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Nitriding of titanium disks and industrial dental implants using hollow cathode discharge

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Abstract

Standard plasma nitriding of commercially pure Ti or various Ti alloys for human body implants (e.g., hip, knee, shoulder and ankle implants) has already proven useful. However, its use in dental implantology is rather limited due to high nitriding temperatures. The small dental implants of complex geometries are frequently distorted. To solve this problem and benefit from the ability of the plasma treatment to modify the implant surface properties (needed for faster osseointegration process), such as creating different surface topographies, increasing surface roughness, changing local chemical properties by formation of different phases, cleaning/sterilizing contaminated surface and increasing the surface wettability, the titanium disk samples and industrial dental implants were nitrided using a hollow cathode discharge (HCD) configuration of a plasma nitriding system in a 20% N_2–H_2 atmosphere at pressures of 150 or 250 Pa and temperatures ranging from 400 to 500 °C for 1 or 2 h. The topography of the samples was characterized by optical and electron microscopy. Phases were determined by X-ray diffraction. The surface roughness and wettability were also quantified. Nitrided layer formation having better stability, increased surface roughness and higher wettability has been observed for samples treated at 450 and 500 °C and at a pressure of 150 Pa. Industrially fabricated dental implants were then nitrided at 500 °C/150 Pa for 2 h. The results show capability of HCD in treating dental implants. A significant change in the surface texture and superior wettability of the plasma-treated dental implants, with no geometric distortions, have been observed.

Keywords: Dental implants; Plasma nitriding; Osseointegration; Biomaterials

1. Introduction

The clinical goal for a dental implant is to obtain secure anchoring of the implant in the bone, ideally for a lifetime. It includes the implant's ability to carry and sustain the static and dynamic load to which it is subjected. It is desirable that this goal is achieved in the shortest possible healing time, with small failure rate and with minimal discomfort for the patient [1]. The acceptance of the implant by the human body, the start of the bone healing process, and the subsequent growth of the new bone tissue on the implant surface is called osseointegration [2–4]. One of the driving forces of the ongoing research activity in dental implantology is the reduction of time of this process. In this respect, the material selection for a dental implant is critical and is based on its various required chemical and physical properties [5]. Today, the majority of dental implants are fabricated from commercially pure Ti (of different grades depending on manufacturer) and from titanium based alloys, such as Ti6Al4V [6,7]. The bioinert properties of Ti and Ti-based alloys have been related to a naturally formed 2–5-nm-thick TiO_2 phase on the surface of titanium [8–10]. However, the effect of various different phases, such as titanium nitrides and oxinitrides, also needs to be studied. TiN is known to possess excellent mechanical properties, chemical stability and biocompatibility [11]. Its use for hip, knee, shoulder and ankle implants has led to increased surface abrasion resistance and reduced bacterial colonization compared to other clinically used implant surfaces [12]. TiN can be produced either by nitriding the Ti

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implant surface or by depositing a TiN coating on the implant surface (in this case, the implant does not necessarily have to be made from Ti). Many PVD and CVD techniques and their variants as well as the use of plasma have proved successful in the formation of various stoichiometric and nonstoichiometric TiN_x compounds (e.g., Refs. [13,14] and references therein). The nitriding process is rather more limited. Several works show the successful use of plasma in nitriding of Ti samples at temperatures around 700 and 800 °C [15–17]. However, due to the high-process temperature, small Ti samples of complex geometry are frequently distorted [18]. We know of no previous studies of nitriding of Ti implants using hollow cathode discharge. The use of plasma can also be beneficial in changing surface topography, in increasing surface roughness, in cleaning/sterilizing and in increasing the wettability of the surface (treated inSections 2 and 3). That is why in the present work, we use hollow cathode discharge in the nitriding of Ti cylindrical samples and industrially fabricated Ti dental implants. The influence of the process parameters such as temperature and pressure on the presence of nitride phases on the surface, surface texture, roughness and wettability is studied.

