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Hydroxyapatite Bilayers Coating on Screw Implant Ti6Al4V ELI with Electrophoretic Deposition Method for Improving Osseointegration

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ABSTRACT

Utilization of an alloy titanium (particularly Ti6Al4V), as fracture fixation in biomedical application has restriction because of will associate with osseointegration failure. An effort to titanium coating by hydroxyapatite monolayer still has poor mechanical properties and may lead to implantation failure. Hydroxyapatite bilayers coating aims to protect releasing hazardous ions from implant to the body and improving the osseointegration at the same time. In this research, nanoparticle hydroxyapatite (first layers) and microparticle hydroxyapatite (second layers) were used as coating materials on implant prototype of Ti6Al4V ELI screws. The coating was carried out by electrophoretic deposition (EPD) method used different voltage (2 and 3 volt) for deposition time of 2 and 3 minutes for forming first layers. The process was then continuing for making second layer at 5 and 10 volt for 2 and 5 minutes. In order to intensify of coatings, hydroxyapatite bilayers-coated titanium was air-dried overnight and then sintered at 700oC for 1 hour. The coating layers were characterized by optical microscope, Scanning Electron Microscope (SEM) and thickness gauge series tester. Result of the study show that nanoparticle hydroxyapatite layers are more uniform, thin, dense than microparticle hydroxyapatite layer. Moreover, the second layer shows less adhesion. The obtained voltage and deposition time for best bilayers coating characteristic are 2 volt/3 minutes for nanoparticles hydroxyapatite and 5volt/5minutes for microparticles hydroxyapatite. By approximately 71%-100% surface coverage and 56 µm thickness of bilayers coating, that parameters can be considered to improve osseointegration.

KEY WORDS: *Hydroxyapatite, bilayers coating, Ti6Al4V, electrophoretic deposition*.

1.0 INTRODUCTION

Alternative biomaterial using titanium alloy (Ti-6A-4V) as implantation materials with biomechanical and biocompatibility characteristic still cannot overcome the problem of immunity and osseointegration response. Titanium biomaterials have low bioactivity properties and negative impact on corrosion with exert long-term period. Afterward this condition stimulates biological environment disruption and may cause trauma or impaired immunity [1]. Baan et al [2], not only the toxic Ti-6Al-4V alloy constituents, but in 2006 the International Agency for Research on Cancer (IARC) classified TiO2 as a carcinogenic factor against body tissue. Another study from Oldani and Dominguez [3] showed that the titanium inert properties had unstable implant result with skeletal tissue, so there is a movement on micro scales and resulting in leakage that can lead to cracks that can degrade the biomechanical properties of titanium. Wang [4] reported that layer formation of fibrosis (encapsulation) in Ti-6A1-4V implant may be failed on osseointegration. Other crucial issues that arise are the release of biomaterials such as Ti4+, Co2+ and Al3+ ions resulting in decreased cellular metabolism such as DNA synthesis, mitochondrial activity, mineralization, and alkaline phosphorus and osteocalcin activity in vitro [5].

Alfarsi et al [6] and Hamlet et al [7] suggest that pure titanium biomaterial induces proinflammatory cytokine activity ie TNF-α, IL-1α, IL-1β and chemokine Ccl-2. The same conditions were also found by Meng and Yang [8] on titanium particles induced proinflammatory cytokines (IL-1, IL-6, TNF-α) and osteoclast differentiation factors (RANKL). Wazen et al [9] suggest that there is a decrease in the expression of TGF-β in vivo on the surface of Ti-6Al-4V biomaterials. The results of in vivo gene expression profile analysis on titanium biomaterials by Ivanoski et al [10] suggest that there is an increase in gene expression associated with an inflammatory response (TNF-α, IL-1 and MCP-1) and low gene expression for osteogenic cell differentiation such as osteoblasts (BMP-2, VEGF, I-kB kinase / NF-kB cascade, TGF-b / BMP, Notch and Wnt signaling). This proves that titanium surfaces are still less bioactive to stimulate new bone tissue growth and improve osseointegration. Therefore, titanium surface modification can be performed without affecting the biomechanical properties of biomaterials as implantation materials.

