Materials Research. 2013; 16(5): 1006-1014
DOI: 10.1590/S1516-14392013005000067

Influence of Different Acid Etchings on the Superficial Characteristics of Ti Sandblasted with Al_2O_3

Bruno Ramos Chrcanovic*, Nathalia Lorrayne Costa Leão, Maximiliano Delany Martins

Laboratório de Nanoscopia – LabNano, Centro de Desenvolvimento da Tecnologia Nuclear – CDTN,
Comissão Nacional de Energia Nuclear – CNEN, Av. Presidente Antônio Carlos, 6627,
Campus da UFMG, Pampulha, CEP 31270-901, Belo Horizonte, MG, Brazil

Received: June 13, 2012; Revised: February 6, 2013

Some implant manufactures use Al_2O_3 instead TiO_2 powder to sandblast the machined dental implant, because Al_2O_3 powder is commercially more easily available and is cheaper than TiO_2 powder. However, Al_2O_3 powder usually leaves aluminum oxide contamination on the surface, which is potentially toxic. In this work, we subjected Ti discs previously sandblasted with Al_2O_3 powder to 5 different acid etchings in order to verify which treatment is able to remove incorporated particles of Al_2O_3 from the surface. One group of samples were only sandblasted and served as control. The samples were analyzed by electron microscopy (SEM, EDS), scanning probe microscopy, and grazing incidence XRD. The control group showed presence of Al_2O_3 on the surface. Three acid etchings were efficient in removing the alumina from the tested samples. Almost all the tested samples showed higher roughness parameters values than the control samples. Titanium hydride was found in almost all test groups. Moreover, the results suggest that there is no incorporation of the whole Al_2O_3 particle into the titanium surface after the collision, conversely a particle fragmentation occurs and what remains on the titanium surface are Al_2O_3 residues.

Keywords: *titanium, aluminum oxide, surface modification, sandblasting, acid etching*

1. Introduction

The design of endosseous dental implants have been revisited extensively to decrease treatment time frames by reducing the healing period for osseointegration[1]. Alterations in surface texture and chemistry are the commonly used modifications to increase the biological response to implants. Preparation of a roughened titanium surfaces has long been held and demonstrated to be an effective way to promote the interfacial biomechanical properties of bone-anchored implants by means of increasing the interlocking capacity of surface and consequently enabling a favorable stress distribution of the functional loading of an implant at the interface[2]. Several earlier biomechanical studies in various animal models found that the surface texture of titanium implants has a significant influence on their anchorage in bone[3-5].

Some authors also demonstrated the biological advantage of a rougher surface compared to machined or polished surfaces. Fu et al.[6] showed that osteoblast cell adhesion, proliferation and alkaline phosphatase (ALP) enzyme activity on sandblasted surface and laser-scanned surface were higher than those on machine-tooled and polished surfaces. ALP activity is considered to play a major role in bone formation and mineralization[6].

Bone interlocking or micromechanical anchorage at the interface is not a feature common to all surfaces; to achieve it, a certain level of roughness seems to be required. Some authors[7,8] showed that machined surfaces do not achieve micromechanical anchorage at the interface. Bone was not found attached to the machined surface when removed, whereas anchorage has been documented for other surfaces with physical and chemical surface modifications[4,7,8]. The surface topography obtained by acid etching can be modulated according to prior treatment, for example, by sandblasting, using acid mixtures, using different temperatures, and using different etching times[9]. A combination of blasting and acid etching has been a commonly used surface modification technique during the last two decades. The reason for the combination of methods is that the blasting procedure hypothetically achieves an optimal roughness for mechanical fixation whereas the additional etching smoothes out some sharp peaks. The resulting surface has an improved potential for protein adhesion, considered to be important for the early bone-healing process[10]. Acid etching is a subtractive method, wherein pits are created on the titanium surface[5]. The etching process corrodes the titanium surface greatly, creating irregular pits of varying depth, and produces a microroughness in the range of 0.5 to 3 μm, depending on the etching conditions. When the implant surface is sandblasted prior to etching, a microroughness is superimposed on top of the macroroughness. Etched surfaces have been documented to lead to more bone apposition[11] and to enhance the interfacial strength as measured by removal torque[3] or push-out tests[12] when compared to machined surfaces.

Regarding the first step of surface modification, the sandblasting process on machined dental implant is usually

---

*e-mail: brunochrcanovic@hotmail.com

made with aluminum oxide (Al_2O_3) or titanium oxide (TiO_2) powder. Some dental implant manufactures use Al_2O_3 to sandblast the machined dental implant before the acid etching process, because Al_2O_3 powder is commercially more easily available and is cheaper than TiO_2 powder. However, as the sandblasting particles used during the roughening step may not be completely removed from the implant surface during the etching process, sharp-edged alumina particles are left and can potentially be released during implant insertion[9] or during the osseointegration process.

The effects of Al_2O_3 are definitely a cause for concern. Although Piattelli et al.[13] showed that residual Al_2O_3 particles on the implant surface could not affect the osseointegration of titanium dental implants, their *in vivo* study confirmed this only for a very short-term, since the rabbits used in the study were euthanized after only 4 weeks. More recently, Canabarro et al.[14] evaluated the response of osteoblasts derived from human alveolar bone on to different modified titanium surfaces. They found that the presence of Al_2O_3 could possibly interfere with the nucleation of apatite crystals during the process of mineralization. Therefore the potential effects of slow and continuous release of trace metals cannot be ignored. In the short term, however, trace elements may be responsible for tissue toxicity and wound breakdown, leading to failure of the implant[15]. Although there are no clear reports of machined titanium implants failing due to contamination of the surrounding tissues by impurities, the mere presence of associated metallic elements in the adjacent tissues is a matter of concern[15]. It is therefore relevant to develop a technique of producing roughness on titanium surfaces with the use of Al_2O_3 powder in the sandblasting process without the addition of surface impurities.

