Crack Analysis on Ti-6Al-4V ELI Coated with Commercial Hydroxyapatite for Implant Material: Literature Review

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Abstract. Ti-6Al-4V Extra Low Intertitial (ELI), a type of titanium alloy that is commonly used for implant material. However, use of Ti-6Al-4V ELI still has some problems. The main one is oxide layer on the surface can be detached during application due to corrosion process. Such corrosion debris is a toxic substance to the human body. It is, therefore, necessary to modify the surface of the implant to avoid corrosion process by using coating method. A good coating material for orthopedic implants comes from ceramics, namely hydroxyapatite (HA). However, there are also an obstacle, HA coating on titanium, sometimes not evenly across the surface, causing cracks on the coating layer surface. There are two methods that are often used in coating materials, namely Electrophoretic Deposition (EPD) and Dip Coating. This study analyzed number of literatures using a searching engine of international reputable journals Science Direct, Pubmed on biomaterials and biomedicine fields using the keywords of Ti-6Al-4V ELI, hydroxyapatite, cracks, EPD method and Dip Coating. This literature review may useful for the readers and researchers, in order to choose the best method for crack reduction in the coated implants. Dip Coating method is better than EPD method in point of view simplicity and cost. Moreover, the coating layer is evenly distributed, no build-up of HA in several surface areas, so that cracks on surface are minimized.

1. Introduction
Ti-6Al-4V Extra Low Intertitial (ELI), an α+β type of titanium alloy, is usually used for biomedical applications. This is due to this alloy has better physical and mechanical properties than stainless steel and pure titanium; namely lighter, more ductile, stronger, lower modulus of elasticity, and better biocompatibility. Currently, Ti-6Al-4V ELI is common for dental implants as well as for orthopedic implants such as bone fixation (plates, screws, pins), spine fixation and artificial joints [1]. However, the use of Ti-6Al-4V ELI still causes problems. Kwok [2] exposed that the use of Ti-6Al-4V ELI has a risk of corrosive attack by body fluids, and the release of metal titanium oxide (TiO₂) particles. Such particles are dangerous because it has adverse effects on the surrounding tissue. The oxide layer on surface can be released due to corrosion process so that it is toxic to the body. This condition can also result in reducing growth of new bone tissue. Another problem is the metal surface is not bioactive, so it is unable to form osseointegration (the link between the bone and the implant material) in the body. It is necessary, therefore, to modify the surface of material by using surface coating method. This coating aims to avoid direct material contact with body tissues, provides protection against the release of unsafe ions from material, and accelerates the occurrence of osseointegration, stimulates the growth of new bone tissue to repair damaged bone tissue. If there is no osseointegration, the implant will have looseness, and then causing of implant failures. A good coating material for orthopedic implants comes from ceramics, namely hydroxyapatite (HA). HA has bioactive, inert and non-toxic properties. The HA coating aims to prevent such bone loosening. In addition, it also aims to protect the surface of implant from corrosion and direct contact to the body tissues [3].

HA is one of the inorganic compounds or calcium phosphate compounds, which make up the hard tissue of the human body such as bones and teeth. HA is biocompatible because it has a structure that resembles the matrix structure of the human bone element Ca₁₀(PO₄)₆(OH)₂.
addition, HA also has bioactive properties, and it can accelerate the regeneration of bone tissue during implantation. According to Cheng et al. [4], Ti-6Al-4V ELI coated with HA has a higher corrosion resistance level than non-coated one. With this good level of corrosion resistance, it is able to provide a positive biological response to the body. However, there is still a barrier. HA coating layer on titanium, sometimes are not evenly across the surface. Juliadmi [5,6] found that coating Ti-6Al-4V with commercial HA (particle size 10 μm) by using Electrophoretic Deposition (EPD) method, produced in an unequal layer over the whole surface of the substrate and there is a buildup of HA and cracks in several surface areas. A larger the particle size of HA produces higher cracks on the layer [7,8].

HA coating of micro particles on Ti-6Al-4V ELI with the EPD method, the layer is easily brittle and many cracks on the surface. Another method that is widely used for hydroxyapatite coating is the dip coating method. This method has a number of advantages, including low cost of coating, easy coating method, can control the desirable coating thickness and can be carried out at room temperature, so it does not change the properties of HA.

From a number of literature studies [8-12], it is found that Dip Coating method can produce a better evenness of the surface layer than the EPD method. In addition to the HA layer that is evenly distributed and without cracks, the implant material must also contain a good porous (8). This cavity is generated from the heating process (sintering). This cavity serves as the retention of bone cells during implantation. The immersion speed of dip coating method has significant effect on the characteristics of Ti-6Al-4V hydroxyapatite-gelatin coating layer, where the increase of immersion speed, an even surface layer of the implant is obtained, so that the attachment of the layer to the substrate is stronger [10]. The same trend is also obtained for HA coated SS316L where no cracks is obtained at the coating layer [11]. It is also found that the layer thickness increases with increasing drawing speed of the sample from the bath [12]. For instance, the withdrawal speed of 5 cm/minute (0.083 mm / s), resulting in a denser HA structure and severe layer on the surface of Ti-6Al-4V. However, it is necessary to prove that the hydroxyapatite coating layer is not easily to cracke under pressure of fluid during application.

