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## The Effects of Surface Roughening Techniques on Surface and Electrochemical Properties of Ti Implants

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#### Abstract

This chapter deals with the effect of commonly used surface roughening techniques for rapid osseointegration on surface and electrochemical properties of dental implants. Dental implants prepared by smooth machining (MAC), double acid etching (DAE), sandblasting and acid etching (SLA), Ti plasma spray (TPS) and anodization (ANO) were included, and their electrochemical properties were compared to untreated commercially pure titanium (cpTi). The treated surfaces demonstrated great differences in surface roughness, morphology, elemental composition and oxide type. Open circuit potential (OCP) and anodic scan potentiodynamic curves showed that electrochemical properties of treated surfaces are inferior to untreated cpTi in an original Ringer's solution and a Ringer's solution enriched with NaF except from the case of ANO where the electrochemical properties upperties were enhanced. Galvanic action between dental implants and prosthetic superstructures and more importantly between the treated root and polished collar of dental implants is also discussed.

Keywords: dental implants, electrochemical testing, corrosion, surface roughness, SEM

#### 1. Introduction

Ti and its alloys (Ti–6Al–4V, Ti–6Al–7Nb, Ni–Ti and others) have a long record of applications in dental field. [1–3]. Although Ti is well known for its biocompatibility and excellent corrosion resistance, there are still concerns for the ionic release of Al and V from Ti alloys as they are connected with adverse biological consequences [4–9]. To overwhelm this complica-

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© 2016 The Author(s). Licensee InTech. This chapter is distributed under the terms of the Creative Commons Attribution License (http://creativecommons.org/licenses/by/3.0), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited. tion, most dental implants are manufactured of commercially pure titanium (cpTi: grade II and IV), although a few implants are still produced by the stronger Ti–6Al–4V alloy.

In first place corrosion of dental implants is not a primary concern as the implant surface is not exposed to oral fluids. Ideally after the implant placement the collar will be covered by the soft tissue at cervical region while root region will be covered by the attached bone. However, under inflammatory conditions like peri-implantitis, the environment can be very acidic and thus much more aggressive. In general, peri-implantitis establishes two changes at the region. The first is a significant decrease in pH value at the region resulting in a more aggressive environment for Ti surfaces. Both cpTi and Ti6Al4V alloys showed inferior corrosion resistance in lower pH while the corrosion rate and kinetic is accelerated [10]. The second is the direct contact of collar and root regions with oral fluids due to the resorption of soft and hard tissues has to be considered. Under these conditions, different corrosion mechanisms can be activated:

**Uniform corrosion:** Ti surfaces cannot withstand the corrosive action of oral fluids and a uniform regular removal of metal from implant surface is occurred [11].

**Pitting corrosion:** A form of localized corrosion, where small surface fissures are developed on the metal surface.

**Crevice corrosion:** Corrosion takes place between two close metallic surfaces as in the case of implant and abutment [12]. Crevice corrosion can be also developed on a deep surface crevice where stagnant conditions of the solution are achieved and oxygen exchange between surface and environment is impossible.

**Galvanic corrosion:** A galvanic couple is developed when dissimilar metallic materials are placed in contact.

**Microbial corrosion:** Microbial corrosion or microbiologically-influenced corrosion is the corrosion form caused or promoted by the metabolic actions of microorganisms which reduce the pH levels.

**Fretting corrosion:** Fretting corrosion is caused due to micro movements of mechanically connected parts of an implant structure.

Recently, a research study claims that corrosion of dental implants might be not the result but the triggering factor for peri-implantitis [13]. In 2009, Alberkston et al [13] claimed that corrosion along with the presence of aggressive bacteria, lesion of peri-implant attachment and excessive mechanical loading, among the four triggering factors of peri-implantitis. They concluded that "peri-implantitis is a general term dependent on a synergy of several factors, irrespective of the precise reason for first triggering of symptoms" and thus corrosion resistance might be associated with the failure of dental implants.

