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Chemical Mechanical Surface Nano-Structuring (CMNS) Implementation on Titanium Based Implants to Enhance Corrosion Resistance and Control Biocompatibility

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ABSTRACT

Titanium is the metal of choice for many implantable devices including dental prostheses, orthopaedic devices and cardiac pacemakers. Titanium and its alloys are favoured for hard tissue replacement because of their high strength to density ratio providing excellent mechanical properties and biocompatible surface characteristics promoting in-vivo passivation due to spontaneous formation of a native protective oxide layer in the presence of an oxidizer. This study focuses on the development of a three-dimensional chemical, mechanical, surface nano-structuring (CMNS) process to induce smoothness or controlled nano-roughness on the bio-implant surfaces, particularly for applications in dental implants. CMNS is an extension of the chemical mechanical polishing (CMP) process. CMP is utilized in microelectronics manufacturing for planarizing the wafer surfaces to enable photolithography and multilayer metallization. In biomaterials applications, the same approach can be utilized to induce controlled surface nanostructure on three-dimensional implantable objects to promote or demote cell attachment. As a synergistic method of nano-structuring on the implant surfaces, CMNS also makes the titanium surface more adaptable for the bio-compatible coatings as well as the cell and tissue growth as demonstrated by the electrochemical and surface wettability evaluations on implants prepared by DI-water machining versus oil based machining.

INTRODUCTION

Nano-scale modification of macro-scale three-dimensional implantable devices is gaining more attention as the cell attachment/detachment mechanisms at the bio-interfaces are profoundly affected by the nanoscale interfacial interactions [1]. It has been shown that the chemical mechanical polishing (CMP) approach that is primarily utilized in microelectronics manufacturing can be extended to induce controlled surface nanostructure on three-dimensional implants to promote or demote cell attachment [2]. By tuning the polishing slurry particle size, solids loading and the chemical composition, both the chemical nature and the surface topography can be modified to make the surface very smooth or rough at nanoscale. This new technique helps produce implant surfaces that are cleaned from potentially contaminated surface layers by removing a nano-scale top layer while simultaneously creating a protective oxide film on the surface to limit any further contamination to minimize risk of infection [3]. The ability of modifying the surface nanostructure is essential to determine the fibroblast and osteoblast cell attachment/detachment mechanisms on the implant surfaces. The control of cell viability helps tune the functionality of the implants, whether the biocompatibility depends on promoting cell attachment, such as in the dental or prosthetic implants, or limited attachment is preferred to maintain the functionality of a device such as for the cardiac valves. There is evidence that surface roughness is an essential part of cell attachment. Rabinovich et al. used atomic force microscopy (AFM) to demonstrate the effects of radius of asperities on the nanoscale to control adhesion on Ti thin film surfaces [4].

Implants are machined by computer numerical control (CNC) method typically in the presence of oil as a lubricant. The use of oil in machining process helps controlling the local heating on implant and makes it easier to shape the titanium rods into the dental implants. Yet, the effects of oil processing on the implant surface properties and biocompatibility are not studied in the past. There are additional surface treatments applied on the machined implants such as sand blasting, etching and various coatings [2]. The current process of record is the sandblasted, large grit, acid-etched implant surface (SLA) technique. The SLA surface enhancement for dental implants is a method that was introduced in 1997 [5]. This treatment creates a micro-scale textured surface with the goal of increased osseointegration by increasing surface roughness. In conventional SLA treatment, hard particles such as zirconia or alumina are used for sandblasting and if they remain on the surface they tend to result in inflammation [2]. In most recent applications, biphasic calcium phosphate (BCP) particles are used for blasting the implant surface as they are biocompatible and hydroxyapatite-like particles and can promote osseointegration. The BCP treatment is followed by an acid etch of 50% sulfuric acid at high temperatures for 1 minute [6]. Osseointegration of the implant occurs with the increased surface roughness allowing for osteoblast cells to adhere to the implant surface [7]. However, BCP particle-based SLA treatments can be prone to delamination at the implant/particle coating interface, since the acid treatment may not clean the surface of the implant from any remaining sand-blasted particles and metallic residue. This can be a potential cause of titanium particle dislocation during implant placement in addition to Ti^{+4} ion release from the surface of the dental implants as a result of the removal of the native surface oxide layer by acid treatment. Both problems may lead to potential periimplantitis and significantly shorten the implant life and discomfort to the patient. In this paper, we investigate the effect of oil versus de-ionized (DI)-water based machining on dental implants as a baseline and compare the BCP and CMP treatments after oil and DI-water machining for surface quality and electrochemical passivation behaviour to investigate the effects of conventional oil based implant machining on post treatment quality and its implications [8].