As the blasting procedure with Al_2O_3 powder produces desired superficial characteristics to osseointegration, but leaves sharp-edged alumina particles on the surface (which may be toxic), it is the aim of the present study to prepare commercially pure titanium (cpTi) grade IV discs sandblasted with Al_2O_3 and submit to 5 different acid etchings described in the literature, in order to verify which acid etching (if any) is able to remove the Al_2O_3 from the previously sandblasted surface.

2. Material and Methods

Eighteen machined cpTi grade IV discs (12.7 × 2.0 mm) were used as the substrate material for the experiment. All discs were cut from a rod using a IsoMet® Low Speed Saw (Buehler®, Lake Bluff, USA) with a Diamond Wafering Blade No. 11-4244 (4” diameter, 0.012” thickness) from the same manufacturer.

The samples were embedded in polymethyl methacrylate, in order to be polished by a polishing machine. The samples were sandblasted at a pressure of 4 bar with Al_2O_3 powder (average granulometry of 250 µm) in a KaVo Strahlstation EWL 5423 (KaVo Dental GmbH, Biberach/Riβ, Germany). The samples were kept manually at a distance of approximately 2 cm from the blast nozzle, and the sandblasting was oriented perpendicular to the disc surface. Then all samples were ultrasonically cleaned in acetone for 30 minutes, in alcohol for 30 minutes, and finally in deionized water for more 30 minutes, to remove loose particles of Al_2O_3.

The discs were separated into a control group with 3 discs and 5 test groups with 3 discs each. Each test group was acid-etched by five different acid etchings (defined as groups AT1 to AT5) previously described in the literature[16-20]. Table 1 presents a detailed description of these 5 acid etching treatments. The firing in vacuum was performed in a VITA Vacumat 40T vacuum furnace (VITA Zahnfabrik H. Rauter GmbH & Co.KG, Bad Säckingen, Germany).

The surface morphology of treated samples was examined by scanning electron microscopy (SEM - JEOL, model JSM-5310, Tokyo, Japan). The SE mode with an acceleration voltage of 25 kV was selected for SEM analysis and the pressure was maintained below 1×10^{-5} Torr. The load current (LC) was approximately 85 µA. For a direct comparison of the surface morphology, the same magnification of 1000× was selected for all samples.

In order to obtain quantitative analysis of the surface roughness, atomic force microscopy (AFM - NTegra Aura, NT-MDT, Moscow, Russia) of the samples was performed. AFM images were acquired in air using semicontact mode with a NSG 01 sharpened gold-coated silicon tip (nominal spring constant of 2.5-10 N/m and nominal resonance frequency of 110-200 kHz, NT-MDT). The scanning area for the measurements was 50 × 50 µm². The images obtained by AFM were characterized by 2nd order extraction filter, using the software “Image Analysis 2.1.2” (NT – MDT, Moscow, Russia). The seven amplitude surface roughness parameters determined by the software were evaluated (S_y, S_z, S_a, S_q, S_{sk}, and S_{ka}). The mean value and standard deviation of

Table 1. Acid-etching groups details.

Acid-etching group	Acid solution	Temperature (°C)	Etching time (min)	Additional treatment	Reference
AT1	1% HF/30% HNO_3	RT	60	-	Orsini et al.[16]
AT2	12% HF	RT	2	-	Cho and Park et al.[17]
	70% HCl/H_2SO_4	80	5	-	
AT3	70% HCl/60% H_2SO_4	60	60	-	Carvalho et al.[18]
AT4	0.11 mol/L HF + 0.09 mol/L HNO_3	RT	10	dried in an oven at 50 °C for 24h	Yang et al.[19]
	5.80 mol/L HCl + 8.96 mol/L H_2SO_4	80	30	dried in an oven at 50 °C for 24h	
AT5	48% H_2SO_4	60	60	firing in vacuum at 600°C for 10min	Iwaya et al.[20]

these parameters were obtained from 15 satisfactory scans of each group (5 from each of the 3 samples), from random sites on the surface.

The surface chemical composition was analyzed by energy dispersive x-ray spectroscopy (EDS - JEOL, model JXA-8900RJ, Tokyo, Japan). A significant area at the center of each sample was chosen, without incorporating chemical analysis of the sample holder. All the analyses were made with a magnification of 200×. The elemental chemical composition was determined by the mean value and standard deviation from the 3 samples of each group.

Moreover, grazing incidence X-ray diffraction (GIXRD) measurements were carried out in a Ultima IV X-ray diffractometer (Rigaku, Tokyo, Japan), using Cu-Kα_1 radiation at 30 kV and tube current of 20 mA, without any filter or monochromator, in the angle range of 10°-90° (2θ) with a grazing incidence of 3°, making the diffraction sensitive to the surface. The step of measurement was set to 0.05° with a scan rate of 0.5° per minute. The divergence slit was set to 1 mm, with a Div H.L. Slit of 2 mm. The results were analyzed in Search-Match software (Crystallographica, Oxford, United Kingdom). GIXRD experiments were carried out in order to distinguish chemical compounds at the sample surface, mainly aluminum and titanium compounds.

3. Results

3.1. *SEM analysis*

Figures 1a to 1f revealed characteristic differences at the microscopic level according to the surface modification methods, as measured by SEM. The control group samples were mainly characterized with facets produced by blasting, with some smooth areas and other very rough areas (Figure 1a). Differences of the pits and facets were obvious between the implants due to differences of the etching processes. Incorporated particles were clearly observed in SEM analyses in the control samples and in the AT5 samples (white little clusters throughout the surface – Figures 1a and 1f). Samples submitted to acid etching classified as number 1 (AT1) showed the presence of shallow pits (Figure 1b). AT2 samples showed a surface with many pits, with large variation in the diameter of the pits (Figure 1c). AT3 samples showed a surface with a great number of pits (Figure 1d). AT4 samples showed a smoothening of the facets on the surface (Figure 1e) when compared with the control group samples, which suggests that the acid etching was not effective to change surface morphology. AT5 showed the presence of similar irregularities, as the facets present in control group, but now with the creation of small pits throughout the surface (Figure 1f).

