Hydroxyapatite coating on cobalt alloys using electrophoretic deposition method for bone implant application

by Dyah Hikmawati

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Abstract. Damage on bone due to osteoporosis and cancer triggered high demand for bone implant prosthesis which is a permanent implant. Thus, a prosthesis coated with hydroxyapatite (HA) is required because it is osteoconductive that can trigger the growth of osteoblast cells. The purpose of this study is to determine the optimum concentration of HA suspension in terms of the surface morphology, coating thickness, adhesion strength and corrosion rate resulting in the HA coating with the best characteristics for bone implant. Coating using electrophoretic deposition (EPD) method with concentrations of 0.02M, 0.04M, 0.06M, 0.08M, and 0.1M was performed on the voltage and time of 120V and 30 minutes respectively. The process was followed by sintering at the temperature of 900 ^{0}C for 10 minutes. The results showed that the concentration of HA suspension influences the thickness and the adhesion of layer of HA. The higher the concentration of HA-ethanol suspension the thicker the layer of HA, but its coating adhesion strength values became lower. The concentration of HA suspension of 0.04 M is the best concentration, with characteristics that meet the standards of the bone implant prosthesis. The characteristics are HA coating thickness of 199.93 ± 4.85 μm, the corrosion rate of 0.0018 mmpy and adhesion strength of 4.175 ± 0.716 MPa.

1. Introduction

Damage on bone due to osteoporosis and cancer triggered high demand for bone implant prosthesis which is a permanent implant. Until now, the fulfilment of the needs for bone implant prosthesis in Indonesia still relies on the imported products. The imported bone implant prosthesis often used today is the cemented type that its application would lead to aseptic loosening. Aseptic loosening is the most common failure mechanisms in replacement joints that cause pain to the patient and eventually will need the repeated surgery. To avoid aseptic loosening, prosthesis coated HA (HA) is required because HA is an osteoconductive which can stimulate the growth of osteoblast cells. Therefore, recent researches tend to focus on the coated implant, which generally coats the metal alloy implants with HA.

Various methods of coating HA to the substrate alloy Ti have been done, including the method of pulsed laser deposition (PLD) [1-5] and RF magnetron sputtered [6]. Both two methods are high-technology and expensive. In addition, the entire coating uses titanium alloy as a substrate, whereas titanium alloys are very expensive which will generally be a problem for all people. The alternative metal besides titanium alloy is a cobalt alloy. Its mechanical properties are equivalent to titanium

alloy, its biocompatibility is slightly below the titanium alloy, but the price is cheaper than titanium alloys [7-9].

A research was done by Aminatun [10] which conducted HA coating on cobalt alloy and titanium alloy with dip coating method. This study resulted in uneven HA coating on the surface of the cobalt alloy substrate. Therefore, it is necessary to find another simple and unexpansive coating method. That method is electrophoretic deposition (EPD). EPD is a method of suspension deposition on the metal surface due to the influence of external electric fields. Factors that affect the quality of the coating on the coating process by the method of EPD are deposition time, the applied voltage, and the concentration of the suspension. Deposition rate is proportional to the deposition time and voltage used. Meanwhile, the concentration of the suspension HA affects the rate of deposition HA particles on the surface of the metal alloy substrate [11]. Until now, there is no precise information on the composition of the suspension concentration of HA-ethanol used in the coating of cobalt alloy. Therefore, it is necessary to do a more in-depth study of the HA coating of cuttlefish bone to cobalt alloy using the EPD method especially in terms of optimization of the suspension concentration of HA-ethanol.

2. Materials and methods

This research was conducted in 4 stages: a) Preparation of a cobalt alloy substrate and HA of cuttlefish bone; b) the coating process by using the EPD method with variation of the concentration of HA suspension; c) the sintering at a temperature of 900°C for 10 minutes; and d) characterization of samples.

