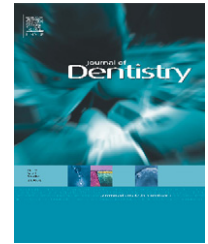


Available online at [www.sciencedirect.com](http://www.sciencedirect.com)

SciVerse ScienceDirect

journal homepage: [www.intl.elsevierhealth.com/journals/jden](http://www.intl.elsevierhealth.com/journals/jden)

## Titanium surface topography after brushing with fluoride and fluoride-free toothpaste simulating 10 years of use

Laiza M.G. Fais<sup>a</sup>, Romeu B. Fernandes-Filho<sup>a</sup>, Marcelo A. Pereira-da-Silva<sup>b</sup>,  
Luis G. Vaz<sup>a</sup>, Gelson L. Adabo<sup>a,\*</sup>

<sup>a</sup> Araraquara Dental School, UNESP-Univ Estadual Paulista, Department of Dental Materials and Prosthodontics, Rua Humaitá, 1680, Araraquara, São Paulo 14801-903, Brazil

<sup>b</sup> University of São Paulo, Department of Physics and Material Science, Av. Trabalhador São-carlense, 400, São Carlos, São Paulo 13566-590, Brazil

### ARTICLE INFO

#### Article history:

Received 14 April 2011

Received in revised form

15 December 2011

Accepted 3 January 2012

#### Keywords:

Titanium

Sodium fluoride

Toothbrushing

Surface properties

Microscopy atomic force

Corrosion

### ABSTRACT

**Objectives:** To conduct a controlled study contrasting titanium surface topography after procedures that simulated 10 years of brushing using toothpastes with or without fluoride.

**Methods:** Commercially pure titanium (cp Ti) and Ti-6Al-4V disks (6 mm Ø × 4 mm) were mirror-polished and treated according to 6 groups ( $n = 6$ ) as a function of immersion (I) or brushing (B) using deionised water (W), fluoride-free toothpaste (T) and fluoride toothpaste (FT). Surface topography was evaluated at baseline (pretreatment) and post-treatment, using atomic force microscope in order to obtain three-dimensional images and mean roughness. Specimens submitted to immersion were submerged in the vehicles without brushing. For brushed specimens, procedures were conducted using a linear brushing machine with a soft-bristled toothbrush. Immersion and brushing were performed for 244 h. IFT and BFT samples were analysed under scanning electron microscope with Energy-Dispersive X-ray Spectroscopy (EDS). Pre and post-treatment values were compared using the paired Student *T*-test ( $\alpha = .05$ ). Intergroup comparisons were conducted using one-way ANOVA with Tukey post-test ( $\alpha = .05$ ).

**Results:** cp Ti mean roughness (in nanometers) comparing pre and post-treatment were: IW,  $2.29 \pm 0.55/2.33 \pm 0.17$ ; IT,  $2.24 \pm 0.46/2.02 \pm 0.38$ ; IFT,  $2.22 \pm 0.53/1.95 \pm 0.36$ ; BW,  $2.22 \pm 0.42/3.76 \pm 0.45$ ; BT,  $2.27 \pm 0.55/16.05 \pm 3.25$ ; BFT,  $2.27 \pm 0.51/22.39 \pm 5.07$ . Mean roughness (in nanometers) measured in Ti-6Al-4V disks (pre/post-treatment) were: IW,  $1.79 \pm 0.25/2.01 \pm 0.25$ ; IT,  $1.61 \pm 0.13/1.74 \pm 0.19$ ; IFT,  $1.92 \pm 0.39/2.29 \pm 0.51$ ; BW,  $2.00 \pm 0.71/2.05 \pm 0.43$ ; BT,  $2.37 \pm 0.86/11.17 \pm 2.29$ ; BFT,  $1.83 \pm 0.50/15.73 \pm 1.78$ . No significant differences were seen after immersions ( $p > .05$ ). Brushing increased the roughness of cp Ti and of Ti-6Al-4V ( $p < .01$ ); cp Ti had topographic changes after BW, BT and BFT treatments whilst Ti-6Al-4V was significantly different only after BT and BFT. EDS has not detected fluoride or sodium ions on metal surfaces.

**Conclusions:** Exposure to toothpastes (immersion) does not affect titanium *per se*; their use during brushing affects titanium topography and roughness. The associated effects of toothpaste abrasives and fluorides seem to increase roughness on titanium brushed surfaces.

© 2012 Elsevier Ltd. All rights reserved.

\* Corresponding author. Tel.: +55 16 236 8395; fax: +55 16 3301 6406.

E-mail address: [adabo@foar.unesp.br](mailto:adabo@foar.unesp.br) (G.L. Adabo).

0300-5712/\$ – see front matter © 2012 Elsevier Ltd. All rights reserved.

doi:10.1016/j.jdent.2012.01.001

### 1. Introduction

The use of titanium, and titanium based alloys, has significantly increased in dentistry with the broader use of osseointegrated implants. Dentists have indeed been encouraged to use these metals in implanted supported structures, crowns, fixed and removable partial dentures,<sup>1,2</sup> orthodontic wires and brackets,<sup>3</sup> based on their favourable properties, such as biocompatibility, low density, low thermal conductivity, sufficient strength to withstand high static and cyclic stresses of the masticatory system, low weight, low cost and good resistance to corrosion.<sup>4</sup>

Resistance to corrosion and biocompatibility are directly related to the passive oxide layer formed on titanium's surface and its alloys.<sup>4,5</sup> The exposure of titanium to air or to solutions leads to spontaneous surface passivation<sup>6,7</sup> and, within nanoseconds,<sup>1</sup> a 4-6 nm thickness film is typically developed,<sup>4</sup> mainly consisting of amorphous or low-crystalline TiO<sub>2</sub>. This film acts as a kinetic barrier against corrosion.<sup>7</sup>

The mere presence of the oxide layer does not maintain the stability, since its surface may not be fully protected in the very complex chemistry of the oral cavity. This layer may be mechanically or chemically removed or destroyed.<sup>4</sup> Whilst titanium shows high resistance to corrosion in artificial saliva,<sup>8,9</sup> 0.9% NaCl,<sup>9</sup> and physiological saline solution,<sup>9</sup> it has been suggested that fluoride ions from toothpastes, dental gels, and mouthrinses can cause deleterious effects on commercially pure titanium (cp Ti), Ti-6Al-4V and Ni-Ti.<sup>1,3,6,8-14</sup> These ions may decrease the polarisation resistance whilst increasing anodic current on the titanium oxide layer,<sup>11</sup> making its surface more prone to corrosion.<sup>9,10,3,15</sup> Associated

with metal ion release<sup>6</sup> these changes could affect chemical composition,<sup>1,6,12,16</sup> microstructure,<sup>8</sup> surface topography,<sup>1,12</sup> surface roughness<sup>1,11</sup> and mechanical properties.<sup>17</sup>

Most studies focused on the chemical effects of fluoride, by submerging titanium in fluoride solutions.<sup>1,3,6,8,12,16,18</sup> In real life, however, removable prosthesis, implanted supported structures, brackets and orthodontic wires must be daily cleaned by brushing. The effects of this procedure on the titanium surface are not conclusive,<sup>2,14,19-21</sup> with a single study focusing on the relationship between the chemical actions of fluoride and the mechanical actions of toothbrushing using toothpastes.<sup>14</sup>

Accordingly, it was conducted a controlled study contrasting titanium surface topography after procedures that simulated 10 years of brushing using toothpastes with or without fluoride. Furthermore, surfaces exposed to fluoride ions contact were analysed under scanning electron microscope (SEM) with Energy-Dispersive X-ray Spectroscopy (EDS), in order to test possible fluoride reactions with cp Ti and Ti-6Al-4V. The null hypothesis was that no significant difference would be found after (1) chemical action of the toothpaste compounds and toothpaste fluoride ions, as well after (2) of the toothbrush bristles, toothpaste abrasives, and toothpaste abrasives + fluoride ions.

