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The Effect of Sintering Temperature on Bilayers Hydroxyapatite Coating of Titanium (Ti-6Al-4V) ELI by Electrophoretic Deposition for Improving Osseointegration

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Abstract. Bilayers hydroxyapatite (HA) coating using electrophoretic deposition (EPD) method has been applied into a biocompatible metal, Ti-6Al-4V ELI, in order to improve bioactivity of the alloy and then to accelerate bone remodeling and osseointegration during implantation. Two steps EPD process was conducted for obtaining based layer consist of HA nanoparticles using voltage 3 volt for 3 minutes. It was then followed by second layer formation consist of HA micro particles using voltage 5 volt for 5 minutes. The coated alloy was then sintered at temperatures of 700°C, 800°C and 900°C for each 10 minutes within vacuum tube furnace at the sintering rate 20°C/s. Surface morphologies were examined using optical microscope and scanning electron microscope (SEM). The result of this study showed that bilayers hydroxyapatite coating onto Ti-6Al-4V surface was produced through EPD with those parameters. Sintering treatment at temperature 800°C gives thin, dense, even and crack-free coatings. The Ti-6Al-4V ELI surface is almost fully covered by bilayers hydroxyapatite (with surface coverage 98.6%) with adequate bonding (without lost weight of coating layers). An improper coating layer is obtained for lower (700°C) and higher (900°C) temperature. The sintered samples at temperature 900°C have micro cracks, void and debonding layers. It is expected such bilayers hydroxyapatite with sintering at 800°C can initiate mineralization and then make a quick osseointegration.

Keywords: bilayers hydroxyapatite, Ti-6Al-4V ELI, electrophoretic deposition, temperature sintering, osseointegration

1. Introduction

Biomaterial implantation for fracture treatment gives an effect directly to body metabolism. Biological responses determined by biomaterial characteristics will influence bone remodeling and osseointegration as the aim of successful implantation. Osseointegration can be adjusted using materials with good mechanical properties combined high biocompatibility characteristic. This properties may be found on orthopedics implant that is titanium alloy, Ti-6Al-4V ELI (*extra low interstitial*) with compositions 80% titanium, 6% aluminum, 4% aluminum and other constituents. In structural, Ti-6Al-4V have phases α/β will transform from HCP- α structure to BCC- β structure at temperature 980°C [1]. Titanium has corrosion resistance cause of spontaneous passivation when contacts oxygen to form surface oxide layers



[2]. This layer will protect in releasing of hazardous material constituents to body environment for long term using. Therefore, surface modification through the coatings was needed in order to prevent corrosion and to improve bioactivity of materials with hydroxyapatite for achieving osseointegration.

Hydroxyapatite are ceramic biomaterials in the molecule form $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ having hexagonal unit [3] having characteristics for coating of biomaterial implant that are biocompatibility, bioactive [4], and osteoconductivity [5]. Particularly, hydroxyapatite nanoparticles, with low porosity, are involved in biological responses within increases density of osteoblast [6] and molecular interaction [7] for osseointegration [8]. Coating using hydroxyapatite micro particles will increase interfacial bonding through apatite mineralization. The combination of hydroxyapatite nanoparticles and micro particles as bilayers coating was aimed to improve bioactivity material to achieve osseointegration.

The coating of bilayers hydroxyapatite using electrophoretic deposition (EPD) need heat treatment to obtain better mechanical property than the other method such as plasma sprayed [9]. The advantages of this method encompass high versatility and controlled product, using low temperature and simplicity procedure. The appropriate sintering temperature will effect for optimum quality of hydroxyapatite coating. Assessment of sintering temperature to bilayers hydroxyapatite (composed by nanoparticles and micro particles) deposited on material Ti-6Al-4V is needed to adjust osseointegration in orthopedic implantation.

2. Materials and Methods

Titanium alloy, Ti-6Al-4V ELI screw materials were used. Materials were abraded with mesh 800, 1000 and 1500 for homogenization of surface roughness. The cleaning was conducted using ethanol, acetone and nitric acid 25% solutions each for 15 minutes with ultra-sonication. Materials were dissolved in NaOH solution for 1 hour and air-dried using hot plate. This procedure based on work Bai et al and Erakovic et al with modification.

