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Development and Characterization of Hydroxyapatite Coating on Titanium Surfaces

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Abstract: Titanium and its alloys have been widely used as implant materials due to several favourable properties like biocompatibility, light weight, high corrosion resistance, wear and fatigue resistance and ability of integrate with bone. Since the implants are placed within the human body, better quality and longer life is in demand. One of the most prominent reasons for implant failure are bacterial infections. Antibacterial drugs are possible solution to bacterial infection but it kills the normal cells and some traces of bacteria are left there which can form biofilms which can further promotes bacterial growth. Surface modification of titanium promotes osseointegration and simultaneously reduce bacterial adhesion. This study is to the modification of the Ti surface by hydroxyapatite coating. Painting method is use to coat the Hydroxyapatite (HA) powder on the titanium surface. For surface characterization, the surfaces were investigated by 3D confocal microscopy and Energy Dispersive X-ray spectroscopy (EDX). The hydrophilicity was assessed by measuring contact angles. The results show that the average roughness increases with the surface coating, thereby the wettability of the surface increases. Surface modification helps to enhance the properties of implant surface. EDX spectra shows that presence of elements (Ca, P and O) which are main constitutes of hard tissue, teeth and tendons and the average surface roughness (Ra) of deposited layer will stimulate better Osseointegration. Surface oxidation states appeared to have a major role in wettability.

Keywords: Hydroxyapatite coating, Painting method, Wettability, Bio implants.

I. INTRODUCTION

Simple bone fractures can be treated by external fixation; bone fractures usually require internal fixation that uses implants (through surgery) to provide temporary support at the fracture site for boost healing of the fracture. Metallic implants, made of titanium and its alloys, stainless steel and cobalt-chromium alloys are the traditional materials used for internal fixations due to their excellent mechanical properties and endurance [1]. In the 1950s titanium was first used in orthopedic applications. Orthopedics is that branch of surgery which dealing with the rectification of deformities of bones. Orthopedic surgeons treat musculoskeletal trauma, spine diseases, sports injuries, and much more by using both surgical and nonsurgical resources. Currently, titanium and its alloys are the main preference for orthopedic devices such as hip joints, bone screws, knee joints, spinal fusion cages, shoulder and elbow joints, and bone plates and scaffolds due to several favourable properties like biocompatibility, light weight, high corrosion resistance, wear and fatigue resistance and ability of integrate with bone.

In the bone surgery, the important and desirable goal is osseointegration. The integration of connective tissues (osteoblasts) in to the surface of implant metal is termed as osseointegration. Osseointegration brings a stable bone-implant connection that can support prosthesis and transfer applied loads without focusing stresses at the border between the bone and the implant. The early healing and relieve patients' pain can facilitate by better Osseointegration. Bacterial infection is more susceptible in Metallic implants [2]. The local defence system is highly affected by the surgical trauma after implantation, and it is highly susceptible time for bacterial infection. The defence mechanism at the implant-tissue interface is affected even after tissue integration due to a smaller number of blood vessels. The reduced defence mechanism causes colonization of bacteria resulting infection [3]. Appropriate alloying or surface treatment (modification) provides sufficient strength requirement for efficient bone healing process. Coating is the simplest method to overcome the problems of fast degradation and high corrosion rate than alloying, which provides a protective layer against the corrosive environment. Surface topography modifications appear promising, since they avoid the spread of antibacterial substances in the neighbouring tissues with the consequent risk of inducing bacterial resistance.

To overcome these surface-related problems on metallic implants materials, a variety of surface modification techniques have been used including chemical treatment, physical and biological methods. Considering that the implant surface is the first part of the implant that interacts with the host. Modification on implant surfaces which inhibit formation of biofilms and retards bacterial adherence has great potential in the design of implants. Surface modification has been essential in enhancing biocompatible and Osseo-conductive properties of the implant [4]. Surface texturing is a process of inducing specific patterns such as micro-pillars, grain structures and micro-holes which can lead to improved optical, tribological, biomedical properties, as well as surface wettability and the surface free energy of the implant material [5]. Laser texturing is found to have significantly reduced the adhesion of bacteria and reduced the formation of biofilm. Hydrophilic implant with a rough surface has also exhibited better osseointegration and antibacterial property [6].