### 2. Materials and methods

The study flow is summarised in Fig. 1. Seventy-two disks specimens (4 mm thick and 6 mm in diameter) were machined from rods of cp Ti Grade 2 (Ti, 99.76%; O, 0.16%; Fe, 0.06%; C, 0.01%; N, 0.001%; H, 0.002%) and Ti-6Al-4V (Ti, 89.78%; Al,

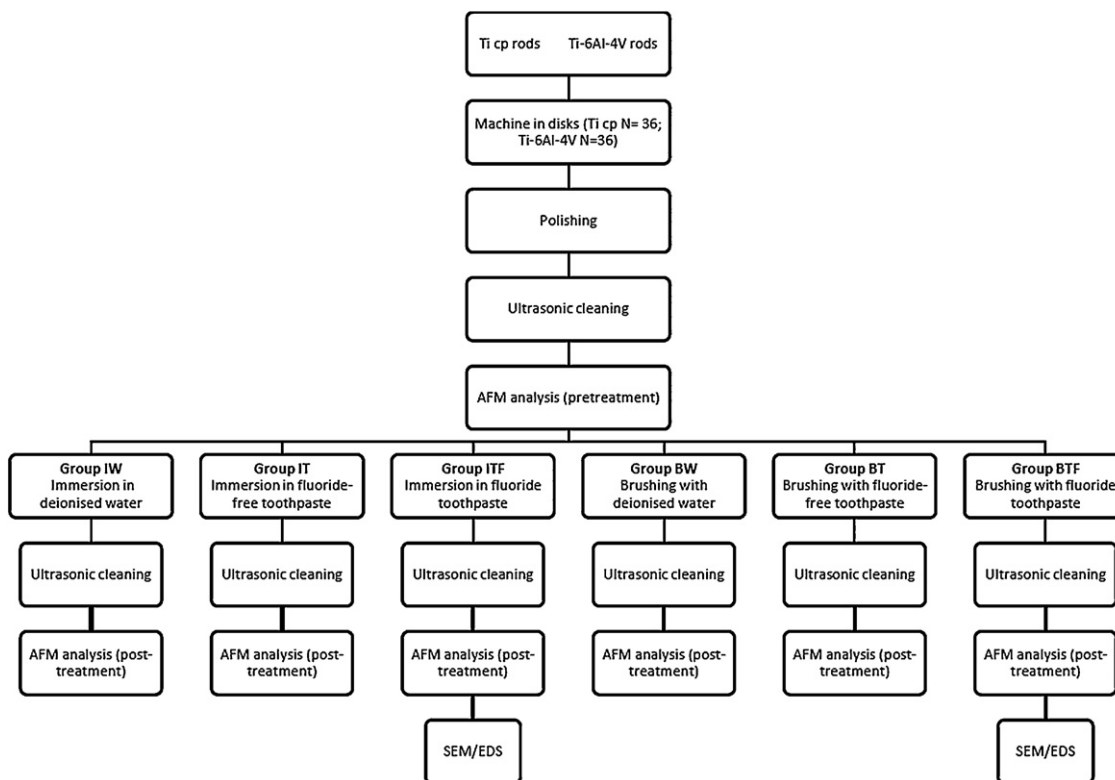


Fig. 1 – Flow chart of the study.

6.06%; V, 4.0%; O, 0.10%; Fe, 0.04%; C, 0.007%; N, 0.004%; H, 0.003%), both provide by Realum (Realum Ind. Com. de metais puros e ligas Ltda, São Paulo, SP, Brazil).

### 2.1. Specimen preparation

Specimens were mirror-polished using a polishing device (Arotec Ind. e Com. Ltd, Cotia, SP, Brazil). Procedures were conducted under running water, at 600 rpm and 0.5 kgf, using 320, 400, 600, 800, 1200, 1500 and 2000 grit SiC abrasive papers (Norton Abrasivos Brasil, São Paulo, SP, Brasil). Final polishing was performed with buffing cloth (Microcloth<sup>®</sup>, Buehler, Illinois, EUA) using 3  $\mu\text{m}$ , 1  $\mu\text{m}$  and 0.25  $\mu\text{m}$  diamond suspensions (Metadi Supreme, Buehler, Illinois, EUA), 0.06  $\mu\text{m}$  colloidal silica (Mastermet, Buehler, Illinois, EUA) and 0.05  $\mu\text{m}$  alumina suspension (Alfa Micropolish II, Buehler, Illinois, EUA). Disks of cp Ti ( $N = 36$ ) and Ti-6Al-4V ( $N = 36$ ) were ultrasonic cleaning (Thornton, Inpec Electronics, Vinhedo, SP, Brazil) in isopropyl alcohol (JTBaker, Xalostec, México) for 3 cycles of 30 min each. Specimens were randomly allocated to the 6 groups ( $n = 6$ ).

### 2.2. Toothpaste slurries

For the immersion and brushing tests, slurries were prepared with 1 part of toothpaste (grams) to 2 parts of deionised water (mL),<sup>2,21</sup> which were mixed immediately before use for 10 min, using a magnetic device.<sup>22</sup> Two types of toothpastes were prepared:

- (1) Fluoride free-toothpaste – 52.5% micronised  $\text{CaCO}_3$ , 25%  $\text{C}_3\text{H}_5(\text{OH})_3$ ; 18% ethyl hydroxyethyl cellulose; 2%  $\text{C}_{12}\text{H}_{25}\text{SO}_4\text{Na}$  and deionised water (qsp);<sup>23</sup> pH equal to 6.3.
- (2) Fluoride toothpaste – 52.5% micronised  $\text{CaCO}_3$ , 25%  $\text{C}_3\text{H}_5(\text{OH})_3$ ; 18% ethyl hydroxyethyl cellulose; 2%  $\text{C}_{12}\text{H}_{25}\text{SO}_4\text{Na}$ , NaF (1500 ppm) and deionised water (qsp);<sup>23</sup> pH equal to 6.3.

### 2.3. Immersion test

Specimens were statically submerged<sup>18</sup> in deionised water (Group IW), fluoride-free toothpaste slurry (Group IT) or in fluoride toothpaste slurry (Group IFT) for 244 h. This time is equivalent to 10 years of 2 min brushing per session, twice a day.<sup>2,21,24</sup> Vehicles (water or slurries) were changed every 12 h, when specimens were washed under running water for 30 s. At the end of the immersion tests, the disks were cleaned for 30 min in isopropyl alcohol (JTBaker, Xalostec, México) using ultrasound (Thornton, Inpec Electronics, Vinhedo, SP, Brazil).

### 2.4. Brushing test

Specimens were brushed by a mechanical device equipped with 6 soft bristle toothbrushes heads (Oral B, straight head #35; Gillette do Brazil, São Paulo, Brazil) with either deionised water (BW), fluoride-free toothpaste slurry (BT) or fluoride toothpaste slurry (BFT). The machine was set to brush at a rate of 60 reciprocal strokes per minute, and to provide a vertical load of 200 g<sup>25</sup> on the specimens. Deionised water (150 mL) or

toothpaste slurries (100 mL of deionised water + 50 g of toothpaste) were inserted into the slurry bath, remaining the specimens statically submerged during brushing.

Brushing lasted 244 h with automatic linear movements<sup>2,21,24</sup> (amplitude of 10 mm) of the toothbrushes heads. Toothbrushes and vehicles were changed every 22,080 strokes, or the equivalent of three months of use. At the end of brushing time, the disks were cleaned in isopropyl alcohol (JTBaker, Xalostec, México) using ultrasound (Thornton, Inpec Electronics, Vinhedo, SP, Brazil) for 30 min.