Hydroxyapatite solution for EPD process was prepared with 1 gram (Sigma Aldrich, USA) dissolved in 100 mL ethanol and homogenized using hot plate stirring for 1 hour prior to coating. The coating was carried out for two step that is to form nanoparticle hydroxyapatite as the first layer (3V for 3 minutes) and after air dried for 24 hours and the second layers was formed of micro particle hydroxyapatite (5V for 5 minutes). The coated materials were air dried for 24 hours and followed by sintering process at 700°C, 800°C, and 900°C temperature (holding 10 minutes and sintering rate 20°C/min) using vacuum furnace (High Temperature Vacuum Tube furnace GSL-1100). Weight measurement of coating layers was determined by weight differences between uncoated and coated material after coating process used balance. Analysis of morphology characteristics was conducted using optical microscope (Olympus LG-PS2) and scanning electron microscope (SEM Hitachi S-3400N at 10.0 kV). Imaging was used to measure coverage surface with computer analysis and the areas were covered up by hydroxyapatite particle calculated as surface coverage regions.

3. Results and Discussion

The surface of Ti-6Al-4V ELI materials covered up by bilayers hydroxyapatite obtained from EPD process (Figure 1). Principally, the nanoparticle coatings have thin, homogeny, and cover up the entire of material surface. The amorphous hydroxyapatite micro particles just coat the certain part of material surface and cohesive bind with hydroxyapatite nanoparticle. Hydroxyapatite micro particle layers are going to be agglomeration and have variance thickness that may be effected by voltage and time parameters of EPD process [10]. Deposited coatings on material surface at moment after the coating process have lower adhesion strength [11]. The following process, sintering, was needed to obtain the increasing of adhesion strength among

the coating layers onto material surface, because deposition and densification was not occurred simultaneously. The sintered layers have more dense structure due to densification that shrinkage and cracking may be occurred [12] and particularly founded in more than the 20 μm thickness [11]. The crack part may increase osseointegration because it role as mechanical interlocking through nucleation apatite mechanism on crack boundary site [13].