2. The role of surface topography and surface wettability

It has been observed that faster osseointegration can be achieved by implant surface texturing [19,20]. Initially, this purely experimental observation was explained as due to the beneficial role of increased surface roughness, since it gives a higher surface contact area and increased adhesion by mechanical interlocking on a macroscopic scale. However, Cordiolli et al. [21] has shown that, for their acid-etched implants of lower surface roughness, higher removal torque from rabbit tibia is necessary than for the rougher grit-blasted and plasma-sprayed implants. The surface topography cannot be simplified to surface roughness, as can be seen frequently in the literature. The special designed cavities, grooves and other topographical features can be very important for bone attachment and growth. It can promote orientation and guide locomotion of specific cell types and has the ability to directly affect cell shape and cell function [20,22–24]. This has been explained by the highly developed ability of biological systems to recognize specially designed features on the molecular scale, the so-called biorecognition, and by the unique synergistic connection between the nanometer and micrometer length scales when cells are present [1,25]. The recognition is programmed into the molecules through the combination of their 3D topographic architecture, the superimposed chemical architecture and the dynamic properties.

The first molecules arriving at the surface on a nanosecond scale are water molecules. The water is known to interact and bind very differently at surfaces depending on the surface properties. The properties of the surface water "shell" are an important factor influencing proteins and other molecules that arrive a little later (micro and millisecond scale). These water-soluble biomolecules also have hydration (water) shells, and the interaction between the surface water shell with the biomolecular water shell influences the fundamental kinetic processes and the thermodynamics at the interface [1]. For example, it may determine if proteins denature or not, their orientation, coverage, etc. When cells arrive at the surface, they "see" a protein-covered surface whose protein layer has properties that were initially determined by the preformed water shells. It has been observed that cell adhesion is generally better on hydrophilic rather than on hydrophobic surfaces [26,27].

3. Why hollow cathode discharge (HCD)?

A sample or dental implant placed into a plasma encounters a complex and hostile environment, which includes interaction with photons, bombardment by electrons, ions, atomic and molecular neutrals and radicals in ground and excitation states. The particle bombardment is a strongly nonequilibrium process. Upon contact with a surface, particles can release a significant part of their energy, producing pressure and thermal spikes. For example, 3283 K spikes and pressures of 1.3×10^{10} Pa (1.2×10^{5} atm) for 7×10^{-11} s have been calculated for impinging particles with an energy of 100 eV [28]. Such pressures and spikes affect the results of the process taking place at the surface in contact with the plasma and are the reason for a frequently observed surface densification, sputtering of the target material, intense heating, formation of metastable materials on the surface, surface structure damage, etc. In the case of surfaces for dental implants, it is possible to create (depending on the conditions) various surface topographies, increase surface roughness, change local chemical properties by formation of different phases, clean/sterilize contaminated surface and increase the wettability of the surface.

The hollow cathode effect is a special situation for the glow discharge between two closely separated cathode surfaces. This effect occurs when the dimension of the cathode fall region becomes as large as the separation distance. The loss of electrons is low because they are repelled by the negative walls of the cathode, and in fact, they oscillate between the sample and the wall. The plasma density (that is the electron concentration) increases and reaches values of about 10^{12} cm^{-3} [29]. As a consequence, the production of ions rises too, and the ion flux density at the substrate surface increases. Due to these factors, such surfaces can be heated to extremely high temperatures even at relatively low bulk substrate temperatures of 200–500 °C. Such enhanced plasma conditions of HCD have been recognized as favorable

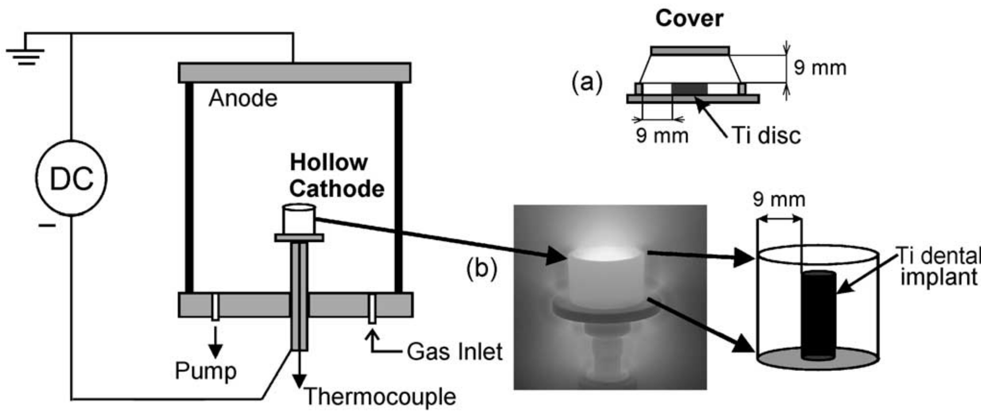

Fig. 1. The Hollow Cathode Discharge (HCD) nitriding system configuration with inserted (a) Ti disc and (b) dental implant.

by various researchers in their search for the formation and stabilization of high temperature and metastable phases on the substrate surface [30,31].

