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Surface modification of Ti implants by plasma oxidation in hollow cathode discharge

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Abstract

As a result of superior biocompatibility and mechanical adequacy, titanium has been widely used in the manufacture of dental implants. On the downside, relatively long periods are normally required to fully integration of the bone into the implant. Surface modification techniques have the potential to shorten the osseointegration time of implants significantly contributing to patient comfort. In this work, plasma discharge in oxidizing atmospheres was used to modify the surface of Ti implants by the production of rough surfaces that consists of a mixture of Ti-oxides. The results showed that considerable improvement on surface roughness and mechanical stability of the oxidized layers could be achieved by confining the effect of the plasma discharge by shielding the cathodic region of the reactor. Processing parameters including temperature, time and pressure were optimized and applied to commercially available Ti implants. Improved wetting was obtained, which is potentially associated to shorter osseointegration periods.

Keywords: D. Titanium; A. Titanium oxide; C. DC plasma; B. Roughness; X. Surface modification

1. Introduction

Numerous varieties of dental implants are currently manufactured from Ti or Ti alloys and subsequently surface treated aiming at reducing the osseointegration period and increasing their applicability to poor quality alveolar bone. To fulfill such requirements, implants must induce positive responses from the surrounding cells and tissues as well as assure cellular adhesion. The degree of integration is directly related to the deposition of a glycoproteinic conditioning film onto the surface of the implant. This process depends on superior wettability of the surface to promote molecular adsorption [1] and improved surface roughness to yield cellular interlocking. Studies have shown that rough surfaces have improved the growth of bone tissue surrounding the implant by increasing the deposition and better distributing proteins on the surface of the implant. [2,3].

Recent studies have also indicated that the surface modification of Ti implants [4] worked towards improving the area of contact between bone and implant thus assisting osseointegration. Surface modification processes can act on different stages of osseointegration, including differentiation of cells present on the metal–bone interface immediately following surgical implantation and on the amount of calcified bone matrix deposited onto the surface of the implant [5]. Roughness also affects the first stages of vascularization of the tissues surrounding the implant immediately after surgery in addition to determining patterns of migration, alignment, orientation, adhesion and, finally the rate of protein production and cellular function [6].

Surface modification techniques applied to implant surfaces can be classified into subtraction or addition processes. Only rough surfaces are produced by subtraction processes including particle blasting, acid etching and, more recently, laser metal cutting [7–12]. Both blasting and etching require the use of chemical neutralization processes to neutralize and rinse off acids and oxides in order to accommodate the use of modified surfaces in organic

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environments. A number of commercially available implants are characterized by hybrid surfaces containing both macro- and micro-retentions produced by a combination of blasting and etching techniques [13]. Addition modification processes can produce either porous or rough implant surfaces. Porous surfaces are usually thicker than rough ones. Whereas the former approach results in layers thicker than 3000 nm with irregularities of 150–300 nm average depth, rough surfaces of average thickness 10–40 nm or 50–70 nm are achieved for Ti and hydroxiapatite, respectively [13]. Plasma spray has been widely used to coat implants with titanium or hydroxiapatite. Modified rough surfaces are usually 50 to 150 nm thick with Ra equal to 1.82 μm for Ti and 1.59–2.94 μm for hydroxiapatite [5]. Another approach is the controlled growth of porous TiO_2 layers by anodic oxidation. Properties such as layer thickness and roughness can be tailored [5].

Several studies have detailed the nature of oxide layers produced by different surface treatment methods. Specific properties of the resulting layers, such as chemical composition, thickness and roughness determine the biological response of the environment [14]. Plasma treatments offer the opportunity of largely varying the properties of surface layers by adjusting a few experimental parameters, such as electron density, energy and distribution function. The interaction of plasma with the surface of a metal involves simultaneous bombardment of plasma species and heat transfer. In addition to heat, plasma also produces other effects such as surface defects and controlled chemical reactions [15]. Plasma is generated applying a voltage between two electrodes in a hermetically sealed system at sufficiently low pressure. Electrons and ions are accelerated in an electric field, colliding with other particles and producing additional ions and electrons in chain reaction [16]. Sputtering of surface atoms, heat dissipation by particle bombardment, creation of defects on the crystal lattice of the cathode (implant), deposition of oxide, adsorption and diffusion [17,18] are some of the events that can take place. Most of the events related to the development of a surface layer take place in the cathode of the plasma set-up. Sputtering does not occur uniformly throughout a bombarded area. On polycrystalline surfaces, different sputtering rates may result from different crystallographic orientations of the grains. As a result, the topography of the surface can be drastically affected [19]. As particles strike the surface, ~90% of their energy is transformed into heat which is absorbed by the cathode [20]. The remainder energy is dissipated as radiation, by convection or conduction through walls and reaction environment. The yielded power depends on the partial pressure of constituents, total pressure and nature of the gas, as well as composition of the cathode. The ionization rate and, therefore, plasma reactivity, can be improved by shielding the discharge in a hollow cathode configuration (Fig. 1). The set-up consists in two parallel surfaces cathodically polarized and positioned at close distance. Their main role is to successively repel the electrons present in the confined region. As a result, the number of collisions between electrons increases, which contributes to an increase in the ionic density of the system. These effects are responsible for increasing the sputtering rate and temperature of the surface. Improved damage, and therefore roughness, can be obtained without significantly increasing the temperature characteristic of the conventional method.