Hydroxyapatite (HA) that is basically pure calcium hydroxide phosphate, has a chemical formula $Ca_{10}(PO_4)_6(OH)_2$. It has favourable osteo-conductive and bioactive properties making it a preferred biomaterial for both dental and orthopaedic biomedical

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applications. Hydroxyapatite has been used for many years as a bioactive implant coating to improve Osseointegration [7]. The chemical composition and crystal structure of Hydroxyapatite is very comparable to the human skeletal system, which is therefore a more suitable material for bone replacement and reconstruction and it has a large capacity for adsorbing proteins. HA is one of the widely used coating materials in orthopaedic and dental applications due to its superior biocompatibility and strong bonding with human bones. HA coating on dental implants is used for long-term survival of implants. HA coating over metal substrate stimulates bone tissue formation, improves corrosion properties, improve the cell adhesion, Osseointegration, reduce the formation of fibrous tissues and gives a longer life to the implants. Hydroxyapatite materials cannot be used as implant to substitute huge bony defect or load-bearing applications; hence this material was commonly used to create thin biofilm over the implant which associates the mechanical performance of implant material and bioactivity of HA [8].

Various coating techniques have been developed for coating HA on implants, such as Plasma Spraying, Physical Vapour Deposition (PVD), Sol-gel, Chemical Vapour Deposition (CVD), Electrochemical Deposition, Electrophoretic Deposition and Pulsed Laser Deposition (PLD) [9]. Commercially Plasma spraying is widely used but high equipment cost, low crystallinity and presence of phases that are unwanted in a coating are common problems faced by this technology [10]. Electrochemical-deposition of HA is regarded as an inexpensive and simple process that can be performed at a room temperature. The chemical composition and thickness of HA coating can easily be controlled by using electrochemical-deposition.

The aim of the present work is to coat hydroxyapatite (HA) powder on the grade 5 titanium surface. The surface chemical composition of HA coatings was characterized by Energy Dispersive X-Ray Spectroscopy and surface topography were analysed by Confocal Laser Microscope. Evaluation of wettability was determined using a Sessile drop test.

II. MATERIAL AND METHODS

A. Material Preparation

Material used for the experiment is commercially sourced medical grade titanium, namely Grade-5 (Ti6Al4V, Alloy). Cut into square pieces using a Wire cut EDM machine having dimensions of 10mm×10mm length, breadth and a thickness of 1mm. To get surface homogeneity samples were sequentially polished with different grades of SiC paper (120-1200). The scratches on the surfaces are further removed by applying diamond lapping paste of 0.5µm. After polishing, to remove the surface residues on surface the samples were cleaned ultrasonically in distilled water, rectified spirit and acetone for 5min and then dried in hot air.

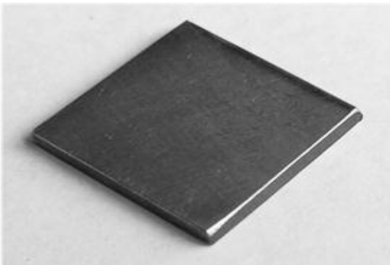

Fig.1. Polished Titanium sample Grade-5

B. Hydroxyapatite Coating

To obtain homogeneous roughness, all the pieces were sanded with 220-1200 grade sandpaper and polished with 1 µm alumina paste. After this procedure, the samples were washed in acetone, using an ultrasound bath for 15 min. Coating process of the hydroxyapatite on titanium was carried out using a suspension of hydroxyapatite in oil of turpentine (OT). The proportion of hydroxyapatite powder and oil of turpentine was one to three (g/mL) and the mixing was performed by using a spatula. The suspension was applied to the surface of the titanium by using a brush. Then the painted samples were placed in a furnace at 800 °C for 30 min.