4. Experimental setup

Ti discs (grade II), 4 mm in diameter and 2-mm high, were top surface polished until an average surface roughness, *Ra*, of 0.2 μm was reached. Then the samples were cleaned in an acetone ultrasonic bath and placed into the plasma nitriding system. In the second part of the study, the industrially fabricated dental implants (Neodent-Titamax liso II), 4 mm in diameter and 15 mm tall (acho que os implantes têm 15 mm de altura), made of Ti (grade II) were used. For them, no additional cleaning process was necessary as they were supplied well sterilized using gamma rays.

The experimental apparatus used for plasma nitriding is shown in Fig. 1. It consists of a vacuum chamber containing an anode and a hollow cathode (all metal parts are made of stainless steel), in which the Ti discs (Fig. 1a) or industrially applied dental implants (Fig. 1b) are placed and well centralized. The conditions for HCD are satisfied in the space between the inner wall of the crucible and the sample (for both, the Ti discs and dental implants) and between the stainless steel cover and the top surface of the Ti discs, which are all at the same negative potential. The distance of sample from the cathode inner wall surface (and from the superior cover in the case of Ti discs) was 9 mm. The nitriding conditions for Ti discs are summarized in Table 1. Samples were treated in flowing 20% N_2–H_2 for 1 or 2 h The flow of the gas mixture was held constant at 11 sccm for all experiments. The pressure was stabilized at 150 or 250 Pa, and the temperature of samples was held constant between 400 and 500 °C. The temperature was measured by a chromel–alumel thermocouple inserted in the substrate holder, as indicated in Fig. 1, and controlled by varying continuously the voltage between the electrodes. Dental implants were nitrided after determining the optimal pressure/temperature conditions (see the Results and discussion section), while keeping other parameters as stated above.

After the treatment, the top surfaces of the nitrided Ti discs were characterized for their texture, roughness, wettability and formed phases, while the treated and as-supplied dental implants were characterized for their texture and wettability. The texture was analyzed by optical and scanning electron microscopy (SEM). The mean value of the average surface roughness, *Ra*, was calculated from measurements of *Ra* in three different directions (angles of 120°),

Table 1
Plasma nitriding conditions and nitrided layer thickness for 12 Ti samples and one dental implant

Sample	Pressure (Pa)	Voltage (V)	Current (A)	Power (W)	Temperature (°C)	Time (h)	Nitrided layer thickness (μm)
1	150	710	0.20	142.0	400	1	7
2	150	810	0.23	186.3	450	1	32
3	150	918	0.27	247.9	500	1	31
4	250	595	0.21	125.2	400	1	4
5	250	690	0.24	165.6	450	1	5
6	250	745	0.30	223.5	500	1	8
7	150	700	0.19	133.0	400	2	5
8	150	790	0.23	181.7	450	2	51
9	150	850	0.27	229.5	500	2	48
10	250	585	0.21	122.9	400	2	–
11	250	650	0.26	169.0	450	2	–
12	250	715	0.30	214.5	500	2	2
Implant	150	1050	0.24	252.0	500	2	–

obtained using a SURTRATONIC 3 Taylor–Robson profilometer. The technique used to characterize the wettability of the surfaces is usually the measurement of the contact angle of a drop of a liquid on the tested surface. In our case, we have used a physiological serum, an EURO-COLINS solution of glucose (3.57%), glycerin (70%) and pigment. As in the case of the dental implants, the contact angle is difficult to estimate, it was adopted a qualitative measure of wettability—coverage of the implant screw by physiological serum after 1 min. Surface phases were studied using Shimadzu XRD-6000 X-ray diffraction equipment.

5. Results and discussion

During optimization of the nitriding process, the pressure was varied while keeping the voltage constant. Two sudden increases in the current were repeatedly detected, a strong one at 150 Pa and a smaller one at 250 Pa, indicating higher thermal efficiency, respectively. During the temperature optimization, the Ti discs treated above 500 °C exhibited dark nonuniform layer formation. These layers proved easy to detach using an ultrasound cleaning procedure [18]. Surface structure degradation took place during intense plasma treatment, and for this reason, the Ti discs were discarded from further experimentation.