### 2.5. Characterisation of titanium surfaces

Atomic force microscopy (AFM) was used to evaluate the surface topography and surface roughness at baseline (pretreatment) and post-treatment (immersion or simulated brushing). AFM analysis was conducted in standard contact mode (Nanoscope IIIA<sup>™</sup>, Digital Instruments, Santa Barbara, USA). Images were analysed using Gwyddion 2.5 (Prague, Czech Republic) and 3D images were normalised in scale Z. Surface roughness was defined as the arithmetical average of the surface height relative to the mean height ( $R_a$ ). Three surfaces of 50  $\mu\text{m}^2$  were randomly chosen in each specimen. The mean values of  $R_a$  were calculated for each specimen.

For each metal, one specimen of IFT and BFT had its surface examined using a scanning electron microscope (SEM) (FEI Quanta 400 FEG ESEM, FEI Company, Hillsboro, Oregon, USA) equipped with an Energy-Dispersive X-ray Spectroscopy (EDS) (INCA 250 energy dispersive X-ray, Oxford Instruments, Concorde, New Hampshire, USA). All analyses were carried out at 20 kV, 137 eV resolution, and 90  $\mu\text{A}$  beam current. Discs were placed directly onto the stub and examined without any preparation or manipulation (i.e. the samples were neither coated nor dehydrated for the analysis).

### 2.6. Statistical analysis

Data were transformed using linear transformation.  $R_a$  measurements were analysed individually for cp Ti and Ti-6Al-4V, in three steps: (1) one-way ANOVA ( $\alpha = .05$ ) was used to compare the six pretreatment groups (baseline) in order to verify the polishing standardisation; (2) within groups (pre-treatment vs. post-treatment) analyses were conducted using the paired Student T-test ( $\alpha = .05$ ); (3) post-treatment comparisons were conducted using one-way ANOVA ( $\alpha = .05$ ) with Tukey post-test ( $\alpha = .05$ ), in order to identify differences amongst the experimental treatments.

## 3. Results

Mean  $R_a$  values with statistical results are displayed in Table 1 (cp Ti) and Table 2 (Ti-6Al-4V). No significant differences were found at baseline for roughness (cp Ti –  $p = 0.99$ ; Ti-6Al-4V –  $p = 0.40$ ), suggesting that groups had similar profiles at baseline.

Cp Ti roughness did not significantly differ after IW, IT and IFT relative to baseline (Table 1), although significant changes were seen for all groups after brushing (BW, BT, BFT). The immersion treatments also did not significantly change the

**Table 1 – Means and standard deviations of Ra (nm) obtained from atomic force microscopy analysis of cp Ti specimens.**

Groups	Pretreatment	Post-treatment
IW – Immersion in deionised water	2.29 (0.55) <sup>Aa</sup>	2.33 (0.17) <sup>Aa*</sup>
IT – Immersion in fluoride-free toothpaste	2.24 (0.46) <sup>Aa</sup>	2.02 (0.38) <sup>Aa†</sup>
IFT – Immersion in fluoride toothpaste	2.22 (0.53) <sup>Aa</sup>	1.95 (0.36) <sup>Aa‡</sup>
BW – Brushing with deionised water	2.22 (0.42) <sup>Aa</sup>	3.76 (0.45) <sup>Bb§</sup>
BT – Brushing fluoride-free toothpaste	2.27 (0.55) <sup>Aa</sup>	16.05 (3.25) <sup>Cb#</sup>
BFT – Brushing fluoride toothpaste	2.27 (0.51) <sup>Aa</sup>	22.39 (5.07) <sup>Db**</sup>

Different uppercase letters indicate significant differences in columns obtained by one-way ANOVA followed by HSD Tukey test.  
 Different lowercase letters indicate significant differences in rows obtained by Student T-test:  
 \*  $p = 0.66$  (pretreatment IW vs. post-treatment IW).  
 \*\*  $p < 0.0001$  (pretreatment BFT vs. post-treatment BFT).  
 †  $p = 0.16$  (pretreatment IT vs. post-treatment IT).  
 ‡  $p = 0.24$  (pretreatment IFT vs. post-treatment IFT).  
 §  $p < 0.0001$  (pretreatment BW vs. post-treatment BW).  
 #  $p < 0.0001$  (pretreatment BT vs. post-treatment BT).

**Table 2 – Means and standard deviations of Ra (nm) obtained from atomic force microscopy analysis of Ti-6Al-4V specimens.**

Groups	Pretreatment	Post-treatment
IW – Immersion in deionised water	1.79 (0.25) <sup>Aa</sup>	2.01 (0.25) <sup>Aa*</sup>
IT – Immersion in fluoride-free toothpaste	1.61 (0.13) <sup>Aa</sup>	1.74 (0.19) <sup>Aa†</sup>
IFT – Immersion in fluoride toothpaste	1.92 (0.39) <sup>Aa</sup>	2.29 (0.51) <sup>Aa‡</sup>
BW – Brushing with deionised water	2.00 (0.71) <sup>Aa</sup>	2.05 (0.43) <sup>Aa§</sup>
BT – Brushing fluoride-free toothpaste	2.37 (0.86) <sup>Aa</sup>	11.17 (2.29) <sup>Bb#</sup>
BFT – Brushing fluoride toothpaste	1.83 (0.50) <sup>Aa</sup>	15.73 (1.78) <sup>Cb**</sup>

Different uppercase letters indicate significant differences in columns obtained by one-way ANOVA followed by HSD Tukey test.  
 Different lowercase letters indicate significant differences in rows obtained by Student T-test:  
 \*  $p = 0.22$  (pretreatment IW vs. post-treatment IW).  
 \*\*  $p < 0.0001$  (pretreatment BFT vs. post-treatment BFT).  
 †  $p = 0.12$  (pretreatment IT vs. post-treatment IT).  
 ‡  $p = 0.08$  (pretreatment IFT vs. post-treatment IFT).  
 §  $p = 0.77$  (pretreatment BW vs. post-treatment BW).  
 #  $p < 0.0001$  (pretreatment BT vs. post-treatment BT).

roughness of Ti-6Al-4V (Table 2). As for Ti-6Al-4V, significant differences were seen after the two brushing treatments (BT and BFT) (Table 2).

Post-treatment comparisons showed significant differences amongst the experimental treatments in cp Ti ( $p < 0.001$ ) and in Ti-6Al-4V ( $p < 0.001$ ). The Tukey HSD showed that the roughness of cp Ti immersion groups (Table 1) was similar across groups and lower than those of BW, BT and BFT (Table 1); BFT had the highest roughness, followed by BT and BW, i.e. the roughness increased from BW to BFT. Similarly, for Ti-6Al-4V no significant differences were seen amongst the immersion groups (Table 2), although IW, IT and IFT were no different than BW, which had, in turn, lower roughness than the brushed groups. BFT had the highest values of roughness.

Three-dimensional topographies (Figs. 2 and 3) corroborated the results of the Ra analyses. Pretreatment surfaces of cp Ti (Fig. 2a, c, e, g, i and k) and Ti-6Al-4V (Fig. 3a, c, e, g, i and k) had homogeneous surfaces. No significant changes were observed in IW (Figs. 2b and 3b), IT (Figs. 2d and 3d) and in IFT (Figs. 2f and 3f). Ti-6Al-4V surfaces after BW were also not significantly changed (Fig. 3h).

Changes were seen on brushed cp Ti (Fig. 2h, j and l). They were minor in BW (Fig. 2h), intermediate in BT (Fig. 2j) and more heterogeneous in BFT (Fig. 2l). Topography of Ti-6Al-4V

showed important irregularities after BT (Fig. 3j) and BFT (Fig. 3l).