EXPERIMENT

Materials: DI-water and oil-based CNC lathe machined; and BCP treated titanium dental implants were provided by MODE Medikal. Rhenus FS 750 was used as the oil lubricant [9] during CNC lathe machining. Quartron SH-3 ultra-high purity commercial colloidal silica slurry, a commercial slurry tuned toward titanium removal in microelectronics manufacturing with a particle size of approximately 0.1µm was provided by Versum Materials. Hydrogen peroxide was added to this consumer slurry at 3wt% concentration to enhance the chemical mechanical polishing. CMNS treatment was performed by using only DI-water and DI water with 3wt% H_2O_2 to investigate the effect of oxidizer and slurry on the surface topography and wettability and optimizing the treatment conditions. In addition, a 0.2µm colloidal silica slurry was prepared in the lab by only pH adjustment to pH 9 and ultrasonication to be used as a buff to clean the implant surface post CMNS treatment with the commercial slurry that is tuned for the titanium polishing.

Methods: A simplified version of the robotic integration [10,11] in-lab three-dimensional CMP set up, shown in Figure 1, was prepared using an electric brush as the polishing pad, a rpm controlled rotating implant holder and a beaker containing the desired slurry as per the planned treatment. The implant was attached to the holder by screwing into place and the toothbrush was affixed next to the dental implant to polish the implant surface at a constant pressure. Four different CMP treatments were tested for CMP optimization, DI-water, DI-water with 3wt % H_2O_2, commercial slurry, and commercial slurry with 3wt % H_2O_2. Further surface cleaning was performed with a 0.2µm buff slurry. All CMP experiments were performed for 5 minutes and implants were rinsed in DI-water, ultrasonicated in ethanol for 1 minute, and air dried. Material removal rates were calculated based on weight measurements before and after CMP treatments over the length of 5 minutes to determine the rate of material removal in ug/min. Implants were weighed using a Denver Instruments Summit Series SI-224 high precision balance with 0.01 mg accuracy.

Surface roughness measurements were performed by using a Zygo NewView 5000 3D surface profiler. Minimum two measurements were taken in the trough of the implant on two different implant samples prepared by same surface treatment and the results were averaged. Post measurement, analyses were conducted by using Zygo MetroPro Micro7k application software.

To determine the surface wettability, which correlates to the surface biocompatibility, static contact angles were measured by using the sessile drop method by a Ramé-Hart goniometer with DROPimage Advanced Software. Measurements were taken at the third trough from the bottom of the implant, described in Figure 2, over a 10 second period for consistency. There were 4 measurements taken on each implant to gain representative data from the implant surface.

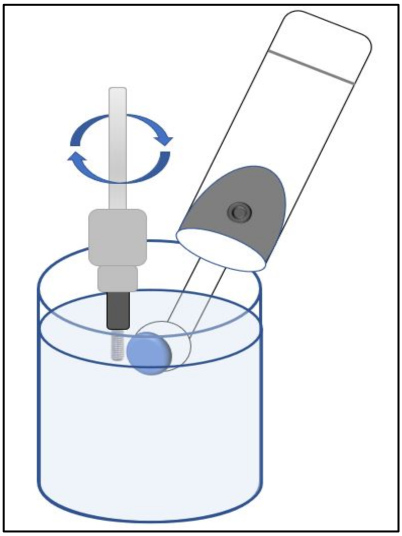

Figure 1: Schematic of the in-lab three-dimensional CMP laboratory set-up comprised of a rotating sample holder with controllable rpm, a power-controlled brush for polishing, and a beaker containing post-treatment slurry.