Oxygen plasma has a severe effect on localized cleaning of the surface structure and subsequent formation of stoichiometric TiO_2. Preliminary results on the surface modification effect of the hollow cathode discharge method revealed the possibility of adjusting processing parameters resulting in the necessary reliability and reproducibility to commercial levels with reduced costs and shorter osseointegration periods. The present study addressed the surface modification of Ti surfaces and dental implants by depositing TiO_2 rough layers in oxygen plasma aiming at improving wetting and therefore reducing osseointegration time. The effect of the main parameters on wetting, chemical composition of the oxide layer, thickness and roughness of Ti surfaces were systematically studied from oxidized surfaces produced in hollow cathode discharge. Finally, the method was used to treat commercially available dental implants. The properties of both bare and coated implants were established.

2. Experimental procedure

2.1. Starting materials

9-mm long samples were cut from pure titanium rods (ϕ=4 mm, L=500 mm) that follow ASTM F67-89 specifications [21]. According to these guidelines the material should be free from external or internal defects. The Ti pellets were ground down using SiC paper and finished with alumina slurry. The average roughness of the polished

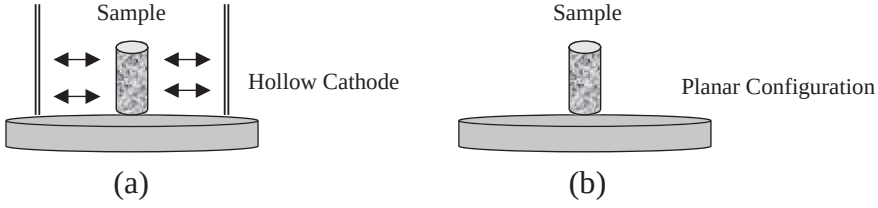


Fig. 1. Schematics of plasma configuration with (a) hollow and (b) planar cathode.

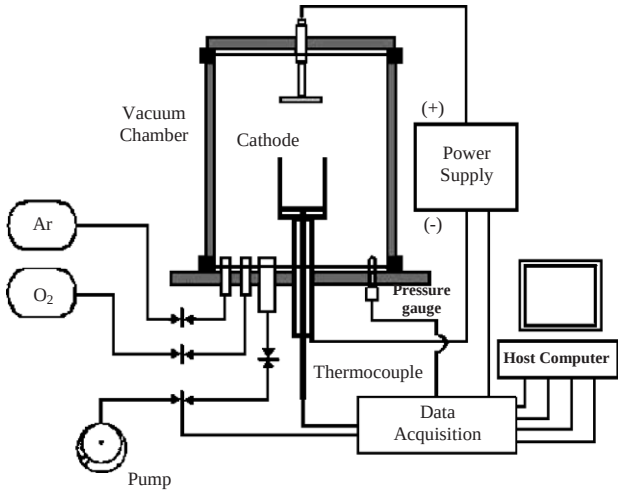


Fig. 2. Schematic representation of plasma reactor chamber set-up.

surfaces, Ra, was 0.2 μm. The same procedure was used to produce samples for microstructural characterization and microhardness evaluation. The polished samples were etched for 1 min using a solution containing 80 mL ethanol, 2 mL fluoridric acid and 20 mL nitric acid.

Prior to plasma treatment, the samples were cleaned in ultra-sound bath for 20 min using petroleum ether and 15 min in acetone and finally dried. The plasma reactor consisted of a stainless steel chamber 400 mm in diameter and 400 mm in length. The hollow cathode consisted of a steel base and a stainless steel tube internally coated with a Ti sheet into which the samples were individually placed and treated. The cathode was negatively polarized using a dc source with maximum voltage 1200 V and current 1.5 A, whereas all the other metallic parts of the chamber were grounded. A type-K thermocouple was inserted in the bottom part of the sample holder to measure a reference temperature for the sample during oxidation. The internal pressure of the chamber was measured using a Baratron capacitive gauge from Edwards Instruments (0.1 Pa full scale). A schematic representation of the plasma reactor chamber set-up is shown in Fig. 2.

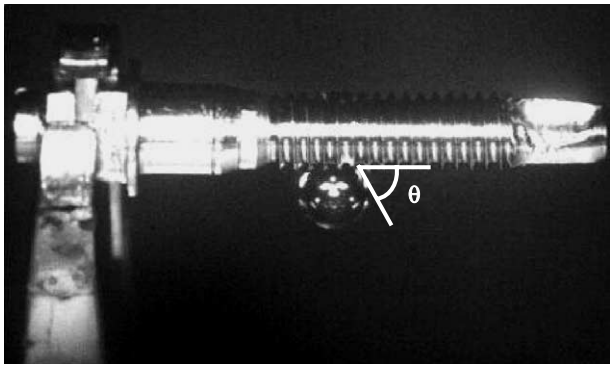


Fig. 3. Wetting angle measured on implant.