Ti-6Al-4V surface modification with bioactive biomaterial i.e. hydroxyapatite aims to improve the integration of bone tissue with implantable biomaterials thus increasing the success of implantation. The bioactive properties and biocompatibility of hydroxyapatite can reduce the immune response and induce the growth of new bone tissue thus stimulating osseointegration. However, poor mechanical strength and hydroxyapatite monolayer solubility may affect the structure and functionality of the implant [11]. Hydroxyapatite monolayer may be degraded in the body environment and associated with an inflammatory response. These characteristics will stimulate protein adsorption on the surface of the implant and further promote the adhesion of cells to the growth of new bone tissue required at the beginning of repair of bone tissue. Although hydroxyapatite degradation triggers the growth of new bone tissue and integrates well with bone tissue, weak bonds with the substrate may degrade the biomechanical properties of Ti-6Al-4V biomaterials. Thus, the hydroxyapatite coating must have good strength on the biomaterials substrate with the level of controlled degradation i.e. the formation of bilayers.

Mechanically, the use of hydroxyapatite coatings has an effect on the mechanical characteristics of biomaterials. Levingstone [12] suggests that multilevel hydroxyapatite coatings consisting of stable/solid and active/amorphous layers with plasma spraying methods have good biocompatibility properties with bone tissue in vitro. In addition to triggering the differentiation and formation of bone tissue by amorphous layers, the implants have a stable bond between substrate biomaterials and hydroxyapatite due to stable/solid layers. Gu et al [13] revealed that the adhesive properties of hydroxyapatite are preferable in stratified coatings compared with one layer of hydroxyapatite and there is an increase in bond strength in the coating. Therefore, the use of hydroxyapatite coating not only gives effect to biological response but also gives effect to osseointegration implantation.

The use of plasma sprayed methods negatively affects the mechanical characteristics of the coating and is associated with implant failure. Sintering processes with temperatures above 1000oC trigger the degradation of the mechanical properties of titanium (phase transformation, grain growth, and surface oxidation) resulting in biocompatibility of biomaterials [14]. An alternative method that uses low temperature to produce a layer of hydroxyapatite bilayers efficiently and effectively is electrophoretic deposition (EPD). The use of EPD is not only based on its high versatility on biomaterial differences [15], but it is also an effective (cost) method that requires only simple equipment [16]. The advantage of the EPD method is the deposition of biomaterials with uniform homogeneity of the microstructure and yields controlled coating thickness with thin and dense forms of substrate with different shapes and three-dimensional and porous complexes [17] The EPD method has been used for homogeneous HA coating on cortical screws which can improve bone fixation and reduce interfacial clearance [18] and can increase the corrosion protection of metals in SBF solution [19]. Therefore, this study examines the coating of hydroxyapatite bilayers on the surface of Ti6Al4V ELI material with prototype screws.

2.0 MATERIALS AND METHODS

Titanium alloy discs, Ti-6Al-4V, was formed by lathe machine in order to make a screw that used as a substrate in this study. Samples abraded by using silica carbide (SiC) paper with 600-grit and 1000-grit followed by polishing machine for facilitate coatings. Material was then immersed and cleaned in distillation water and methanol used ultrasonic bath for 15 minutes and followed with NaOH solution for 1 hours. The samples were air dried with Stirring Hot Plate machine for 5 minutes.

The EPD suspension was prepared by adding 1 gram hydroxyapatite powders to 100 mL ethanol solution. The pH value was adjusted to 4.0 by addition of HNO3 solutions. The graphite and titanium were anode and cathode, respectively. The deposition process was carried out by different deposition voltages and times for the first layers The coating was carried out by electrophoretic deposition (EPD) method used different voltage (2 and 3 volt) for deposition time of 2 and 3 minutes for forming first layers that is 2V2M, 3V2M, 2V3M and 3V3M. The process was then continuing for making second layer at 5 and 10 volt for 2 and 5 minutes that is 5V2M, 10V2M, 5V5M, and 10V5M. In order to intensify of coatings, hydroxyapatite bilayers-coated titanium was air-dried overnight and then sintered at 700oC for 1 hour. The as-deposited coatings sample heated used vacuum furnace (High Temperature Vacuum Tube Furnace GSL-1100) in order to increase density of coatings. Morphology analysis of coating surface was examined using optical microscope (Olympus GX71) and scanning electron microscope (Hitachi S3400N operating at 15.0 kV) and thickness gauge series tester.

3.0 RESULTS AND DISCUSSIONS

Figure 1 show that commonly electrophoretic deposition method of nanoparticle and microparticle is effective in resulting bilayers coating on biomaterial Ti6Al4V ELI screws surface. Levingston [12] reported that hydroxyapatite bilayers coating could be obtained by plasma sprayed method. Hence, using of this method may affect the alteration of coating composition and will affect for implantation process in body tissue.