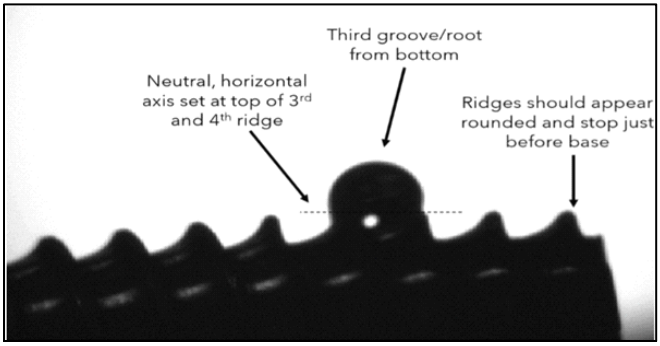

Figure 2: DROPimage describing the location of the droplet, the third trough/groove from the bottom of the sample, where contact angles were measured.

Electrochemical potentiodynamic based tests were conducted on dental implants exposed to freshly prepared simulated body fluid (SBF) solution [12] at 36.6 ± 0.1 °C. To maintain a near constant exposure area of the implant, only the last three troughs including the lower base were kept open while all the remaining implant surface was thoroughly masked by using PTFE tape as can be seen in Figure 3. The exposure was calculated by assuming it to be the total curved surface area of a frustum of a cone plus the apical flat base area of the implants. Electrical connection was made through the hollow inside of the implant by using the metallic tail of an alligator clip. Saturated calomel electrode (SCE) connected with a Luggin capillary, and a 26-guage thick platinum wire (99.90% pure) were used as the reference and the counter electrodes, respectively.

Measurements were performed and analysed by using the Gamry Reference 3000 Potentiostat and its dedicated Gamry Echem analyst software. After a 1-h open circuit potential (E_{oc}) stabilization, potentiostatic transients at 0 ± 100µV were collected for 10 mins for each specimen. Followed by a 10 mins delay, potentiodynamic polarization curves were also recorded from -1V up to +2V from E_{oc}, with a scan rate of 10mV/min. Following the electrochemical testing, samples were rinsed in running DI water and flushed with dry hot air until completely dry. For testing Ti coupons, a Gamry Flat specimen holder was used with a fixed exposure area (circle with diameter=1 cm). Each test measurement was triplicated to ensure statistical data reproducibility.

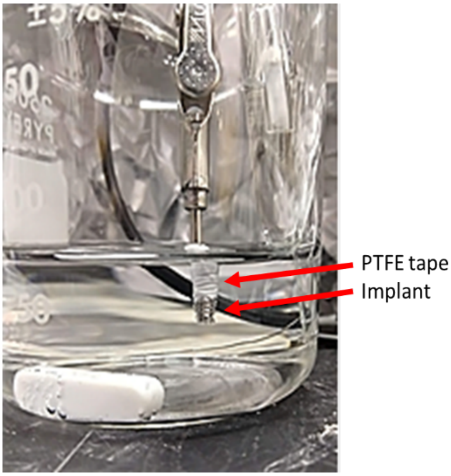

Figure 3: Electrochemical cell experimental set-up for testing dental implants. Electrical connection is made by the metallic tail of an alligator clip. PTFE tape masks the top of the implant while the bottom three troughs remain exposed.

RESULTS AND DISCUSSIONS

The dental implant samples machined with oil and DI-water were initially polished with only DI water, DI water and 3wt% oxidizer, commercial slurry, and commercial slurry with 3wt% oxidizer. Figure 4a illustrates the material removal rates calculated after CMNS treatment with the commercial slurry as compared to the DI water used as the polishing media. It can be seen in that DI-water CMNS treatments resulted in negligible removal rates even in the presence of the oxidizer in the environment. Furthermore, there was an increase in the implant weight after the treatment with the commercial polishing slurry. This can be attributed to abrasive silica particles remaining on the surface of the implant after polishing treatment with the slurry that is tuned to control the titanium removal in the absence of the chemical component provided by the oxidizer. To further optimize the CMNS implementation on the surfaces of the dental implants, a 0.2µm silica-based buff slurry was prepared (adjusted to pH 9 and stabilized by ultrasonication) and used on all the implants treated with the commercial slurry. Figure 4b shows that the implementation of a buff procedure was able to clean implant surfaces from the residual particles effectively and in the absence and presence of the 3wt % addition of H_2O_2 on the