2.2. Plasma oxidation

Preliminary tests aimed at establishing optimum pressure and temperature conditions were done. The pressure range between 2.2 and 4.0 mbar (220 and 400 Pa) was fully studied since pressures values below 1.5 mbar (150 Pa) resulted in little or no growth of the oxide coating layer, whereas values above 5.0 mbar (500 Pa) usually affected the

Table 1
Correlation between plasma oxidation parameters and properties of oxide layer

Pressure (mbar)	Cathode	Temperature/time (°C/min[a])	Color	Peeled-off	Oxides
2.2	Hollow 3.5 mm	400	Dark	Yes	TiO_2 TiO Ti_4O_7 TiO_4
		500	Dark	Yes	TiO_2 TiO Ti_4O_7 TiO_4
		700	Dark	Yes	TiO_2 TiO Ti_4O_7 TiO_4
	Hollow 9.0 mm	400	White	Partially	Ti_4O_7 TiO TiO_2
		500	White	Yes	Ti_4O_7 TiO TiO_2
		700	White	Yes	Ti_4O_7 TiO TiO_2
	Planar	400	Dark	Yes	TiO_2 TiO Ti_4O_7 TiO_4
		500	Dark	Yes	TiO_2 TiO Ti_4O_7 TiO_4
		700	White	Partially	Ti_4O_7 TiO TiO_2
2.6	Hollow 9.0 mm	400	White	Yes	Ti_4O_7 TiO TiO_2
		400/30 min	Silver	No	TiO_2 TiO Ti_4O_7 TiO_4
		500	White	Partially	Ti_4O_7 TiO TiO_2
		500/30 min	White	Partially	Ti_4O_7 TiO TiO_2
		500/10 min	White	Yes	Ti_4O_7 TiO TiO_2
		700/10 min	White	Yes	Ti_4O_7 TiO TiO_2
4.0	Hollow 3.5 mm	400	White	Partially	Ti_4O_7 TiO TiO_2
		500	White	Yes	Ti_4O_7 TiO TiO_2
		700	–	–	
	Hollow 9.0 mm	400	White	Yes	Ti_4O_7 TiO TiO_2
		500	Silver	No	TiO_2 TiO Ti_4O_7 TiO_4
		700	White	Yes	Ti_4O_7 TiO TiO_2
	Planar	400	Silver	No	TiO_2 TiO Ti_4O_7 TiO_4
		500	Silver	No	TiO_2 TiO Ti_4O_7 TiO_4
		700	White	Yes	Ti_4O_7 TiO TiO_2

[a] Oxidation treatment time was 60 min unless stated otherwise.

homogeneity of the coating layer. Previous studies on plasma oxidation using the planar cathode configuration also suggested that temperatures between 400 and 700 °C should be used. Both planar and hollow cathode configurations were used. The distance between sample edge and casing was set to 3.5 or 9.0 mm.

The chamber was initially pumped down to 10^{-2} mbar (1 Pa), purged with 99.9% pure argon and pumped down again to 10^{-3} mbar (0.1 Pa). The source was turned down and adjusted to 500 V under argon atmosphere to establish a glowing discharge at approximately 180 to 284 °C. After 20 min, a mixture of 90% analytical argon and 10% commercial oxygen (99.5% pure) was introduced at constant flowing rates of 45 cm^3/min for the former and 5 cm^3/min for the latter until the target working pressure was reached. The temperature was then adjusted.

2.3. Titanium pellets and implant characterization

The microstructure, wetting, roughness, visual aspect and microhardness of the oxidized surfaces were characterized. The wetting angle was established from sessile drop tests performed both on plain and implant surfaces. The samples were stored in surgical paper until the test was done. They were handled using sterilized Ti tweezers thus preventing surface contamination. A digital Kacil Model FS 25 μL micropippete was used to drop a solution containing 3.57% glucose physiological liquid (EUROCOLINS), 70% glycerin and dye. The physiological liquid selected is used to transport human organs. It is valid for 30 to 40 h and simulates the intracellular environment. The volume of the drop was 0.25 ml. The wetting angle was estimated from digital pictures taken after 5, 60 and 300 s using a Nikon Dental Eye II digital camera. The wetting angle on implants was estimated using the set-up shown in Fig. 3.

Wetting experiments were performed on samples and implants previously submitted to a rigorous cleaning and sterilization protocol including the following steps:

- Immersion in a solution of 2.5 ml DEIV 3E solution (enzymatic detergent) and 500 ml bidistilled water in ultrasonic bath for 10 min to remove grease, proteins and carbohydrates.
- Immersion in absolute alcohol and ultrasonic cleaning during 10 min.
- Immersion in distilled water and ultrasonic cleaning during 10 min.
- Water evaporation under hot air for 1 min.
- Sterilization in autoclave at 121 °C for 20 min.

Steps 1 to 3 were repeated twice. The results represent averages of at least five measurements.

