International Journal of Science and Research (IJSR)
ISSN (Online): 2319-7064
Index Copernicus Value (2015): 78.96 | Impact Factor (2015): 6.391

Using Hydrofluoric Acid to Enhance Titanium Surface Topography

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Abstract: ***Purpose:*** ***The aim was to explore the effect of different concentrations of HF acid etch on titanium surface topography (with different time interval).*** ***Materials and Methods:*** ***Pure polished titanium discs were subjected to various concentration of HF acid etch(0.2 wt % and 0.5 wt %) for for four time intervals of 1.5 min, 2 min, 2.5 min and 3 min. at room temperature. After etching the discs were rinsed immediately with distilled water. Polished titanium surfaces were used as a control. Surface roughness was measured using profilometry. Topography was examined using scanning electron microscopy (SEM).*** ***Results:*** ***Etching of titanium discs with 0.2 wt% or 0.5 wt% HF acid had a clearly visible effect on polished titanium surfaces. For etching with 0.5 wt% HF, a steady increase in Ra value with etching time was observed reaching a maximum value of 0.147 µm at 3 min. Highly significant differences were found between Ra value in 3 min etching and both 1.5 and 2 min etching given in P= 0.001. For etching with 0.2 wt% of HF, a relatively different pattern was observed. The Ra values increased for 1.5 and 2 min acid exposure then slightly decreased at 2.5 min acid exposure before increasing again for a 3 min etching period. Highly significant differences were found between the 1.5 min group and both 2 min and 3 min group given P = 0.004, 0.001 respectively. SEM picture shows grain pattern (A honeycomb pattern) of the titanium surface following treatment with 0.5 wt % HF acid etching.*** ***Conclusions:*** ***This research showed that a slight difference in concentration, or duration have significant impact on titanium surface topography. Titanium is an amenable material for designing of implant and it is possible to modify the surface using a variety of protocols. Roughness resulting from HF acid etching varied according to acid concentration, duration of acid etching procedure and original surface roughness of the substrate.***

Keyword: Dental implant, titanium, surface modification, hydrofluoric acid, roughness

1. Introduction

Dental implants have become an important option in treatment plans within dentistry to replace missing teeth. However, implant failure and peri-implant diseases are still a problem facing implantologists. The long term success of an implant is hieghly dependent upon the ability of the material to integrate with the surrounding bone and connective tissue.[1] Many efforts have been made to develop materials that can accelerate osseointegration , [2] enhance gingival attachment to provide a soft tissue seal that prevents bacterial invasion, [3] and resist bacterial adhesion and colonization and/or having bactericidal effects.[4]

The biological response to a dental implant is determined by a number of physical and chemical features of the implant surface. These include mechanical properties and physicochemical properties (oxide composition and thickness, wettability, surface free energy and surface topography). Any interaction between the body tissues and the implant material such as adsorption of protein will be affected by these properties and any changes in one of these groups will affect the other parameters. [5,6,7,8]

The formation of osteoid and mineralization depend upon initial adhesion of a fibrin blood clot and mesenchymal stem cells onto the implant surface.[9] Bone will be formed in direct contact with the implant surface as a result of a series of changes and modifications of the tissue/implant interface. The amount and rate of bone formation and bone/implant mechanical interaction is affected by the implant surface characteristics. [7].

Dental implants differ from other load-bearing implants such as orthopedic implants because they cross between two different environments (oral cavity and inside body tissue). This is a challenging environment and an implant therefore needs to cope with the normal microbiota associated with the oral cavity, provide a seal to prevent bacterial invasion inside the body, endure different masticatory forces, withstand variation in pH and temperature and even galvanic current, [10] as well as being able to osseointegrate with bone

A certain amount of roughness (pore or micro texture surface) is essential for promotion of gingival tissue ingrowth. A surface roughness value of 0.2 µm seems to be the ideal surface roughness for the transmucosal part of a dental implant (threshold roughness). This roughness has been suggested to be the most suitable roughness to obtain a stable soft tissue seal around the supragingival part of a dental implant. If it is smoother than this it will prevent cell attachment.[11,12]