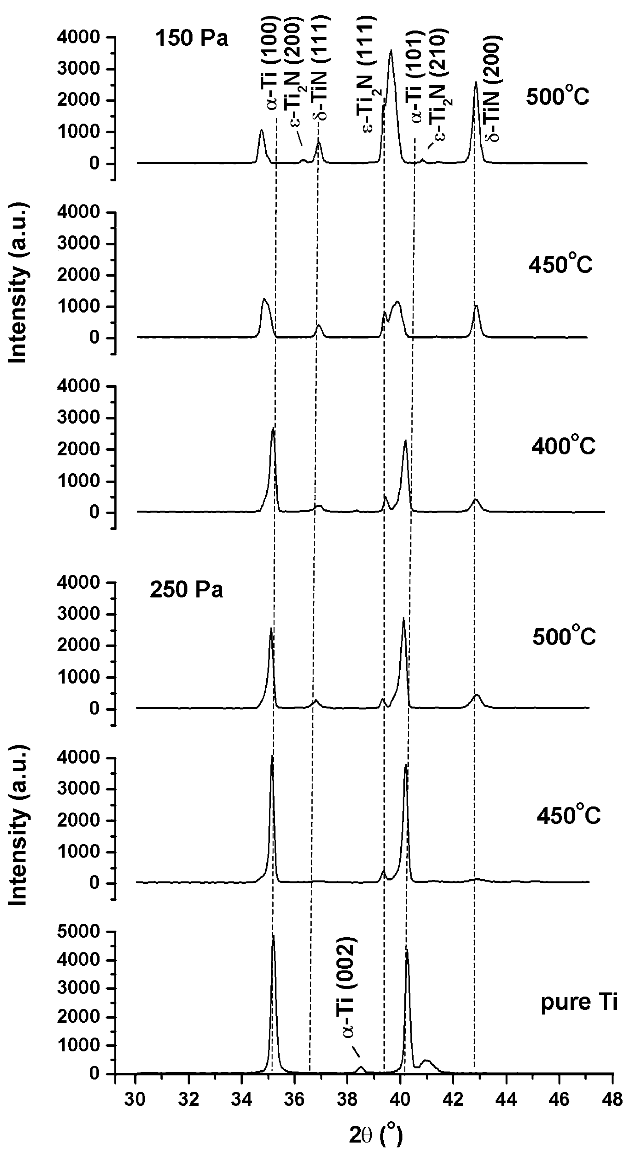

Fig. 2. X-ray diffraction spectra of pure Ti and the samples nitrided at pressures of 150 and 250 Pa, at temperatures of 400, 450 and 500 °C for 1 h.

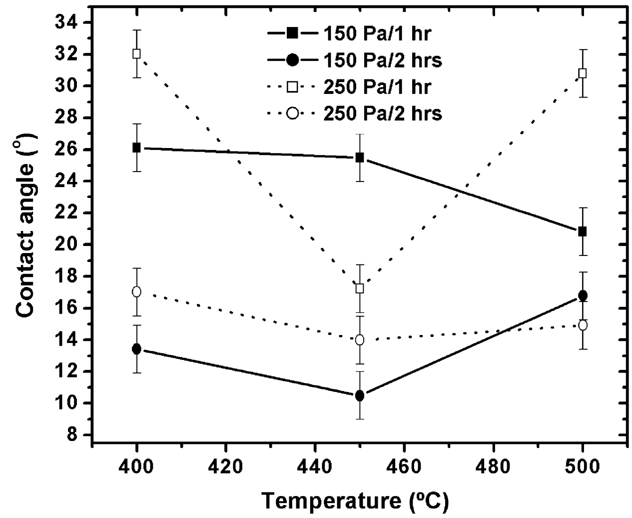

Fig. 3. Contact angle of the drop of a physiological serum on the top of Ti discs as a function of temperature for four combinations of pressure/time conditions (150 and 250 Pa, 1 and 2 h).

