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Development of 3-D Chemical Mechanical Polishing Process for Nanostructuring of Bioimplant Surfaces

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This study focuses on the development of a three dimensional chemical mechanical polishing (CMP) process to induce smoothness or controlled nano-roughness on the bio-implant material surfaces, particularly for an application on the dental implants. CMP 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. Hence, we propose CMP as a synergistic method of nano-structuring on the implant surfaces and focus on extending the process to a 3-D platform to implement it on the dental implants.

Introduction

Biomaterials are widely used for dental prostheses, orthopedic devices, cardiac pacemakers and catheters. Titanium and its alloys are favored as biomaterial for hard tissue replacement due to their excellent mechanical properties and surface characteristics, which promote biocompatibility due to spontaneous formation of a thick oxide layer in the presence of an oxidizer [1]. The surface morphology and oxide layer thickness of titanium implant can be changed trough different surface treatments [2]. However, the surface of titanium maybe contaminated during casting due to its highly reactive nature, which in turn lessens the biocompatibility and the mechanical properties at the tissue/bio-implant interface [3]. Metals tend to form native oxides when they are exposed to oxidizing environments, which may be a self-protective layer in some cases. One of the main processes where the protective metal oxide films are closely investigated is the Chemical mechanical planarization for metals (CMP). In CMP process, the top film surface of the metal is exposed to the slurry chemicals. This interaction forms a chemically altered top film that is removed by the mechanical abrasion of the nanoparticles. The chemically altered top films have to be protective oxides to enable planarization by stopping chemical corrosion on the recessed metal surfaces while the elevated structures are polished [4]. It has been shown by an earlier study that the application of CMP on Ti films has been very successful in terms of creating a thin titanium oxide film on the surfaces and promoted biocompatibility [5]. The effects of oxidation of Ti films on cell activity improvement as well as hydroxyapatite formation have also been demonstrated in the literature [6, 7].

In this study, CMP technique is used to induce nano-smoothness and controlled nano-roughness on the titanium surfaces. It has been demonstrated earlier through inducing nano and micro patterns on various biomaterials that these structures help increase the cell growth capability of the bio-implants [8]. However, for applications like artificial cardiac valves surfaces demoting cell growth may be needed for continuous functionality. Biocompatibilities of the titanium surfaces treated by CMP can be controlled by altering them to a very smooth or nano-structured surface structure and bring the advantage of applying the same process for many different applications. Our aim is to create engineered Ti based dental implants with self-protective surfaces to minimize chemical and bacterial reactivity, while promoting their biocompatibility through surface patterning.

CMP process, as it is used in microelectronics manufacturing for planarization functions in 2-dimension. In order to polish 3-dimensional bio-implant surfaces, the number of degrees of freedom (DoF) has to be increased in the system. One solution to accomplish this is to utilize a 6-DoF robotic arm to hold the polishing piece. Robotic arm is a mechanical arm that has similar functions to a natural human arm. It consists of joints, which give robotic arm the capability of rotary and linear motion. A 6-DoF robot can easily reach any point in its workspace and in any desired orientation. This ability of the robotic arm provides the necessary DoF in the 3-D CMP system that is required for the homogenous polishing of the 3-D implant materials. In the proposed design a 6-DoF robotic arm is integrated to the regular desktop CMP tool. The arm holds the dental implant in combination with a force torque sensor that can hold the implant material towards the polishing pad under a constant pressure. The pad material is chosen to be soft and easily deformable to be able to deform to the shape of the implant. When pad is rotated with a constant RPM value, the dental implant can be polished by keeping a constant pressure on the contacted area. Figure 1 illustrates the proposed 3-D CMP process.

