Surface properties of heat treated with different durations of titanium alloy dental implants

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ABSTRACT

Background: The surface properties of the titanium alloy plays a significant role in the bond of the dental implant with living bone and modification of the implant surface could enhance osseointegration. This study was aimed to investigate the effect of different durations of heat treatment on the surface properties of titanium alloy for dental implants.

Materials and methods: Twenty disks of (Ti-6Al-4V) alloy were prepared. The sample was divided into four test groups to study the effect of different duration of heat treatment to the surface topography; surface chemistry, titanium oxide layer thickness, blood contact angle, & blood drop diameter of titanium alloy samples were investigated to evaluate the effect of different durations of heat treatment at a temperature of 750°C.

Results: The surface topography, surface chemistry, titanium oxide layer thickness, blood contact angle, & blood drop diameter of titanium alloy samples improved highly significantly as the duration of heat treatment increased.

Conclusions: The heat treatment of 750°C for 90 minutes showed the highest improvement in the surface properties which in turn will lead to enhancement in the osseointegration of the dental implant.

Keywords: heat treatment, titanium alloy, surface properties. (J Bagh Coll Dentistry 2013; 25(3):49-56).

INTRODUCTION

The surface properties of the titanium alloy plays a significant role in the structural and functional bond of the dental implant with the living bone Therefore, modification of the implant surface was proposed as a method for enhancing osseointegration. Surface topography, wettability, surface chemistry, and thickness of titanium oxide layer are all considered to be very critical factors that could influence osseointegration.[1-4] Wettability is one of the surface characteristics of an implant that may influence the speed and strength of osseointegration.[5,6] Measurement of the contact angle of a liquid is one way to quantify the surface free energy of solids or the ability of the liquid to wet the solid.[7,8]

Titanium biocompatibility is due the alloy's ability to form a surface oxide film spontaneously and immediately when subjected to oxygen. This titanium oxide layer (TiO_2) covers and protects the underlining metal from corrosion. The protective effect of this layer against corrosion prevents the release of toxic metal particles which can induce an osteolytic reaction that may lead to implant loosing and failure.[7] This titanium oxide layer cannot meet all the clinical requirement due to its small thickness which is between 5-10 nm. This film forms spontaneously at ambient temperatures and pressure and is called native oxide. Titanium oxide films can also be artificially grown by heating, acid etching and electrolytic oxidation, also known as anodizing.[8]

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In order to increase the thickness and stability of oxide layer, various strategies have been utilized to improve the mechanical and biological properties of titanium alloy and some of these strategies were the sol-gel, anodizing, and hydrothermal methods [9-15] Elias et al.[16] analyzed the influence of sandblasting, acid etching and anodizing on the dental implant surface and their results showed that the surface treatment lead to a change in the surface Wettability. The implants with treated surfaces showed greater roughness, higher friction coefficient, lower contact angle and demanded a larger insertion torque than machined implants.

These methods have disadvantages such as cost, complexity, and the time needed, while heat treatment of titanium alloy was shown to be lower in cost, easier, simple, needs less time, and with hopeful results. Heat treatment of titanium alloy result in enhancement of surface roughness, surface area, oxide layer thickness, Wettability, and protein and osteoblast adherence.[5] Lee et al.[18] stated that "as the temperature of the thermal treatment increased the surface characteristics and biocompatibility of titanium increased". They investigated the effect of three different thermal treatment temperatures (300°C, 500°C, and 750°C) for 30 minutes on the surface characteristics of commercially pure titanium. They found that the only effective thermal treatment for the commercially pure titanium was at 750°C for 30 minutes since it showed greater improvement in the surface characteristics, and cellular interactions of the TiO_2 layer.

The hypothesis for this research was that the surface properties of the titanium alloy changed as the time of heat treatment increased at 750°C. So, this study was aimed to investigate the effect of

different durations (30 minutes, 60 minutes, and 90 minutes) at the effective heat treatment temperature of 750°C on the surface topography, titanium oxide layer thickness (TiO_2), surface chemistry, contact angle, and diameter of blood drop of grade 5 titanium- aluminum- vanadium alloy (Ti-6Al-4V).

