Studying the effect of surface conditioning on the corrosion performance of titanium dental implants

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Abstract. The biocompatibility of dental implants is dependent on good interaction between implant-human body tissue and a good osseointegration. The surface roughness plays an important role enhancing bone healing and promoting biomechanical properties at the bone/implant interface. The increase in surface roughness can simultaneously improve cell migration and attachment of an implant, and enhance the osseointegration process. However surface roughness has shown to be detrimental to corrosion, raising the need to achieve a balance between good osseointegration and corrosion performance. This study characterised the corrosion performance of commercially pure titanium grade 4 with different surface conditionings. Implants in the form of 15 mm discs and implant screws were tested in basic Ringers lactate solution of pH 5.5 at 37°C and in modified Ringers of pH 2. Corrosion tests included open circuit potential (OCP), potentiodynamic polarization test (PDP) and mass loss corrosion tests. Metallurgical characterisation showed that titanium Grade 4 consisted of equiaxed alpha (α-Ti) grains. The OCP test showed that the machined implants were nobler than the roughened implants. The corrosion rates obtained were very low, below 0.13 mm/y which is an acceptable corrosion rate for biomaterial design and application. Mass-loss tests showed that the alloys passivated regardless of the surface conditioning. The machined surface had a corrosion resistance higher than that of the roughened surface finish in all conditions.

1. Introduction
Dental implants made of titanium, especially commercially pure titanium, have become a well-established treatment modality for the replacement of missing teeth and are state of the art in the field of dental restoration [1]. The concept of osseointegration was introduced by Branemark in the mid 1960’s [2]. Osseointegration is defined as a direct structural and functional connection between ordered, living bone and the surface of a load-carrying implant. It is critical for implant stability, and is considered a prerequisite for implant loading and long-term clinical success of end osseous dental implants [3].

In order to improve the speed and strength of bone formation and to allow more rapid loading of the implants, researchers have investigated the effects of modifying implant surfaces. The surface modification is considered to start from the topographical change of the surface or increasing the roughness of the titanium surface [1]. Surface roughness has an important role in enhancing bone healing and promoting biomechanical properties at the bone/implant interface through increasing the mechanical retention and allowing good stress distribution [4]. Rough surfaces are often used in clinical situations where acceleration and enhancement of osseointegration and bone interlocking is required such as in cases with poor bone quality or reduced bone volume. Based on current knowledge smooth implants are
those with an average roughness of $S_a$ less than 0.5µm, minimally rough implants have a $S_a$ 0.5-1µm, moderately rough implants have a $S_a$ 1-2µm and rough implants have a $S_a$ above 2µm [2].

Alumina ($\text{Al}_2\text{O}_3$) is frequently used as a blasting material and produces surface roughness varying with the granulometry of the blasting media [5], [6]. However, the blasting material is often embedded into the implant surface and residue remains even after ultrasonic cleaning, acid passivation and sterilization. Alumina is insoluble in acid and is thus hard to remove from the titanium surface. In some cases, these particles have been released into the surrounding tissues and have interfered with the osseointegration of the implants. Moreover, this chemical heterogeneity of the implant surface may decrease the excellent corrosion resistance of titanium in a physiological environment [5].

The aim of this study is to characterise the corrosion performance of a machined and roughened surfaces of a commercially pure titanium grade 4.

2. Materials and Experimental Procedure

2.1 Material and Implants Preparation

Commercially pure titanium grade 4 was selected for this study because titanium has been the material of choice in several disciplines of dentistry. Titanium has excellent characteristics such as biocompatibility, osseointegration, high wear and corrosion resistance, low compatibility issues and high strength. Recent attention has been directed towards further development of this material. Table 1 shows the chemical composition of titanium grade 4.

For this study two surface treatments were selected namely machined, and roughened. The roughened samples were prepared by $\text{Al}_2\text{O}_3$ blasting. Implants are usually blasted and then etched with acids such as hydrochloric, sulphuric, hydrofluoric and nitric acid. The acid attack on the surface of the dental implants results in uniform roughness with pits and craters of micrometric size, this leads to an increase in surface area. These pores enhance bioadhesion and the osteoblasts properties [2]. Each manufacturer has its own method of acid etching, by controlling the temperature, exposure time and concentration of acids.