Although Ti oxide can be instantly rebuilt after an unexpected damage, a recent study has pointed out that the breakdown of the oxide film is followed by a dissolution process which finally deteriorates the corrosion resistance if this happens repeatedly [14]. In a retrieval analysis study, the corrosion and pitting potential of an intra-oral aged implants were found lower compared to unused ones. The retrieved implants showed lower passivation range and

polarization resistance, indicating that in vivo aging deteriorates the electrochemical properties of Ti implants [15]. Moreover, a retrieval study of four failed dental implants showed that all had been corroded during intra-oral service [16]. The authors concluded that surface oxidation of dental implants might be changed due to the acidic environment developed by bacteria biofilms and/or the inflammatory conditions at the region. This process may permanently breakdown the oxide film facilitating the release of debris and metal ions around the implant. The latter might also hinders the re-integration of bone on implant surface. [16]

Given that corrosion has not yet considered among the risk factors of implant failure there are no specific guidelines to clinicians to minimize the possibility of in vivo corrosion (i.e minimize galvanic coupling between implant and supestructure alloys). Unfortunately, till today, there are no comparative studies on the electrochemical behavior of contemporary dental implants with different surface treatments. A few studies have employed advanced techniques such as electrochemical impedance spectroscopy to characterize the electrochemical properties of anodized and machined dental implants [17–19]. However, the diversity of the applied methods and solutions used for testing makes comparison between the surface treatments rather invalid. A few papers have studied the galvanic coupling of Ti with different dental alloys used for the preparation of implant-retained superstructures providing data for suitable and nonsuitable combinations [20–23]. However, the aforementioned results cannot be directly extrapolated in clinical practice as the experimental conditions are far from intra-oral environment.

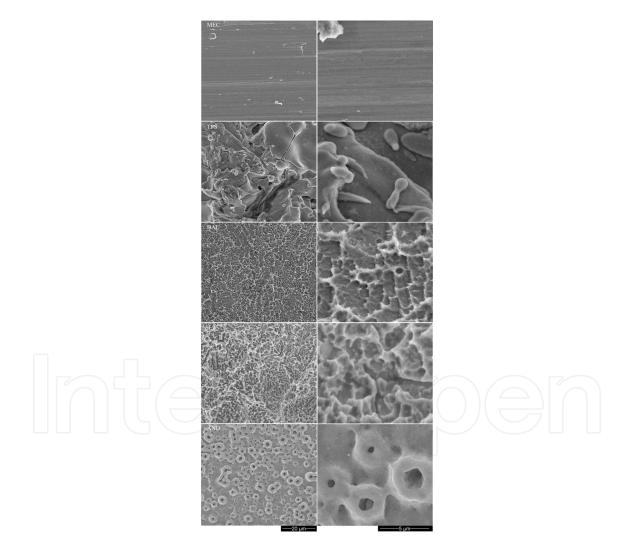
# 2. Effect of surface roughening techniques on morphology, roughness, composition and oxide type of modified Ti implant surfaces.

The modification of implant surface in a way to accelerate the osseointegration process is a topic of intense research and competition among implant companies. A variety of surface roughening techniques have been implemented till today including Ti plasma spray (TPS), double acid etching (DAE), sandblasting with large grit and acid etching (SLA), anodization (ANO), machining (MAC) (**Table 1**), laser etching and others [24].

| Implant (Manufacturer)                           | Surface treatment          | Code |
|--|----------------------------|------|
| Ice (3i, Palm Beach Gardens, FL, USA)            | Smooth machining           | MAC  |
| IMZ TPS (Friedrichsfeld, Mannheim, GER)          | Ti plasma-sprayed          | TPS  |
| OsseotiteFull (3i)                               | Double acid etched         | DAE  |
| SLA Active (Institute Straumann, Basel, CH)      | Sandblasting, acid etching | SLA  |
| Replace Select (Nobel Biocare, Göteborg, Sweden) | Anodized                   | ANO  |

Table 1. Dental implants, manufacturer, surface roughening technique and code for commercially available products.