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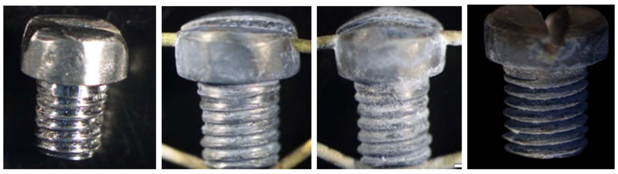

Figure 1: Hydroxyapatite bilayers coating by electrophoretic deposition at 2V3M and 5V5M; (a) uncoated sample, (b) nanoparticle-coated sample, (c) microparticle-coated sample, and sintered sample.

Titanium surface was covered up by nanoparticle hydroxyapatite entirely, uniform, and thin, while a little amount of microparticle hydroxyapatite was found as second layers. At second layers was seen particle agglomeration as shown in the Figure 2. Differences of particle size have impact nanoparticle hydroxyapatite migrate easily in suspension beneath electric field. Movement of larger particle needs higher electric energy.

The else influence factors for morphology characteristic of bilayers coating is charge difference. Nanoparticle hydroxyapatite adhered conveniently owing to charge difference with negative-charged titanium surface. Therefore, when EPD process of second layers was applied on nanoparticle hydroxyapatite that is positive charged, microparticle hydroxyapatite have difficult attachment.

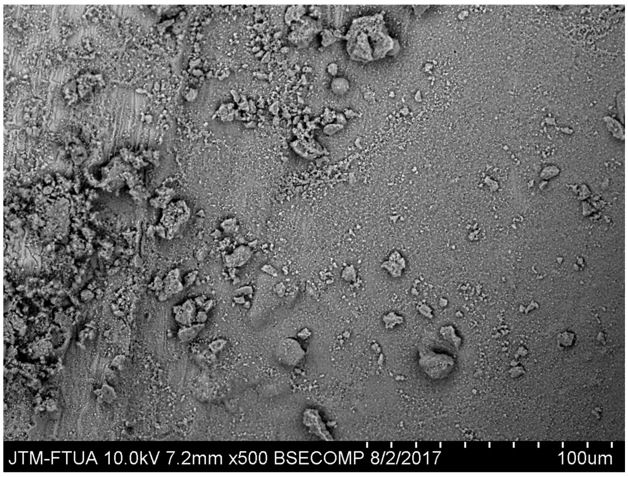

Figure 2: SEM assessment of hydroxyapatite bilayer coating at surface Ti6Al4V ELI screw

The given voltage and deposition time within electrophoretic deposition method lead to an influence for coating structure too. At lower treatment, 2V2M dan 5V2M, the optimal hydroxyapatite bilayer coating wasnot achieved. The same condition was found at highest treatment that is 3V3M and 10V5M. The voltage of 2V fo 2M is sufficient to deposite nanoparticle hydroxyapatite already, but is not enough to move microparticle hydroxyapatite so amount of particles adhered is sligh. The high energy was needed in order to deposit larger particles.