3.2. *AFM analysis*

The qualitative and quantitative surface topography demonstrated different degrees of roughness. Table 2 presents the mean values of tridimensional roughness parameters for the control group and acid-etched samples (groups AT1 to AT5), as determined by AFM. It can be observed that the surface of the samples from group AT1 showed smaller values of the amplitude roughness parameters than the control group, whereas the samples from AT2, AT3, and AT4 groups showed higher values. AT5 showed closest values of S_a, S_q, and S_z as compared to the control group.

3.3. *EDS analysis*

EDS analysis of the surfaces showed titanium and oxygen to be the most common elements in all groups, followed by aluminum (Table 3). The presence of oxygen showed a modest variation in atomic concentration (%at) between the groups (about 40%). There was a higher variation in concentration between the samples with the elements titanium and aluminum. Groups control and AT5 showed a smaller %at of titanium (Figure 2a). Aluminum was found in higher concentrations in groups control, AT3, and AT5, with values ranging 6.5-7.5% in these groups (Figure 2b). It was not found in group AT2, and showed low concentration in groups AT1 and AT4 (0.3% and 1.4%, respectively). Sulfur was only detected in groups AT3 and AT4, at low concentrations (about 1%).

3.4. *XRD analysis*

Figure 3 presents a typical GIXRD diffractogram for a sample from the control group, where diffraction peaks were labeled according to Miller indices, as described elsewhere[21]. The diffractogram analysis confirmed the presence of titanium (Ti) and aluminum oxide (Al_2O_3). The GIXRD results obtained for the samples from groups submitted to acid etching showed the presence of Ti in group AT1 (Figure 4a), Ti and titanium hydride (TiH_2) in group AT2 (Figure 4b), Ti, Al_2O_3, and TiH_2 in group AT3 (Figure 4c), Ti and TiH_2 in group AT4 (Figure 4d), and Ti, Al_2O_3, TiH_2, and rutile (TiO_2) in group AT5 (Figure 4e).

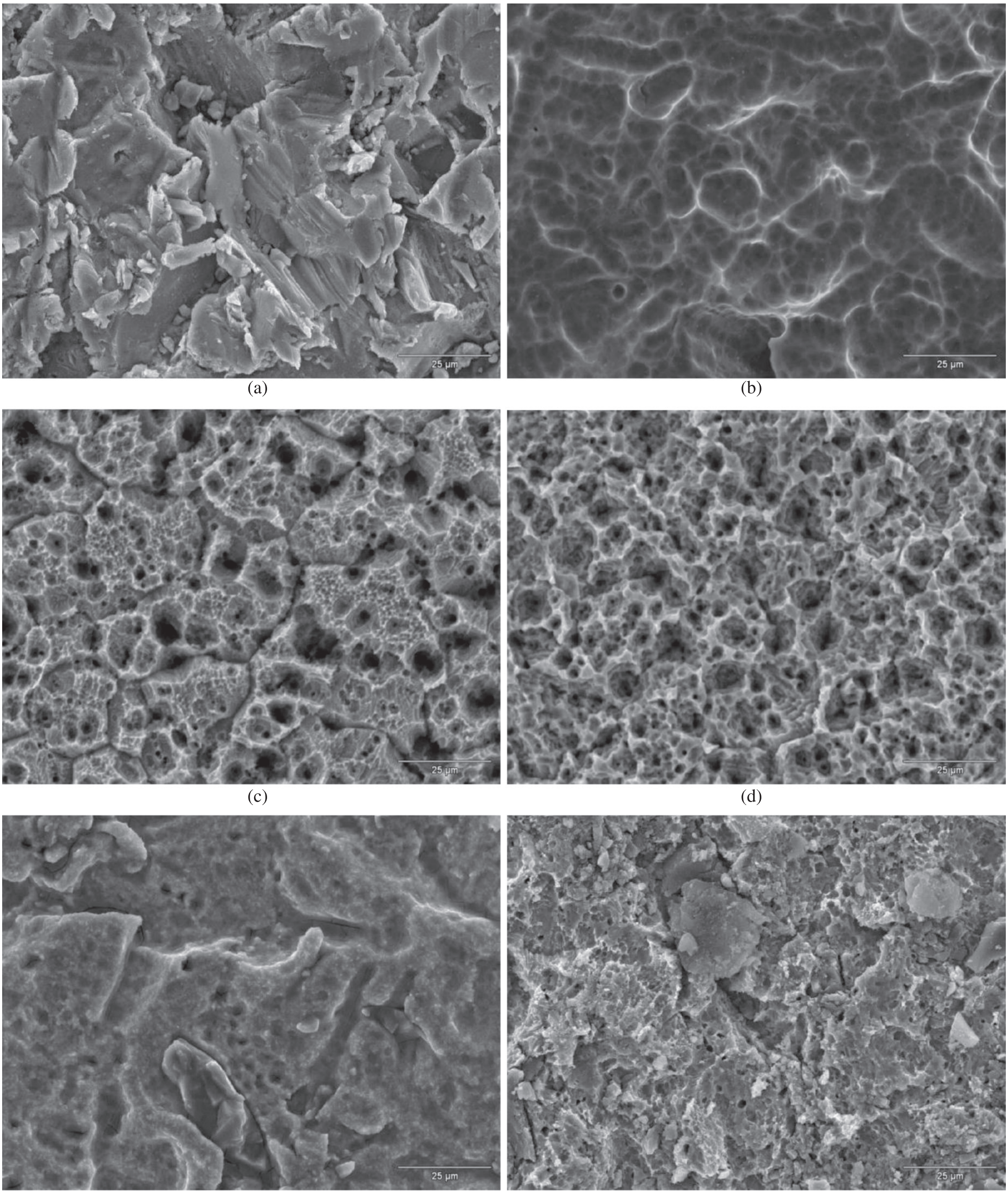
4. Discussion

Surface contamination of the alloys is a recognized problem[22] and must be avoided in order to retain the surface characteristics of the metal as well as to prevent additional metallic ion release into the host tissues. This is particularly essential in metals/alloys intended for surgical implantation, i.e. endosseous dental implants, where potentially both local and distant toxic effects may occur.