2.1. Preparation of a cobalt alloy substrate and HA of cuttlefish bone

Cobalt alloy substrate was synthesized through fusion method using tri arc melting furnace on the current of 200 A with a composition of 62.25% Co-31.5% Cr-5% Mo-0.5% Mn-0.5% Si-0.25%N which was adapted to ASTM F75 (American Society for Testing and Materials F75) and was then continued with homogenization process at a temperature of 1300°C for 2 hours. The materials that were used are powder chromium [Cr (99+) - Merck], powder cobalt [Co (99+) - Sigma-Aldrich], molybdenum powder [(Mo (99+) - Merck], powder manganese [Mn (99+) - Merck], silicon powder (Si - Merck) and powder Cr2N (Nilaco). After that, the alloy was cut using wire cut with varying sizes of 0.5 mm x 0.8 mm and thickness of 2-3 mm, rubbed with coarse 80-grit silicon, washed with distilled water and then soaked in ethanol [12]. HA of cuttlefish bone was made by hydrothermal method. First of all, extraction of $CaCO_3$ from the lamella cuttlefish bone, then it was heated at a temperature of 350°C for 3 hours. Subsequently, the mixture suspension $CaCO_3$ 1M and $NH_4H_2PO_4$ 0.6M was heated at the temperature of 200°C for 12 hours in a closed vessel. The mixture powder from the heating was washed with distilled water until pH neutral, followed by methanol. The final process was sintering at a temperature of 900°C for 1 hour [8].

2.2. The coating process using the EPD method

HA suspension was made in ethanol with various concentrations of 0.02 M, 0.04 M 0.06 M, 0.08 M and 0.10 M. After that, the coating process was done by using the EPD method with cobalt alloy served as the cathode and platinum as the anode. The coating process was done at a constant voltage and coating time which was at a voltage of 120 V for 30 minutes. Samples of the coating were dried at room temperature.

2.3. The sintering process

The sintering process was done on dried samples layer a tube furnace STF & TZF Models at a temperature of 900°C with 10 minutes of holding time, the increasing rate of 10°/min and the rate of decline 5°/min, under vacuum conditions flowed with argon and with the flow rate of 3l / min [12].

2.4. Characterization of sample

The crystal structures of HA coating samples on cobalt alloy were characterized using X-ray diffractometer PAN alyticalX'Pert PRO and its surface morphology was characterized using Scanning Electron Microscopy (SEM- Fei Inspect S50). XRD test was characterized using a source with a wavelength of CuK_α = 1.54060Å, at the angle = 5°-60°, 0.0170° step size, scan step time 135.2550s, operated at 40 kV and 30 mA. SEM test was performed at a voltage of 20 kV with WD = 15.2 to 15.7 mm. Adhesion strength test was characterized using Shimadzu autograph AG-10TE and corrosion test used the potentiostatmeter. Adhesion strength test and corrosion test have been repeated three times. Adhesion strength used Equation 1 and the value of corrosion rate used Equation 2.

$$\sigma = \frac{F}{A} \quad (1)$$

With σ is adhesion (MPa), F is the force applied (N) and A is the surface area of the HA layer [13].

$$corrosion\ rate(mpy) = \frac{0{,}13 \cdot I_{corr} \cdot EW}{\rho} \quad (2)$$

0.13: metric conversion factors and time, I_{corr}: current density when E_{corr} (uA/cm^2),
ρ : density (g /cm^3), EW: equivalent weight [14]

3. Results and discussion

3.1. Morphology and thickness of HA layer

HA layers on cobalt alloy from various concentrations of HA suspensions characterized by SEM on surface morphology and a cross-sectional, are presented in Fig. 1 and Fig. 2.