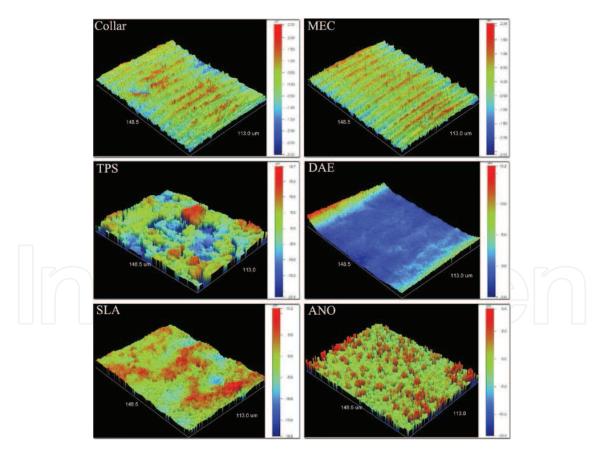
Today, products prepared with the aforementioned techniques are available in dental market as there is no clear evidence for the superiority of one surface modification over the others. The different surface roughening techniques provide characteristic surface patterns on Ti implant surfaces. MAC is characterized by parallel serrations with a rather smooth surface (**Figure 1**). TPS provides surfaces with a random distribution of small granules resemble to solidified droplets probably due to plasma spray process along with a random distribution of surface cracks (**Figure 1**). DAE and SLA depict some similarities due to the final step of acid etching, although SLA illustrates shallow grooves probably due to grit blasting before etching. ANO is characterized by valleys and open craters although the size, the shape and the distribution of these craters are significantly dependent on operational parameters during anodization.



**Figure 1.** Secondary electron images from the root surface of dental implants in 4000 (left) and 24000 (right) nominal magnifications. Parallel serrations are shown on MAC surface due to surface grinding. TPS provides surfaces with a random distribution of small granules along with surface cracks. DAE and SLA illustrate some similarities due to the final step of acid etching although SLA demonstrates shallow grooves associated to grit blasting before etching. ANO is characterized by open craters and valleys.

3D profilometric images (**Figure 2**) provide a better idea for the highest (red) and lowest (blue) areas of each surface. For MAC the highest points are the ridges of serrations while for TPS randomly distributed granular regions. The highest points for SLA are region surrounding valleys while the top of craters constitutes the highest points for ANO. **Table 2** presents representative values for roughness parameters from dental literature. In general, the implants' surfaces are classified based on Sa (average roughness over the complete 3D surface) in smooth (0.0–0.4  $\mu$ m), minimally rough (0.5–1.0  $\mu$ m), moderately rough (1.0–2.0  $\mu$ m) and rough (>2  $\mu$ m) [25]. The first category includes the well-polished implant collars while MAC and DAE are classified as minimally rough surfaces. SLA and ANO belong to moderately rough surfaces and TPS to rough ones. Despite this general classification, it must be noted that manufacturers can modify the procedural parameters, and thus commercially available implants might have big differences in their surface roughness even if they are prepared by the same surface roughening technique.

From corrosion standpoint, this difference in surface roughness might trigger the crevice corrosion mechanism. In this mechanism, the surface can withstand the corrosive environment but the stagnant solution in the crevice changes the chemistry increasing the aggressiveness of solution.



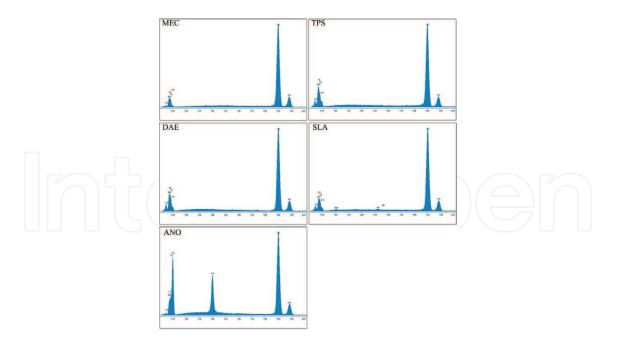
**Figure 2.** Representative 3D profilometric images from the collar (representative from all implants) and the surfaces of differently modified root surfaces. Red areas are the highest and blue the lowest areas of each surface. Note the difference in scale among 3D images.

|        | Sa [26] | Sa [27] | Ra [24] |
|--------|---------|---------|---------|
| Collar |         | 0-0.4   |         |
| MAC    | 0.9     | 0.5     | 0.2     |
| TPS    | 5.2     |         | 7.0     |
| DAE    | 0.9     | 0.5     |         |
| SLA    | 2.6     | 1.6     | 1.2     |
| ANO    | 1.7     | 2.0     |         |
|        |         |         |         |

**Table 2.** Sa (average roughness over the complete 3D surface) and Ra (average roughness along X or Y axes) values for collar and root regions of implants from dental literature.