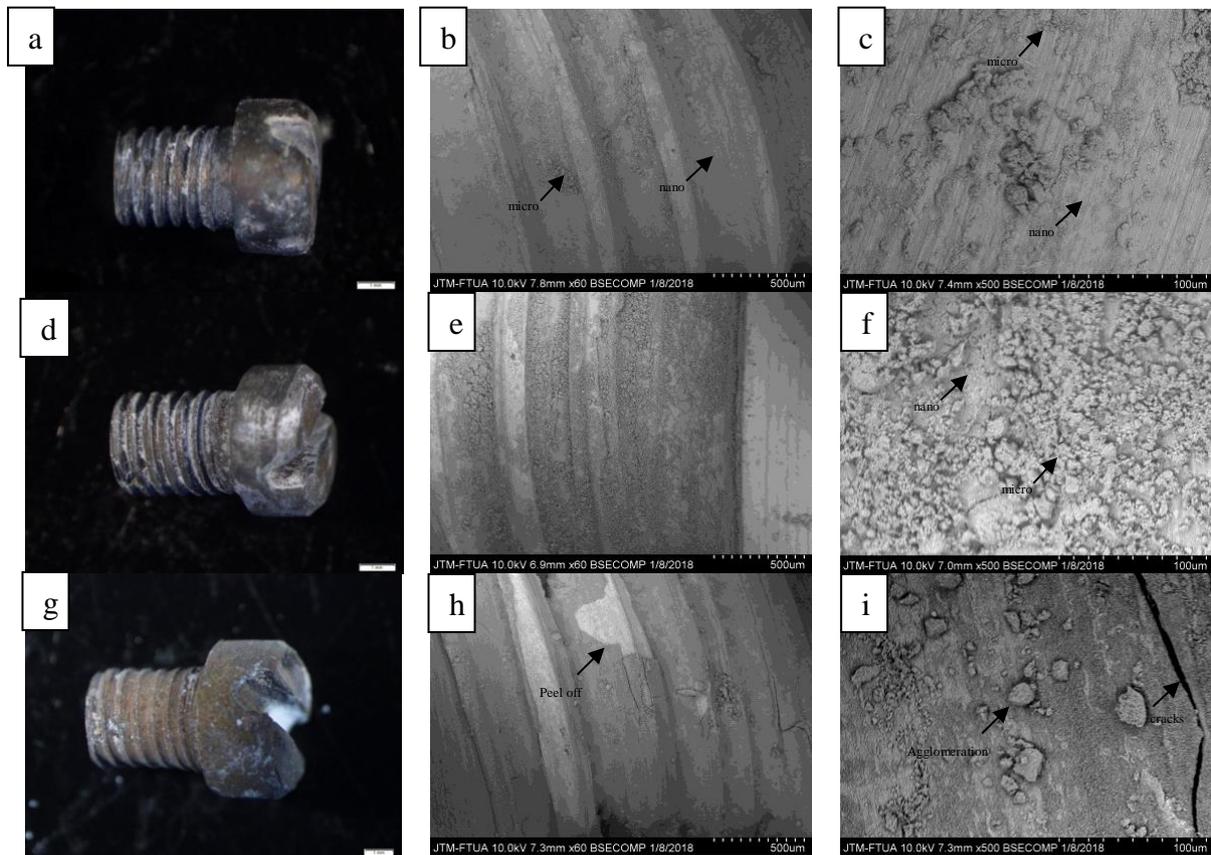


Figure 1. Morphology characteristic of hydroxyapatite bilayers coating on Ti6Al4V ELI surface effected by different sintering temperature; (a), (b) and (c) 700 °C; (d), (e) and (f) 800 °C; (g), (h) and (i) 900 °C

Sintering affects the density of bilayers hydroxyapatite coatings. Although the high temperature treatment at 900°C improves densification and reduces porosity, the coatings crack followed by peeling of the certain layers. High porosity, one of the EPD process flaws, promotes corrosion and releases titanium material ions induced by body environment. Porosity reduction by high temperature promote cracks might be caused by the difference of material thermal coefficient [14]. That will effect expansion and shrinkage difference between coating and material at heating and cooling of sintering process thus resulting thermal stress [17,18]. The Ti-6Al-4V materials have thermal coefficient $\sim 10.3\mu\text{m}/\text{mK}$ lower than hydroxyapatites ($\sim 14\mu\text{K}/\text{mK}$) that effects resulting of residual tensile stresses promoted the cracking [17]. It proved that crack propagation more associate to used sintering rather than EPD process [15].

Nanoparticle and micro particle hydroxyapatite well bonds to Ti-6Al-4V ELI material surface when sintering was given at 800°C temperature. The dense, even and non-cracks of nanoparticle hydroxyapatite role as the protecting toward possibility of material corrosion and acting in biology activity at implantation. The loosening micro particle hydroxyapatite may be dissolute acting directly for bone remodeling through the forming of interfacial coatings. Using nanoparticle hydroxyapatite as intermediate between micro particle hydroxyapatite and material surfaces have suitability of thermal coefficient with titanium material cause of a

number of atoms at grain boundaries increasing particle mobility [18]. It caused sintering with 800°C temperature for 10 minutes no promote cracks propagation. The previous study reports that the 800°C temperature for 1 hour is optimum condition for hydroxyapatite sintering in vacuum condition because not causes structural hydroxyapatite changes and cracks [13,21] with adhesion strength 47 ± 0.5 MPa [19]. Araghi et al [20] stated that optimum temperature effects the stable chemical characteristic of hydroxyapatite coatings because have good adhesion to material surface. Hydroxyapatite coating implanted by in vivo may occurs dissolution in the form of calcium and phosphate ions so promote nucleation and apatite crystal formation [23,24]. Densification founded relatively slow when sintered at 700°C temperature because there is still releasing of hydroxyapatite micro particles while hydroxyapatite nanoparticles bond well with material surface. The low sintering temperature is still possible to form the weak bonding with the material surface [18,25].

Table 1. Surface coverage and coating mass value of hydroxyapatite bilayers on Ti6Al4V ELI treated by different sintering temperature

Sintering Temperature (°C)	Surface coverage (%)	Coating mass (μg)
700	88.92 ± 4.24	$- 3.10^{-2} \pm 0.00$
800	98.59 ± 0.49	0
900	26.99 ± 18.03	$13.10^{-2} \pm 0.00$

The alteration of hydroxyapatite particle weight attached on material surface (Figure 2) shows that sintering may associate with surface coverage values (Table 1). The lowest value of surface coverage happened at high sintering temperature 900°C, but it was found the increasing of coating weight and may be caused by too high temperature. High temperature will promote oxidation of materials that may cause forming of oxide layers on material surface so there is more coating mass. Materials Ti-6Al-4V ELI is reactive toward high temperature making oxidation thus sintering should be conducted at optimum temperature in intense vacuum condition [16]. Contrary, high temperature beyond 900°C effects the losing of hydroxyapatite coating weight in small amount [11]. The low temperature of sintering is still insufficient to increase bonding between hydroxyapatite particle and materials. However, high temperature around 900°C will effect densification, peeled off, and uncovered coating layers on material surface. For different materials and method, stainless steel coated by hydroxyapatite using investment casting, Nuswantoro et al [24] found the better sintering temperature is around 800°C-900°C which resulting high cristallinity, surface coverage, purity and hardness of hydroxyapatite coatings.