The roughness parameter, Ra, for both bare and modified surfaces were evaluated using a Robson Taylor SURTRONIC 3 equipment. The cut-off was set to 0.25 mm, i.e., evaluation length of 1.25 mm. This value was adequate for the statistical analysis on Ti-rods 4.00 mm in diameter. Measurements were carried out in three different directions at angles of approximately 120°. Vickers microhardness was obtained using a CARL ZEISS JENA mph-100 test machine. Results represent the average of at least three measurements. Changes in color and detaching of the oxidized layer upon ultrasound cleaning were studied. The samples were cross-sectionally cut and the exposed surfaces were etched and observed under optical and scanning electronic microscope (Philips XL 30 ESEM). Furthermore, the presence of crystalline phases on the surface of the implants was analyzed by X-ray diffraction using a Siemens D-5000 apparatus. Cu Kα radiation was used to scan the angular range $20° \leq 2\theta \leq 120°$ at 0.02° steps. The holding time per step was set to 1.5 s.

Finally, optimized processing conditions were selected and employed to previously characterized commercial implants (3.3 mm in diameter and 15.0 mm long in height). Wrapped and sterilized implants from different manufacturers were used. The microstructure, wetting and visual aspect of the oxidized implants were analyzed.

3. Results and discussion

The surface of titanium pellets was modified in plasma under different conditions and characterized according to

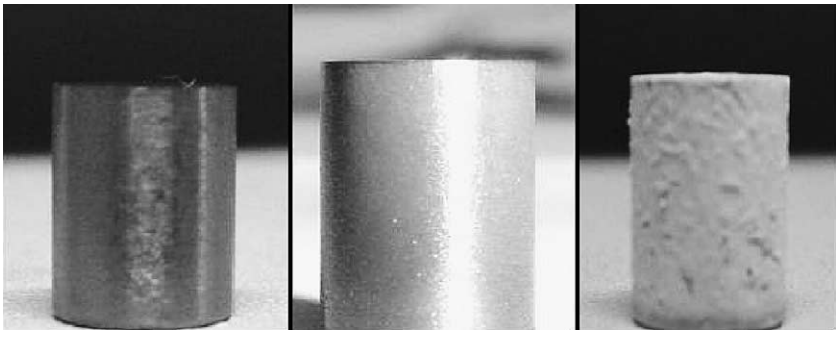


Fig. 4. Visual aspect of oxidized samples illustrating (a) dark layer, (b) silvery layer and (c) white layer.

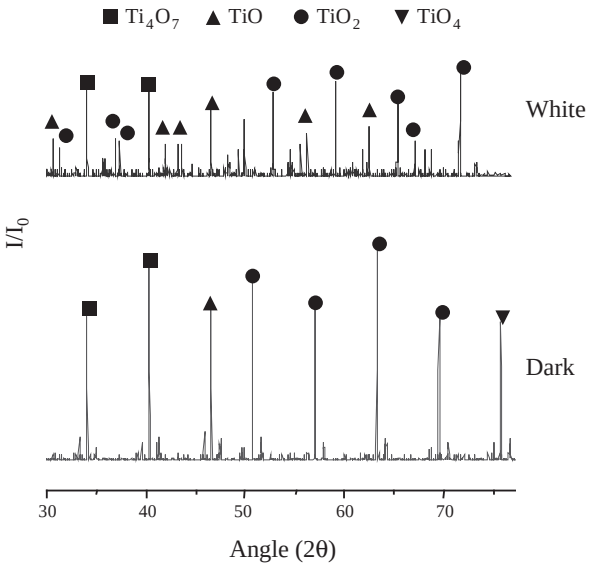


Fig. 5. X-ray diffraction pattern of whitish and dark oxidized layers.

visual aspect, thickness and crystallography of the oxide layer, wettability, roughness and hardness. Characteristics of modified Ti surfaces could be correlated with the plasma oxidation parameters (Table 1). The best conditions determined on Ti pellets were used to modify commercially available smooth Ti implants.

The visual aspect of oxidized pellets was used as the first and most simple characterization aspect due to its commercial importance. Three main colors (hues) were observed upon oxidation and directly related to the composition of the oxide formed and thickness of the oxide layer. Different oxidation parameters (pressure, temperature, holding time and cathode configuration) basically resulted in dark, silvery and whitish pellets, as shown in Fig. 4. The difference in color was attributed to differences in the composition and thickness of the oxide layer [22]. X-ray analyses of plasma oxidized Ti pellets (Fig. 5) revealed that the whitish aspect

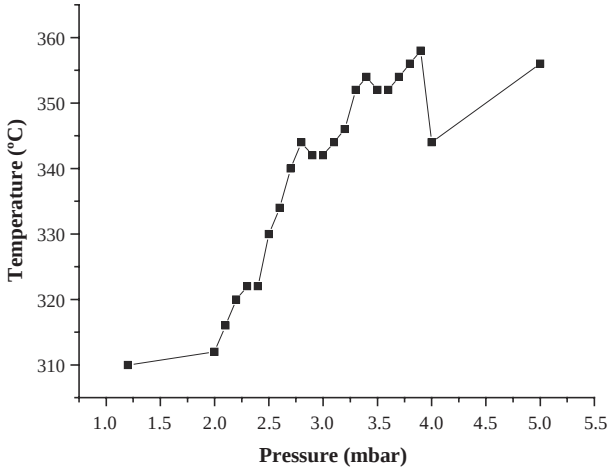


Fig. 6. Effect of hollow cathode on the processing temperature as a function of pressure.