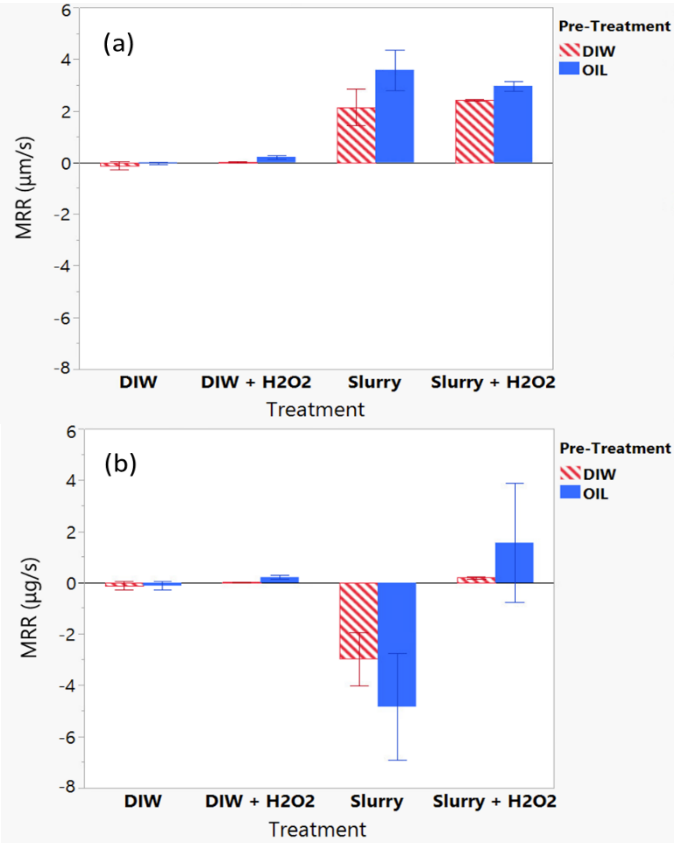

Figure 4 Material removal rates for slurry treatments using (a) commercial slurry and (b) commercial slurry then 0.2µm buff slurry. Two replicates were used. Legend refers to the pre-treatment used; DI-water (DIW) or oil lubricant (OIL).

titanium dental implants and help identify the absolute material removal on the samples treated with the slurry in the presence of the oxidizer.

In order to understand the biocompatibility of the oil versus DI-water based machining on the dental implants, surface roughness and wettability analyses were conducted as detailed in the experimental section. The baseline CNC machined implants, which were either prepared with DI-water or with machining oil, were measured for the surface roughness values as summarized in Figure 5.a. It can be seen that post machining, both the DI-water and oil processed samples measured an average surface roughness value of approximately 0.5 μm. Implants prepared through BCP particle treatment measured to have a higher average surface roughness for both DI-water and oil machined surfaces as expected. Performing CMNS with DI-water, DI-water with H_2O_2, or commercial slurry alone increased the surface roughness values by about 20%. The addition of 3wt % H_2O_2 to the commercial slurry provided significant increase in averaged surface roughness for the DI-water machined implants, which is statistically the same as the BCP treatment. However, the oil machined implants did not show a significant change in roughness, which can be attributed to the fact that the oil on the surface inhibits the surface from getting effectively structured because of the lubrication between the titanium and the abrasive particles. In addition to the surface topography, surface wettability is also an indirect measure of the biocompatibility. The implant surfaces are shown to attach more cells when the surface roughness is increased [13], and the surface hydrophobicity is enhanced. Therefore, an increase in the contact angle is considered to be favourable for the dental implants. Figure 5.b summarizes the contact angle measurements collected on the implant samples with various treatments. It can be seen that there were consistently high values for all the oil machined implants which were above 100 degrees indicating hydrophobicity. For baseline CNC machined and BCP treated implants in DI-water and oil, no significant difference is noted for the recorded contact angle values. However, DI-water machined implants treated with the commercial slurry in the absence and presence of H_2O_2 proved to be more hydrophilic post CMNS treatment. It is believed that the machining oil is left on the implant surface regardless of the post treatment and since the oil is hydrophobic in nature the implant surface remains hydrophobic after the treatment. Since the DI-water machined implants turn hydrophilic post CMNS implementation (with the commercial slurry both with and without H_2O_2), show a decrease in contact angle, and the oil machined ones do not, it is believed that the machining oil is left on the surface which can compromise the surface biocompatibility of the implant surface.

