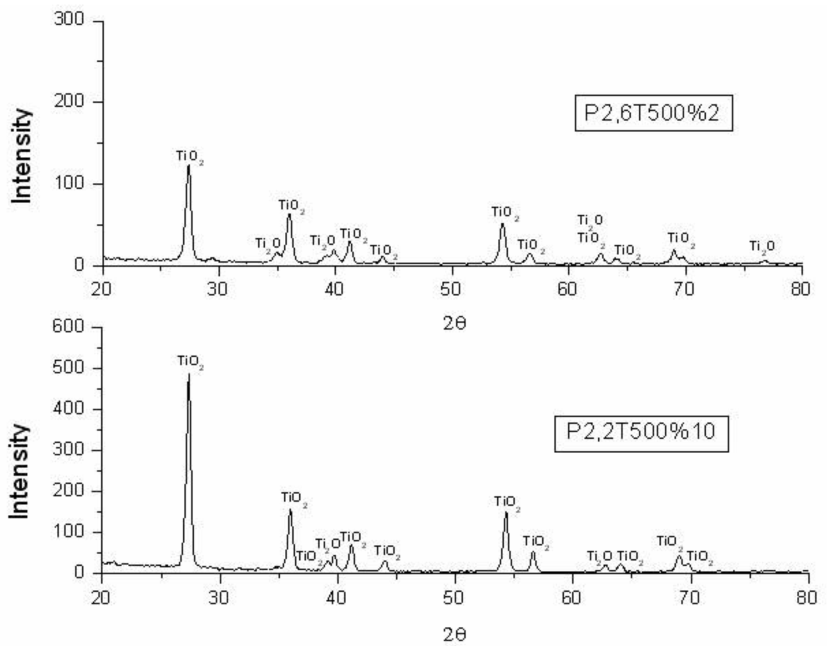


Figure 8. X-ray diffraction patterns of samples (a) p2.6t500%2 and (b) p2.2t500%10.

4. Conclusions

Titanium pellets were plasma oxidized in hollow cathode discharge between 400 and 500°C. The content of oxygen was adjusted between 2 and 20% and the total pressure of the system was set to values ranging from 2.2 to 4.0 mbar. The results obtained during the characterization of oxidized titanium pellets indicated that total pressure between 2.2 and 2.6 mbar, oxygen vol.% between 2 and 10% and temperature between 400 and 500ºC were adequate to optimize wetting and texture of titanium for application in dental implants. Stable TiO_2 oxide coating layers capable of yielding improved performance can be obtained under the following specific set of experimental conditions: p2.6t500%2 and p2.2t500%10.

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