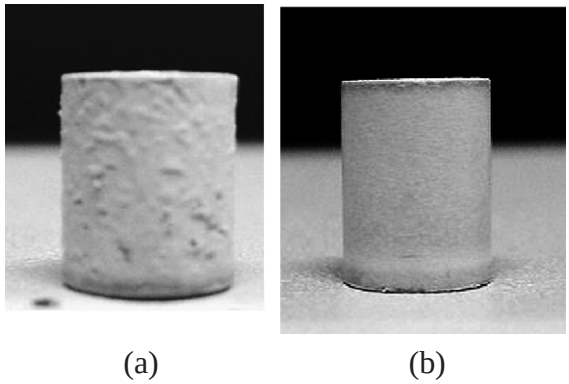


Fig. 7. (a) Oxidized sample depicting whitish layer before ultrasound cleaning and (b) oxidized layer partially peeled off.

corresponded to layers containing a mixture of Ti_4O_7, TiO and TiO_2. The presence of stable TiO_2 in the white layer may be a result of atomic sputtering and subsequently formation of surface oxides which further stabilized to TiO_2 by surface diffusion. Successive impingement of oxygen ions onto such stable layer may have assisted in the diffusion of oxygen to deeper areas and the consequent formation of TiO and Ti_4O_7 [18]. Darker surfaces also contained Ti_4O_7.

The color of the samples and, therefore, the thickness and composition of the oxide layer directly depended on the processing conditions, which determined the rate of ionic impingement against the titanium surface. In the hollow cathode configuration, plasma density increases and the environment is populated with highly energetic particles. The rate of bombardment is intensified with respect to the planar configuration, which increases the thermal gradient between the surface and the bulk of the sample. This scenario contributed to the kinetics of the oxidation reactions, even at relatively lower temperatures, which ultimately imposed the whitish hue of the surface (mixture of Ti_4O_7, TiO and TiO_2) over the darker aspect. An example of such effect could be seen from samples oxidized at 400 or 500 °C for 60 min under 2.2 mbar. Whereas oxidation in hollow cathode resulted in whitish hue, darker surfaces were observed simply switching to planar configuration.

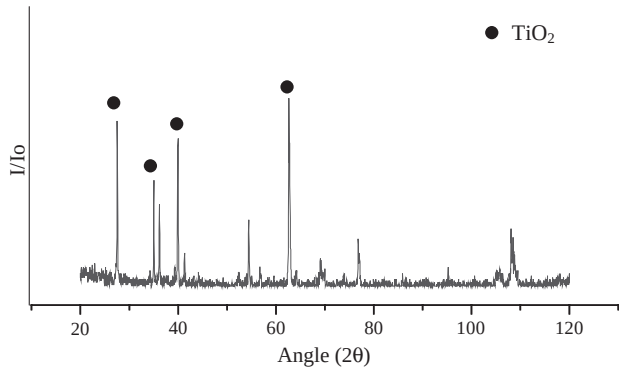


Fig. 8. X-ray diffraction pattern of peeled-off sample after ultrasonic-bath cleaning.

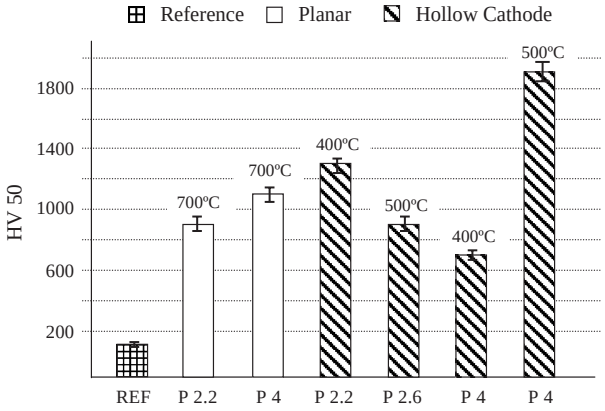


Fig. 9. Microhardness of reference and oxidized Ti pellets.

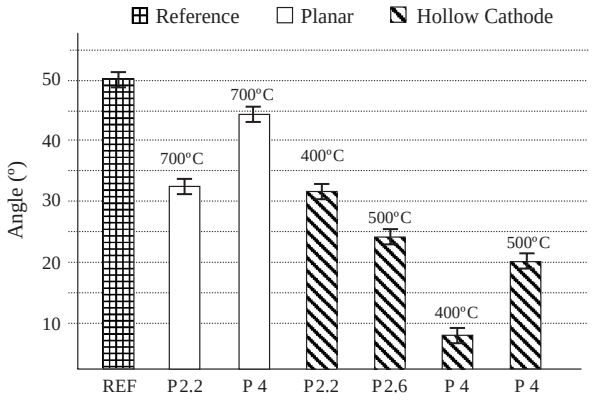


Fig. 11. Contact angle of reference and oxidized Ti pellets.