Populations of macrophages have been shown to undergo increased metabolic activity lasting up to 90 days in the case of rough-surface implants, by which time smooth-surface implants were quiescent and encapsulated by fibrous tissue. Therefore, whatever the nature of the contaminant, its effects on the implant surface characteristics, and the consequent reaction at the implant-tissue interface, need to be recognized as one possible factor in clinical failure[23].

One possible contaminant of great concern is the residues of Al_2O_3 from the sandblasting process. Al Jabbari et al.[24] has recently demonstrated that alumina fragments embedded on the alloy surface resist steam jet cleaning, suggesting that the fragments are very firmly retained. A similar conclusion was reached from previous findings that Al content after sandblasting with Al_2O_3 did not decrease significantly after hot steam cleaning[25]. Acid etching seems to be the only method of removing or significantly reducing the presence of residues of Al_2O_3 on the surface of a metal/alloy after sandblasting with Al_2O_3. The results of the present study suggests the same, since the samples were ultrasonically cleaned for 90 minutes in three different ways (acetone, ethyl alcohol, and deionized water), and even after this procedure, the samples of the control group showed a considerable presence of Al_2O_3 in the surface, as observed in the GIXRD diffractogram (Figure 3). Thus, the particles are somehow incorporated into the titanium surface. However, it can also be suggested that the Al_2O_3 particles were fragmented after collision with the titanium surface, since no whole Al_2O_3 particle (250 µm diameter) were observed in any of the SEM images from the samples of the control group.

Nonetheless, the acid etching may affect the surface roughness and morphology, but not always in a negative way. As already mentioned, etched surfaces have been



(a) (b) (c) (d) (e) (f)

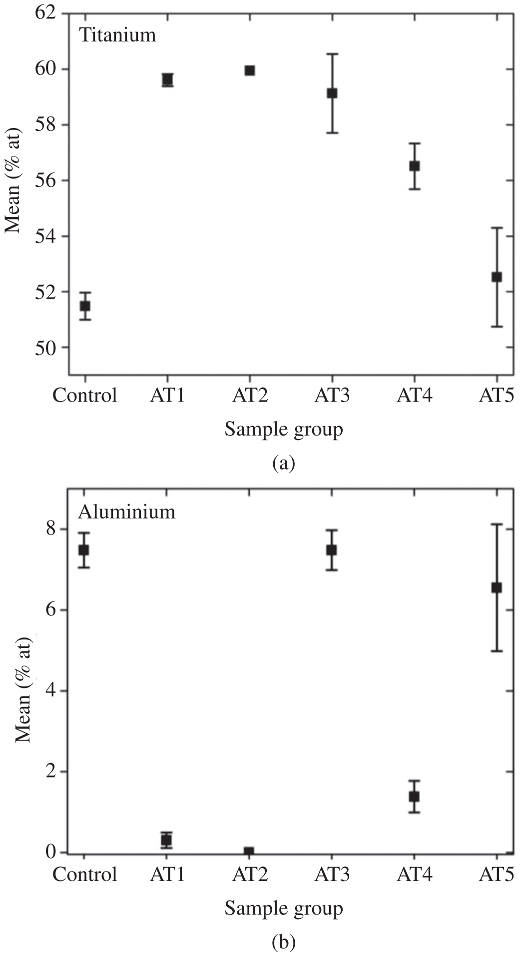
Figure 1. SEM pictures of groups control (a), AT1 (b), AT2 (c), AT3 (d), AT4 (e), and AT5 (f) (original magnification 1000× – scale bar 25 µm).

Table 2. Mean values (±SD) of tridimensional roughness parameters as determined by AFM (scanning area of 50 × 50 μm^2).

Group	S_y (μm)	S_z (μm)	Average-mean height (μm)	S_a (μm)	S_q (μm)	S_{sk}	S_{ku}
Control	4.53 ± 0.81	2.58 ± 0.49	2.35 ± 0.46	0.53 ± 0.15	0.68 ± 0.18	0.17 ± 0.25	0.52 ± 1.00
AT1	4.31 ± 1.09	2.20 ± 0.68	2.11 ± 0.71	0.38 ± 0.11	0.51 ± 0.13	–0.11 ± 0.53	1.51 ± 1.42
AT2	6.39 ± 0.74	3.18 ± 0.36	3.29 ± 0.36	0.82 ± 0.18	1.01 ± 0.21	–0.16 ± 0.19	–0.19 ± 0.26
AT3	6.49 ± 0.68	3.24 ± 0.34	3.24 ± 0.39	0.79 ± 0.10	0.98 ± 0.12	0.05 ± 0.20	–0.10 ± 0.43
AT4	6.02 ± 0.76	2.99 ± 0.38	3.08 ± 0.43	0.70 ± 0.15	0.88 ± 0.17	–0.15 ± 0.19	0.19 ± 0.52
AT5	5.48 ± 1.21	2.72 ± 0.60	2.71 ± 0.69	0.56 ± 0.21	0.71 ± 0.26	–0.07 ± 0.27	0.66 ± 1.06

Table 3. Atomic concentration (%at) of elements according to the sample groups, as determined by EDS analysis (mean values from 3 samples).