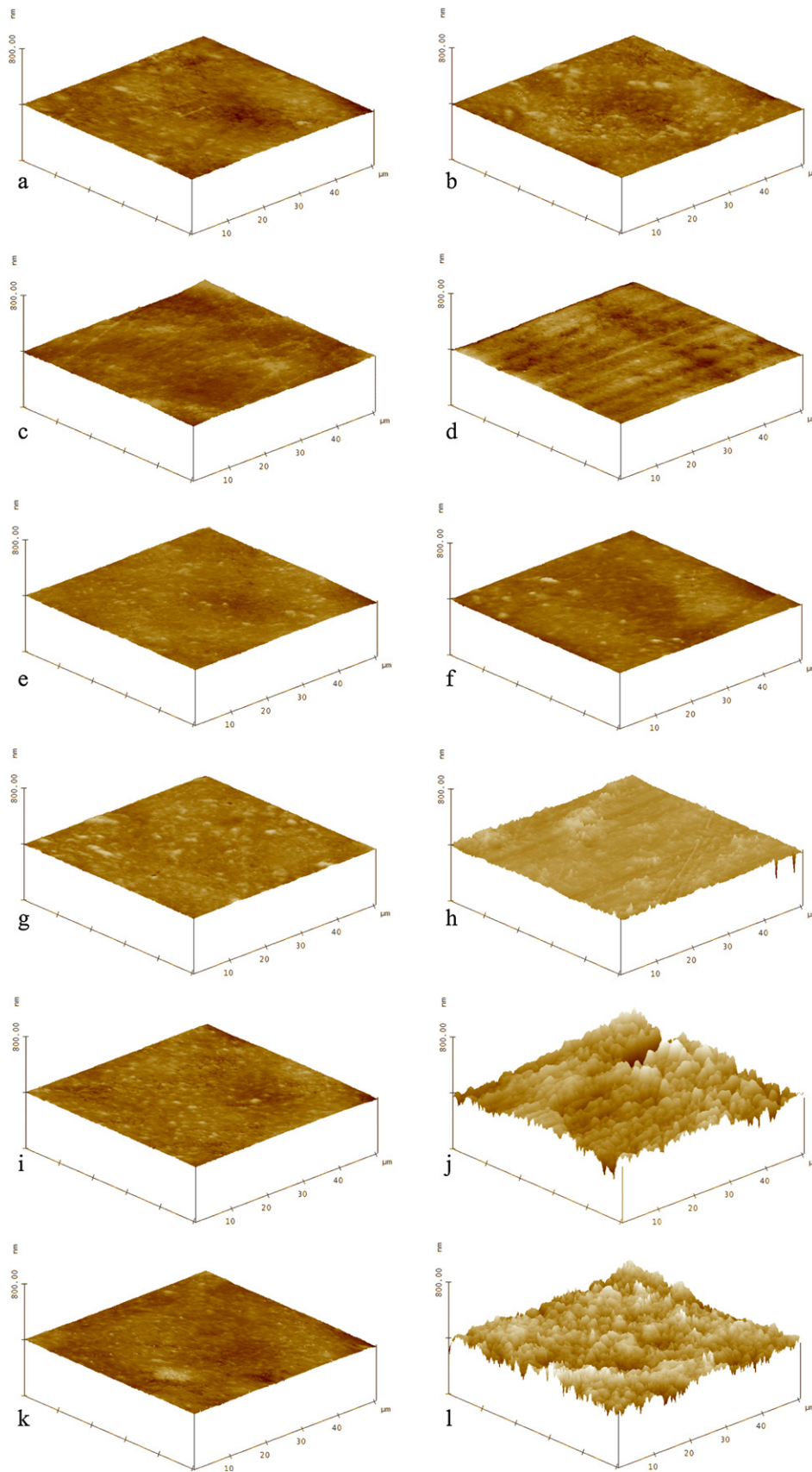
Post-treatment microstructures (1500× magnification) of the IFT and BFT surfaces are shown in Fig. 4. Regardless of microstructural differences between cp Ti and Ti-6Al-4V, IFT surfaces (Fig. 4a and c) were even and completely featureless whilst BFT surfaces (Fig. 4b and d) exhibited an uneven surface with significant grooves and some pores. The EDS point-analyses of these surfaces (600×) did not detect traces of sodium or fluorides (Figs. 5–8).

#### 4. Discussion

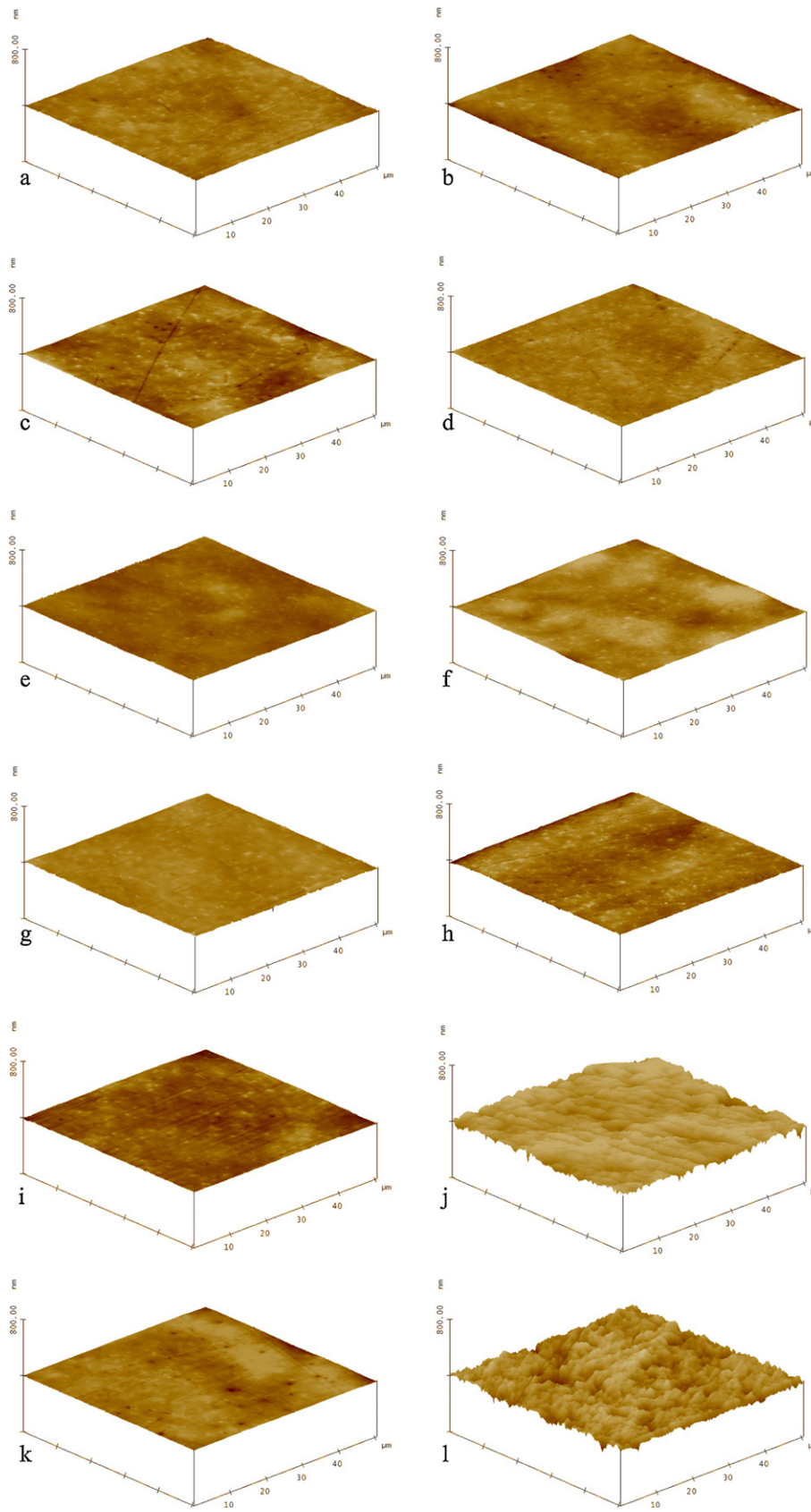
The null hypothesis was rejected based on the data (3D topographies and Ra measurements) when metals were brushed, suggesting that the presence of abrasives on the toothpastes affected the roughness and topography of titanium based materials. Major changes happened likely due to the combined effects of fluoride ions and toothpaste abrasiveness during brushing.