Increasing the pressure from 2.2 to 4.0 mbar and oxidizing Ti pellets in hollow cathode during 60 min resulted in white/silvery layers regardless of the temperature (400–700 °C). Similar results were observed with the planar configuration. The nature of the oxides formed depended on the temperature and the color of the surface changed from silver (400 or 500 °C) to white (700 °C). An intermediate pressure value was also studied. This value (2.6 mbar) was selected from the maximum slope of the plot of the temperature as a function of the pressure (Fig. 6) to maximize the hollow cathode effect. Surfaces with an intermediate silvery aspect were obtained setting the pressure to 2.6 mbar and oxidizing samples at 400 °C during 30 min. Increasing the holding time to 60 min changed the color of the sample to white. Higher temperatures (500 or 700 °C) also yielded the whitish hue regardless of the holding time (10, 15, 30 or 60 min).

The oxidizing conditions which yielded darker samples were left out due to adverse esthetics to dental implants. On the other hand, whitish oxidized layers partially peeled off upon ultrasonic cleaning. Such change in visual aspect can be seen in Fig. 7. X-ray analyses of samples depicting peeling off revealed a change in the composition of the layer, having TiO_2 as the predominant phase present (Fig. 8). It could be reasonably concluded that considerably thick oxidized layers peeled off due to excessive brittleness and residual stress built up, both deleterious to the adherence of the oxidized layer to the substrate.

Therefore, from an aesthetical standpoint only experimental processing conditions, which produced uniform silvery layers, were used to the remaining of the work. Selected samples were then submitted to microhardness, roughness and wetting tests along with microstructural analysis. Significant increase in the microhardness of oxidized samples with respect to bare Ti (reference sample) could be noticed for some conditions (Fig. 9), suggesting that the embrittlement could be assisted by the higher values of microhardness.

Related studies on thermal oxidation [22] established attempts to correlate thickness and color of oxidized layers. White layers have been attributed to thicknesses in excess of 170 nm whereas the silvery aspect corresponded to thickness between 70 and 170 nm. As it can be seen from Fig. 10, stable silvery layers around 1000 nm thick could be produced in the hollow cathode configuration of the plasma reactor. It is worthwhile mentioning at this point that the passivating and adherent characteristic of relatively thick oxidized layers

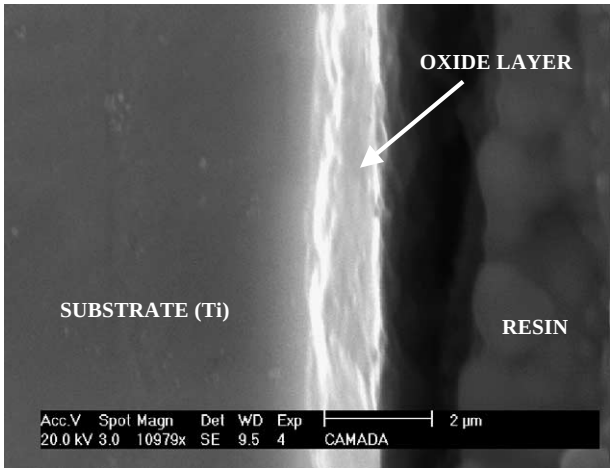


Fig. 10. SEM cross-sectional view of oxidized pellet.

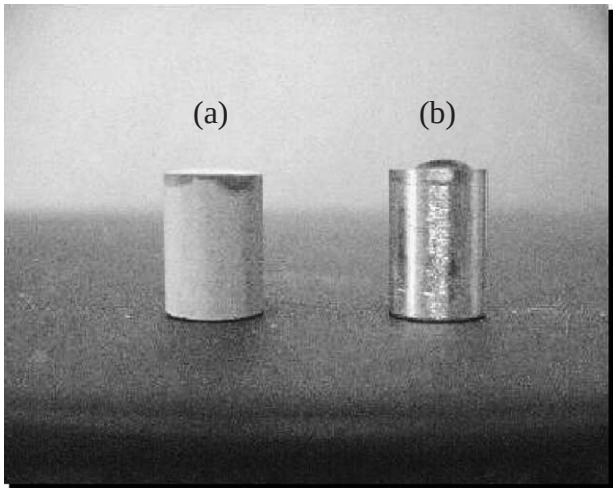


Fig. 12. Wetting on (a) oxidized and (b) bare Ti pellet.