Group	Ti	O	Al	S
Control	51.5	41.0	7.5	-
AT1	59.6	40.1	0.3	-
AT2	60.0	40.0	-	1.0
AT3	59.1	40.6	7.5	1.2
AT4	56.5	40.8	1.4	-
AT5	52.5	40.9	6.5	-



(a)

(b)

Figure 2. Graphic presentation of atomic concentration of titanium (a) and aluminium (b) in the sample groups, as determined by EDS analysis.

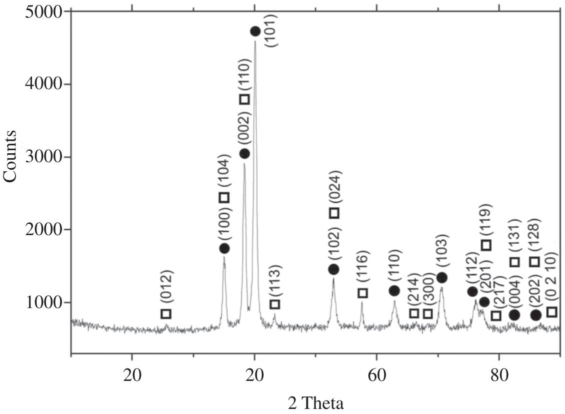


Figure 3. Typical GIXRD diffractogram for the control group sample, showing peak identification (Miller indices). Ti (circle), Al_2O_3 (square).

documented to improve bone apposition[11]. In the groups AT2 and AT3, SEM images showed that the etching has created micropits over the surface macrorugosities obtained by sandblasting, as compared to the control group, which is also reflected in higher values of the amplitude roughness parameters for these samples. However, specific to dental implants, studies have shown that histologic and biomechanical characteristics were improved due to increases in the as-machined surface texture by varied methods resulting in average implant surface roughness (S_a) ranging from 0.5 to 2 μm[26,27]. Thus, the values found in the present study for the roughness parameter S_a in all studied groups except AT1 seem to be appropriate (0.56-0.82 μm, see Table 2).

Another observation concerning the surface roughness is that the observed values of the dimensional amplitude roughness parameters (S_y, S_z, average, S_a, S_q) were higher than the control sample, agreeing with An et al.[23]. On the other hand, Bathomarco et al.[29] have observed the opposite, i.e. that the chemical etching lead to a decrease in the surface roughness. This divergence may result from differences in the conditions of blasting procedure. While the present study used Al_2O_3 particles with 250 μm in diameter with a blast pressure of 4 bar, the other study[29] used titanium oxide (TiO_2) particles with 50 μm in diameter with a blast pressure of 3 bar.

Buser et al.[4] compared machined, dual-etched and titanium plasma-sprayed (TPS) implants with sandblasted + etched surfaces (as performed in the present study) in a pig model. The R_a for the machined, etched and TPS surfaces was 0.15, 1.3 and 3.1 µm, respectively, and 2 µm for the blasted + etched surface. The removal torque was significantly higher for the blasted + etched implants. The results can be interpreted in a way that optimal roughness also exists for blasted + etched surfaces or that the additional micropits added to the surface may be more important than a further increase of the height deviation[10]. Similar findings were found in a rat model by Abron et al.[30] and by Marinho et al.[31]. They have found the strongest bone response with blasted + etched implants in comparison with machined surfaces.