Implant surfaces are further differentiated in elemental composition as appeared by EDX analysis (**Figure 3**). All spectra showed C and N which should be appended to surface contamination while O should be attributed to surface oxide film. For SLA, Na and Cl were also identified and might be appended to residues of NaCl solution where the implant is placed to avoid atmospheric contamination. P in ANO has been retained from the solution used during anodization.

Although Ti oxide is spontaneously formed when Ti is exposed to atmospheric oxygen, a recent study employing Raman analysis illustrated great differences among the oxide type developed on different surfaces [28]. According to the results of this study, MAC surface contains mainly

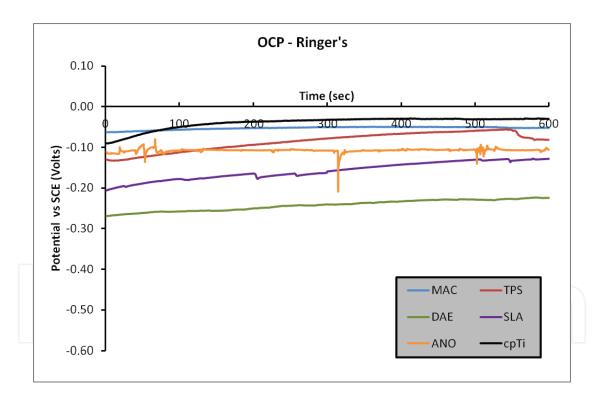


**Figure 3.** X-ray EDS spectra from the root surface of dental implants prepared by different surface roughening techniques. All surfaces illustrated the presence of Ti while C and N should be appended to surface contamination. The presence of O is involved with oxide film. Na and Cl were also identified for SLA and might be appended to residues of NaCl solution where the implant is stored. P in ANO has been retained from the solution used during anodization.

amorphous Ti oxide and less anatase, TPS amorphous and less rutile, DAE mainly  $Ti_2O_3$  and amorphous and less rutile, SLA mainly Brookite and lesser rutile and ANO anatase and less rutile. Given the big differences in all the aforementioned properties, different electrochemical properties are anticipated.

#### 3. Electrochemical properties

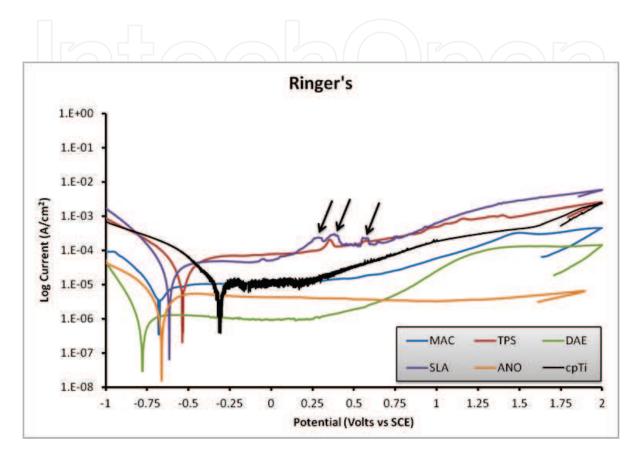
All the surfaces show an almost steady open circuit potential (OCP) in Ringer's (**Figure 4**), indicating a rapid establishment of equilibrium between surface and solution. The OCP values range from -0.28 up to -0.05 V while cpTi showed -0.05 V close to previous reported values [29]. OCP curves illustrate that the potential of all surfaces is quickly stabilized. MAC and TPS showed values close to cpTi while SLA and ANO showed slightly lower OCP values. A few peaks at ANO curve might be appended to reactions taking place at the surface craters. However this is only a speculation and it needs further experimental verification. DAE showed the lowest OCP value. All the treated surfaces showed lower OCP values compared to cpTi a finding which has been also detected for sandblasting compared to reference Ti surface [30].



**Figure 4.** Open circuit potential (OCP) curves in Ringer's solution. All implants show an almost steady curve over the time, indicating a rapid establishment of equilibrium between surface and solution. The ionization tendency is increased towards lower OCP values.