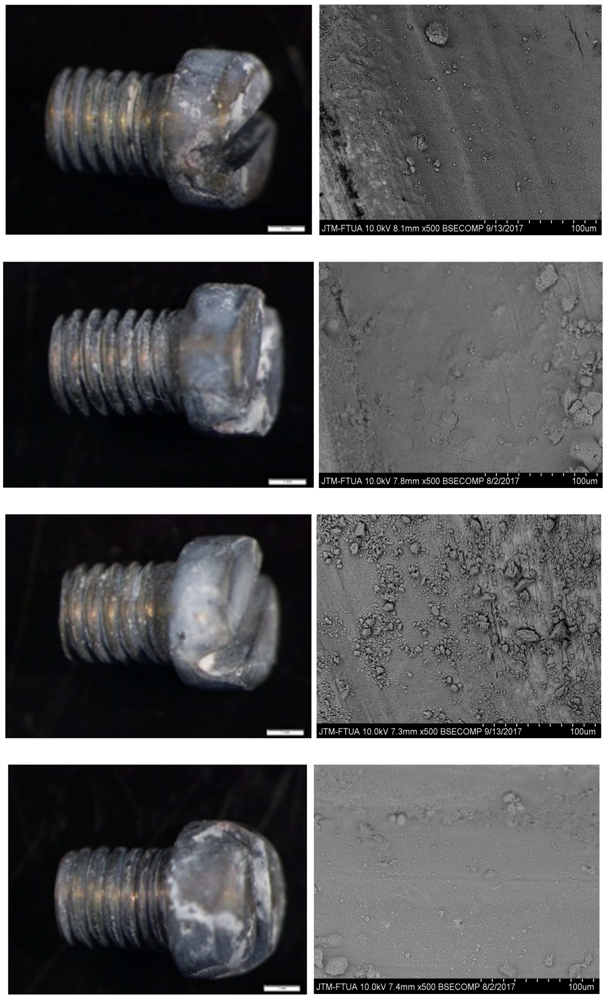

Figure 3: Morphology characteristic of hydroxyapatite bilayers coating at different treatment; (a) 2V2M and 5V2M, (b) 3V2M and 10V2M, (c) 2V3M and 5V5M, and (d) 3V3M and 10V5M

Deposition increase along with the raising of voltage and deposition time. The excess energy and time will influence for degradation the quality of coating such as less adhesion of intraparticle and then peeling off easily. The optimal result in this study was found at 2V3M and 5V5M treatment. Titanium surface was coated by nanoparticle and microparticle hydroxyapatite as bilayers coating properly. The voltage 2V is sufficient to deposite nanoparticle hydroxyapatite for 3M. During 5M, microparticle hydroxyapatite can be deposited through voltage 5V. It can be shown in coating characteristic such as surface coverage and coating thickness value.

Through over 2V3M and 3V3M treatment, titanium surface was covered up properly by nanoparticle hydroxyapatite bilayers as shown in the Table 1. However, it was resulted microparticle layer that coat titanium surface entirely yet. Voltage have contribution to coat the entire of titanium surface evenly. Herewith, time have impact for movement and deposition of particles in suspension. The previous research report that the too

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high voltage affect particle agglomeration cause of current turbulence. In the relative short time, particles can migrate, deposite, and arranged improperly The resulting coating have uneven structure and less adhession.

Table 1: Surface coverage value of hydroxyapatite bilayerscoating by electrophoretic deposition method at different treatment of voltage and time deposition

Surface Coverage (%)	2V2M and 5V2M	3V2M and 10V2M	2V3M and 5V5M	3V3M and 10V5M
First layer	95,26	99,60	100,00	100,00
Second layer	32,18	57,53	71,93	60,90

Deposition time determine the deposition rate on surface titanium. The increas of deposition time followed by the rise of particle number that migrate and depsoite. The coating thickness was influenced by the increase of deposition time [20] . This study obtains the coating thickness is around 33-55 µm as shown in Figure 4 that means appropriate with biomedical application in orthopaedic application.

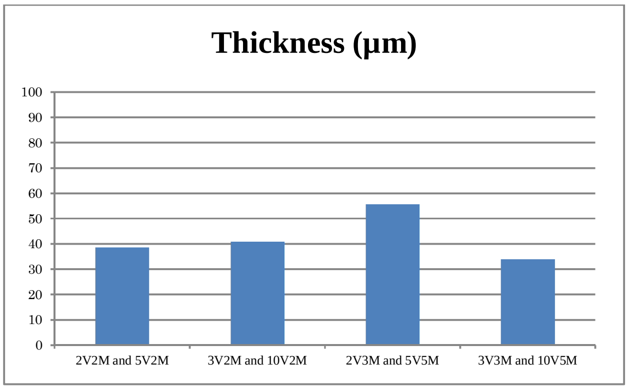

Figure 4: Thickness value of hydroxyapatite coating layers by electrophoretic deposition

4.0 CONCLUSION

In conclusion, the uniform, thin and dense layers can be obtained by nanopaarticle hydroxyapatite coating and followed by less adhesion of microparticle hydroxyapatite layer. The obtained voltage and deposition time for best bilayers coating characteristic are 2 volt/3 minutes for nanoparticles hydroxyapatite and 5volt/5minutes for microparticles hydroxyapatite. By approximately 71%-100% surface coverage and 56 µm thickness of bilayers coating, that parameters can be considered to improve osseointegration. Therefore, coatings with electrophoretic deposition method used nanoparticle and microparticle hydroxyaatite as bilayers coating is effective for resulting the coating suitable for biomedical application. There is needed advanced research for assessment the biomecanical properties and biological response for bilayers coating.

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