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"EVALUATION AND COMPARISON OF SURFACE MODIFICATIONS OF COMMERCIALLY PURE GRADE-I TITANIUM BY COMBINATION TECHNIQUE OF BLASTING WITH ALUMINA FOLLOWED BY ACID ETCHING AND OXIDATION WITH NAOH "

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ABSTRACT:. The aim of this study is evaluate two different techniques of modification of titanium surface and to compare the surface roughness levels, surface wettability and surface configuration of variously treated surfaces of titanium (commercially pure titanium grade I). Commercially pure titanium (Grade I) sheets of 0.2mm thick and 4.5mm diameter are used for this study. Blasting of titanium with Alumina, combined with Acid etching using Hydrofluoric acid, Hydrochloric acid and sulfuric acid. And Oxidation treatment is done with Sodium hydroxide, Surface roughness levels were measured with the help of surface profilometer and surface analyzer. Surface wettability is measured with help of contact angle measurement using light microscope and surface configuration was determined with the help of scanning electron microscopy. Scanning electron microscopic studies concluded that samples with alumina blasting followed by acid etching revealed uniform rough configuration of the surface.

KEYWORDS: combination technique, oxidation treatment, surface wettability, surface roughness, surface configuration

INTRODUCTION

Branemark reported a scientific transition in the nature of interfacial screw-host bone behavior involving commercially pure titanium implants in 1977, and the field of dental implants entered new era of therapeutic possibilities. Since its beginning, modern implantology has held great promise for helping patients with compromised esthetics, speech, or masticatory function. As clinical studies documenting long term success with implants began to appear, more and more practitioners have embraced the new technology. The role of implant surface in determination of osseointegration has been recognized for many years. In 1990s several investigators pursued detailed investigation of the effect of surface topography on the extent of bone formation[1]. Dental implants' surface morphology, including micro geometry and roughness, has been shown to have a significant effect on implant integration. The surfaces of titanium dental implants have been modified by additive methods (titanium plasma spray) or by subtractive methods (acid-etching, sandblasting) to increase the surface area. Morphometric analysis have shown differences in bone –implant contact percentages with varying of surface characteristics as well as sensitivity of cells to surface microtopography[2].

Aim of the study

How can implant topography be represented or categorized is also important. Three-dimensional measures are needed to account for the isotropic deviations of topographic elements from the mean surface plane. Contacting instruments such as profilometer and non-contacting optic instruments are used for this purpose. Thus the aim of the study is

1. To evaluate combination and oxidation methods of surface modification of the titanium surface.
2. To compare the surface roughness level of variously treated surfaces of the titanium.
3. To measure the surface wettability of the variously treated surfaces of the titanium.
4. To determine the surface configuration of variously treated surfaces of titanium

Materials

1. Commercially pure titanium, ASTM grade I (99.7%Ti, 0.2%Fe,0.1%O2,o.o5%N) sheets of 0.2mm-thickness and 4×4.5 mm diameter. **(Fig.1.)**
2. Hydrofluoric acid 2%
3. Hydrochloric acid 10%

4. Sulfuric acid 10%
5. AL2O3 grains of 100 microns in size
6. NAOH 5.0M
7. Nitric acid 5%
8. Distilled water

Instruments

1. Glass measuring jars
2. Glass beakers
3. Glass pipettes
4. Artery forceps
5. Wooden tongue blade
6. Wooden frame
7. Motor and pestle

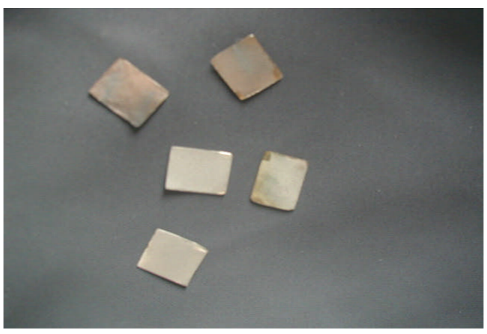


Fig.1. Titanium sheets of 4X4.5 mm

Fig.2. Blasting procedure

Fig.3. Acid etching procedure

Equipment

1. Sand blaster (M.S surgicals)
2. Vacuum furnace (Multimat, MACH2 DENTSPLY)
3. Ultrasonic cleaner
4. Perthometer (MAHR S2)
5. Surface analyzer (Vecco)
6. Optical microscope
7. Scanning electron microscopic machine (XL 30 SEM Phillips)
8. Incubator (TECHNICO)