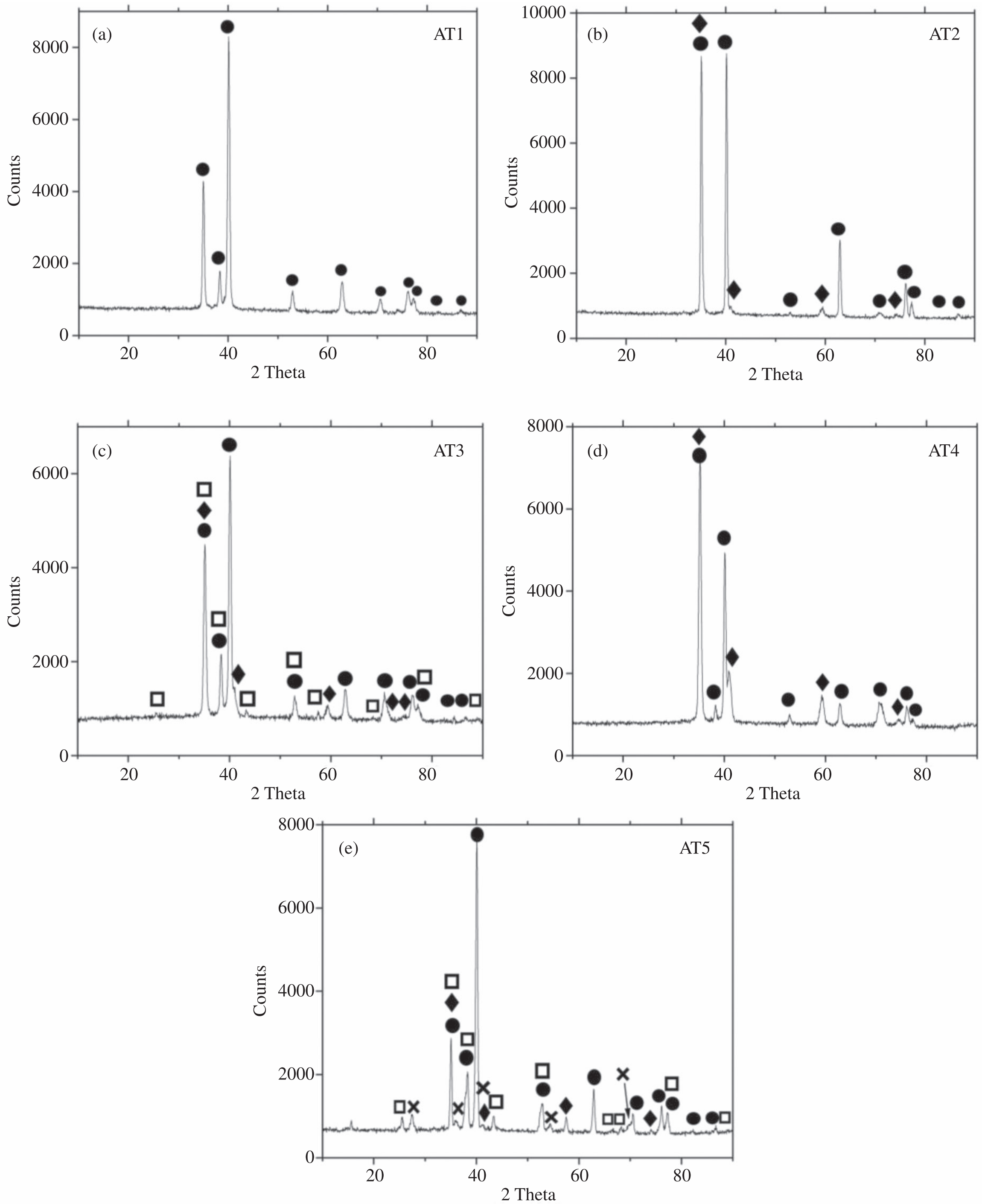


Figure 4. Typical GIXRD diffractograms of samples from groups AT1 to AT5 (a to e, respectively). Peak identification according to crystal structures: Ti (circle), TiH_2 (diamond), Al_2O_3 (square), rutile (X).

It has been reported that the etching process modifies the Ti surface composition of SLA-treated implants, and XRD and metallographic microscopy analysis indicated the presence of 20 to 40% of titanium hydride (TiH_x, $x \leq 2$) in addition to Ti[32]. Before attacking the metallic titanium, the acids must first dissolve the protective titanium oxide layer. During the course of the corrosion process of titanium, native hydrogen ions (H^+) are released[33]. These small ions diffuse rapidly into the metal because the latter is left without its dense protective oxide layer. Therefore, the sub-surface is enriched with hydrogen[34]. When hydrogen saturation is reached, titanium hydride is formed. Titanium hydride may be biologically important because a hydride layer is much better suited as a template for binding biomolecules chemically onto a titanium surface[35]. In the present study, as the surface of the samples were also modified by acid etching after sandblasting, it was not surprising that titanium hydride was found in almost all test groups (from AT2 to AT5), as demonstrated by GIXRD analysis. As the AT1 samples did now show the presence of titanium hydride on the surface, it can not be suggested that the acid-etching classified here as AT1 is weak. Two observations favor this opinion. First, AT1 was able to remove almost all content of Al from the surface. Second, according to the observations of Szmukler-Moncler et al.[36], for cp Ti, the absorbed hydrogen could not be related to the vigor of the etching bath.

EDS analysis of the surfaces showed titanium and oxygen to be the most common elements in all groups, most probable due to the natural formation of a passivating titanium oxide layer (mainly TiO_2) just after sample surface preparation. It was previously observed, by using XPS analysis, that dental implants surfaces treated only by sandblasting and acid etching consists of oxidized titanium[37]. TiO_2 can exist in three crystalline forms named anatase, rutile, and brookite, all with different physical properties. The quasi-amorphous oxides can be crystallized by heating to temperatures of 400-500 °C, which leads to transformation to more crystallized phases[38]. Thus, the presence of rutile phase in group AT5 can be explained by the thermal treatment by which the samples of this group were subjected (firing in vacuum at 600 °C for 10 minutes).

As the substrate, Ti was detected in all samples (control and test groups). The GIXRD diffractograms also showed the presence of Al_2O_3 in groups AT3 and AT5, demonstrating a similarity with the results of EDS, which also showed a greater presence of Al in the same test groups. As the chemical analysis performed by EDS does not distinguish compounds, the results suggest that the aluminum signal comes from alumina.

Sulfur in the samples of groups AT3 and AT4 can be the originated from the H_2SO_4 used in the acid etching process. As this acid was also used to etch samples from groups AT2 and AT5 and were not detected by the EDS analysis, it can be suggested that whether the EDS technique was not sufficiently sensitive as to detect low concentrations of sulfur in these groups or differences in the acid etching processes of each group may have influenced the absence of this element in the samples of groups AT2 and AT5, because acid mixture, bath temperature, and etching time may affect the chemistry of the surfaces[5].

Considering that the observed roughness parameter values, morphology, and atomic concentration of Al for the samples from group AT5 are similar to the control group, it can be suggested that the AT5 was not effective in changing the roughness and the chemical composition of the titanium disc surfaces when compared to samples only sandblasted (control group), except that the heat treatment has led to a higher crystallinity of TiO_2 on the surface in the form of rutile phase.

It was stated that the sandblasting particles used during the roughening step are not completely removed from the implant surface during the etching process[9]. Therefore sharp-edged alumina particles are left and could potentially be released during implant insertion. This raises questions regarding the added value of sandblasting prior to etching on the anchorage of etched implants[5]. However, it was demonstrated in the present study that some acid etchings can completely (or almost completely) remove the aluminum from a titanium surface previously sandblasted with Al_2O_3.

5. Conclusions

The present study demonstrated that the acid etchings here named as AT1, AT2, and AT4 are efficient in removing residues of Al_2O_3 from the previously sandblasted surface. This is suggested based on the surface sensitive analyses presented here (SEM, EDS, GIXRD, and AFM). Moreover, it can also be suggested that there is no incorporation of the whole Al_2O_3 particle into the titanium surface after the collision (for the blasting parameters used, 4 bar and 250 µm average particle diameter), conversely a particle fragmentation occurs and what remains on the titanium surface are Al_2O_3 residues. Last but not least, since the present study has used discs as the substrate material, the observed results can not be directly extrapolated to complex surfaces like those in cylindrical threaded titanium implants.

Acknowledgements

This work was supported by the Brazilian agencies CNPq and FAPEMIG. The authors would like to thank Eduardo Antônio de Carvalho (CDTN/CNEN), Rolf Ankli (Dental Atelier Rolf Ankli Art & Experience), and Sai Sunil Kumar.