This study analyzed number of literatures using a searching engine of international reputable journals Science Direct, Pubmed on biomaterials and biomedicine fields using the keywords of Ti-6Al-4V ELI, hydroxyapatite, cracks, EPD method and Dip Coating. This study to identify relevant studies regarding to choose the best method for crack reduction in the coated implants. The inclusion criteria used for this review involved the coating layer studies written in English language up to May 2018. Three of the authors independently evaluated the titles and abstracts of potentially relevant previous studies. Selected studies were individually read and analyzed concerning the focus of the present review, which was to discuss and summarize important key publications regarding crack analysis on Ti-6Al-4V ELI coated with commercial hydroxyapatite for implant material. Author names, journal, publication year, objectives, methods, and main outcomes were retrieved from the selected relevant articles.

2. Results and discussion
Dip Coating method consists of three steps as shown in figure 1. First, the immersion step. In this case, the implant material is dipped in HA solution. Second, the implant material that has been dyed is pulled upwards. The pulling velocity factor will determine the thickness and evenness of the surface layer of implant material obtained. In this method, it is necessary to pay attention to controlling the withdrawal speed, in order to obtain the desired coating results. Third, the evaporation process, in which the solvent evaporates from the liquid, forming a thin layer.
Coating Ti-6Al-4V ELI with micro-HA (particle size 10 μm) by using Electrophoretic Deposition (EPD) method, produced in an unequal layer over the whole surface of Ti-6Al-4V ELI and there is a buildup of HA and cracks in several surface areas [5,6. Not only that, the HA layer also disclosed some cracks [7]. Nevertheless, the coating of Ti-6Al-4V ELI with HA 125 μm, the HA layer is also not evenly distributed and this will simultaneously cause cracks to appear on the surface of Ti-6Al-4V ELI.

A larger the particle size of HA produces higher cracks on the layer [7]. The larger of HA particle size has the greater cavity (porosity). The 125 μm size of HA particles is quite large, the ethanol used as the HA solvent, trapped in the cavity formed during the HA coating process, is also quite large. This will cause cracks on the surface of layer during the sintering process, because the trapped ethanol evaporates quickly.

Similar results were obtained from the study of Gnanavela et al [8]. HA coating of micro particles on Ti-6Al-4V ELI using EPD method, obtained the best morphological results at a voltage of 8 volts and a time of 8 minutes, but the layer is easily brittle and many cracks on surface. The cracks in the HA layer were also caused by the nature of the ceramics not having good crack toughness during the sintering process.

This cavity is generated from the heating process (sintering). This cavity serves as the retention of bone cells during implantation. The immersion speed of dip coating method has significant effect on the characteristics of Ti-6Al-4V hydroxyapatite-gelatin coating layer, where the increase of immersion speed, an even surface layer of the implant is obtained, so that the attachment of the layer to the substrate is stronger [10]. The variations in the withdrawal speed used were 0.089 mm/s, 0.120 mm/s, 0.178 mm/s and 0.198 mm/s. The higher the withdrawal speed, an even surface layer of the implant is obtained, so that the attachment of sample to the substrate is stronger. At the variation of withdrawal speed of 0.198 mm/s, the thickness and shear strength values were 125.28 μm and 13.96 MPa. In this study, commercial HA mixed with 30 percent gelatin was used.
The same trend is also obtained for HA coated SS316L where no cracks is obtained at the coating layer [11]. It is also found that the layer thickness increases with increasing drawing speed of the sample from the bath [12]. For instance, the withdrawal speed of 5 cm/minute (0.083 mm/s), resulting in a denser HA structure and severe layer on the surface of Ti-6Al-4V. However, it is necessary to prove that the hydroxyapatite coating layer is not easily to cracke under pressure of fluid during application. Acquired the HA layer evenly on the surface of Stainless Steel (SS) 316L as an implant material with dip coating method, there were no cracks. The HA used is commercial HA plus additive solvent P2O5, Na2CO3 and KH2PO4, and cracks were not found when the sintering temperature was 600°C.

Figure 3. Ti-6Al-4V ELI has a crack free surface [13].

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, encourages 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]. It will effect expansion and shrinkage difference between coating and material at heating and cooling of sintering process thus resulting thermal stress [15,16]. The Ti-6Al-4V materials have thermal coefficient ~10.3μm/mK lower than hydroxyapatites (~14 μK/mK) that effects resulting of residual tensile stresses promoted the cracking [15]. It proved that crack propagation to used sintering rather than EPD process [17].

Nanoparticle and micro particle hydroxyapatite well bonds to Ti-6Al-4V ELI material surface when sintering was given at 800°C temperature. The non-cracks of nanoparticle hydroxyapatite role as the protecting toward possibility of material corrosion and acting in biology activity at implantation. The loosenning 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 number atoms at grain boundaries increasing particle mobility [18]. It caused sintering with 800°C temperature for 10 minutes have not 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 [19,20] with adhesion strength 47 ± 0.5 MPa [21].

4. Conclusions

1. Dip Coating method is better than EPD method in point of view simplicity and cost. EPD coating method produces an uneven layer over whole of Ti-6Al-4V ELI surface and there is
a buildup of HA in some surface areas. The HA layer also showed some cracks. The larger the particle size of the coating, the more cracks will occur in layer.

2. Dip Coating method can control thickness of the HA layer, namely by varying the speed of implant material withdrawal during immersion. The coating layer is evenly distributed, no build-up of HA in several surface areas, so that cracks on surface are minimized.

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