All the samples were machined, roughened (not acid etched) and sterilised by Southern Implants (PTY) LTD. The discs were 15 mm in diameter and 2 mm thick; whereas the implants tested were one of their standard products, see Figure 1. The surface area of the implant was reported to be 414.15 mm².

| Elements (wt %) | N | C | O | Fe | Ti |
|---------------|---|---|---|----|----|
|               | 0.05% max | 0.08% max | 0.4% max | 0.5% max | Rem/balance |
Figure 1. Roughened samples in the as-received condition (a) discs (b) implants.

2.2 Material Characterisation
A metallurgical characterisation was performed on each type of surface treatment to study the basic features or reference condition of each surface treatment before corrosion testing. The samples were characterized using both optical and electronic characterization techniques.

2.2.1 Chemical Analysis
The discs were analysed in the as-received condition using a Zeiss EVO-MA15 scanning electron microscope (SEM) fitted with Bruker energy dispersive spectroscopy (EDS) detector. EDS is a chemical microanalysis technique used in conjunction with scanning electron microscopy (SEM) for the elemental analysis or chemical characterization of a sample. Thus it gives a local elemental composition of the sample.

2.2.2 Phase Analysis
The discs were analysed in the as-received condition using a Bruker D8 Advance powder diffractometer, with Linxeye detector with Fe filtered Co-K alpha radiation. This method makes use of the net intensity of the main peaks of the phases, and identification is based on the crystal structure of phases that occur in amounts of greater than 3 mass %. The EVA software was used to identify the phases. Amorphous phases are not detected and the phases specified may not necessarily reflect the actual composition of phases identified.

2.2.3 Metallography
The discs were sectioned and mounted in an epoxy resin, ground and polished to a 1μm surface finish. The implants were then etched with Kroll’s reagent (3 mL HF, 6 mL HNO₃ and 100 mL H₂O) to reveal their microstructures. This was performed to confirm the condition of the implants. Optical micrographs were taken at 2219x and 1109x magnification.

3. Corrosion Testing
The corrosion tests were performed in a basic Ringers lactate solution at 37°C, which is frequently used in in vitro experiments on organs or tissues. Several situations can acidify the pH of saliva such as infections, certain foods (sugary food, pickled foods, sour candies, fruits, soft drinks and juices), mouthwash products, smoking, chronic/systemic diseases and medication, may also contribute to the corrosion of dental implants [7]. In an effort to simulate this aggressive nature of the mouth it was decided to also perform tests in modified Ringers lactate solutions with respect to pH and sulphide (S²⁻) content. Sulphide was included in the study because sulphur products are of particular concern in regards to titanium dental implants because periodontopathic bacteria secretes considerable amounts of
sulphide by products, such as hydrogen sulphide (H₂S), methylmercaptan (CH₃SH), and dimethyl sulphide ((CH₃)₂S), as a result of their metabolism [8].

The pH was adjusted using sulphuric acid (H₂SO₄) while the addition of sulphide was obtained by an addition of sodium sulphide (Na₂S). Table 2 below shows the chemical composition of the Ringer’s lactate solutions used.

Table 2. Chemical composition of the solutions.

| Solutions | Sodium chloride (NaCl) | Potassium chloride (KCl) | Calcium chloride dihydrate (CaCl₂.2H₂O) | Sodium lactate (NaC₃H₅O₃) | Sulphide (S²⁻) | pH |
|-----------|------------------------|--------------------------|------------------------------------------|---------------------------|----------------|----|
| Solution 1| 30g                    | 0.3g                     | 0.2g                                     | 3.1g                      | -              | 5.5|
| Solution 2| 30g                    | 0.3g                     | 0.2g                                     | 3.1g                      | -              | 2  |
| Solution 3| 30g                    | 0.3g                     | 0.2g                                     | 3.1g                      | 0.5ppm         | 2  |

3.1 Electrochemical Testing

Two electrochemical corrosion tests were performed on the discs to assess and study the effect of different surface treatments. All the tests were performed at 37°C (body temperature, in the three Ringers lactate solutions detailed.

PC driven “ACM Gill AC” potentiostat was used to perform the electrochemical tests. The 10 mm discs were inserted in a sealed PVC holder. One graphite rod acted as a counter-electrode and a Haber-Luggin capillary made the junction with a saturated calomel reference electrode (SCE). Figure 2 shows the corrosion test set-up. All potential values are with respect to the SCE. Nitrogen was bubbled continuously through the solution during testing to create an anaerobic environment around a dental implant simulating that experience in the mouth.