Methods

Titanium plates of 4.5mm length X 4mm wide and 0.02mm thick are used for this study. Titanium plates are cut from the commercially pure (grade I) titanium sheet. All the twenty five plates were standardized to 4.5mm length X 4mm wide and 0.02mm thick and are ultrasonically cleaned before being subjected to following surface modifications

1. **Mechanical chemical group:**

Al^2O^3 blasting +Acid etching with 2% Hydrofluoric acid[2]

Alumina of 100 microns size particles is filled in the conventional sandblasting machine. Titanium sheet of 0.2mm-thickness and 4×4.5 mm diameter is fixed in the wooden frame that is specially made to hold the specimens. The wooden frame along with, the specimen, are held 5cm away from the blasting tip and blasting of the surface is done on both sides for 10 minutes at 80 Lb pressure. Following which ultrasonic cleaning of the sample is done. The cleaned sample is etched with 2% hydrofluoric acid by placing it in the beaker containing acid for 10 minutes **(Fig.2.)**

Al^2O^3 blasting +Acid etching with 20% Hydrochloric acid and sulfuric acid[3]:

Alumina of 100 microns size particles is filled in the conventional sandblasting machine. Titanium sheet of 0.2mm-thickness and 4×4.5 mm diameter is fixed in the wooden frame that is specially made to hold the specimens. The wooden frame, along with the specimen, are held 5cm away from the blasting tip and blasting of the surface is done on both sides for 10 minutes at 80 Lb pressure. Following which ultrasonic cleaning of the samples done. The cleaned sample is etched with by placing it in the beaker containing 20% of Hydrochloric acid and sulfuric acid for 10 minutes.

Fig.4. Surface profilometer


Fig.5. Surface analyzer


Fig.6. contact angle measured with optical microscope is shown on the computer screen attached to it

$Al^{2}O^{3}$ blasting +Acid etching with heat-treated 20% Hydrochloric acid and sulfuric acid[4]:

Alumina of 100microns size particles is filled in the conventional sandblasting machine. Titanium sheet of 0.2mm-thickness and 4×4.5 mm diameter is fixed in the wooden frame that is specially made to hold the specimens. The specimen is fixed in a wooden frame is held 5cm away from the blasting tip and blasting of the surface is done on both sides for 10 minutes at 80 Lb pressure. Following which ultrasonic cleaning of the sample is done. And the sample is placed test tube containing acid is heated on the direct flame intermittently for 10 minutes.

2. **Oxidation treatment group[5]:**

NAOH solution of 5.0M is prepared. The samples are soaked in the prepared in NAOH solution is kept in the incubator at 60 degree centigrade for 24 hours followed cleaning with distilled water and it is air dried in air atmosphere for 40 degree centigrade for 24 hours the substrate is heated to 600 degree centigrade in vacuum furnace at the rate of 5 degree rise in centigrade for every minute for 1 hour and allowed to cool to room temperature.

3. **Chemical and oxidation treatment group[5]:**

Treatment of surface with $HF/HNO^{3}/H^{2}O$ (1/1/1) followed by NAOH Treatment

Nitric acid and hydrofluoric acid 5% is prepared by adding 5 ml of concentrated acid to 95 ml of water. One part of nitric acid and one part of hydrofluoric acid with two parts of water is taken in the glass beaker. The titanium sheets are etched with this solution for 1 minute followed by NAOH treatment. **(Fig.3.)**

3. Methods of Measuring Surface Roughness

Surface Profilometry[6]: Contact profilometry is method of measuring the surface texture of a materi**al.** MAHR Perthometer (S2) a surface textures measuring and recording instrument is used for this purpose**.(Fig.4)**

Parts:

1. Stylus
2. Tracing head
3. Block made of metal
4. Microprocessor

The titanium sheets are positioned in the flat block made of metal, and stylus is attached to the tracing head.