References

1. Berglundh T, Abrahamsson I and Lindhe J. Bone reactions to longstanding functional load at implants: An experimental study in dogs. *Journal of Clinical Periodontology*. 2005; 32(9):925-932. PMid:16104954. http://dx.doi.org/10.1111/j.1600-051X.2005.00747.x
2. Pilliar RM, Deporter DA, Watson PA and Valiquette N. Dental implant design: Effect on bone remodeling. *Journal of Biomedical Materials Research*. 1991; 25(4):467-483. PMid:2050711. http://dx.doi.org/10.1002/jbm.820250405
3. Klokkevold PR, Nishimura RD, Adachi M and Caputo A. Osseointegration enhanced by chemical etching of the titanium surface: A torque removal study in the rabbit. *Clinical Oral Implants Research*. 1997; 8(6):442-447. PMid:9555202. http://dx.doi.org/10.1034/j.1600-0501.1997.080601.x
4. Buser D, Nydegger T, Oxland T, Cochran D, Schenk RK, Hirt HP et al. Interface shear strength of titanium implants with a

sandblasted and acid-etched surface: a biomechanical study in the maxilla of miniature pigs. *Journal of Biomedical Materials Research*. 1999; 45(2):75-83. http://dx.doi.org/10.1002/(SICI)1097-4636(199905)45:2<75::AID-JBM1>3.0.CO;2-P

5. Szmukler-Moncler S, Perrin D, Ahossi V, Magnin G and Bernard JP. Biological properties of acid etched titanium implants: effect of sandblasting on bone anchorage. *Journal of Biomedical Materials Research Part B*: Applied Biomaterials. 2004; 68(2):149-159. PMid:14737762. http://dx.doi.org/10.1002/jbm.b.20003
6. Fu J, Hu Y, Guo Z, Zhang Y, Hao Y and Li S. Effect of surface micro-topography of titanium material on the behaviors of rabbit osteoblast in vitro. *Applied Surface Science* 2008; 255(2):286-289. http://dx.doi.org/10.1016/j.apsusc.2008.06.064
7. Gotfredsen K, Berglundh T and Lindhe J. Anchorage of titanium implants with different surface characteristics: An experimental study in rabbits. *Clinical Implants Dentistry and Related Research*. 2000; 2(3):120-128. http://dx.doi.org/10.1111/j.1708-8208.2000.tb00002.x
8. Bernard JP, Szmukler-Moncler S, Pessotto S, Belser U and Samson J. Histological and SEM analysis of reverse-torqued Branemark and ITI implants in the canine mandible and maxilla. In: *Proceedings of the 10th Annual Meeting of the Academy of Osseointegration*; 2002; Dallas. Dallas; 2002.
9. Szmukler-Moncler S, Testori T and Bernard JP. Etched implants: A comparative surface analysis of 4 dental implant systems. *Journal of Biomedical Materials Research Part B*: Applied Biomaterials. 2004; 69(1):46-57. PMid:15015209. http://dx.doi.org/10.1002/jbm.b.20021
10. Wennerberg A and Albrektsson T. Effects of titanium surface topography on bone integration: a systematic review. *Clinical Oral Implants Research*. 2009; 20(Suppl 4):172-184. PMid:19663964. http://dx.doi.org/10.1111/j.1600-0501.2009.01775.x
11. Lazzara RJ, Testori T, Trisi P, Porter SS and Weinstein RL. A human histologic analysis of Osseotite and machined surfaces using implants with 2 opposing surfaces. *International Journal of Periodontology and Restorative Dentistry*. 1999; 19(2):3-16.
12. Baker DA, London RM and O'Neil RB. Rate of pull-out strength gain of dual-etched titanium implants: A comparative study in rabbits. *International Journal of Oral Maxillofacial Implants*. 1998; 14(5):722-728.
13. Piattelli A, Degidi M, Paolantonio M, Mangano C and Scarano A. Residual aluminum oxide on the surface of titanium implants has no effect on osseointegration. *Biomaterials*. 2003; 24(22):4081-4089. http://dx.doi.org/10.1016/S0142-9612(03)00300-4
14. Canabarro A, Diniz MG, Paciornik S, Carvalho L, Sampaio EM, Beloti MM et al. High concentration of residual aluminum oxide on titanium surface inhibits extracellular matrix mineralization. *Journal of Biomedical Materials Research A*. 2008; 87(3):588-597. PMid:18186053. http://dx.doi.org/10.1002/jbm.a.31810
15. Darvell BW, Samman N, Luk WK, Clark RK and Tideman H. Contamination of titanium castings by aluminum oxide blasting. *Journal of Dentistry*. 1995; 23(5):319-322. http://dx.doi.org/10.1016/0300-5712(94)00003-X
16. Orsini G, Assenza B, Scarano A, Piattelli M and Piattelli A. Surface analysis of machined versus sandblasted and acid-etched titanium implants. *International Journal of Oral and Maxillofacial Implants*. 2000; 15(6):779-784. PMid:11151575.
17. Cho SA and Park KT. The removal torque of titanium screw inserted in rabbit tibia treated by dual acid etching. *Biomaterials*. 2003; 24(20):3611-3617. http://dx.doi.org/10.1016/S0142-9612(03)00218-7
18. Carvalho DR, Carvalho PS, Magro Filho O, De Mello JD, Beloti MM and Rosa AL. Characterization and in vitro cytocompatibility of an acid-etched titanium surface. *Brazilian Dental Journal*. 2010; 21(1):3-11. PMid:20464314. http://dx.doi.org/10.1590/S0103-64402010000100001
19. Yang GL, He FM, Yang XF, Wang XX and Zhao SF. Bone responses to titanium implants surface-roughened by sandblasted and double etched treatments in a rabbit model. *Oral Surgery Oral Medicine Oral Pathology Oral Radiology and Endodontics*. 2008; 106(4):516-524. PMid:18602288. http://dx.doi.org/10.1016/j.tripleo.2008.03.017
20. Iwaya Y, Machigashira M, Kanbara K, Miyamoto M, Noguchi K, Izumi Y et al. Surface properties and biocompatibility of acid-etched titanium. *Dental Materials Journal*. 2008; 27(3):415-421. PMid:18717170. http://dx.doi.org/10.4012/dmj.27.415
21. Chrcanovic BR, Pedrosa AR and Martins MD. Chemical and topographic analysis of treated surfaces of five different commercial dental titanium implants. *Materials Research*. 2012; 15(3):372-382. http://dx.doi.org/10.1590/S1516-14392012005000035
22. Hruska AR and Borelli P. Quality criteria for pure titanium casting, laboratory soldering, intraoral welding, and a device to aid in making uncontaminated castings. *Journal of Prosthetic Dentistry*. 1991; 66(4):561-565. http://dx.doi.org/10.1016/0022-3913(91)90524-Z
23. Salthouse JN and Matlaga BF. Effects of implant surface on cellular activity and evaluation of histocompatibility. In: Winter GD, Leray JI and De Groot K, editors. *Evaluation of biomaterials*. London: Wiley; 1980.
24. Al Jabbari YS, Zinelis S and Eliades G. Effect of sandblasting conditions on alumina retention in representative dental alloys. *Dental Materials Journal*. 2012; 31(2):249-255. http://dx.doi.org/10.4012/dmj.2011-210
25. Wang CS, Chen KK, Tajima K, Nagamatsu Y, Kakigawa H and Kozono Y. Effects of sandblasting media and steam cleaning on bond strength of titanium-porcelain. *Dental Materials Journal*. 2010; 29(4):381-391. PMid:20668358. http://dx.doi.org/10.4012/dmj.2009-119
26. Albrektsson T and Wennerberg A. Oral implant surfaces: Part 1 - Review focusing on topographic and chemical properties of different surfaces and in vivo responses to them. *International Journal of Prosthodontics*. 2004; 17(5):536-543. PMid:15543910.
27. Buser D, Broggini N, Wieland M, Schenk RK, Denzer AJ, Cochran DL et al. Enhanced bone apposition to a chemically modified SLA titanium surface. *Journal of Dental Research*. 2004; 83(7):529-533. PMid:15218041. http://dx.doi.org/10.1177/154405910408300704
28. An S-H, Matsumoto T, Miyajima H, Sasaki J-I, Narayanan R and Kim K-H. Surface characterization of alkali- and heat-treated Ti with or without prior acid etching. *Applied Surface Science*. 2012; 258(10):4377-4382. http://dx.doi.org/10.1016/j.apsusc.2011.12.119
29. Bathomarco RV, Solorzano G, Elias CN and Prioli R. Atomic force microscopy analysis of different surface treatments of Ti dental implant surfaces. *Applied Surface Science*. 2004; 233(1-4):29-34. http://dx.doi.org/10.1016/j.apsusc.2004.04.007
30. Abron A, Hopfensperger M, Thompson J and Cooper LF. Evaluation of a predictive model for implant surface topography effects on early osseointegration in the rat tibia model. *Journal*