Several factors influence material's surfaces during toothbrushing and some may explain the differences found between cp Ti and Ti-6Al-4V. Variables such as microstructures, hardness, tensile properties, fracture toughness, fatigue

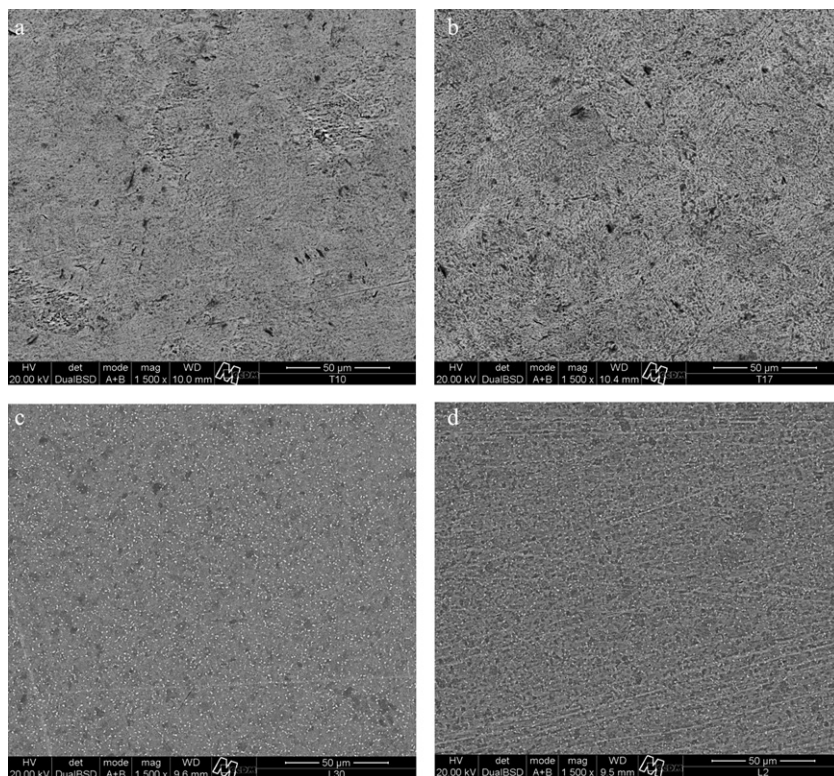




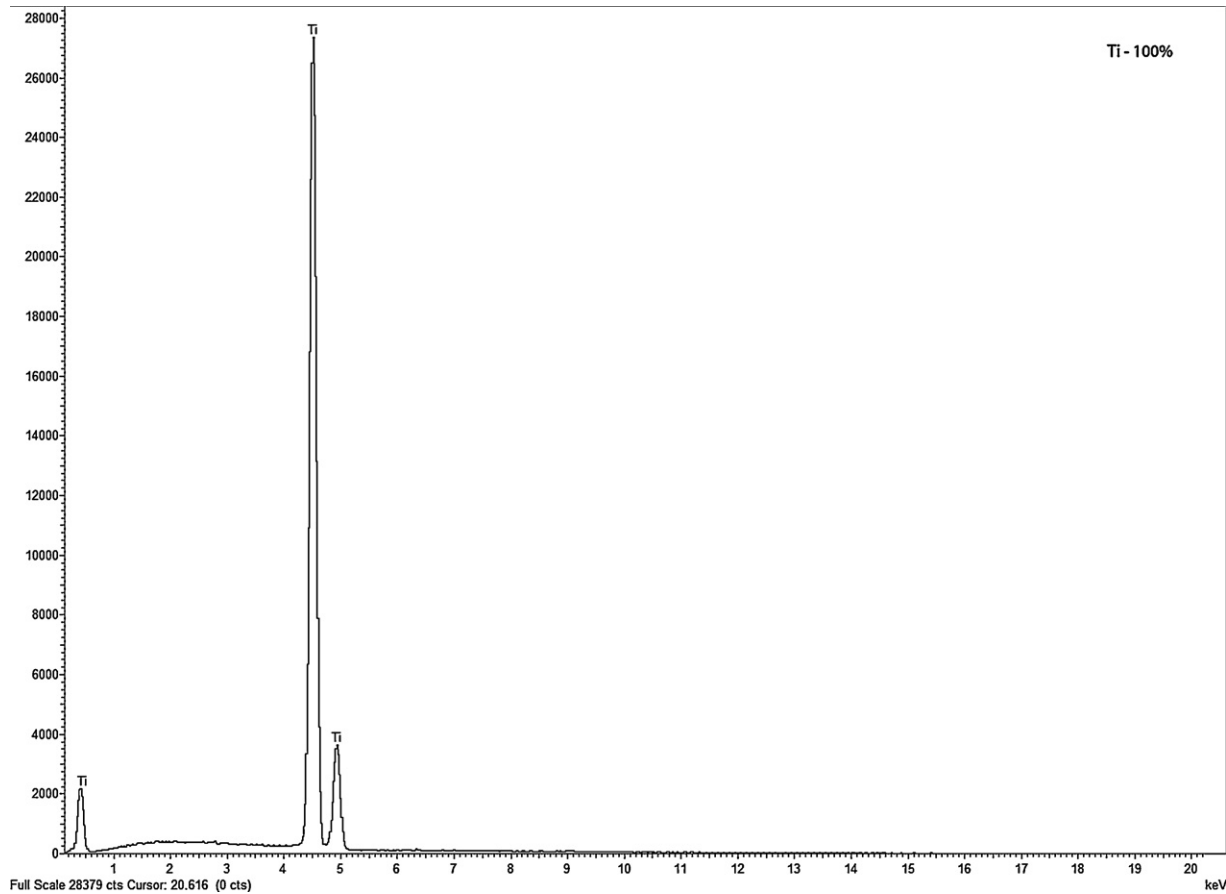
**Fig. 2 – 3D atomic force microscopy images of cp Ti. Group IW pretreatment (a) and post-treatment (b); Group IT pretreatment (c) and post-treatment (d); Group IFT pretreatment (e) and post-treatment (f); Group BW pretreatment (g) and post-treatment (h); Group BT pretreatment (i) and post-treatment (j); Group BFT pretreatment (k) and post-treatment (l). The colour becomes lighter on proceeding from the valleys towards the peaks.**



**Fig. 3** – 3D atomic force microscopy images of Ti-6Al-4V. Group IW pretreatment (a) and post-treatment (b); Group IT pretreatment (c) and post-treatment (d); Group IFT pretreatment (e) and post-treatment (f); Group BW pretreatment (g) and post-treatment (h); Group BT pretreatment (i) and post-treatment (j); Group BFT pretreatment (k) and post-treatment (l). The colour becomes lighter on proceeding from the valleys towards the peaks.