MATERIALS AND METHODS

Titanium disk shaped samples were prepared from grade 5 titanium- aluminum- vanadium alloy (Ti-6Al-4V) with dimensions of 6mm diameter and 1mm thickness, five samples for each test group. The sample surface was polished with silicon carbide grit paper 400 then 1200. After polishing, the sample was cleaned of any remaining particles generated during polishing. This was commenced by the use of acetone and ethanol for 10 minutes, and rinsed with deionized water between and after the application of each solvent.[18] All the samples were placed in a desiccator to eliminate any moisture and for storage.[17]

The samples were divided into four test groups; control group (**A**) received no treatment, group (**B**) was treated with 750°C for 30 minutes, group (**C**) was treated with 750°C for 60 minutes, and group (**D**) was treated with 750°C for 90 minutes. They were heated inside a heavy duty box furnace **(**CARBOLITE, Parsons Lane, Hope, England). The heat treated samples were immediately transferred to a desiccator until testing. During handling, the samples were carefully held at the disk edges with tweezers to avoid any damage and/or contamination of the sample surfaces.

Scanning electron microscope (SEM)

To assess the oxide layer thickness, test samples were embedded in cold cure acrylic resin and then cross-sectioned.[18] The surface topography and oxide layer thickness were observed by scanning electron microscopy (VEGA Easy Probe SEM ^{TM}).

X-ray diffraction (XRD)

The surface chemical composition of the titanium samples was analyzed by the study of the X-ray diffraction patterns generated by the X-ray diffractometer (XRD-6000 Shimadzu X-ray Diffractometer) for the titanium alloy samples.

Blood contact angle measurement

Blood was obtained from a male donor of 21 years of age and was immediately mixed with 3.8% sodium citrate and used for the blood contact angle measurement at room temperature.[19] A drop of blood of 2 µl volume was placed on the titanium disk sample with the use of an adjustable volume pipette of 0.5 – 10 µl to ensure a standard size of blood drop for all the samples. A picture was taken for the blood drop after 15, 30, 45, 60, and 75 seconds of placement on the disk sample surface. The measurement of the blood contact angle from the pictures was performed by the use of the Corel Draw X3 analyzing software.[16, 17]

Diameter of blood drop

A picture was taken for the blood drop on the surface of the titanium samples after 2 minutes of blood drop placement. The diameter was measured by recording the average of five different diameter measurements of the blood drop on the titanium sample surface. The measurement was carried out with the use of the software program Dimaxis version 2.3.3.

Statistical analysis

The data of the titanium oxide layer thickness, blood contact angle, and blood drop diameter for each test group was analyzed using the Statistical Package for Social Sciences (SPSS) version 17.0. Descriptive Statistics, One way analysis of variance (ANOVA) and least significant difference (LSD) test was used to assess the significant differences at a significance level of $p<.05$.

RESULTS

Surface topography

The surface topography of the test groups differed from that of the control group, as shown in figure (1). The surface of the test groups tended to be rougher and more irregular. The crystallites of the surface of the test groups were larger, rougher, & more tapered in shape and this increased with the increase of time of the heat treatment. This was contrary to the surface of the sample of the control group which was smaller, smoother, & more regular.

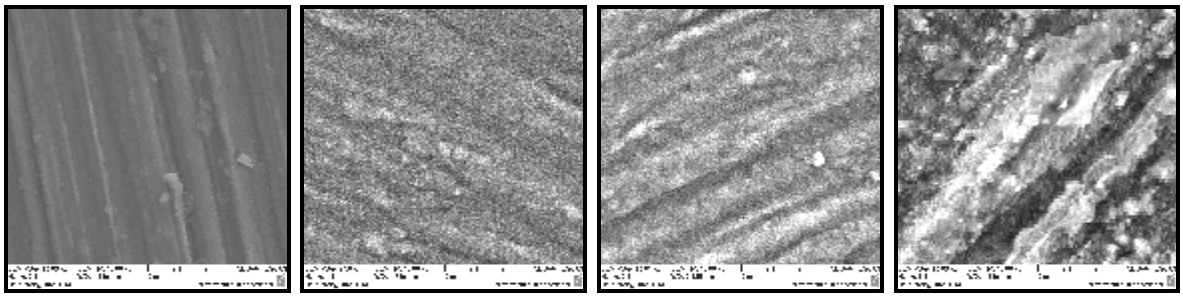

Figure 1. SEM images of the surface topography and morphology of the test groups A, B, C, &D from left to right respectively.

Thickness of titanium oxide layer

The SEM image of the cross sectioned samples of the test groups revealed that the greatest thickness was for group D (19.2µm) and the least was for the control group (1.6µm) (figures 2 & 3). The thickness of the titanium oxide layer increased highly significantly as the time of heat treatment increased ($p<0.01$)(table 1,2 & 3).