Experimental

CMP and bacteria growth analyses were conducted on titanium foils with 1mm thickness and 99.6% purity (TI000430) obtained from Goodfellow Cambridge Ltd. The purchased

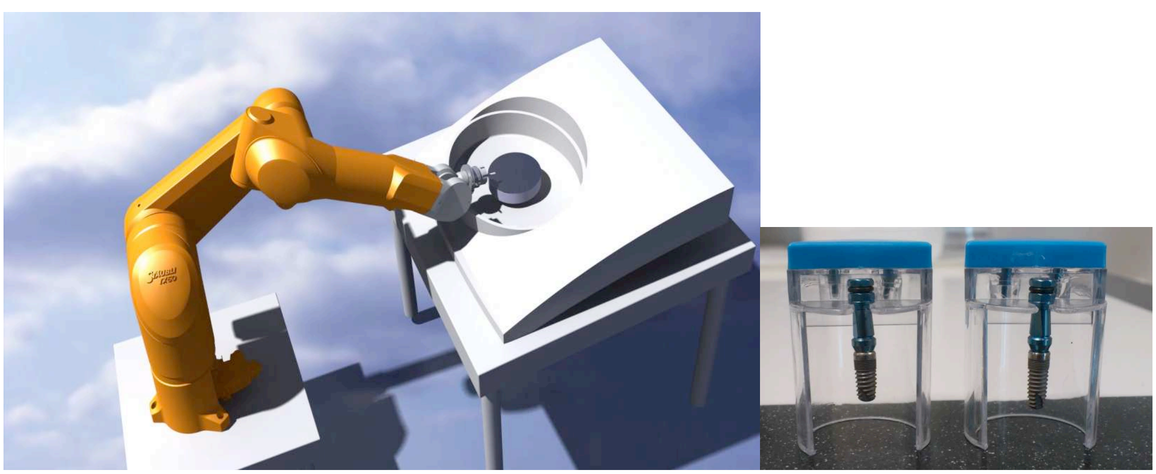

Figure 1. Schematic image of 3-D CMP process design and the picture of dental implants.

foil, which was 300x300mm in size was cut to 14x14 mm pieces to fit to the holder of the CMP tool. The original sample surface considered as baseline for the testing was annealed. In order to compare the properties of the original surface against the surfaces prepared through CMP, polishing was conducted by using a desktop Tegrapol-31 polisher and 5% weight alumina (Al_2O_3) slurry with 50nm particle size. Slurries were prepared at pH 4 using nitric acid through ultrasonicating long enough by repeated pH adjustment until the slurry was fully stabilized. CMP tests were conducted at 70 N downforce, which is equivalent to a 7.88psi pressure on the used sample size. Initial samples were polished with regular CMP set up in 2-D using a Suba IV subpad stacked under a polytex buff pad to obtain a smooth surface. In addition, two sizes of sand paper (silicon carbide 150C and P320) were used in place of the polishing pad to create the microstructures through CMP. Samples were polished for 2 minutes with ~3% H_2O_2 as an oxidizer to promote chemical activity. Material removal rates were calculated through weighing the samples pre and post polish by a high precision balance (four digits after zero). All samples were cleaned in ultrasonic bath with pH adjusted DI water for 5 minutes and dried with nitrogen gas before they were characterized. Same experimental conditions in 3D level applied to dental implant samples obtained from ImplantKa Limited.

Surface Characterization

All samples were characterized for wettability through contact angle measurements using simulated body fluid (SBF) with a KSV ATTENSION Theta Lite Optic Contact Angle Goniometer using the sessile drop method. The microstructures of specimens were examined using a Nanomagnetics Atomic Force Microscope (AFM) with contact mode and the surface roughness values were recorded on 10 x 10 µm scan area. X-Ray Diffraction analyses were conducted on bare Ti sample and CMP applied sample in the absence of H_2O_2.

Biological Activity Analyses

The infection resistances of the CMP induced titanium plates were conducted through bacteria growth analyses. Titanium plates were sterilized with an autoclave at 120ºC for 20 minutes before the microbiological analysis. Cronobacter Sakazakii (Gram-) bacteria was used and the bacteria growth was observed over 1, 3 and 7 days and quantified by measuring the thickness of the colonies grown on the sides of the plates. For the fibroblast cell attachment testing, titanium plates were sterilized with UV radiation. L929 fibroplast cells were incubated in the laboratory for the proliferation on the samples. After 15 days of incubation period, cell morphology was assessed as 10^4 cell/cm^2 by counting under microscope with thoma lamella. To simulate the osteoblast (bone cell) response hydroxyapatite (HA) growth test were implemented. HA was deposited on the processed titanium plates as described in literature [9] and the results were evaluated through weight differences pre and post deposition. The surface roughness values were quantified by taking AFM images.