The overall aim of acid etching an implant surface is to make pits to allow bone ingrowth. The surface of the etched implants can be affected by several parameters, such as the original surface roughness, type and concentration of acid, temperature, and time.[13,14]

Fluoride solutions have been used to treat titanium dental implants surfaces. Titanium is very sensitive to fluoride ions and can react with them readily resulting in an increased micro roughness. Fluoride also has the advantage of changing the dental implant surface to a bioactive material (7). Lamoll et al., [15] studied the surface topography, chemistry and biocompatibility of polished titanium surfaces treated with hydrofluoric acid solution (HF). They suggested that treating titanium implants with HF acid can lead to specific surface changes that improve the biocompatibility of titanium surfaces. They also reported that the fluoride penetrated deep into the titanium.

In research studies and also in some dental implant companies details of surface modification without precise information on procedure are generally given. For example in case of acid etching the duration and concentration of acid used is often not provided. In this study, It has been felt that it is important to highlight the importance of providing detailed information of surface modification.

The aim was to explore the effect of different concentrations of HF acid etch on titanium surface topography (with different time interval).

2. Materials and Methods

Specimens preparation and polishing

Discs of 5 mm in diameter (± 0.1 mm) were punched out from 100 x 100 x 1 mm of annealed titanium sheets (99.6+%) (Goodfellow Cambridge Limited, Huntingdon, England). Discs were cleaned in an ultrasonic bath at room temperature with ethanol for 15 min then allowed to dry at room temperature.

In order to have an accurate evaluation of surface changes (especially at nano-level) and for proper comparison between groups, a uniform clean surface was obtained (mirror polished surface) on one side of each disc. To facilitate polishing, discs were mounted within a specific ring using an epoxy resin system for embedding and impregnation of the specimens (Struers A/S, Ballerup, Denmark) and these were then polished with a Struers A/S machine.

The polishing procedure was conducted in three steps the first step was conducted using a disc grinding paper (silicon carbide grinding paper), grit 500 (Paper), 200 mm diameters at 300 rpm, 25 N, for 1 min, under water flow.the second step was conducted using a MD Largo disc (MALOT), 200 mm diameter at 150 rpm, 30 N for 4 min with DiaPro Allegro/largo polishing liquid as a lubricant. The third and final step was conducted using a MD-Chem polishing cloth disc (MACHE) at 150 rpm, 30 N, for 5 min using OP-S 0.04 µm colloidal silica suspension with 10% H_2O_2.

A mirror surface image was obtained using this procedure. The discs were then cleaned in an ultrasonic bath at room temperature with ethanol for 15 min, and then with distilled water. Discs were then dried in an oven at 40 ˚C for 1 h and left to dry at room temp. The discs were stored in a sealed container.

Hydrofluoric acid etching

Hydrofluoric acid (HF) is powerful acid and reacts readily with titanium without the need for heat. The etching procedure was conducted at room temperature for two different concentrations of HF acid (0.2 wt % and 0.5 wt %) (Sigma-Aldrich) for four time intervals of 1.5 min, 2 min, 2.5 min and 3 min. at room temperature. After etching the discs were rinsed immediately with distilled water.

After each surface modification the discs were ultrasonicated in ethanol for 5 min and then distilled water for 10 min at room temperature. The discs were then incubated in the oven at 40 ˚C for 1 h and allowed to dry at room temperature.

Scanning electron microscopy (SEM)

Topographic inspection was conducted using a scanning electron microscope (SEM Tech Ltd, Bonsall, Derbyshire, UK). All samples were attached by adhesive to aluminum SEM stubs and examined at 20 kV in the secondary emission mode in a PC-controlled ISI 60 scanning electron microscope.

Measurement of surface roughness

Non contact optical Proscan profilometry was used to measure the surface roughness (Proscan 2000, Scantron Industrial Products Ltd. Monarch centre, Taunton, England). Four discs per surface were measured. The measurements were conducted in an X and Y direction, and the scanned area was 2 x 2 mm. The measurement was taken for 20 lines in the Y axis; 250 spots in each line were measured twice. The final analysis was conducted in an area of 1.2 mm x 1.2 mm in order to avoid edge effects. Ra measurement was calculated for each sample: Ra: is the arithmetic mean of the absolute values of the surface point departures from the mean plane within the sampling area.[16] (Macdonald et al., 2004).