**Figure 5** illustrates representative anodic scan curves along with a small part of reverse scanning while the electrochemical data are presented in **Table 3**. SLA and TPS demonstrate a few oxidation peaks (pointed by the black arrows) while all curves show negative hysteresis implying that the oxide film can be reformed after an unexpected breakdown. Similar  $E_{corr}$ 

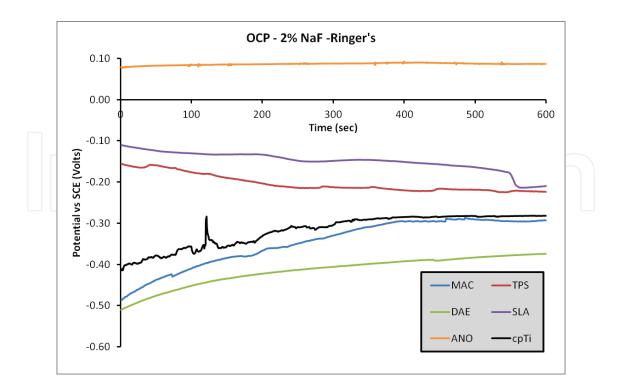
values have been reported in dental literature (-0.35 V [31], -0.4 V [32] and -0.18 V [29]). However, all  $E_{corr}$  values of treated surfaces moved cathodically denoting an increase tendency of surface to react. All surfaces show a passivation region and  $E_{pit}$  of cpTi was found close to previously reported values (0.45 V [32]. ANO showed the highest  $E_{pit}$  (**Table 3**) compared to others.



**Figure 5.** Anodic scans from dental implants with different surface modifications. Oxidation peaks (pointed by black arrows) were identified for TPS and SLA. All the surfaces showed a breakdown potential ( $E_{pit}$ ) and negative hysteresis in reverse scanning (a small part of reverse scanning curve at 2 V is appeared for all materials).

|      | E <sub>corr</sub> | I <sub>corr</sub> | E <sub>pit</sub> | Hysteresis |  |
|------|-------------------|-------------------|------------------|------------|--|
|      | (V)               | (µA/cm²)          | (V)              |            |  |
| срТі | -0.27             | 3.8               | 0.22             | Negative   |  |
| MAC  | -0.84             | 3.6               | 0.55             | Negative   |  |
| TPS  | -0.52             | 20.3              | 0.43             | Negative   |  |
| DAE  | -0.79             | 7.4               | 0.29             | Negative   |  |
| SLA  | -0.62             | 39.4              | 0.04             | Negative   |  |
| ANO  | -0.68             | 3.4               | 1.26             | Negative   |  |

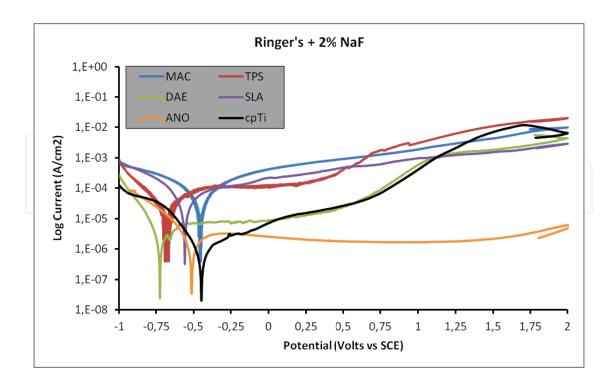
**Table 3.**  $E_{corr}$ ,  $I_{corr}$ ,  $E_{pit}$  and type of hysteresis from the anodic scan curves obtained in Ringer's solution. Higher  $E_{corr}$  and  $E_{pit}$  lower  $I_{corr}$  and negative hysteresis benefit the corrosion resistance.



**Figure 6.** OCP curves in 2% NaF+Ringer's solution. ANO showed an increase in OCP values compared to Ringer's solution. However, the OCP values of the rest implants moved cathodically although potential is again quickly stabilized as in the original Ringer's solution.

Many researchers have focused on the effect of fluoride ions on the corrosion resistance of dental implants as many dental products such as toothpastes, mouthwashes, prophylactics gels and others are proposed for the oral hygiene of patients with dental implants. However, Ti oxide is very vulnerable to fluoride ions and thus the corrosion resistance of dental implants is seriously compromised [33–35]. Generally, in F<sup>-</sup> containing media the surface of Ti showed a strongly bound complex  $Na_2TiF_6$  followed by a huge increase in surface roughness [36]. However, the presence of F<sup>-</sup> reduces the corrosion resistance of dental alloys too [37]. In Ringer's solution with 2% NaF all OCP curves moved cathodically in a range from -0.4 to -0.2 V. Previous studies reported that OCP of cpTi in Ringer's solution is ranged between -0.08 [29] and 0.05 V [38], implying that the surface roughening techniques applied have moved the OCP cathodically. Surprisingly, ANO showed an increase in OCP in the 2% NaF+Ringer's solution, while the OCP of the rest implants moved cathodically due to the more aggressive nature of this reagent. However, the potential is again quickly stabilized as in the original Ringer's solution.