Fig. 2. Hydroxyapatite powder

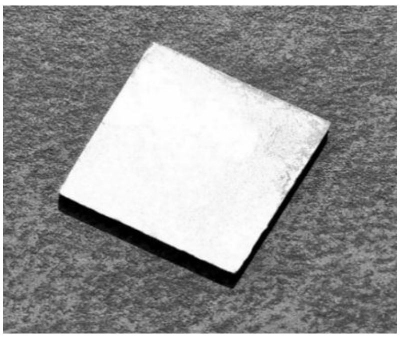

Fig. 3. Hydroxyapatite coated Ti plate

C. Surface Topography

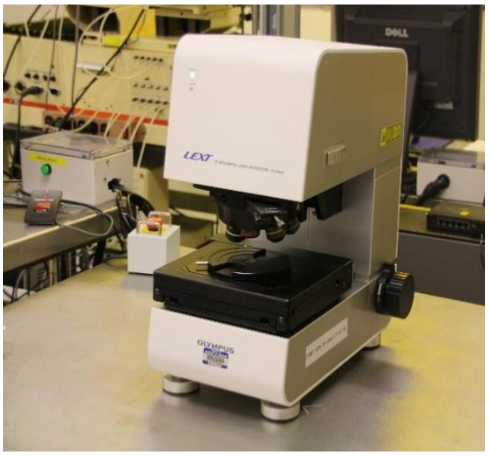

Fig.4. Olympus LEXT OLS 4000 Confocal Laser Microscope

The surface topography of the polished and HA coated surface were analysed by Olympus LEXT OLS 4000 Confocal Laser Microscope. 2D and 3D surface images were captured using laser imaging mode. The scanned area was 256 × 256μm^2. Images were recorded under various magnification scale using a 405nm Laser and Photomultiplier Detector. The Minimum Z-Resolution was 10 nm and Minimum XY-Resolution was 120 nm. The surface parameter includes R_a (Average roughness), R_{sk} (Skewness of surface), R_{ku} (Kurtosis of surface) were measured randomly in several locations from the polished and HA coated surfaces.

D. Surface Chemistry Analysis

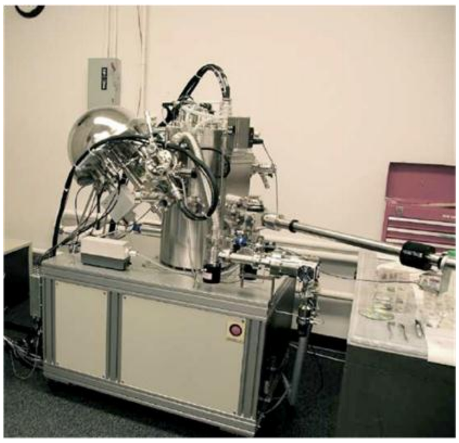

Fig.5. Energy Dispersive X-Ray Spectroscopy

The surface chemistry of HA coated Titanium grades 5 was tested by Energy Dispersive X-Ray Spectroscopy using Phi 5000 Versaprobe Scanning Esca Microprobe equipped with x-ray source with a focused beam <10 μm to 300 μm. It is an analytical technique used for the elemental analysis or chemical characterization of a sample.

E. Wettability Analysis

Fig.6. KRUSS Drop Shape Analyser – DSA25

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Wettability (contact angle) at room temperature was determined using a Sessile drop test by dropping micro-litre droplets on the surface. Distilled water was used as the testing liquid in order to avoid the chemical reaction with the surface. The contact angle values were analysed using a multifunctional video-based camera system KRUSS Drop Shape Analyser - DSA25. The image capture and data analysis were made by KRUSS ADVANCE Software.

III. RESULTS AND DISCUSSION

A. Surface Topography

Images obtained by confocal microscopy shows neat well-defined coated surface. The surface of the coated plate can be compared with the polished surface as reference plate. To quantify the topography of the titanium substrates we can use the combination of the three microscopy techniques. The surface roughness parameters of the titanium surfaces are shown in Table.1.