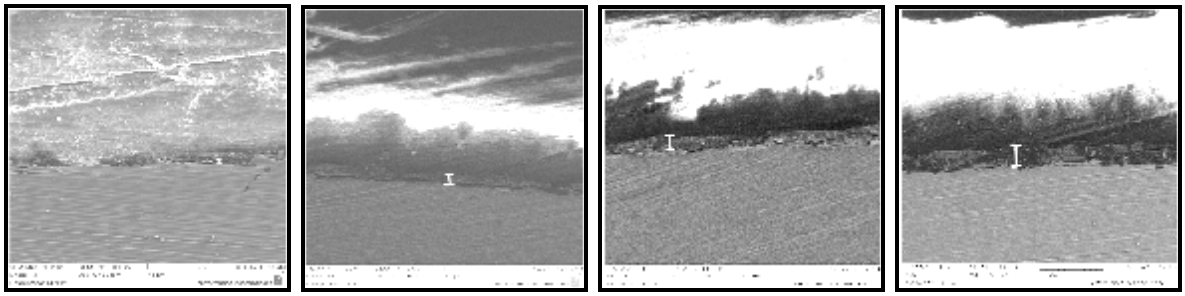

Figure 2. SEM image of the TiO_2 layer thickness of groups A, B, C, & D from left to right respectively.

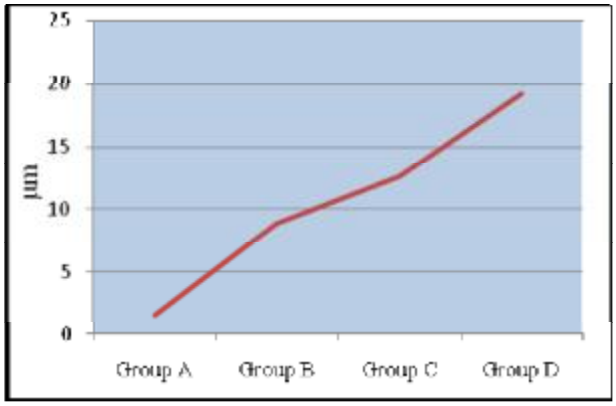

Figure 3.TiO_2 layer thickness (µm) for all test groups.

Table 1. Descriptive Statistics of the TiO_2 layer thickness (µm) for all test groups.

Test groups	N	Mean	S.D.
A	5	1.6340	0.35956
B	5	8.9340	0.76989
C	5	12.6660	1.06263
D	5	19.2140	1.98598

Table 2. One- way ANOVA of the TiO_2 layer thickness for all test groups

	Sum of Squares	df	Mean Square	F-test	Sig.
Between Groups	808.167	3	269.389	185.936	0.000
Within Groups	23.181	16	1.449		
Total	831.349	19			

Table 3. Multiple Comparisons LSD for the TiO_2 layer thickness (µm) for all test groups

Test groups	Mean Difference	S.E.	Sig.
A- B	-7.30000*	0.76127	0.000
A- C	-11.03200*	0.76127	0.000
A- D	-17.58000*	0.76127	0.000

*** The mean difference is significant at the 0.05 level.**

X- ray diffraction (XRD)

The X- ray diffraction patterns (figure 4) for the test groups when compared with the control group showed that the intensity of the XRD peaks of the test groups decreased, some peaks were eradicate, and new peaks were generated. The titanium peak was eradicated and the anatase and/or rutile phases appeared for all test groups.

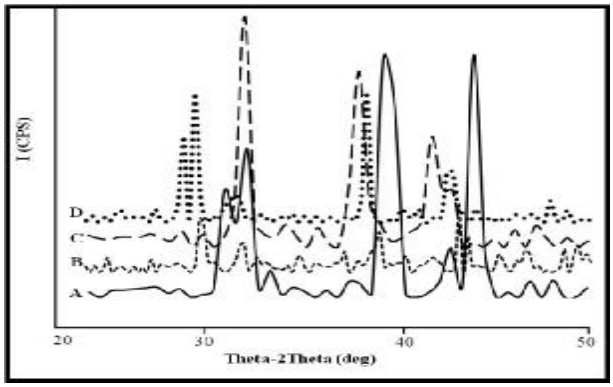

Figure 4. XRD patterns of test groups

Blood contact angle

The Blood contact angle of all test groups (figure 5 & 6) decreased with increase in the time of heat treatment. This change was highly statistically significant for all the test groups when compared with the control group ($p<0.01$) (table 4,5 & 6).

Figure 5. Blood contact angle for groups A, B, C, &D from left to right respectively.