Similar to Ringer's solution the anodic scan curves showed that surface roughening techniques move  $E_{corr}$  value to lower values while passive region was vanished for cpTi, MAC and SLA. In addition, DAE and MAC showed positive hysteresis denoting that in the case of oxide breakdown the reformation of the oxide film is impossible under these conditions (**Figure 7**). Again ANO showed the best corrosion resistance properties demonstrating the highest (1.32 V)  $E_{pit}$  value (**Table 4**).



**Figure 7.** Representative anodic scans from dental implants with different surface modifications. All surfaces showed a breakdown potential while MAC and DAE demonstrated a positive hysteresis in reverse scanning (a small part of reverse scanning curve at 2 V is appeared for all materials).

|      | E <sub>corr</sub> | <b>I</b> <sub>corr</sub> | E <sub>pit</sub>       | Hysteresis |
|------|-------------------|--------------------------|------------------------|------------|
|      | (V)               | (µA/cm²)                 | (V)                    |            |
| срТі | -0.42             | 1.7                      | Without passive region | Negative   |
| MAC  | -0.47             | 46.2                     | Without passive region | Positive   |
| TPS  | -0.69             | 19.1                     | 0.20                   | Negative   |
| DAE  | -0.72             | 4.0                      | 0.18                   | Positive   |
| SLA  | -0.68             | 83.8                     | Without passive region | Negative   |
| ANO  | -0.56             | 1.8                      | 1.32                   | Negative   |

**Table 4.**  $E_{corr}$ ,  $I_{corr}$ ,  $E_{pit}$  and type of hysteresis from the anodic scan curves acquired in 2% NaF+Ringer's solution. Higher  $E_{corr}$  and  $E_{pit}$  lower  $I_{corr}$  and negative hysteresis benefit the corrosion resistance.

There is limited knowledge for the effect of surface roughening techniques on electrochemical properties of dental implants. OCP and anodic scans showed that sandblasting deteriorates the electrochemical properties of Ti surface, a finding that has already been reported by previous studies [30]. A speculation for this behavior is that the residual stresses developed in the subsurface during sandblasting have a detrimental effect on corrosion properties. The same trend was identified for both the Ti6Al4V and Ti6Al7Nb alloys after sandblasting in phosphate-buffered solution (PBS) [39]. However, all previous studies on ANO surfaces agreed that ANO has a positive effect on electrochemical properties. This has been tested in a variety of reagents

including PBS and media with cells simulating inflammatory conditions [17], Ringer's [40], PBS [41] and 0.9% NaCl [42]. Interestingly the same findings were found for Ti6Al4V and Ti6Al7Nb [42]. Recent data showed that no correlation was identified between roughness parameters and electrochemical properties in both the aforementioned solutions meaning that surface roughness cannot affect the corrosion resistance and thus the electrochemical properties are not dependent on how rough the surface is [26].

#### 4. The galvanic aspect

Galvanic coupling can be easily developed in the oral cavity between dental implants and implant-retained superstructures especially under peri-implantitis conditions. Concerning the galvanic couple of Ti with dental alloys, a few studies have been conducted employing different reagents. **Tables 5**, **6** and **7** illustrate potential differences of various galvanic couples between Ti and dental alloys. The values are sorted in descending order from the highest positive value towards the lower negative value. In most cases, the precious alloys show positive values implying that Ti will be under anodic control. In this scenario if the galvanic corrosion is triggered, then the alloy under cathodic control (precious alloys) remains immune while Ti will be dissolved. In contrast Ti is in cathodic control with all base Co–Cr and Ni–Cr alloys which means that Ti will be protected while the base alloys will be corroded under the galvanic action [21]. Given that galvanic action is triggered when the difference in potential is above 0.2 V the couples with minimal difference to Ti is ideal to avoid galvanic action and corrosion of one of the two alloys. As implant-retained superstructures are replaced easier than implants themselves, it is recommended that dental implants should be under minimal cathodic control.