Fig. 2 shows XRD spectra of Ti samples nitrided at pressures of 150 and 250 Pa (i.e., in conditions of higher and lower ionization) and at temperatures of 400, 450 and 500 °C for 1 h. The samples' spectra are compared with that of pure Ti. The sample treated at 250 Pa and 450 °C is dominated by peaks of Ti (hexagonal α-Ti and high-temperature cubic β-Ti). At 500 °C, new peaks of δ-TiN appeared. All XRD spectra of samples treated at 150 Pa have well-defined reflections of δ-TiN. These peaks are more intense when treatment temperature and time are increased. New peaks of ε-Ti_2N are detected at 500 °C. Such a strong difference in the XRD spectra between samples treated at 150 and 250 Pa indicates different kinetics at the surface of these samples during plasma nitriding. This shows that the effect of the hollow cathode at lower pressure is more pronounced and, in fact, that the degree of ionization (directly related to the current density at substrate surface) is governing the process of nitriding of Ti in the system configuration.

It was also observed that the peaks related to hexagonal α-Ti decrease their intensity, lose their symmetry and shift to the left part of the spectra when increasing the treatment temperature. This behavior is more pronounced at 150 Pa. The peaks could not be assigned to any other possible phase. However, in the literature, the shift has been related to lattice expansion and distortion due to inserted interstitial nitrogen [32]. Since in this case the treatment atmosphere

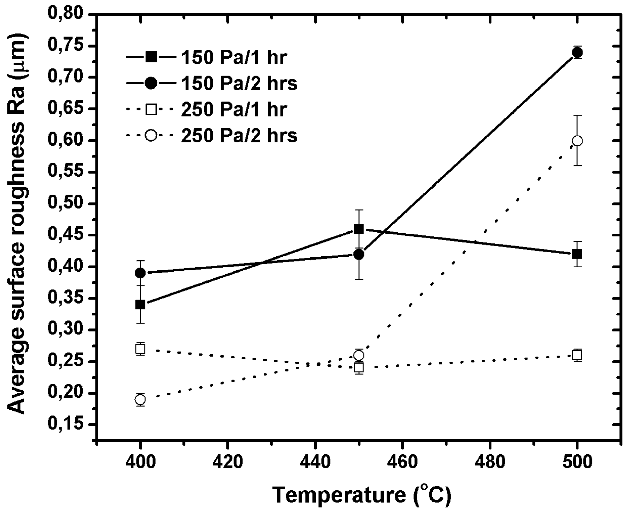

Fig. 4. Average surface roughness values of nitrided Ti discs as a function of temperature for four combinations of pressure/time conditions (150 and 250 Pa, 1 and 2 h).

was a mixture of nitrogen and hydrogen, we suggest that the observed behavior may be caused not only by incorporated nitrogen but also by incorporated hydrogen. The observed phenomenon correlates with internal stress, which suggests that this may be the reason for structure degradation and failures, demonstrated by easy detachment of nitrided surface layers at higher temperatures (>500 °C) [18].

The wettability, expressed as the contact angle, of all nitrided Ti samples (listed in Table 1) is shown in Fig. 3 as a function of treatment temperature. The contact angle of all treated samples lies below 32°, while for pure Ti (cleaned in ultrasonic acetone bath), the contact angle is 50°. All samples nitrided for 2 h have a contact angle below 18°. The Ti sample nitrided at 150 Pa and at 400 and 450 °C shows the highest wettability, with contact angles below 14°.

The average surface roughness *Ra* of nitrided Ti samples has been found to depend also on plasma conditions (Fig. 4). At temperatures at or below 450 °C, the *Ra* values are approximately two times higher for Ti samples nitrided at a pressure of 150 Pa than those nitrided at a pressure of 250 Pa. A significant increase in the *Ra* values has been observed for both samples treated at 500 °C for 2 h.

All the above-described phenomena such as roughness changes, increase of surface wettability and various formed nitride phases depend on the plasma conditions used. The enhanced plasma conditions (higher degree of ionization, higher current density at the substrate surface) at a pressure