**Fig. 4 – Scanning electron microscope images (1500×) of samples exposed to fluoride ions; cp Ti – Group IFT (a), Group BFT (b); Ti-6Al-4V – Group IFT (c) and Group BFT (d).**



**Fig. 5 – Semi-quantitative composition of cp Ti after immersion in fluoride toothpaste (Group IFT).**

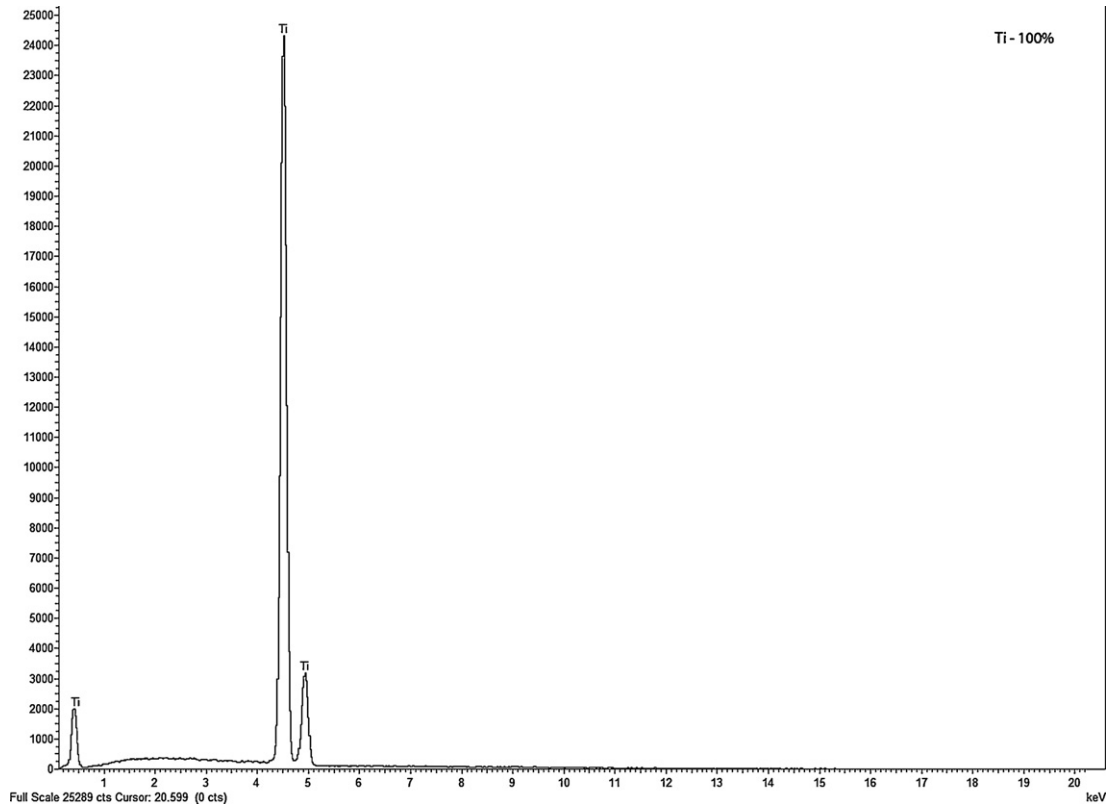


Fig. 6 – Semi-quantitative composition of cp Ti after brushing with fluoride toothpaste (Group BFT).

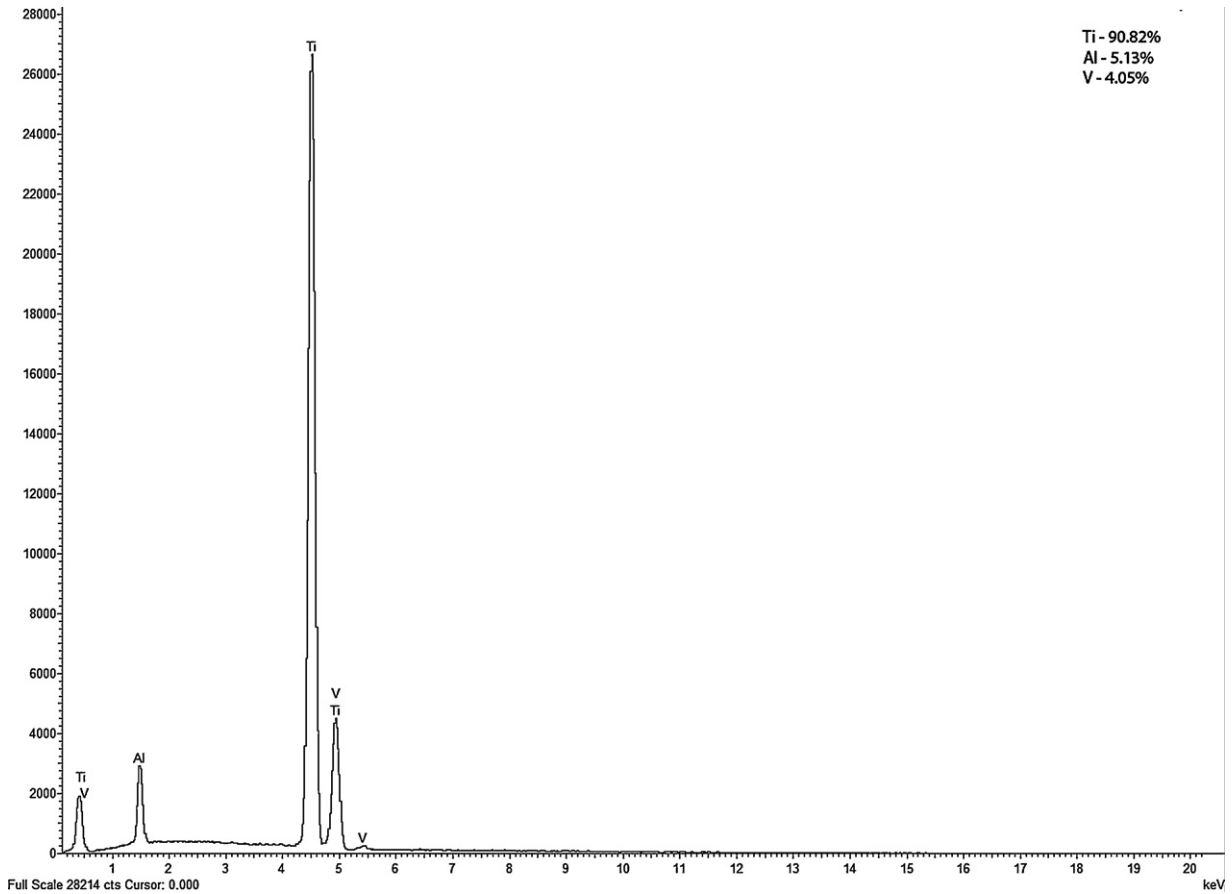
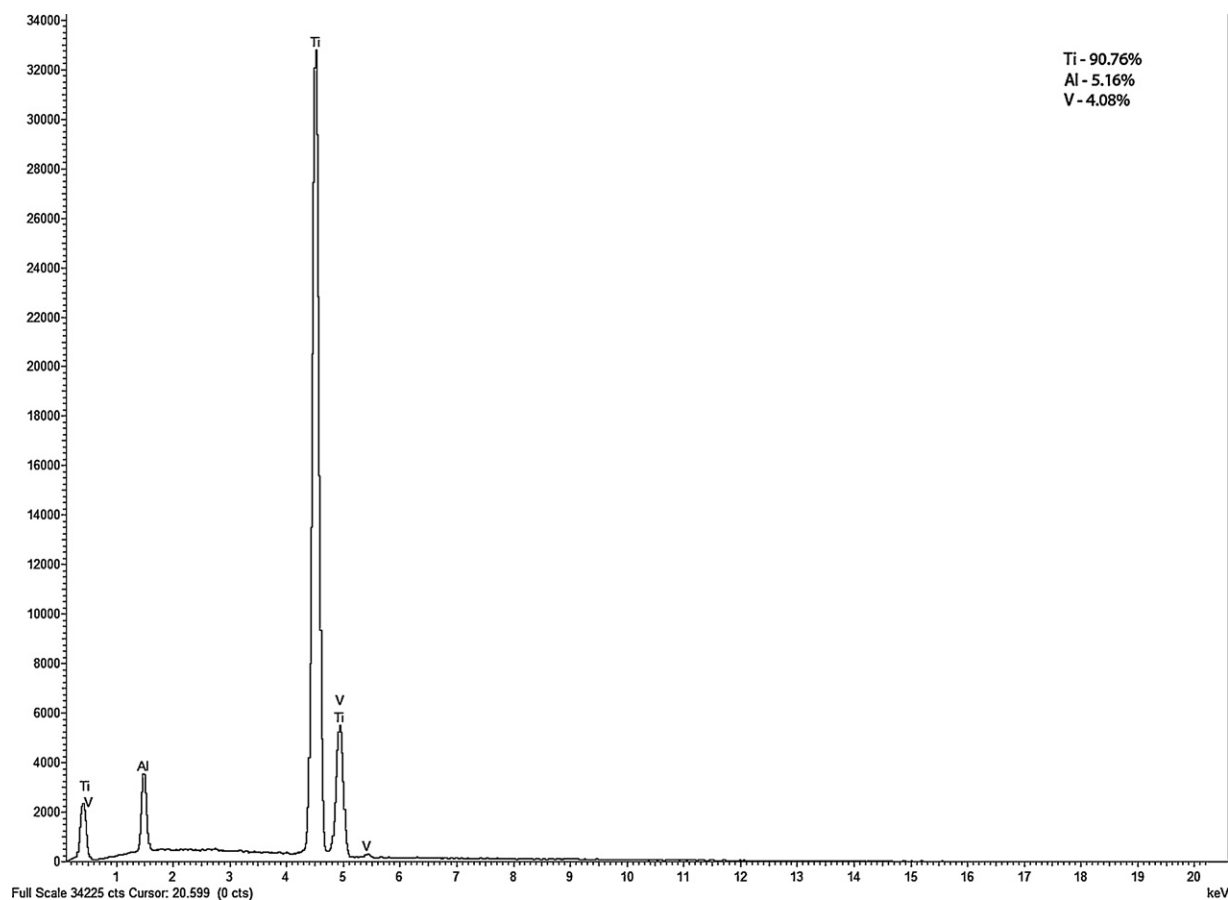