All the samples were cleaned with distilled water in an ultrasonic cleaner for this study. The stylus is kept in contact with the long axis of the titanium sheets with

Table-I. **Results for surface roughness measurements using surface profilometer**

Surface Modified Samples	Sample 1 Ra	Sample 2 Ra	Sample 3 Ra	Sample 4 Ra	Sample 5 Ra	Mean Ra
GROUP 1	0.412µm	0.464µm	0.498µm	0.563µm	0.590µm	1.7452
GROUP 2	0.197µm	0.360µm	0.290µm	0.370µm	0.212µm	1.7944
GROUP 3	0.256µm	0.274µm	0.296µm	0.264µm	0.271µm	1.8042
GROUP 4	0.197µm	0.164µm	0.186µm	0.192µm	0.164µm	0.5054
GROUP 5	0.185µm	0.196µm	0.184µm	0.210µm	0.195µm	0.2872

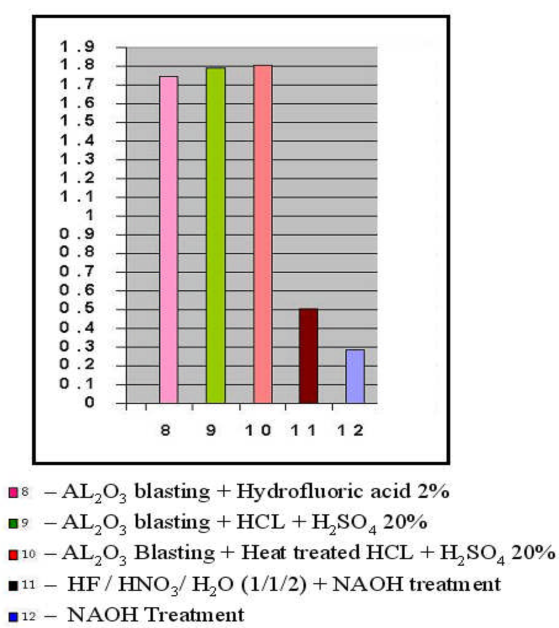
Table-II. **Results for surface roughness measurements using surface analyzer**

Modification of the surface	Sample 1 Ra	Sample 2 Ra	Sample 3 Ra	Sample 4 Ra	Sample 5 Ra	Mean Ra
GROUP 1	440.70ηm	563.60ηm	486.68ηm	610.12ηm	590.82ηm	538.384
GROUP 2	459.80ηm	570.60ηm	650.91ηm	590.25ηm	660.40ηm	586.392
GROUP 3	661.25ηm	739.80ηm	680.25ηm	654.81ηm	560.14ηm	659.250
GROUP 4	94.60ηm	106.74ηm	139.80ηm	146.00ηm	139.64ηm	125.496
GROUP 5	124.08ηm	112.06ηm	180.07ηm	156.12ηm	160.11ηm	146.488

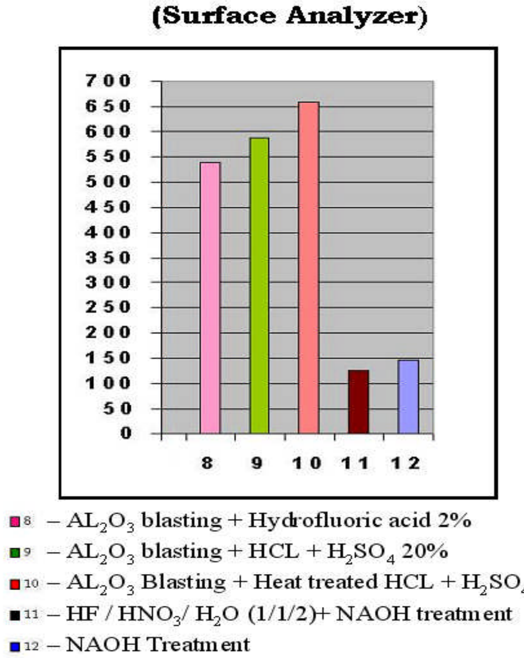
Table-III. Results for surface wettability measurements using contact angle measurement