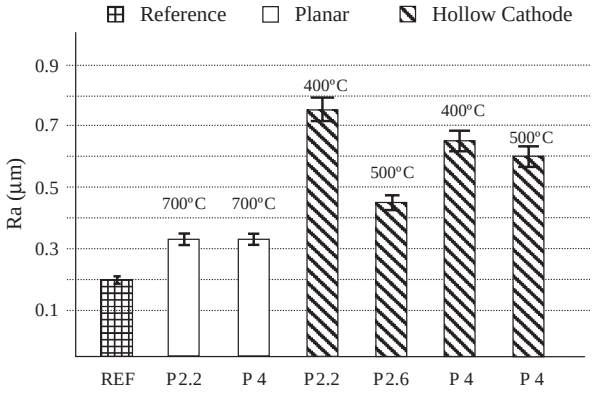
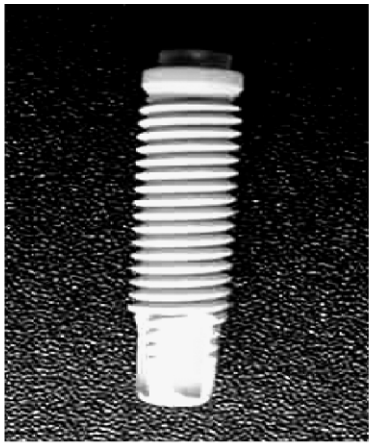


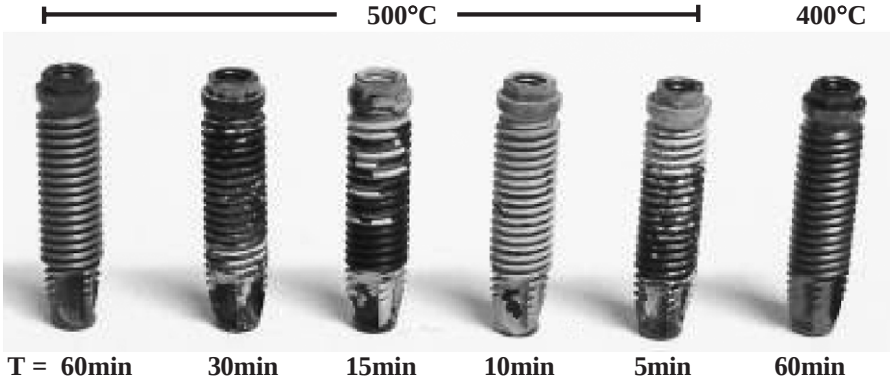
Fig. 13. Roughness (average Ra) of reference and oxidized Ti pellets.

either deposited or formed onto Ti surfaces are positive aspects to the biocompatibility and wetting behavior of dental implants [23–25]. Moreover, the corrosion resistance of Ti implants is also attributed to the stability and nature of the superficial oxide layer. Finally, amongst a number of parameters responsible for long-range osseointegration, surface tension plays an important role on bioadhesion [26].

Adequate surface tension not only assures superior wetting of the implant surface to organic fluids but also contributes to mechanical soundness and durability. Further studies on the relationship of surface tension and cell adhesion are still under way and no detailed conclusion can be established at this point. Nevertheless, it is quite evident that cell adhesion depends on the surface tension of both counterparts of the joint; i.e., oxide layer and organic fluids. Adhesion should be maximum when the magnitudes of the surface tension of both components are similar, thus minimizing interfacial stress concentrations [27]. Wetting experiments can be carried out to at least estimate the usefulness and qualitative behavior of the surface tension between an implant and organic fluids. Therefore, the contact angle between implant surface and organic fluid can be considered a valid parameter to indicate cellular adhesion [1]. The ability of a layer to wet organic fluids can be associated to a trend towards primary deposition of biomacromolecules on the implant/tissue interface, due to its revealed potential to adsorb the precursor biofilms. Improved wetting was observed for all samples oxidized in plasma atmosphere compared to bare Ti (Fig. 11). The



(a)



(b)

Fig. 14. (a) Visual aspect of implant oxidized in hollow cathode at 500 °C and (b) series of implants showing peeling off except for rightmost image (stable silvery layer).

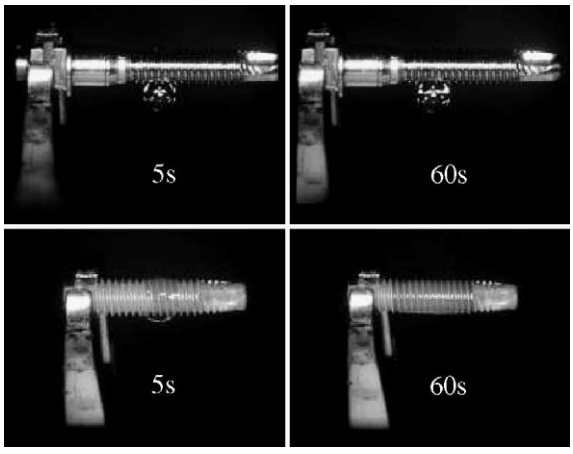


Fig. 15. Pending drop wetting experiment on (a) bare and (b) oxidized implant.

contact angle for oxidized surfaces varied from 8° to 44°, whereas that of untreated pellets was approximately 50°, as it can be visualized from Fig. 12. The set of parameters for improved wetting varied as a function of the pressure. Plasma oxidation also produced considerable changes on the roughness of Ti pellets. Average Ra increased from 0.2 μm to 0.32–0.75 μm upon oxidation, as shown in Fig. 13. Pellets oxidized in hollow cathode clearly depicted the highest Ra values, confirming the boosting effect of the shield on the ionization rate. A combined analysis using Figs. 11 and 13 clearly revealed a decrease in the contact angle for treatment conditions resulting in rougher surfaces, thus suggesting an improvement to the osseointegration behavior of the surface.