Fig. 7 – Semi-quantitative composition of Ti-6Al-4V after immersion in fluoride toothpaste (Group IFT).





**Fig. 8 – Semi-quantitative composition of Ti-6Al-4V after brushing with fluoride toothpaste (Group BFT).**

resistance, and fracture behaviour<sup>10</sup> seem to be related to the material surface; abrasiveness,<sup>21</sup> viscosity,<sup>2</sup> fluoride concentration and pH<sup>2</sup> seem to be determined by the toothpaste compounds. Variables related to the characteristics of the toothbrushes<sup>25</sup> may also be of importance.

The current study suggest that the abrasive action of the toothbrush bristles did not change the Ra and the 3D-AFM topography of Ti-6Al-4V, and was associated with only slight changes in cp Ti BW. Alternatively, substantial changes were seen after brushing with fluoride-free toothpaste and with fluoride toothpaste [about 6.8 and 9.6 times higher than the cp Ti control group (IW) and about 5.5 and 7.8 times higher than the Ti-6Al-4V control group (IW)]. Furthermore, 3D topography was significantly altered likely due to the presence of fluorides plus mechanical action of abrasives.

The influence of brushing with non-fluoride toothpaste on roughness and topography has been described,<sup>2,21</sup> but controversies exist about the effects of abrasiveness in fluoride toothpastes. Siirila and Kononem<sup>14</sup> described that toothbrush bristles influence titanium more extensively than fluoride abrasive toothpastes. Noguez et al.<sup>20</sup> failed to detect significant differences on titanium roughness after using fluoride toothpastes with different abrasiveness. Discrepancies may be due to the different methodologies since the first authors performed manually brushing, whilst the other used electric toothbrushes with rotating oscillation, with lower abrasion power.<sup>25</sup>

Available data suggest that changes on 3D AFM surface topography, Ra values and SEM micrographs in titanium immersion tests, were associated with higher fluoride concentrations and/or acidic NaF solutions,<sup>3,8,11,12,14,18</sup> likely because of the reactions that occur with the NaF and the protective oxide layer. When NaF agents are in contact with titanium, sodium and fluorides ions are released. Fluoride ions combine with hydrogen generating hydrofluoric acid (HF), which reacts with the oxide layer, dissolving titanium. In severe corrosion rates, titanium fluoride, titanium oxide fluoride, or sodium titanium fluoride compounds could be formed on the surface.<sup>1,6,12,16</sup>

In the current study, the IF was not associated with 3D topographic changes or different roughness. Since sodium or fluoride compounds are not detected on the surface, it was suggest that reactions were not enough to change titanium surfaces. These results may have been driven by the low concentration of fluoride and by the pH value.<sup>8,9,13,15,18,26</sup> In this study, fluoride toothpaste with 1500 ppm F<sup>-</sup> and pH = 6.3 was used. According to Nakagawa et al.<sup>9,13,15</sup> titanium changes induced by fluoride can be predicted by pH and fluoride concentration. According to this predictive model, for a fluoride concentration of 1500 ppm, corrosion should only occur if pH is lower than 4.7 for cp Ti and 5.1 for Ti-6Al-4V. Accordingly, at least 10,000 ppm F<sup>-</sup> seem to be necessary in order to corrode titanium when toothpastes with pH equal to 6.3 are used.

The significant increase in roughness of BFT samples relative to BT suggest that even for potentially non-corrosive

toothpastes (1500 ppm F, pH = 6.3), the action of fluoride was influenced by changes in surfaces wear caused by toothpaste abrasives, which may destroy the oxide film<sup>21</sup> and may also produce internal stress that increase current density, facilitating corrosion.<sup>19</sup> Thus, the instantaneous repassivation of the oxide layer, that is typically gradually reorganised and stabilised<sup>5</sup> may be affected by fluoride ions.<sup>4</sup> Nonetheless, EDS spectra findings (Figs. 5–8) support the concept that fluoride (from the toothpaste used in our study) did not cause severe corrosion or formation of insoluble fluoride compounds on the surface of titanium, highlighting the importance not only of fluoride concentration, but also of the pH. Reclaru and Meyer<sup>26</sup> found deposition of fluoride when titanium was immersed in a 1000 ppm F<sup>-</sup> solution at a pH = 3.5. The formation of crystals of Na<sub>2</sub>TiF<sub>6</sub>, Na<sub>5</sub>Ti<sub>3</sub>F<sub>14</sub> and Na<sub>2</sub>TiF were observed, respectively, by Huang,<sup>16</sup> Kaneko et al.<sup>27</sup> and Mabilieu et al.,<sup>12</sup> using solutions with 10,000 ppm F/pH = 6.0, 9,000 ppm F/pH = 6.5 and 25,000 ppm F/pH ranging from 4.5 to 5.3. Sartori et al.<sup>18</sup> did not find fluoride ions or crystals on the surface of implants after immersion in NaF solution (1500 ppm F<sup>-</sup> and pH ranging from 5.3 to 7.4).

In the present study, experimental treatments were defined in order to disentangle the effects of fluoride from the effects of abrasives and brushing on titanium topography. Regarding the use of titanium and its alloys as osseointegrated implants in dentistry, two aspects should be considered: (1) areas in contact with bone tissue have typically higher roughness in order to facilitate osseointegration, whilst (2) abutments and other structures that will be exposed to the oral environment must have smooth surfaces, crucial for controlling biofilm formation.<sup>28,29</sup> Whilst implants and components used as medical devices must have roughness lower than 10 nm,<sup>30</sup> no standardisation has been defined regarding surface roughness of dentistry abutments.<sup>31</sup>

This study has some limitations. For example, although it simulated 10 years of exposure, its *in vitro* nature should be cautiously extrapolated for clinical practice. Methods used to simulate brushing for long periods imply continuous brushing for several hours, which could accentuate abrasive effects and influence of fluoride. Future studies must test clinical conditions, focusing also on plaque accumulation, ion release, and mechanical strength, as well as on other oral cavity variables, such as presence of proteins, fluctuations on fluoride concentrations, changes in pH and temperature.