Modification of the surface	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Mean contact angle
GROUP 1	95°	114°	85°	106°	96°	99.38
GROUP 2	117°	107°	113°	100°	97°	107.16
GROUP 3	105°	107°	98°	99°	97°	101.50
GROUP 4	80°	65°	68°	76°	68°	71.40
GROUP 5	90°	80°	65°	70°	60°	73.00

Graph – 1
Roughness Measurement
(Surface Profilometer)



Graph – 2
Roughness Measurement
(Surface Analyzer)



various surface treatments and recordings were made for average 3.8mm length of all the sheets and microprocessor gives calculations and recordings of the surface roughness. Average Roughness (Ra): is the arithmetic mean of all values of the roughness profile 'R' with the measuring length lm. **(Graph.1)**

Surface Analysis[6]:

It is a non-contacting method of recording the surface of the substrate. Ultrasonically cleaned samples were placed on the plat form and surface topography is measured under 10^{-9} magnification and the computer image of the surface is made. The measurements of the roughness parameters are calculated by the microprocessor. **(Fig.5.) (Graph.2)**

Scanning Electron Microscopy[4]

The surface topography of all the surface modified samples is studied by coating it with gold and scanning them under the scanning electron microscope at high magnifications (500x, 2000x).

4. Method of Measuring Surface Wettability

Contact Angle Measurement[7]: One drop of distilled water was deposited on the surface of the modified sample, with the help of optical microscope **(Fig.6.)** two observers measured and calculated the contact angles of three drops of water for each sample. The contact angles are obtained by following equation

$$\theta = \tan^{-1}(2h/d)$$

Total specimens were divided in to five groups according to the surface modification. And 5 samples were done for each group.

Group 1: AL_2O_3 blasting + Hydrofluoric acid 2%
Group 2: AL_2O_3 blasting + HCL + H_2SO_4 20%
Group 3: AL_2O_3 Blasting + Heat treated HCL + H_2SO_4 20%
Group 4: HF / HNO_3/ H_2O (1/1/2) + NAOH treatment
Group 5: NAOH Treatment

Roughness average (Ra) and contact angle was totally measured for 60 samples.

Statistical Analysis

The statistical package SPSS-PC+(Statistical package for social science, version 4.0.1) was used for statistical analysis. Mean was estimated for all the five samples for each study group. The mean values were compared by One way analysis for variance. Mean value is calculated by using this formula:

$$\text{Mean} = \frac{\sum x}{n}$$

$\Sigma\chi$= Sum of total readings for group
n= number of specimens

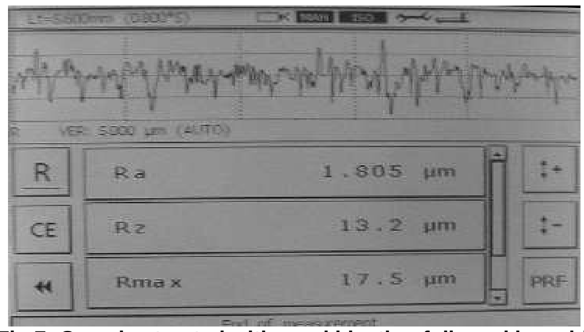


Fig.7. Samples treated with sand blasting followed by acid etching with combination of 20% HCLandH_2SO4 showing higher roughness average(Ra) values

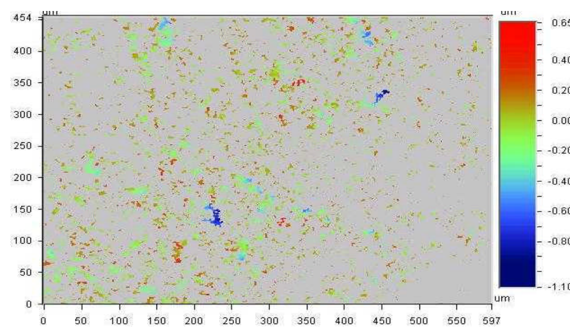


Fig.8. The image of sample treated with sand blasting revealing the deeper red and shallow green depressions and blue elevations on the surface