Electrochemical polarization tests were performed on baseline machined and BCP treated implants and three-dimensional CMNS implemented Ti coupons (to control the removal rates) treated with the four different blurry preparation as outlined in the previous experimental results. Initially the CMNS treated Ti coupons were tested for the corrosion performance to investigate the effect of CMP treatment on corrosion prevention on titanium. Figures 6.a and 6.b illustrate the DC polarization curves for each of the specified sample treatments. In addition, their preliminary corrosion parameters including the corrosion potential (E_{oc}) and DC Linear Polarization Resistance (LPR) are reported in Table I. The LPR values, which correspond to the ability of the test surface to resist anodic polarization (corrosion), were calculated by taking the slope of the polarization curves in the range of ± 10mV vs E_{corr} [14].

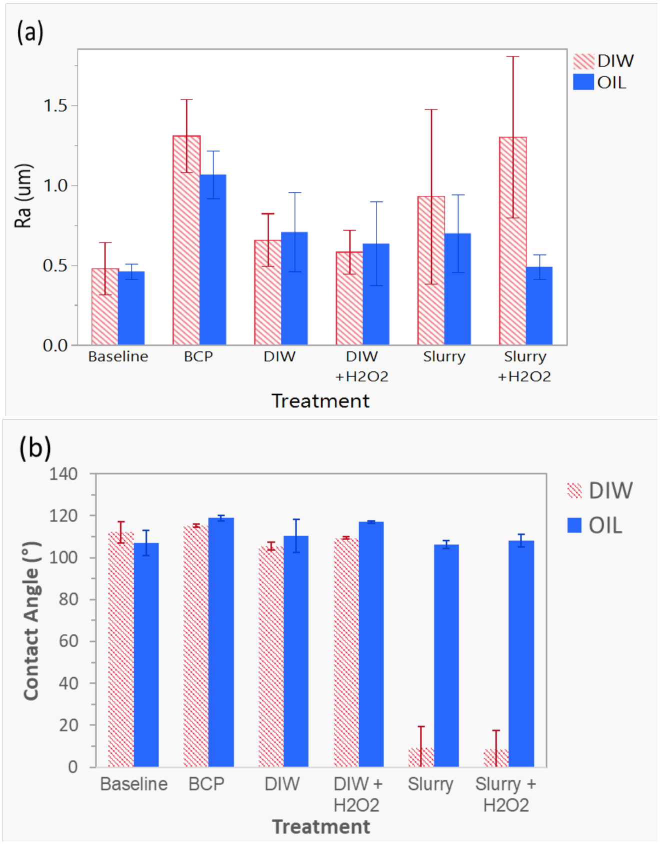

Figure 5: (a) Average surface roughness and (b) contact angle measurements for DI-water vs. oil machined dental implants with various surface treatments. Legend refers to the pre-treatment used; DI-water (DIW) or oil lubricant (OIL).