of Prosthetic Dentistry. 2001; 85(1):40-46. PMid:11174677. http://dx.doi.org/10.1067/mpr.2001.112415

31. Marinho V, Celletti R, Bracchetti G, Petrone G, Minkin C and Piattelli A. Sandblasted and acid-etched dental implants: a histologic study in rats. *International Journal of Oral Maxillofacial Implants*. 2003; 18(1):75-81. PMid:12608672.
32. Perrin D, Szmukler-Moncler S, Echikou C, Pointaire P and Bernard JP. Bone response to alteration of surface topography and surface composition of sandblasted and acid etched (SLA) implants. *Clinical Oral Implants Research*. 2002; 13(5):465-469. PMid:12453122. http://dx.doi.org/10.1034/j.1600-0501.2002.130504.x
33. Donachie Junior MJ. *Titanium*: A Technical Guide. 2nd ed. Materials Park: ASM International; 2000. p. 85-94.
34. Aronsson BO, Hjörvarsson B, Frauchiger L, Taborelli M, Vallotton PH and Descouts P. Hydrogen desorption from sandblasted and acid-etched titanium surfaces after glow-discharge treatment. *Journal of Biomedical Materials Research*. 2001; 54(1):20-29. http://dx.doi.org/10.1002/1097-4636(200101)54:1<20::AID-JBM3>3.0.CO;2-Z
35. Videm K, Lamolle S, Monjo M, Ellingsen JE, Lyngstadaas SP and Haugen HJ. Hydride formation on titanium surfaces by cathodic polarization. *Applied Surface Science*. 2008; 255(5):3011-3015. http://dx.doi.org/10.1016/j.apsusc.2008.08.090
36. Szmukler-Moncler S, Bischof M, Nedir R and Ermrich M. Titanium hydride and hydrogen concentration in acid-etched commercially pure titanium and titanium alloy implants: a comparative analysis of five implant systems. *Clinical Oral Implants Research*. 2010; 21(9):944-950. PMid:20465551.
37. Castilho GAA, Martins MD and Macedo WAA. Surface characterization of titanium based dental implants. *Brazilian Journal of Physics*. 2006; 36(3b):1004-1008. http://dx.doi.org/10.1590/S0103-97332006000600055
38. Nam SH, Choi JW, Cho SJ, Kimt KS and Boo JH. Growth of TiO_2 anti-reflection layer on textured Si (100) wafer substrate by metal-organic chemical vapor deposition method. *Journal of Nanoscience and Nanotechnology*. 2011; 11(8):7315-7318. PMid:22103185. http://dx.doi.org/10.1166/jnn.2011.4813