Statistics

Statistical analysis was carried out using Excel and SPSS (Statistical Package for Social Sciences)

After verification of the normal distribution and the homogeneity of the variance, an analysis of the variance (ANOVA) was used to asses any significant differences among selected group. For multiple comparisons test (Post Hoc multiple comparisons) LSD (least significant difference) was used to determine the specific differences between the means of the group members.

The probability value (P-value) was considered significant at $P < 0.05$ and highly significant if $P < 0.01$.

3. Results

The morphology and the surface roughness of titanium discs was analysed, and found to be different from one to another after various surface modifications.

HF acid etching

Etching of titanium discs with 0.2 wt% or 0.5 wt% HF acid had a clearly visible effect. Polished titanium surfaces changed from a bright mirror surface to dull with few black patches in the case of 2 or 2.5 min exposure to 0.2 wt% HF. A shiny black to dark green colour on light reflection was observed following 3 min etching with 0.2 % HF. Etching of titanium surfaces with 0.5 wt% HF for 1.5 min resulted in a grey to green to silver colour which varied according to the light reflection on these surfaces. Longer efigxposures of 2, 2.5 and 3 min resulted in a dull silver colour on the disc surface.

Fig 1 shows mean surface roughness (mean Ra value) in µm for titanium surfaces etched with different concentrations of HF acid for different times as measured by profilometry. For etching with 0.5 wt% HF, a steady increase in Ra value with etching time was observed reaching a maximum value of 0.147 µm at 3 min. Highly significant differences were found between Ra value in 3 min etching and both 1.5 and 2 min etching given in P= 0.001. While significant differences were found in Ra value between 2.5 min etching time and (1.5, 2, 3 min) etching time given in P=0.027, 0.039, 0.041 respectively.

For etching with 0.2 wt% of HF, a relatively different pattern was observed. The Ra values increased for 1.5 and 2 min acid exposure then slightly decreased at 2.5 min acid exposure before increasing again for a 3 min etching period. Highly significant differences were found between the 1.5 min group and both 2 min and 3 min group given P = 0.004, 0.001 respectively. Significant differences were observed between the 2.5 min group and both 1.5 min and 3 min etching groups given P = 0.026, 0.030 respectively.

Despite the different effects of the two concentrations of HF that were observed with the naked eye, it appears that the highly significant difference was found only in the 2.5 min group while a significant difference was found for the 1.5 min etching group.

SEM

Figures 2 and 3 show SEM images at different magnifications of titanium surfaces etched with 0.2, 0.5 % HF respectively which confirms Ra results presented above. It was interesting to find such marked differences in imaging for different concentrations of the same acid (HF).

A few bright spots on the surfaces without differences in surface texture from polished surfaces were seen following etching for 1.5 min with 0.2 wt% HF acid, but within only another 30 sec. a large number of relatively big irregular holes appeared on the surface that diminished in number and size within the next 30 sec. to virtually disappear after etching for 3 min duration (Figure 2).

However, exposure of polished titanium surface to 0.5 % HF resulted in very different surface modifications. A honeycomb pattern was observed for 1.5 min etching with the titanium surface (Figure 3). This general view continued with all the extended etching times, but with less prominence and fine needle like scratches appearing after 2 and 2.5 min etching duration, that started to disappear after 3 min acid exposure (Figure 3).

Figure 4. SEM picture shows grain pattern of the titanium surface following treatment with 0.5 wt % HF acid etching.

4. Discussion

The results showed that a range of treatments of titanium produced different surface topographies, as first indicated by Xavier et al.,[17], significant differences in surface roughness were obtained.