## 5. Conclusions

Within the limitations of this study, it was concluded that after simulated 10 years, exposure to toothpastes (immersion) with fluoride concentration of 1500 ppm and a pH = 6.3 does not affect titanium *per se*; their use during brushing affect titanium topography and roughness. The associated effects of toothpaste abrasives and fluorides seem to increase roughness on titanium brushed surfaces.

## Acknowledgements

This investigation was supported by CNPQ and FAPESP (State of São Paulo Research Foundation), Grant no. 08/028710.

## REFERENCES

1. Stajer A, Ungvari K, Pelsoczi IK, Polyanka H, Oszko A, Mihalik E, et al. Corrosive effects of fluoride on titanium: investigation by X-ray photoelectron spectroscopy, atomic force microscopy, and human epithelial cell culturing. *Journal of Biomedical Materials Research Part A* 2008;**87**:450–8.
2. Hossain A, Okawa S, Miyakawa O. Surface texture and composition of titanium brushed with toothpaste slurries of different pHs. *Dental Materials* 2007;**23**:186–92.
3. Huang HH. Variation in surface topography of different NiTi orthodontic archwires in various commercial fluoride-containing environments. *Dental Materials* 2007;**23**:24–33.
4. Sivakumar B, Kumar S, Narayanan TSNS. Fretting corrosion behavior of Ti–6Al–4V alloy in artificial saliva containing varying concentrations of fluoride ions. *Wear* 2010;**270**:317–24.
5. Hanawa T, Asami K, Asaoka K. Repassivation of titanium and surface oxide film regenerated in simulated bioliquid. *Journal of Biomedical Materials Research* 1998;**40**:530–8.
6. Matono Y, Nakagawa M, Matsuya S, Ishikawa K, Terada Y. Corrosion behavior of pure titanium and titanium alloys in various concentrations of Acidulated Phosphate Fluoride (APF) solutions. *Dental Materials Journal* 2006;**25**:104–12.
7. Ehrensberger MT, Sivan S, Gilbert JL. Titanium is not “the most biocompatible metal” under cathodic potential: the relationship between voltage and MC3T3 preosteoblast behavior on electrically polarized cpTi surfaces. *Journal of Biomedical Materials Research Part A* 2009;**93**:1500–9.
8. Al-Mayouf AM, Al-Sawayih AA, Al-Mobarak NA, Al-Jabab AS. Corrosion behavior of a new titanium alloy for dental implant application in fluoride media. *Materials Chemistry and Physics* 2004;**86**:320–9.
9. Nakagawa M, Matsuya S, Shiraishi T, Ohta M. Effect of fluoride concentration and pH on corrosion behavior of titanium for dental use. *Journal of Dental Research* 1999;**78**:1568–72.
10. Kononen MH, Lavonius ET, Kivilahti JK. SEM observations on stress corrosion cracking of commercially pure titanium in a topical fluoride solution. *Dental Materials* 1995;**11**:269–72.
11. Popa MV, Vasilescu E, Drob P, Vasilescu C, Demetrescu I, Ionita D. Long-term assessment of the implant titanium material–artificial saliva interface. *Journal of Materials Science Materials in Medicine* 2008;**19**:1–9.
12. Mabilieu G, Bourdon S, Joly-Guillou ML, Filmon R, Basle MF, Chappard D. Influence of fluoride, hydrogen peroxide and lactic acid on the corrosion resistance of commercially pure titanium. *Acta Biomaterialia* 2006;**2**:121–9.
13. Nakagawa M, Matsuya S, Udoh K. Corrosion behavior of pure titanium and titanium alloys in fluoride-containing solutions. *Dental Materials Journal* 2001;**20**:305–14.
14. Siirila HS, Kononen M. The effect of oral topical fluorides on the surface of commercially pure titanium. *International Journal of Oral & Maxillofacial Implants* 1991;**6**:50–4.
15. Nakagawa M, Matsuya S, Udoh K. Effects of fluoride and dissolved oxygen concentrations on the corrosion behavior of pure titanium and titanium alloys. *Dental Materials Journal* 2002;**21**:83–92.
16. Huang HH. Effects of fluoride concentration and elastic tensile strain on the corrosion resistance of commercially pure titanium. *Biomaterials* 2002;**23**:59–63.
17. Roselino Ribeiro AL, Noriega JR, Dametto FR, Vaz LG. Compressive fatigue in titanium dental implants submitted to fluoride ions action. *Journal of Applied Oral Science* 2007;**15**:299–304.
18. Sartori R, Correa CB, Marcantonio Jr E, Vaz LG. Influence of a fluoridated medium with different pHs on commercially pure titanium-based implants. *Journal of Prosthodontics* 2009;**18**:130–4.

19. Molina C, Nogue L, Martinez-Gomis J, Peraire M, Salsench J, Sevilla P, et al. Dental casting alloys behaviour during power toothbrushing with toothpastes of various abrasivities. Part II: Corrosion and ion release. *Journal of Materials Science Materials in Medicine* 2008;19:3015–9.
20. Nogue L, Martinez-Gomis J, Molina C, Peraire M, Salsench J, Sevilla P, et al. Dental casting alloys behaviour during power toothbrushing with toothpastes with various abrasivities. Part I: Wear behavior. *Journal of Materials Science Materials in Medicine* 2008;19:3041–8.
21. Hossain A, Okawa S, Miyakawa O. Effect of toothbrushing on titanium surface: an approach to understanding surface properties of brushed titanium. *Dental Materials* 2006;22:346–52.
22. Heintze SD, Forjanic M, Ohmiti K, Rousson V. Surface deterioration of dental materials after simulated toothbrushing in relation to brushing time and load. *Dental Materials* 2010;26:306–19.
23. Worschech CC, Rodrigues JA, Martins LR, Ambrosano GM. Brushing effect of abrasive dentifrices during at-home bleaching with 10% carbamide peroxide on enamel surface roughness. *The Journal of Contemporary Dental Practice* 2006;7:25–34.
24. Wataha JC, Lockwood PE, Noda M, Nelson SK, Mettenburg DJ. Effect of toothbrushing on the toxicity of casting alloys. *The Journal of Prosthetic Dentistry* 2002;87:94–8.
25. Dyer D, MacDonald E, Newcombe RG, Scratcher C, Ley F, Addy M. Abrasion and stain removal by different manual toothbrushes and brush actions: studies in vitro. *Journal of Clinical Periodontology* 2001;28:121–7.
26. Reclaru L, Meyer JM. Effects of fluorides on titanium and other dental alloys in dentistry. *Biomaterials* 1998;19:85–92.
27. Kaneko EH, Hatorri M, Hasegawa K, Yoshinari M, Kawada E, Oda Y. Influence of finish on the electrochemical properties of dental alloys. *Bull Tokyo Dental Collection* 2000;41:49–57.
28. Rimondini L, Fare S, Brambilla E, Felloni A, Consoni C, Brossa F, et al. The effect of surface roughness on early in vivo plaque colonization on titanium. *Journal of Periodontology* 1997;68:556–62.
29. Subramani K, Jungh RE, Molenberg A, Hammerle CH. Biofilm on dental implants: a review of the literature. *International Journal of Oral Maxillofacial Implants* 2009;24:616–26.
30. Truong VK, Lapovok R, Estrin YS, Rundell S, Wang JY, Fluke CJ, et al. The influence of nano-scale surface roughness on bacterial adhesion to ultrafine-grained titanium. *Biomaterials* 2010;31:3674–83.
31. Bollen CM, Lambrechts P, Quirynen M. Comparison of surface roughness of oral hard materials to the threshold surface roughness for bacterial plaque retention: a review of the literature. *Dental Materials* 1997;13:258–69.