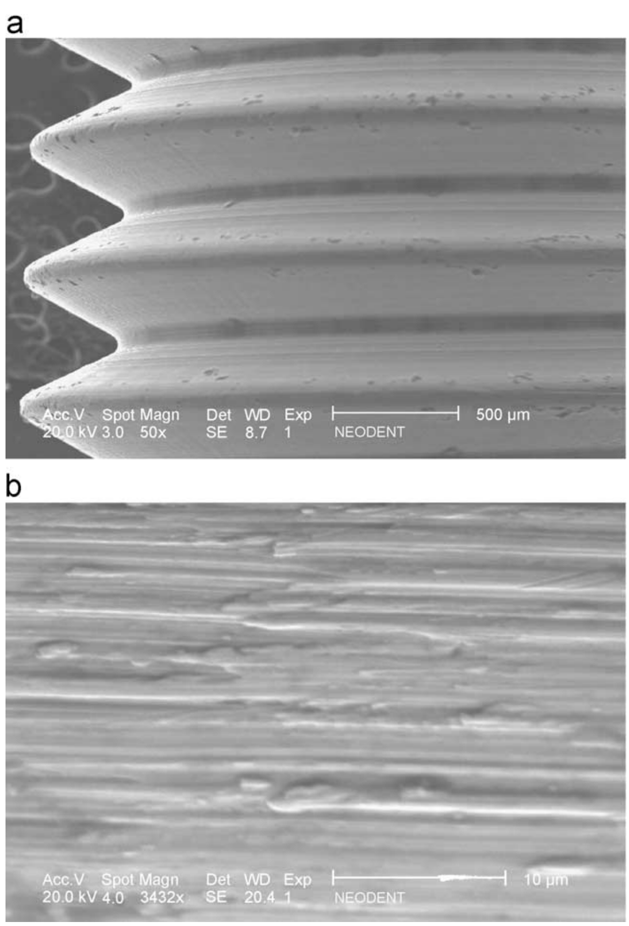

Fig. 5. (a) SEM image of the surface of the as-supplied dental implant with its (b) detail.

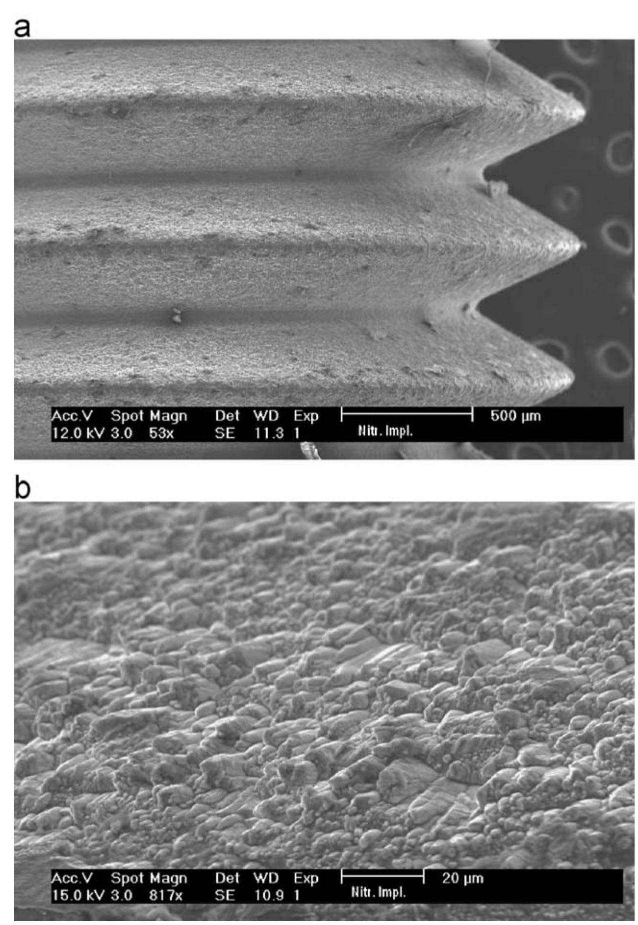

Fig. 6. (a) SEM image of the surface of the nitrided dental implant (150 Pa, 500 °C and 2 h) with its (b) detail.

of 150 Pa and at a given configuration of the hollow cathode are responsible for the creation of nitrided layers, in contrast to the situation when nitrided at 250 Pa or in a conventional planar cathode systems at the same substrate temperature (measured by a thermocouple inserted in the substrate holder). The pressure difference between 150 and 250 Pa during nitriding in conventional cathode systems without additional ionization makes no significant difference, but in the hollow cathode configuration, the pressure selection is crucial.

Increased particle bombardment is also responsible for a stronger texturing effect by sputtering of the surface. The top oxide surface and many loosely surface-bond species are removed during sputtering. After the treatment, the modified Ti surface (textured, nitrided) contains many open dangling bonds. As well of increased roughness and surface phase modification, such unsaturated surface is responsible for increased surface wettability.