Table 1. Surface roughness parameters

Specimens	**Roughness Parameters**		
	R_a (µm)	**R_{sk}**	**R_{ku}**
Grade 5 Polished	0.323	0.221	2.837
Hydroxyapatite coated	2.105	-0.0628	3.947

The arithmetic average roughness (R_a) value of roughness profile determined from deviations about the centre line within the evaluation length. The most common parameter for a machining process and product quality control. R_a value is easy to define, easy to measure even by a least sophisticated profilometers and gives the overall description of surface amplitude. Skewness (R_{sk}) evaluates the degree of asymmetry of surfaces. In cases of asymmetric distribution, it can be characterized as positive or negative. Kurtosis (R_{ku}) describes the distribution sharpness and the normal distribution takes the value 3. For $R_{ku}>3$ the surface has sharp peaks (spiky), $R_{ku}<3$ the surface has peaks are bumpy.

For Grade 5 the polished sample have average roughness R_a values in the range of 0.323µm and the hydroxyapatite coated sample have a surface roughness R_a value in the range of 2.105µm. Surface roughness increased after coating. Coated surface shows higher kurtosis value ($R_{ku} >3$) and negative skewness ($R_{sk} < 0$), so we can conclude that troughs and peaks are present. But the peaks are more prominent than the troughs in coated surface. The coating thickness of hydroxyapatite was measured using SEM cross-sectional morphology values approximately 90.6 ± 8.0 µm.

Bacterial adhesion can be controlled by the surfaces with microscale topography. Bacterial adhesion on Ti substrates is reduced with increasing roughness, which is associated with the decreased number of adhesion points and a reduced attachment area.

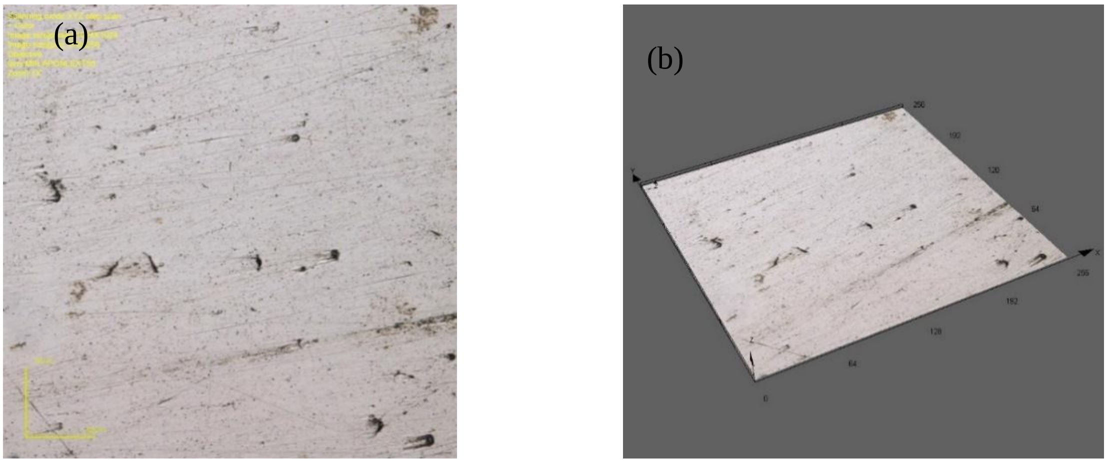

Fig.7. (a) and (b) Confocal microscopy images of Ti grade 5 Polished surface

SEM images in Fig.8 are taken form the HA coated on titanium surface. The white colour distributed over the surface is due to the presence of HA coating. It was evident that the deposited layer was dense and uniform. Some isolated particles were recognized on the layer from Fig. 8 (b), this may due to accumulation of slighter particles. This kind of isolated particle agglomerations increases the surface roughness and helps in improving osseointegration.