| Couple                               | Potential |
|--------------------------------------|-----------|
|                                      | (V)       |
| (Ti)/(60Pd-28Ag-6Sn-6In)             | 0.067     |
| (Ti)/(40Au-35Ag-7.9Pd-7Cu-5In-3.5Zn) | 0.002     |
| (Ti)/(63.5Co-30Cr30-5Mo-1Si)         | -0.027    |
| (Ti)/(61Ni-26Cr-11Mo-1.5Si)          | -0.031    |
| (Ti)/(61Co-25Cr-7Mo-5W-1.5Si)        | -0.107    |

Table 5. Difference in potential between Ti and dental alloys in modified artificial saliva with pH 7.2 [20].

However, all previous values used smoothly machined or polished Ti surfaces which achieved great difference in OCP values with treated root surfaces (**Figures 4** and **6**). DAE have almost 0.2 V difference with MAC surface which can be representative of collar. This means that the exposure of DAE surface and collar to Ringer's solution is close to galvanic threshold. Differences with MAC surface (collar) is even higher in the case of 2% NaF+Ringer's solution denoting that galvanic corrosion is still possible between collar and root of the implant itself

in some cases. Of course, the presence of superstructure facilitates the galvanic phenomena more. However there is limited knowledge on this matter and definitely further research is required in this topic while the development of guidelines for clinicians to minimize intraoral corrosion of dental implants might have a beneficial effect on longevity of implant-retained restorations.

| Couple                                     | Potential |
|--|-----------|
|  | (V)       |
| (Ti)/(68.9Ag-26Pd26-4Cu-0.9Au-0.1In-0.1Zn) | -0.09     |
| (Ti)/(76.5Au-12Ag-8Cu-2Pd-1.5Pt)           | -0.14     |
| (Ti)/(66.5Ni-22Cr-9Mo-1.6Si0.5Fe-0.4Ce)    | -0.22     |
| (Ti)/(67Co-28.5Cr-4.5Mo)                   | -0.31     |

Table 6. Difference in potential between Ti and dental alloys in artificial saliva at 37°C [12].

| Couple   | Potential |
|--|-----------|
|  | (V)       |
| (Ti)/(60Au-24Pt-15Pd)                              | 0.210     |
| (Ti)/(85.5Au-6.5Pt-4.8Pd-1.5Ag)                    | 0.175     |
| (Ti)/(51.5Au-38.4Pd-8.5In-1.5Ga)                   | 0.148     |
| (Ti)/(65Ag-23Pd-6.4Cu-2In)                         | 0.099     |
| (Ti)/(68.5Au-11.7Cu-11Ag-3.8Pd-3.5Pt-1.5Zn)        | 0.097     |
| (Ti)/(71Au-14.5Cu-9Ag-2Pd-2Pt-1.5Zn)               | 0.088     |
| (Ti)/(63Ni-21.7Cr-10.8Mo-1.8Fe-1.5Si-1W)           | -0.132    |
| (Ti)/(65.2Ni-21.6Cr-10.5Mo1.3Si-0.7Fe-0.5Mn-0.2Yt) | -0.167    |
| (Ti)/(79.2Ni-14.5Cr-6Mo-0.3Co)                     | -0.191    |
| (Ti)/(77.5Ni-13.3Cr-3.1Mo-2Ti-1.5Be-1Si-0.5Co)     | -0.229    |
| (Ti)/(78.4Ni-13.Cr-4.5Mo-3.4Al-0.6Fe)              | -0.274    |

Table 7. Difference in potential between Ti and dental alloys in Fusayama reagent with pH 5 at 37°C [21].

#### 5. Conclusions

- Surface roughening techniques significantly affect the roughness, morphology, elemental composition, oxide type and electrochemical properties of Ti implants.
- Electrochemical properties of dental implants are inferior compared to untreated cpTi apart from that of ANO where the electrochemical properties are enhanced.

- Galvanic action might be seriously implicated in corrosion under clinical conditions, a factor associated recently to peri-implantitis.
- Extensive research must be exerted in order to minimize the galvanic phenomena among treated root, polished collar and implant-retained superstructure.
- ANO of Ti surface significantly increases the electrochemical properties of dental implants but these findings must be verified by clinical data.

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