The results presented guided the choice of appropriate surface modification parameters for preliminary tests on commercially available implants. The hollow cathode configuration was used and the distance between cathodes was 9 mm. Pressure was set to 2.6 mbar (260 Pa) and temperature to 400 °C or 500 °C. With these conditions, implants were treated for periods varying from 5 to 60 min. All implants oxidized at 500 °C developed whitish layers (Fig. 14a) which peeled off upon ultrasound cleaning. Plasma treating at 400 °C for 1 h resulted in stable silvery oxidized layers, as shown in Fig. 14b. Wetting significantly improved with respect to the corresponding untreated implant, resulting in full spreading after contact with a liquid drop for 60 s (Fig. 15). The pending drop method was used to evaluate wetting in implants due to the intricate geometry of the part. The resulting morphology of the surface compared to that of bare implants can be visualized in Fig. 16. The roughness of the implant significantly improved with the formation of a network of homogenously dispersed irregularities. Studies have shown that relatively rougher surfaces depict higher contents and better distribution of protein deposits onto Ti surfaces, which positively affects the cellular response to osseous healing [28].

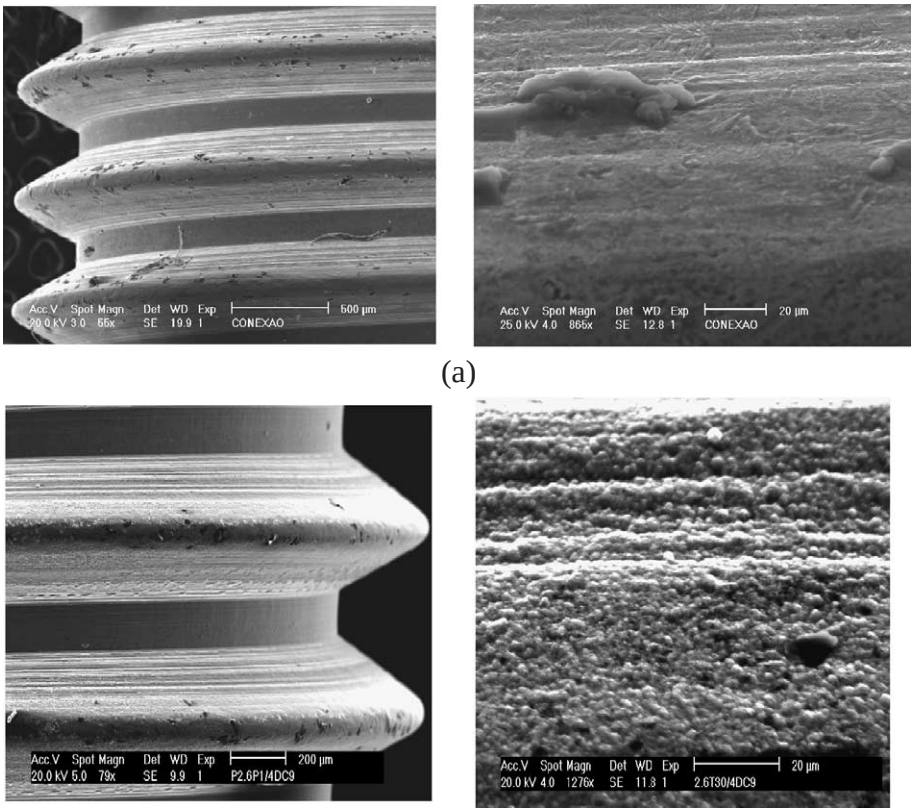


Fig. 16. SEM images of (a) bare and (b) oxidized implant.

Furthermore, investigations on cellular adhesion to bones as a function of surface roughness have produced superior results with rough surfaces, confirming the beneficial effect of surface oxidation on the deposition of osteoblastic cells and corresponding improvement in osseointegration [29].

4. Conclusions

Titanium surfaces were oxidized using plasma bombardment. The hollow cathode configuration improved ionic impingement rate resulting in improved roughness and oxidation at lower processing temperatures. A direct relationship between surface color and composition of the oxides formed could be established. Relatively rough layers consisting of a mixture of oxides peeled off upon ultrasound cleaning and were discarded. Stable oxide layers predominantly consisting of TiO_2 could be formed and resulted in improved wetting of the implant in contact with physiological fluid. Oxidation at 400 °C under 2.6 mbar (260 Pa) using the hollow cathode configuration yielded the best results in terms of wetting, visual aspect, surface morphology and stability of the oxide layer. Commercially available Ti implants were successfully oxidized in plasma under these conditions and revealed significant improving in characteristics potentially related to shorter osseointegration periods.

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