For implants, it can be inferred that the use of oil for CNC machining tends to result in oil remaining on the metal surface as suggested from the previous contact angle measurements. The oil left on the surface acts as a sealant for the metal from the oral fluid exposure (simulated body fluid in this case). This can be observed from the significantly higher LPR values of oil machined implants in comparison to the DIW machined implants. Furthermore, oil machined implants show a relatively larger passivation region as well as smaller current densities in their polarization curves (Fig. 5a). This behaviour has proven to be beneficial towards successful osseointegration, unless a potential bacterial attack leads to the loss of this surface passivation [15]. In the case of the BCP-SLA treatment, it has been shown that it helps enhancing the corrosion performance [16,17] as compared to baseline machining with oil which is consistent with a significant increase in E_{oc} values for oil machined implants. For DIW machined implants, both the LPR as well as the E_{oc} are lower after SLA treatment, suggesting a galvanic reaction is occurring with the additional porous cathodic BCP layer leading to a reduced passivity to protect the metal from the corrosive SBF solution. However, the source of oxygen as well as the mechanisms for enhanced Ti passivation in the case of oil machining, and further testing under simulated saliva environment will be necessary to understand the machining medium effect on in-vivo corrosion behaviour.

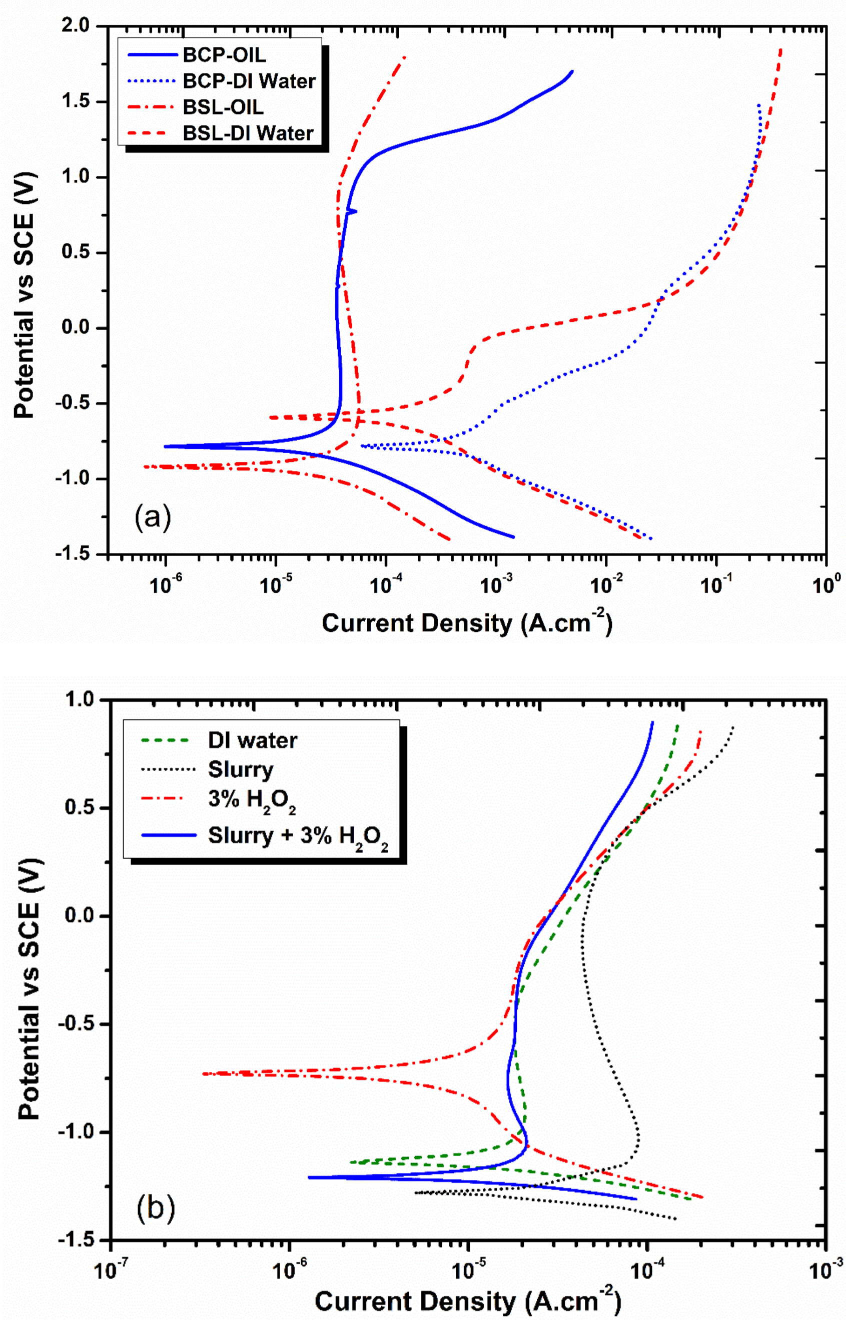

Figure 6: Electrochemical analysis of (a) DI-Water vs. oil machined baseline (BSL) dental implants and SLA treatments (BCP). (b) Ti plates after 3D CMNS treatment using four different polishing conditions, all in SBF solution at 36.6 °C.

Table I: Corrosion parameters acquired from electrochemical tests on both Ti implants and coupons under different treatment conditions.

Concentration of Oxidizer	**Ti implants**		**CMP Polishing Environment**	**Ti coupons**	
	E_{oc} vs SCE (V)	**LPR ($\Omega.cm^{-2}$)**		**E_{oc} vs SCE (V)**	**LPR ($\Omega.cm^{-2}$)**
Baseline – DIW	-0.696 ± 0.104	528.79 ± 31.8	**DIW**	-1.138 ± 0.024	12600 ± 1224.5
Baseline – Oil	-0.898 ± 0.019	3260.65 ± 151.4	**3% H_2O_2**	-0.729 ± 0.015	33220 ± 1310.9
BCP – DIW	-0.766 ± 0.015	116.02 ± 29.9	**Slurry**	-1.298 ± 0.035	2223.8 ± 156.2
BCP – Oil	-0.761 ± 0.022	3327.2 ± 276.2	**Slurry + 3% H_2O_2**	-1.238 ± 0.03	4697.5 ± 421.6