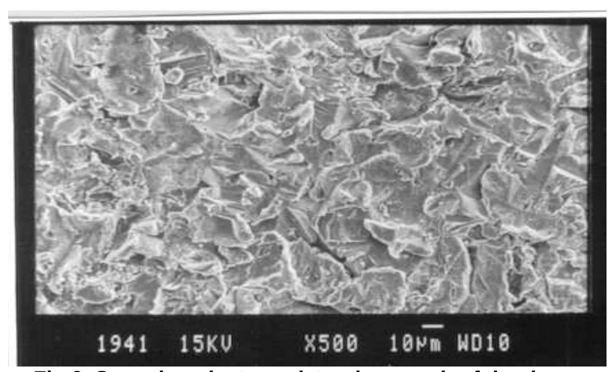


Fig.9. Scanning electron pictomicrograph of titanium surface blasted with alumina followed by etching with HCLandH_2SO4 showing an uniform surface.

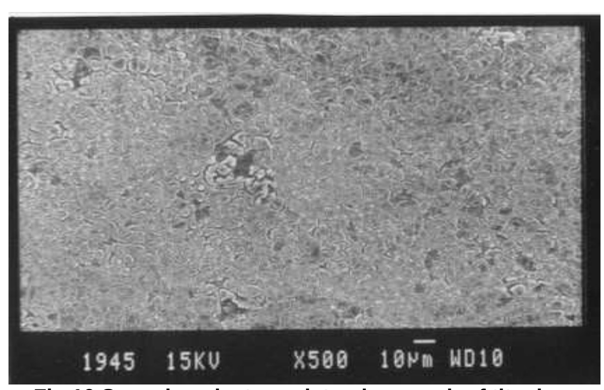


Fig.10.Scanning electron pictomicrograph of titanium surface treated with NAOH showing an uniform coating formed on the surface

Results

Results for surface roughness measurements using surface profilometer and surface analyzer are tabulated**.(Table.I and Table 2.)** Results for surface wettability measurements using contact angle measurement are tabulated **(Table.3).** Contact angle measurement will indicate the surface wettability of the samples**.(Table-3 , Graph-3)**

The surface roughness measurements with the help of surface analyzer revealed that samples treated dual etching with hydrochloric acid and sulfuric acid showed highest mean roughness values.**(Fig.7. and Fig.8)** The contact angle measurement revealed that samples blasted with biphasic material (TCP +HA) and treated with 2% hydrofluoric acid a showed lowest contact angle measurement**.(Table.3)**

Discussion

Implant surface technology is considered as Alternative Avenue for improving osseointegration. Implant features significantly influences the formation and maintenance of bone at implant surface.

The objective of this study is evaluating different methods of modification of the surface modifications of the titanium surfaces and comparing the roughness value, and surface wettability of variously treated samples.

Advantages of increased surface roughness on commercially pure titanium surfaces[8]:

1. Increased surface area of the implant adjacent to bone
2. Improved cell attachment to the implant surface
3. Increased bone present at the interface
4. Increased biomechanical interaction of the implant with the bone (surface area reduces stress next to the implant)

An increase in surface area is one mechanism to reduce stress next to the implant because stress equals force divided by the area. However increasing surface area as a goal of engineering may represent a limited approach to improving implant bone relation available. Clinical evaluations do not indicate the negative effects of rough surface implants on clinical or radiographic measures of performance.

There are two ways to modify the surface layer. Creation of convex, or concave texture. Additive treatments such as plasma spray coating of Hydroxyapatite particles or titanium beads or physical or chemical vapor depositions create convex surface morphology. It is possible that deposited particles can fracture from the surface. In contrast, mechanical treatments such as sand blasting or chemical treatments with acid or alkaline can create a concave surface.

This research project dealt with mainly with concave surface modification.