3.1.1 Open circuit potential (OCP)

The open circuit potential (OCP) also known as the corrosion potential was determined by measuring the voltage difference between the electrodes immersed in the solution with respect to a standard saturated calomel reference electrode. The electrodes were immersed in the solutions and the potential
was recorded as a function of time. The OCP was recorded at four hours when the potential was stable (at equilibrium).

3.1.2 Potentiodynamic polarization test (PDP)

When the OCP was stable the potentiodynamic polarisation tests were recorded for each surface treatment. During these tests the potential of the treated sample is manipulated while measuring the current response. Each scan was stated after the OCP was recorded from −250 mV to +1500 mV versus the corrosion potential at a scanning speed of 10 mV/min. The corrosion current densities were determined by Tafel extrapolation of the rate-determining segment of the polarisation curve, and the corrosion rate was calculated by introducing the values of density and equivalent weight.

3.2 Mass-Loss Testing

Mass-loss corrosion tests were performed to assess the corrosion performance of the actual implants. To simulate the crevice conditions an implant would experience in the jaw, a crevice former was made using cast-able mounting resin, see Figure 3. This resin is non-metallic and inert, and would not chemically respond to the environment. Eight implants were exposed fully immersed in each solution in separate beakers to prevent contamination. The tests were performed for 30 days while maintaining the temperature at 37°C with the aid of a water bath.

![Figure 3. Implants crevice set-up.](image-url)

4. Results and Discussion

4.1 Material characterisation

4.1.1 Chemical Analysis

Figure 4 shows the SEM micrographs of the machined discs. The machined implants showed striations on the surface due to the machining process while the roughened samples had a granular appearance. The EDS spectra, see Figure 5, shows that the roughened surface was contaminated with an aluminium oxide phase, where the machined sample was purely titanium.
4.1.2 Phase Analysis

Figure 6 shows the XRD pattern of a machined and roughened discs. The XRD pattern confirmed the EDS analysis and showed that the machined sample contained only titanium (α-Ti), where the roughened sample also showed TiO₂ and Al₂O₃. The Al₂O₃ phase probably originates from the blasting materials during roughening and the TiO₂ was probably due to a passivation response on the implants surface.
4.1.3 Metallography

Figure 7 shows the cross section of the discs. The machined disc had a smooth surface while the roughened showed a rough surface due to alumina blasting. Figure 8 show the micrograph of the implants in the as-etched condition. The microstructure consisted of equiaxed alpha (α) grains in an annealed condition.

Figure 7. Implants showing the cross section of the disc implants at 2219x magnification (a) machined (b) roughened.

Figure 8. Titanium grade 4 micrograph showing equiaxed α grains at 1109x magnification.
4.2 Electrochemical Testing

4.2.1 Open Circuit Potential

The dynamic behaviour of the passive oxide film can be monitored by measuring the variation of open circuit potential with time, which reflects the thinning or thickening of oxide film for passive metals [9]. The OCP shift in the noble direction for the alloys suggests the formation of a passive film that reduces the corrosion rate. The OCP recorded was the last measurement after four hours. Figure 9 shows a graphical representation of the OCP results and Table 3 shows the detailed results. At four hours the OCP of the samples stabilised although the roughened showed an initial decrease in OCP. This indicates a breaking/dissolution of the air oxide film that was formed on the exposed surfaces due to the atmosphere, and could also be as a result of the aluminium contamination on the surface of the samples. The presence of the aluminium on the roughened samples also decreased the OCP as compared to the machined titanium.

![Figure 9. OCP plots in all solutions.](image)

Table 3. OCP results

| Samples    | OCP (mV)                        |
|------------|---------------------------------|
|            | Ringers pH 5.5                   | Ringers pH 2 | Ringers pH 2+S |
| Machined   | 63                              | 85           | 11             |
|            | 150                             | 97           | 28             |
| Roughened  | -241                            | 32           | -292           |
|            | -302                            | -306         | -106           |

4.2.2 Potentiodynamic Polarization Test

Figure 10 shows a graphical representation of the corrosion rates obtained while Table 4 gives the overall results. The Potentiodynamic polarisation test showed that corrosion rates obtained were very low, below 0.13mm/y which is an acceptable corrosion rate for biomaterial design and application [10]. Figure 11 shows the potentiodynamic polarisation scans.

Higher corrosion rates were observed in both the pH 2 and pH 2+S\(^2\) solutions, and the effect was more pronounced on the roughened samples. The decrease in pH had little effect on the corrosion performance of the machined sample, however with the addition of sulphide S\(^-\) the corrosion rate increased.
significantly. The roughened samples showed significantly higher corrosion rates as compared to the machined samples. All samples showed an active to passive behaviour, and no pitting breakdown was observed.