For 3-Dimensional CMNS treated Ti coupons, the presence of oxidizer (3wt% H_2O_2) is critical to surface passivation region and E_{oc} as can be observed from the polarization curves. The exposure areas can be measured accurately and was the one major reason needed to start with reliable electrochemical measurements on these coupons. Polishing of the coupons in the slurry medium allows removal of the simultaneously formed oxide and an opportunity of a new passive protective layer formation due to concurrent chemical and mechanical actions. The simultaneous chemical and mechanical actions in CMNS can be controlled through the added oxidizer concentration as can be seen in Figure 6.b. The LPR values reported in Table I suggest that a combination of a very dilute slurry with H_2O_2 will deliver highly uniform and protective titanium oxide passive layer. This could either be an additional benefit to that of oil machining or could be useful in enhancing the DIW machined implants as the hydrocarbons of the essential oils could have an adverse effect in reduced bioactivity or bone-implant integration [18]. Further understanding of the effect of slurry design, process parameters, bacterial corrosion, and cell attachment mechanisms will be crucial towards designing an optimum process of record towards enhanced osseointegration and corrosion resistance of dental implants.

SUMMARY

CMNS implementation was performed by using a 3D CMNS method on titanium dental implants machined by using DI-water and oil. Surface nature of the treated implants were investigated by surface roughness, contact angles, and corrosion resistance evaluations after CMNS optimization. Micro-roughness is observed for SLA implants treated with BCP particles that is known to promote osteoblast cell adhesion. CMNS treated implants by using the commercial slurry in the presence of H_2O_2 prove to help with the increase in surface roughness as compared to the baseline CNC machining in DI-water. Surface wettability increases for DI-water machined implants with CMNS treatment when commercial slurry with and without 3wt % H_2O_2 is used. The detailed electrochemical analyses of the implants in SBF solution at 36.6 °C show that oil CNC machined implants have superior corrosion resistance over DIW machined with the downside of leaving the oil residue on the implants. CMNS treatment can be implemented towards designing corrosion resistant and enhanced bioactive implant surfaces towards eliminating Ti^{4+} ion dissolution and periimplantitis. Further studies are ongoing to understand the cell attachment and biocompatibility on the surface after CMNS treatments.

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