Acid etching is one of the major surface modifications that has been used in previous studies and is used commercially on a number of implant types (e.g. Osseotite, 3i implant Innovations, West Palm Beach, USA). The clinical performance of these implants and the associated shortened healing times when compared to machined surface implants has been widely documented.[18]

The benefit of acid etching alone to improve osseointegration was illustrated by Klokkevold et al., [19] who showed that the deep pits created during the etching process were filled with bone which contributed to bone interlocking. Many dental implant manufacturers started to use this procedure to prepare titanium surfaces. [20] However, it has been shown that on some occasions the pits are too small to permit bone ingrowth, and it is thought that this is may be due to either using a weak acid mixture, a low etching temperature, or a short etching time.

Sul et al., [21] showed that the surface morphology of the dual acid etching implant "Osseotite implant" is characterized by needle-like margin structure ≤2 µm wide and ≤1 µm depth with a crystallo graphically etched appearance. Klokkevold et al.,[22] compared the anchorage of etched Osseotite implants and machined surfaces after 1, 2, and 3 months in the rabbit tibia model, and found that the acid etched surface had a higher removal torque than the machined surface after 1 and 2 months of healing respectively.

The etching process is thought to convert the titanium surface by creating a micro-roughness of 0.5–3 µm with the formation of irregular different depth pits.[23] It has been suggested that the dissolution of the implant surface can depend on the orientation of the individual titanium grains.[24] However this is in agreement with this research as titanium grain appeared so clear after etching with 0.5% of HF acid and a clearer picture appear with increase time.

The primary interaction with implant starts at a thin interface zone of about 1 nm in width, which includes rapid adsorption of connective tissue components and blood proteins at a molecular level. This procedure is controlled by physical and chemical properties of the material such as structure, defects, oxide thickness, roughness and contamination.[25] These biocompatibility properties are not only important for first tissue interactions, but also for the long term success of an implant. In addition to the biocompatibility of the implant surface to bone tissue (bone/implant interface) it should have the ability to adhere to sub epithelial connective tissue to form a hemidesmosomal attachment easily (soft tissue/implant interface). According to the results from this research it can be concluded that etching with HF acid will produce smooth surfaces making them good surfaces to manufacture supra-gingival part of dental implant.

Topography of the biomaterial surface plays an important role in determining the cellular response.[26] (He et al., 2008). The biological response to a dental implant is determined by a number of physical and chemical features of the implant surface, which include mechanical properties and physicochemical properties (oxide thickness, chemical composition, crystallinity, surface wettability, surface energy, and surface topography).[27] (Mabboux et al., 2004). Any interaction between the body tissues and the implant material will be affected by these properties and any changes in one of these groups may affect the other parameters. [6, 7,28]

The behaviour of HF acid appeared to differ according to its concentration. HF (0.2 wt %), appeared to act in a similar manner to other acid types [13]. This behaviour and onset of action was different from the action reported by Lamolle et al., [15]. However, the results of etching with 0.5 wt % of HF were in agreement with the findings of Lamolle et al., [15] in which they found that the action of HF was time dependent and initially showed no effect.

5. Conclusions

This research showed that a slight difference in concentration, or duration have significant impact on titanium surface topography.

Titanium is an amenable material for designing of implant and it is possible to modify the surface using a variety of protocols.
Roughness resulting from HF acid etching varied according to acid concentration, duration of acid etching procedure and original surface roughness of the substrate.

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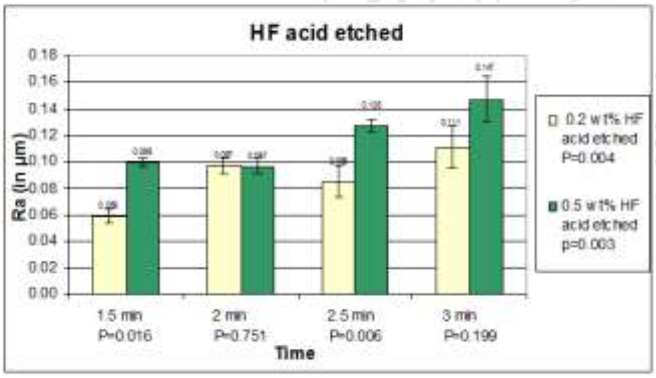

Figure 1: Average Ra values (in µm) and standard deviation of titanium surfaces etched with different concentrations of HF acid separately as quantified by profilometry. P values in the legend represent the significance between different etching times in the same acid group. P values in X axis represent the significance between different acids in the same etching time group.