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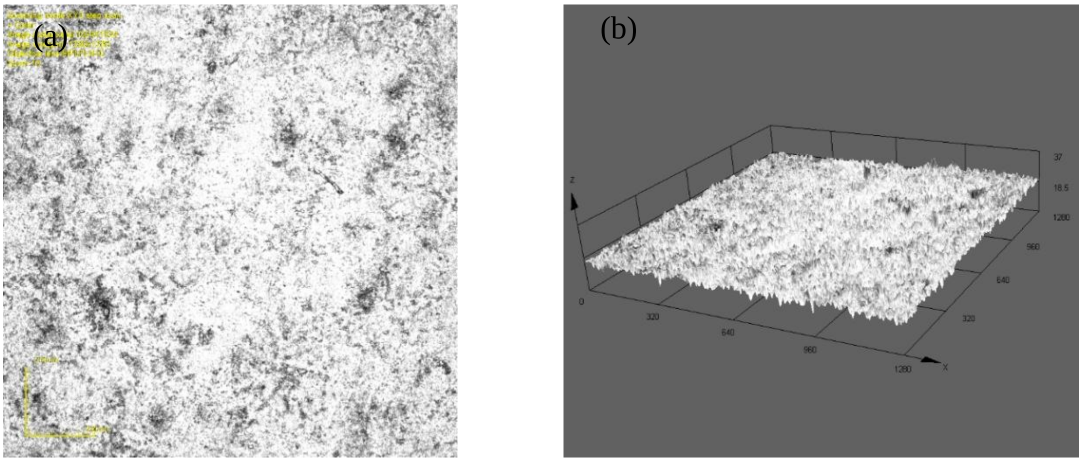

Fig.8. (a) and (b) Confocal microscopy images of Hydroxyapatite coated Ti surface

B. Surface Chemistry Analysis

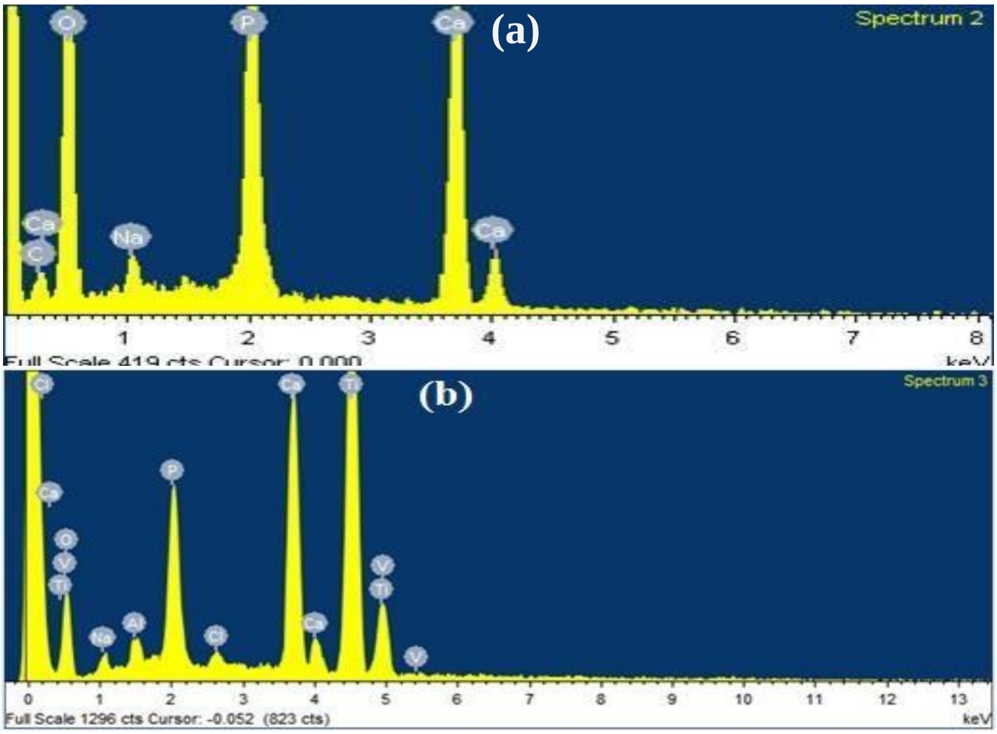

Fig.9. EDX images of (a) Hydroxyapatite powder (b) HA coatings on Ti grade 5

The EDX spectra obtained for hydroxyapatite powder (fig. 9.a) and HA coatings on grade 5 (fig. 9. b) are given. EDX spectra of the layer which comprises of the characteristic peaks of calcium (Ca), phosphate (P) and oxygen (O) elements, which approves that the layer was Hydroxyapatite. In Figure 9 (a), the elements and allocation of the elements are presented in Hydroxyapatite powder is given. The presence of Ca is 19.9%, P is 11.75% and oxygen is 41.4%. In Figure 9 (b), the elements and allocation of the elements are presented in HA coated grade 5 alloy are given. The presence of Ti is 35%, Ca is 15.77%, P is 9.73% and oxygen is 45% are also evidenced on the coated surface of the