The industrially applied dental implants were treated at a chosen (optimized) pressure of 150 Pa and at a temperature of 500 °C for 2 h. In Fig. 6a and b, the texture of the surface of the nitrided implant is revealed and compared with the as-supplied dental implant (Fig. 5a,b). Fig. 5b shows that the surface of the as-supplied dental implant has a typical texture of machining (turning) with circumferential parallel lines perpendicular to the long axis of the implant. In dental implantology, this surface is normally considered smooth [21]. The *Ra* of such a finished surface is typically between 0.30 and 1 μm, depending on various process parameters. In contrast, examination of the surface of the nitrided dental implant seen in Fig. 6b indicates that the surface has been strongly textured by plasma particle bombardment. The circumferential parallel lines are no longer visible. The surface shows formation of microcavities and seems to be rougher than the as-supplied implant, although no independent confirmation of the roughness could be made due to technical difficulties.

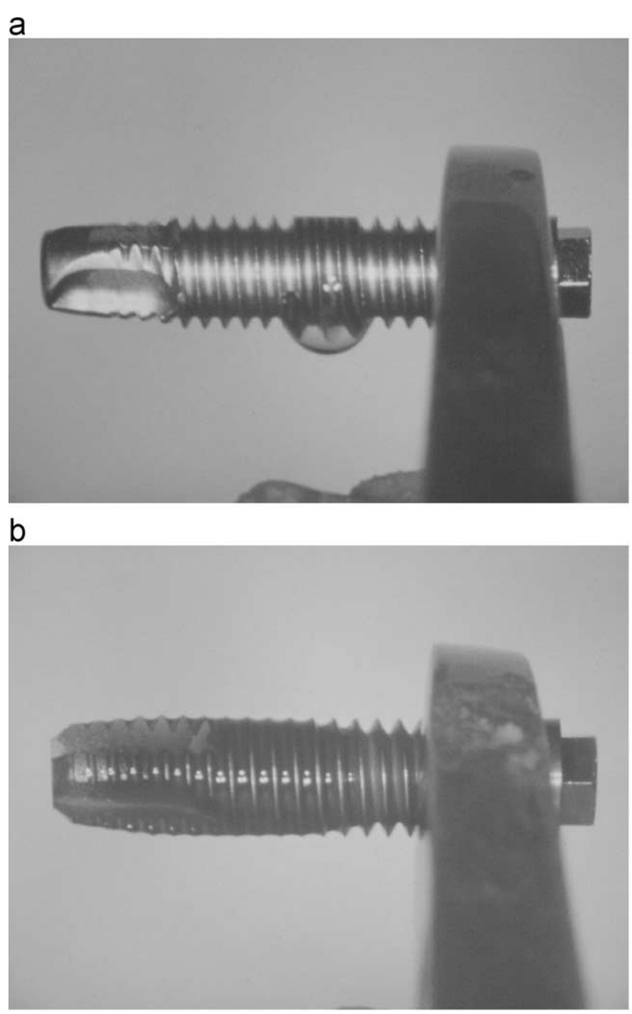

Fig. 7. Wettability test: the physiological serum drop coverage of the surface of (a) as-supplied and (b) nitrided dental implant after 60 s. Scale: dental implant screw is 4 mm in diameter and 9 mm long.

The wettability of both (treated and untreated) dental implants is compared in Fig. 7a and b. The photos were taken 60 s after the drop of physiological serum had been placed on the surface of each implant. A higher surface coverage is observed for the nitrided dental implant.

All the results obtained above suggest possible enhanced osseointegration in implants surrounded by tissue. The ongoing clinical testing is expected to confirm our expectations.

6. Conclusions

In this work, it was concluded that:

- It is possible to obtain good nitrided Ti samples at lower temperatures (450 and 500 °C) than quoted in the literature for conventional planar cathode plasma nitriding (700 °C or higher). This is attributed to enhanced ionization at 150 Pa due to the hollow cathode effect. Furthermore, no distortion was observed during plasma treatment of dental implants of complex geometry at a lower temperature.
- According to the described and accepted general knowledge about the implant–living organism interaction in the literature, our plasma-treated Ti samples and industrial dental implants both show activated surface properties such as higher wettability and surface roughness. In this respect, the best results were obtained using hollow cathode treatment in intense ion bombardment conditions at 150 Pa/(450 or 500 °C) for 2 h.