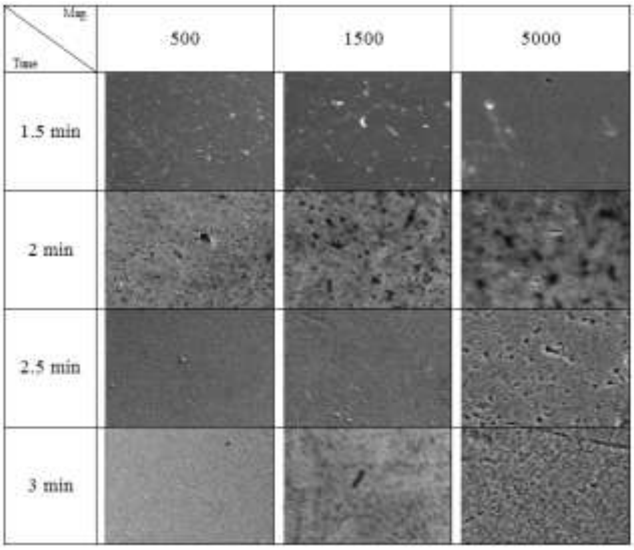

Figure 2: SEM images of titanium surfaces etched with 0.2 wt % HF acid for different times and at different magnifications.

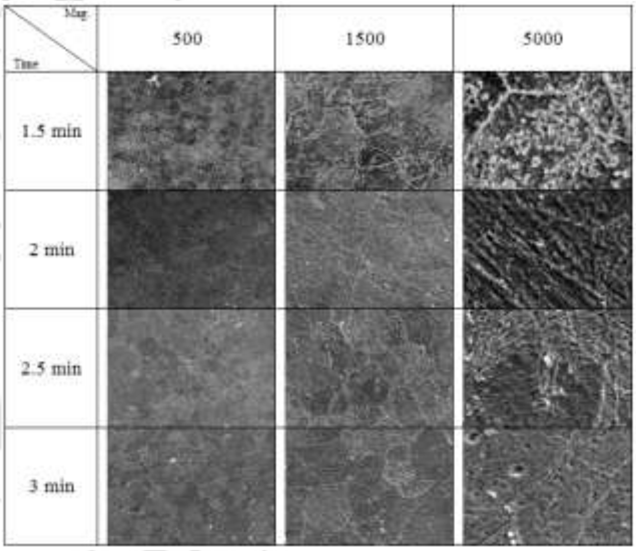

Figure 3: SEM images of titanium surfaces etched with 0.5 wt % HF acid for different times and at different magnifications.

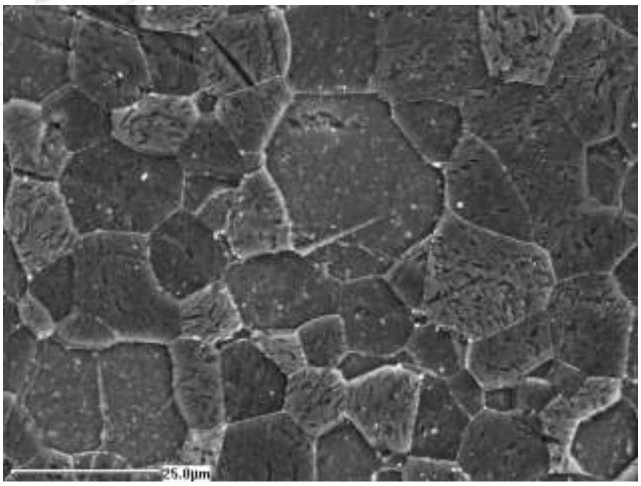

Figure 4: SEM picture shows grain pattern of the titanium surface following treatment with 0.5 wt % HF acid etching