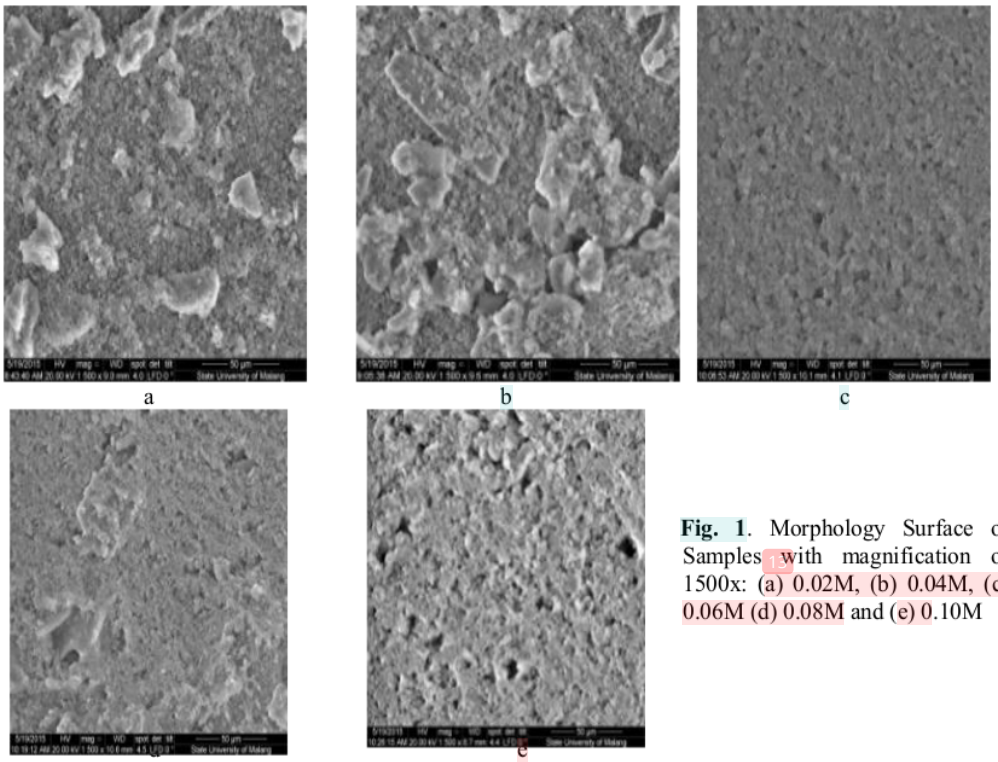

Fig. 1. Morphology Surface of Samples with magnification of 1500x: (a) 0.02M, (b) 0.04M, (c) 0.06M (d) 0.08M and (e) 0.10M

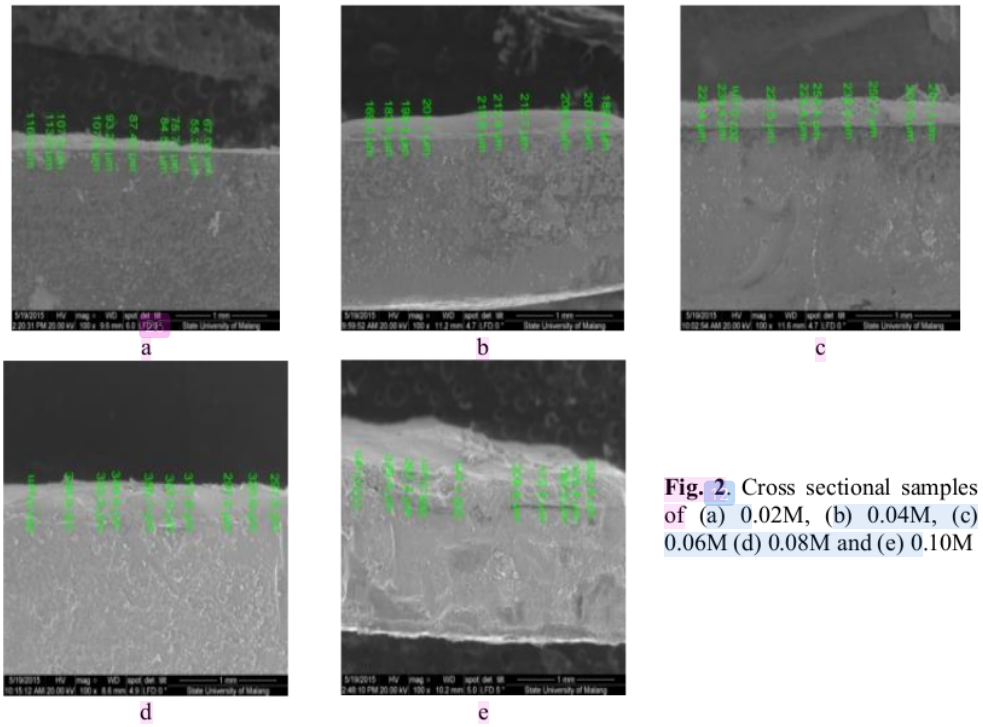

Fig. 2. Cross sectional samples of (a) 0.02M, (b) 0.04M, (c) 0.06M (d) 0.08M and (e) 0.10M

Based on the results of SEM magnification of 1500x in Fig.1, it appears that the HA is covering cobalt alloy substrate. However, it seems that the coating formed is uneven and there are some which coagulates as in Fig. 1a and 1b. SEM test was also done on a cross section sample presented in Fig. 2. It was intended to determine the thickness of the HA coating on the surface of the substrate in each sample. The average thickness of a layer of HA obtained from SEM measurements is presented in Fig. 3.