Results and Discussion

We have demonstrated in previous work that the application of CMP on titanium surfaces resulted in significant changes in the surface characteristics [10]. Contact angle values reflecting on the wettability of the surface were higher as the surface roughness was increased through induced micro level roughness. Surfaces with smoother finish, such as in the one exposed to CMP with polytex pad in the presence of oxidizer resulted in more wettability and hence a lower contact angle and the surfaces with the induced micro roughness resulted in a higher contact angle. AFM analyses of the original untreated titanium plate compared to surface with CMP conducted using polymeric pad in the presence of 3% H_2O_2 showed 118.77 nm and 78.05 nm RMS surface roughness, respectively. Furthermore, it was also observed that the CMP treatment in the presence of oxidizer showed the formation of an amorphous oxide film [11]. In order to analyze the biocompatibility of the prepared surfaces, controlled bacteria growth analyses were conducted. The sample surfaces intentionally scratched tend to accumulate more bacteria colonies as compared to the smoother surfaces. Particularly the sample processes through proper CMP process allowed the least amount of bacteria growth around the titanium plate and oxidizer used samples enable to the limit of the growth during the evaluation process.

HA attachment test showed an increased growth as a function of the increasing surface roughness as summarized in Table I. The fibroblast type L929 cell attachment was also observed to increase with the increasing surface roughness. However, the samples with very rough surfaces demoted the amount of cell attachment, which is believed to be due to the presence of very sharp edges on the surface topography resulting in the rapture of the cells when they try to attach on the surface. On the other hand, the use of oxidizer during the CMP process promoted the cell growth.

Figure 2 illustrates the results obtained on the 3D implant samples by mainly comparing the wettability through measurement of contact angle at the various locations of the dental implant. CMP induced dental implant sample wettability analyses were similar to the responses obtained on the flat titanium plates. The wettability behavior of the implant surface's different regions showed changes according to step height of the screws, which is given in the Figure 2.

TABLE I. L929 cell growth after 5th day and HA deposition response.

Samples	Average Cell Number x10^4 cell/cm^2	HA attachment amount(g)
As is	55.33	1.50
CMP without H_2O_2	51.94	1.59
CMP with 3% H_2O_2	61.08	1.45
CMP with 3% H_2O_2+Ab. P. (45um)	55.53	1.80
CMP with 3% H_2O_2 + Ab. P. (90um)	52.38	2.10

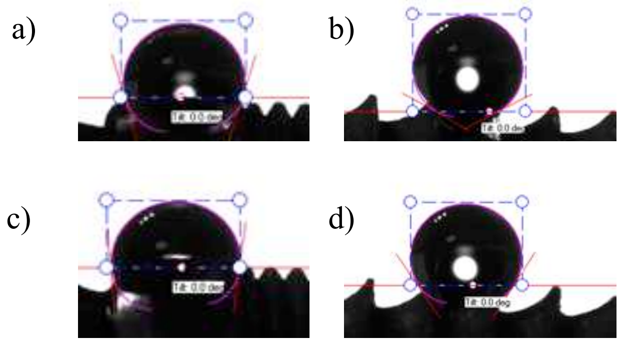

Figure 2. Wettability analyses on different part of dental implant with as received (a & b) and CMP induced in the presence of oxidizer (c & d).

Summary

It is known that the increased surface microstructure and surface oxidation can promote the adhesion of the biological species on the implant surfaces. In this study, CMP process is proposed as an alternative technique to induce microstructure or smoothness to the titanium surfaces to enable more biocompatible surfaces by simultaneously forming a protective oxide layer. Wettability analyses through contact angle measurements were shown to be a valid and easy approach to detect the surface roughness that affects the bioactivity on the surfaces. Biocompatibility analyses conducted by cell attachment also showed difference in the cell growth by increased surface structuring. Hydroxyapatite growth also correlated to increase in surface roughness. The 3D CMP design is under development for the dental implant CMP and as a part of this study, a new design with robotic arm integration is proposed and being tested.

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