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References

[1] B. Kasemo, Surf. Sci. 500 (2002) 656.
[2] C.A. Simmons, S.A. Meguid, R.M. Piliar, J. Orthop. Res. 19 (2001) 187.
[3] P.-I. Brånemark, B. Svensson, D. van Steenberghe, Clin. Oral Implants Res. 6 (1995) 227.
[4] T. Jemt, U. Lekholm, Int. J. Oral Maxillofac. Implants 10 (1995) 303.
[5] R. Thull, Biomol. Eng. 19 (2002) 43.
[6] C.B. Johansson, C.-H. Han, A. Wennerberg, T. Albrektsson, Int. J. Oral Maxillofac. Implants 13 (1998) 315.
[7] P.P. Binon, D.J. Weir, S.J. Marshall, Int. J. Oral Maxillofac. Implants 7 (2) (1992) 168.
[8] B. Kasemo, J. Prosthet. Dent. 49 (6) (1983) 832.
[9] T. Albrektsson, H. Hansson, K. Bengt, K. Larsson, I. Lundstrom, D.H. McQueen, R. Skalak, Ann. Biomed. Eng. 11 (1) (1983) 1.
[10] B. Kasemo, J. Lausmaa, in: P.-I. Branemark, G.A. Zarb, T. Albrektsson (Eds.), Tissue-Integrated Prostheses: Osseointegration in Clinical Dentistry, vol. 4, Quintessence Pub., Chicago, 1987, p. 99, cap.
[11] J. Park, D.-J. Kim, Y.-K. Kim, Keun-H. Lee, Ki-H. Lee, H. Lee, S. Ahn, Thin Solid Films 435 (2003) 102.
[12] B. Groessner-Schreiber, A. Neubert, W.D. Muller, M. Hopp, M. Griepentrog, K.P. Lange, J. Biomed. Mater. Res. 64A (4) (2003) 591.
[13] L. Combadiere, J. Machet, Surf. Coat. Technol. 88 (1996) 17.
[14] L. Combadiere, J. Machet, Surf. Coat. Technol. 88 (1996) 28.
[15] S.C. Mishra, B.B. Nayak, B.C. Mohanty, B. Mills, J. Mater. Process. Technol. 132 (2003) 143.
[16] J.R. Sobiecki, T. Wierzchon, J. Rudnicki, Vacuum 64 (2002) 41.
[17] C.S. Javorsky, T.R. Strohaecker, J.A.T. Borges da Costa, M.A.Z. Vasconcellos, Nucl. Instrum. Methods Phys. Res., B Beam Interact. Mater. Atoms 175–177 (2001) 726.
[18] C.L.B. Guerra Neto, MSc thesis, Department of Physics, Universidade Federal do Rio Grande do Norte Natal–Brazil, 2001.
[19] D.M. Brunette, Int. J. Oral Maxillofac. Implants 3 (1998) 231.
[20] N. Sycaras, A. Iacopino, V.A. Marker, Int. J. Oral Maxillofac. Implants 15 (5) (2000) 675.
[21] G. Cordioli, Z. Majzoub, A. Piattelli, A. Scarano, Int. J. Oral Maxillofac. Implants 15 (5) (2000) 668.
[22] K.D. Chesmel, C.C. Clark, C.T. Brighton, J. Black, J. Biomed. Mater. Res. 29 (1995) 1101.
[23] B. Chehroudi, T.R.L. Gould, D.M. Brunette, J. Biomed. Mater. Res. 23 (1989) 1067.
[24] E.T. Den Braber, J.E. De Ruijter, H.T.J. Smits, L.A. Ginsel, A.F. Von Recum, J.A. Jansen, J. Biomed. Mater. Res. 29 (1995) 511.
[25] K. Anselme, Biomaterials 21 (2000) 667.
[26] G. Altankov, T. Groth, J. Mater. Sci., Mater. Med. 5 (1994) 732.
[27] T.G. Ruardy, J.M. Schakenraad, H.C. Van der Mei, H.J. Busscher, J. Biomed. Mater. Res. 29 (1995) 1415.
[28] H. Tsai, D.B. Bogy, J. Vac. Sci. Technol. A5 (1987) 3287.
[29] H. Morgner, M. Neumann, S. Straach, M. Krug, Surf. Coat. Technol. 108/109 (1–3) (1998) 513.
[30] M. Benda, J. Musil, Vacuum 55 (1999) 171.
[31] J. Musil, J. Vlcek, Czechoslov. J. Phys. 48 (10) (1998) 1209.
[32] S.L.R. da Silva, L.O. Kerber, L. Amaral, C.A. dos Santos, Surf. Coat. Technol. 116/119 (1999) 342.