Figure 10. Graphical representation of the corrosion rates of the alloys in all solutions.

Figure 11. Plot of potential against the current.
Table 4. Potentiodynamic polarisation corrosion rates of the alloys in all solutions.

| Samples       | E_{corr} (mV SCE) | i_{corr} (mA/cm²) | Av. Corrosion rates (mm/y) |
|---------------|-------------------|-------------------|---------------------------|
|               |                   |                   | Individual | Average |
| Ringers pH 5.5|                   |                   |            |         |
| Machined      | -296              | 5.1 x 10⁻⁵         | 0.0005     | 0.0004  |
|               | -374              | 3.5 x 10⁻⁵         | 0.0003     |         |
| Roughened     | -35               | 4.7 x 10⁻⁵         | 0.0004     |         |
|               | 87                | 1.4 x 10⁻⁴         | 0.0013     | 0.0008  |
| Ringers pH 2  |                   |                   |            |         |
| Machined      | 37                | 3.2 x 10⁻⁵         | 0.0003     | 0.0003  |
|               | 60                | 3.7 x 10⁻⁴         | 0.0003     |         |
| Roughened     | 27                | 2.6 x 10⁻⁴         | 0.0023     |         |
|               | -379              | 1.3 x 10⁻³         | 0.0120     | 0.0018  |
| Ringers pH 2+S²|                   |                   |            |         |
| Machined      | -346              | 1.8 x 10⁻⁴         | 0.0016     |         |
|               | -244              | 1.4 x 10⁻⁴         | 0.0013     |         |
| Roughened     | -62               | 7.2 x 10⁻⁵         | 0.0006     | 0.0016  |
|               | 2                 | 2.8 x 10⁻⁴         | 0.0025     |         |

4.3 Mass-loss Testing
Mass-loss evaluations were performed after 7 and 30 days exposure. The corrosion rates were determined based on the mass-loss incurred during the exposure and the average corrosion rates were calculated, see Table 5. The corrosion rates obtained were very low in both 7 and 30 days exposure, less than 0.02mm/y indicating that the alloys tested were in the fully passive condition. Figure 12 shows the implants after testing. No change in colour/discolouration was observed on the surface of the implants after exposure.

Table 5. Mass-loss corrosion rates in all solutions.

| Sample       | Time (Hours) | Corrosion rates Av. (mm/y) |
|--------------|--------------|----------------------------|
|              |              | Individual | Average |
| Ringers      | 168          | <0.02      | <0.02   |
|              | 720          | <0.02      | <0.02   |
| Roughened    | 168          | <0.02      | <0.02   |
|              | 720          | <0.02      | <0.02   |
| Ringers pH 2 | 168          | <0.02      | <0.02   |
|              | 720          | <0.02      | <0.02   |
| Roughened    | 168          | <0.02      | <0.02   |
|              | 720          | <0.02      | <0.02   |
| Ringers pH 2+S²| 168      | <0.02      | <0.02   |
| Roughened    | 168          | <0.02      | <0.02   |
|              | 720          | <0.02      | <0.02   |
5. Conclusions
The aim of this study is to characterise the corrosion performance of a machined and roughened surfaces of a commercially pure titanium grade 4. The following can be concluded:

- Metallography showed that the implants consisted of equiaxed alpha (α) grains in an annealed condition.
- The chemical composition and phase analysis showed that the machined implants consisted of titanium while the roughened implants showed a presence of aluminium particles embedded in the titanium matrix during the roughening process.
- The corrosion performance of Grade 4 titanium with machined and surface roughening were studied in standard and experimental ringers solutions. Although the implants performed quite well in the 30 day mass loss tests it is evident that longer exposure periods are required to effectively measure the effect of the surface roughness on the corrosion performance. These tests may take years, given examples from human trials.
- The electrochemical corrosion tests did however measure a significant difference in the corrosion performance of the machined and roughened samples. The increase in corrosion rate of the roughened samples can be attributed to both surface roughness and contamination of Al₂O₃ on the surface. The presence of this Al₂O₃ and TiO₂ played a significant role.
- Using electrochemistry it also determined that small changes in the environment pH and sulphide can have a significant influence on corrosion, where the sulphide addition has a larger influence on corrosion than the pH reduction, specifically related to the machined samples.

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7 References

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