Various methods of surface modifications of the titanium surface: [53]

I. Mechanical chemical group:
Combination of Acid etching and Sand blasting

1. AL2O3 blasting +acid etching with 2% Hydrofluoric acid
2. AL2O3 blasting +acid etching with 20% Hydrochloric acid and sulfuric acid
3. AL2O3 blasting +acid etching with heat activated 20% Hydrochloric acid and sulfuric acid

II. Oxidation treatment group:

1. Treatment of sodium hydroxide followed by in air oxidation at 600 °C for 1 hour.

III. **Chemical oxidation treatment group:**

1. Treatment of surface with HF/HNO3/H2O (1/1/1) followed by NAOH Treatment.

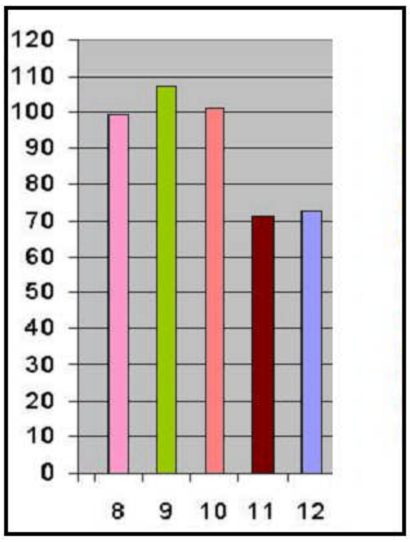
The surface modification was done in above-mentioned five different ways for five samples.

Huyn Min Kim[5] and coworkers determined a method of modifying the surface with sodium hydroxide to improve the bone implant contact. Based on this the treatment of titanium with 5.0 M of NAOH treatment is done .The scanning electron photo micrographs showed a uniform layer of sodium titanate and, these samples also showed lowest contact angle measurement.

Measurement of wettability of a surface, expressed by the contact angle, might be predictive index of cytocompatibility. Cell adhesion to and spreading on a biomaterial are dependent among, other factors on the surface wettability of the biomaterial; therefore the surface roughness affects wettability. W. Aubreysoskolne[9] stated that cell adherence to rough titanium surfaces is greater than to the machines surfaces and Lyndon F.Cooper[8] stated that increased titanium surface topography improves the bone to implant contact and the mechanical properties of the enhanced interface, growing clinical evidence for increased bone to implant contact at altered implant surface confirms the advantages of the increased functional area.

The surface modifications of the titanium found to increase the surface area of titanium that would result greater surface coverage by bone. The contact angle representing the surface wettability also affects the bone implant contact.

Graph – 3
Contact Angle Measurement



8 – AL_2O_3 blasting + Hydrofluoric acid 2%
9 – AL_2O_3 blasting + HCL + H_2SO_4 20%
10 – AL_2O_3 Blasting + Heat treated HCL + H_2SO_4 20%
11 – HF / HNO_3/ H_2O(1/1/2)+ NAOH
12 – NAOH Treatment

Carl E. Misch [10]concluded that functional surface area is inversely proportional to the stress next to the implant. Increase in the surface area results in decrease in stress next to the implant.

Summary

This study evaluated different methods of surface modifications of the titanium and compared the surface roughness and surface wettability of variously treated surfaces of titanium.

Titanium substrate with following treatments such as Blasting with alumina (100µ), Blasting followed by acid etching with HCL and H_2SO_4 and Blasting followed by dual etching with heat treated HCL and H_2SO_4 Showed highest surface roughness values. Along with the above mentioned surface modified samples, surface blasted with biphasic material (combination of Hydroxyapatite and tricalcium phosphate) showed uniform rougher surface in scanning electron pictomicrograph. **(Fig.9. and Fig.10.)**

Measurement of the wettability of the surface is expressed by the contact angle. Samples treated with 5.0M NAOH treatment at 600^{0}C for one hour and samples treated with Hydrofluoric acid, Nitric acid and Water (1/1/2) followed by NAOH treatment at 600^{0}C for one hour and those treated with Hydrofluoric acid 2% showed lowest contact angle Measurements.

CONCLUSION

1. The surface roughness measurements with the help of surface profilometer and surface analyzer revealed that samples treated with blasting with alumina and combination treatment including blasting with alumina followed by acid treatment with HCL and H_2SO_4 showed highest mean roughness values.
2. The scanning electron photomicrographs showed that samples blasted with alumina and biphasic material, and samples blasted with alumina followed by acid etching showed uniform rough configurations of the surface.
3. The contact angle measurement revealed that samples treated with 2% hydrofluoric acid and Hydrofluoric acid, Nitric acid and Water (1/1/2) treatment followed by NAOH showed lowest contact angle measurement.

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