The 700°C temperature revealed that the bonding of bilayers hydroxyapatite with material surface is low. It may caused by founding particle peeling of is around 11.08% of coated surface area with weight loss of hydroxyapatite particles is around $3.10^{-2}\mu\text{g}$. The better bonding of coating was discovered at 800°C temperature with material was covered up by hydroxyapatite approximately 98.59% with no peeling off the particles. It is needed optimum temperature is approximately 800°C in resulting the better bilayers hydroxyapatite coating on titanium materials. Chen et al [25] stated that sintering temperature at 800°C have not effect to purity of nanoparticle hydroxyapatite compounds and increasing hardness of coating layers. This coating layers also have good biocompatibility. At that sintering temperature, there is no more degradation of titanium and no metal-induced decomposition of hydroxyapatite [25]. For bilayers hydroxyapatite coating on titanium in screw form, temperature sintering at 800°C is effective in resulting good surface coverage, dense and homogeneous coating.

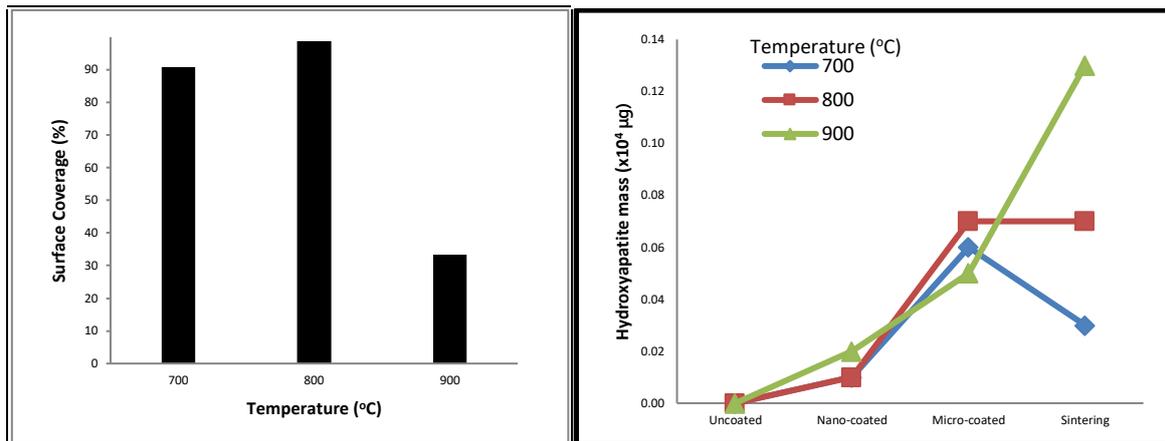


Figure 2. Surface coverage average of hydroxyapatite bilayers coating on Ti6Al4V ELI and Hydroxyapatite mass was coated on Ti6Al4V ELI surface by electrophoretic deposition and effected by sintering

The two step coating using hydroxyapatite nanoparticle and microparticle followed by sintering results good mechanical strength in which the first layers (undercoat) make a diffusion barrier to decomposition of substrat materials that results no crack, dense and no phase transformation coatings [16]. Forming first layer as interfacial can be applied in order to prevent decomposition of materials. Beside of protecting for harmful ion releasing from material, the interfacial layers act as reduction of decomposition due to sintering. Using of electrophoretic deposition is potential method [25] in resulting of bilayers hydroxyapatite suitable for biomedical application particularly for orthopedic due to increase osseointegration.

4. Conclusions

Sintering treatment at temperature 800°C gives thin, dense, even and crack-free coatings. The Ti-6Al-4V ELI surface is almost fully covered by bilayers hydroxyapatite (with surface coverage 98.6%) with adequate bonding (without lost weight of coating layers). An improper coating layer is obtained for lower (700°C) and higher (900°C) temperature. The sintered samples at temperature 900°C have micro cracks, void and debonding layers. It is expected such bilayers hydroxyapatite with sintering at 800°C can initiate mineralization and then make a quick osseointegration.

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