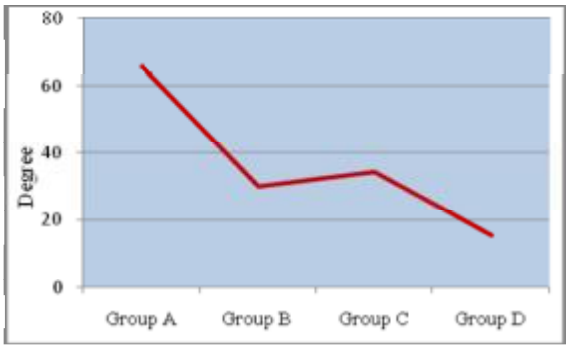

Figure 6. Blood contact angle for the test groups.

Table 4. Descriptive statistics for the blood contact angle (degree).

Test groups	N	Mean	S.D.
A	5	65.8500	5.39850
B	5	30.1000	1.75535
C	5	34.2500	1.82859
D	5	15.4000	1.40979

Table 5. One- way ANOVA test for the blood contact angle.

	Sum of Squares	df	Mean Square	F-test	Sig.
Between Groups	6763.075	3	2254.358	240.105	0.000
Within Groups	150.225	16	9.389		
Total	6913.300	19			

Table 6. LSD Multiple Comparisons for the blood contact angle(degree).

Test groups	Mean Difference	S.E.	Sig.
A- B	35.75000*	1.93794	.000
A- C	31.60000*	1.93794	.000
A- D	50.45000*	1.93794	.000

***The mean difference is significant at the 0.05 level.**

Diameter of blood drop

The diameter of blood drop formed on the surface of the samples of the test groups increased as the time of the heat treatment increased. The greatest diameter was for group D (3.9mm) while the smallest diameter was for the control group (2.2mm) (figure 7 & 8). Statistical analysis showed a highly significant increase in the diameter of blood drop for all test groups when compared with the control group ($p<0.01$) (table 7,8 & 9).

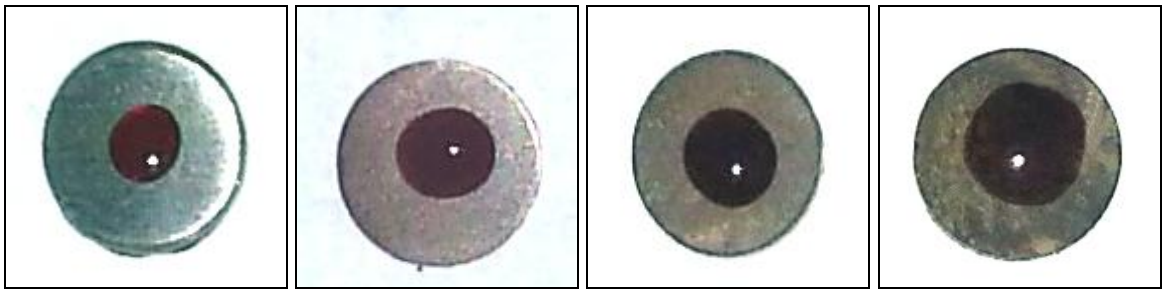

Figure 7. Diameter of blood drop for test groups A, B, C, & D from left to right respectively.

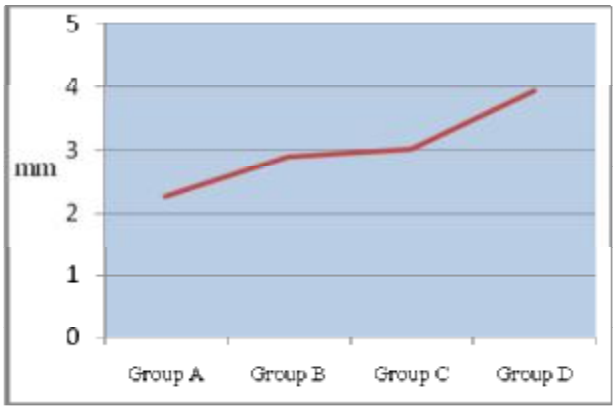

Figure 8. Diameter of blood drop for the test groups.

Table 7. Descriptive Statistics for the diameter of blood drop (mm).

Test groups	N	Mean	S.D.
A	5	2.2540	.09017
B	5	2.8980	.14184
C	5	3.0020	.10354
D	5	3.9340	.20107

Table 8. One- way ANOVA for the diameter of blood drop.

	Sum of Squares	df	Mean Square	F-test	Sig.
Between Groups	7.187	3	2.396	120.684	0.000
Within Groups	.318	16	.020		
Total	7.504	19			

Table 9. LSD test Multiple Comparisons for the diameter of blood drop (mm).