grade 5. The standard percentage of Ca is 18% and P is 10%. The Ca/P and Ca/O ratios were found to be 1.62 and 0.35, respectively, which is in equivalent with the theoretical Ca/P and Ca/O ratios of HA powder which is 1.67 and 0.38 respectively. This shows that the presence of HA helps in bio-growth of the substrate. The elements (Ca, P and O) are main constitutes of hard tissue, teeth and tendons. The average surface roughness (R_a) of deposited layer was 2.105µm measured using confocal microscopy. Many literatures verified that the surface having rough surface will stimulate better Osseointegration.

C. Surface Wettability Analysis

The contact angle values of the polished and hydroxyapatite coated samples are show in Fig.10. The hydrophilicity of the surface is enhanced after surface modification. It has been reported that contact angle greater than 90^0 are hydrophobic surface and have less than 90^0 are hydrophilic surface.

The polished titanium surfaces surface exhibited hydrophilicity and is less than 90^0. Hydroxyapatite coated surface become super hydrophilic due to presence of oxide films in the surface. From XPS results the surface is additionally oxidized after HA coating, which makes oxygen vacancies and water molecules involve in these vacancies delivering hydrogen bonding. Thus, oxidized surface enhances the surface wettability.

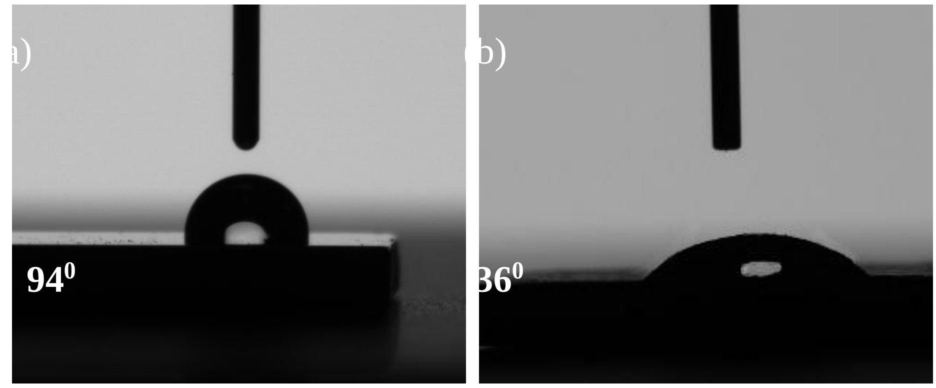

Fig.10. Contact angle measurement of (a) Ti grade 5 polished (b) Hydroxyapatite coated surface

Considering this high wettability is usually required for inducing cell adhesion and the surface wetting is the primary step that leads to bone formation. The present wettability is promising, since hydroxyapatite coated surface present a hydrophilic behaviour with a contact angles generally smaller than those observed for the polished surface.

IV. CONCLUSIONS

This work is focused on the study of osteogenic behaviour of grade 5 titanium surfaces with hydroxyapatite coated, and aims at improving the wettability on the implant surfaces. The surface roughness of the specimen surfaces increased significantly after hydroxyapatite coating. Bacterial adhesion on substrates is reduced with increasing roughness. Hydroxyapatite layer was successfully deposited on the titanium surface by painting method. It is a simple, low-cost methodology, when compared to other coating process. The deposited layer was uniform and free from pores and voids, some isolated particle was formed. It was believed that surface roughness of the layer increased by this isolated particle and promote Osseointegration. Also, the Ca/P ratio of the layer was close to that of standard Hydroxyapatite. Hydroxyapatite coated surface become super hydrophilic due to presence of oxide films in the surface. High wettability is usually required for inducing cell adhesion. EDX spectra shows the presence of elements Ca, P and O, which are the main constitutes of hard tissue, teeth and tendons and the average surface roughness (R_a) of deposited layer was 2.105μm the rough surface will stimulate better Osseointegration.

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