Test groups	Mean Difference	S.E.	Sig.
A- B	-.64400*	.08911	0.000
A- C	-.74800*	.08911	0.000
A- D	-1.68000*	.08911	0.000

***The mean difference is significant at the 0.05 level.**

DISCUSSION

The hypothesis that the surface properties of the titanium alloy enhanced as the time of heat treatment increased at 750°C temperature was accepted.

All the test groups showed a change in the surface properties of the titanium alloy including the surface topography, titanium oxide thickness, surface chemistry, blood contact angle, & blood drop diameter. The differences in these changes among the test groups, increased as the time of heat treatment increased, to reach the maximum readings for the samples with surface properties treated at 750°C for 90 minutes.

Surface topography and morphology of heat treated titanium alloy (figure 1) revealed an increase in the surface irregularities and a change in the shape and size of the surface crystals as the time of heat treatment increased; larger, rougher, & more tapered. The temperature of transition of titanium to an anatase/rutile phase was at 750°C for 30 minutes as stated by Lee et al.[18] and the sample were subjected to this temperature for more than that duration of time which may explain that this transition was more for those samples subjected for a longer duration of time. This transition may explain the increased changes in the surface topography and chemical composition as the heat treatment prolonged. The irregularities in the shape and change in the size of the crystal of heat treated titanium surface was also found by both Pookmanee & Phanichphant [20] and Ninsonti et al.[21] but at different temperatures and durations than that of this research.

The enhancement in the thickness of titanium oxide layer (figure 2) increased as the time of the heat treatment increased and this may be related to the enrichment of titanium matrix with oxygen, as the solubility of oxygen to the titanium matrix increased as the time of heat treatment of titanium alloy increased.[22,18] This may explain the improvement in the thickness of oxide layer which increased as the time of heat treatment increased.

The surface chemistry was analyzed by comparing the X- ray diffraction pattern of the control group with the patterns of the test groups (figure 4) and it showed a decrease in the intensity of the peaks related to the titanium alloy of the heat treated test groups and this may be related to the fact that the increase in thickness of the titanium oxide layer prevented the x-ray beam from penetrating completely to the alloy but rather was blocked partly by the oxide layer. This was confirmed by the SEM image of cross section of the test samples which revealed this increase in thickness of the oxide layer (figure 2), and this was in agreement with the results of MacDonald et al.[23] who stated that the heat treatment produced thick titanium oxide layers on the surface of the titanium alloy. Therefore the heat treated titanium alloy disk did not display a titanium or aluminum peak. New peaks were also generated in the X-ray diffraction patterns of the test groups when compared with the control group

and this was a result of transition of the alloy to the anatase/rutile phase as discussed previously. This agreed with the results of Lee et al.[18] in which they declared the appearance of additional peaks in the XRD patterns of heat treated titanium.

In this research, as the time of heat treatment of titanium alloy increased the blood contact angle decreased and the diameter of the blood drop increased to reach the best results at 750 °C for 90 minutes. This meant that there was an increase in the wettability and this is one of the vital implant surface factors that may influence osseointegration.[1,4] The increase in wettability and surface energy was attributed to the anatase/rutile phase transition that occurred at high temperatures and could affect the surface topography, surface irregularities, chemical structure, and crystal structure.[24, 25] Thus, in turn, increased the wettability and surface energy.[26]

The increase in titanium oxide layer, as discussed earlier, may be one of the reasons responsible for the increase in wettability of the test sample surfaces. The oxide layer of pure titanium exhibits a high surface energy, wettability, as stated by Tengvall & Lundstrom [27] and thus the increase in this layer may have attributed to an increase in the wettability of the test samples.

Surface roughness and surface topography may also have played a role in the increase in the wettability of heat treated titanium alloy sample surfaces as was declared by MacDonald et al.[23], Scharnweber et al.[28] and Rupp et al.[29]. They found that surface roughness of titanium was shown to have a significant influence on the wettability behavior of the titanium surfaces. This also confirms the results of this research in which the surface topography irregularities increased as the time of heat treatment increased.

Chemical structure changes may be another cause for the changes in the wettability of treated titanium as was confirmed by Turkyilmaz [1], Scharnweber et al.[28], and Pegueroles et al.[30]. This coincided with the results of this research which showed changes in the surface chemistry and was confirmed by the X-ray diffraction patterns.

As a conclusion, the surface properties of grade 5 titanium alloy improved as the time of heat treatment increased. The 750°C for 90 minutes showed the highest improvement in the surface topography, titanium oxide layer thickness, surface chemistry, blood contact angle, and blood drop diameter which in turn will lead to enhancement in the osseointegration of the dental implant.

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