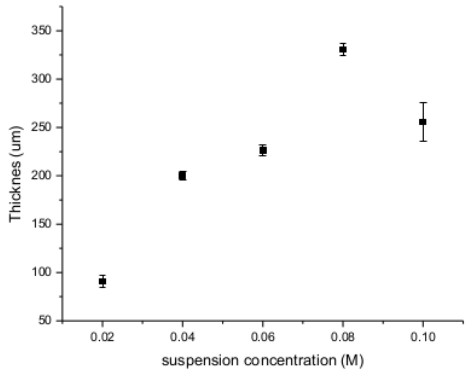

Fig. 3. The thickness of HA layer variation suspension concentrations of HA

Based on Fig. 3, it can be seen that the higher the suspension concentration of HA-ethanol of the concentration of 0.02M up to 0.08M, the greater the value of the HA layer thickness. However, it is not the case at a concentration of 0.10 M, HA coating thickness is lower than in samples of 0.08 M. It is presumed that at a suspension concentration of HA 0.10 M, HA coating that has been coating the surface of the cobalt alloy substrate was not strong enough to hold the HA particles continuously onto the surface of the substrate due to the influence of high power voltage of 120 V so that the outside of the HA layer falls back into suspension, causing the HA layer formed become thinner. Best terms of HA layer thickness as the medical applications standard which do not cause any clinical problems is 50-200µm, seen from the aspect of solubility of the SBF [15]. Based on Fig. 3, it shows that the samples which meet the medical implant applications standard are suspension concentration of HA 0.02 M and 0.04 M respectively in a row with an average thickness of 90.92 ± 6.57 µm and 199.93 ± 4.85 µm.

3.2. Adhesion strength HA layer

Adhesion strength of HA layer on the cobalt alloy substrate was done by conducting shear strength test to determine the strength of HA layer attached to the cobalt alloy substrate. The adhesion strength of HA layer is presented in Fig. 4.

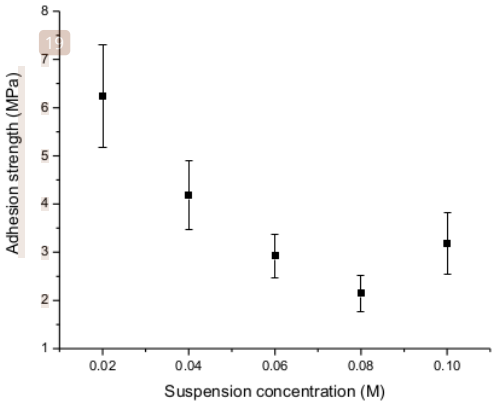

Fig. 4. Adhesion strength vs. suspension concentration of HA

Based on Fig. 4, the highest adhesion strength of HA layer is at 0.02 M of 6.248 MPa. The sample of 0.02 M has the lowest HA layer thickness among other samples. The low strength of adhesion is because the hold time is too short in the sintering process at the temperature of 900^0C, so that the HA coating is still not strong enough to retain its position attached to the substrate cobalt alloy.

This shows that the thicker the layer of HA, the lower the adhesion strength of HA coating. According to Fig.4, it also reveals that the higher the concentration of the suspension of HA-ethanol used in the coating process, the lower the adhesion strength of HA coating. The adhesion strength values are still far from the results from the research conducted by Bunyamin [16] which results in adhesion strength of HA coating layer in SS316L with the thickness of 20-25 µm by 20-25 MPa, whereas HA coating on Ti 6Al 4V with the thickness of 25-40 µm has the adhesion strength of 10-14 MPa. The low of adhesion strength in this study is because the resulted layer is very thicker than the expected.

3.3. The corrosion rate in the SBF solution

In this study, the corrosion test was done to all samples in a solution of *simulated body fluid* (SBF). The result of corrosion tests to all samples' concentrations is presented in Fig. 5. According to Fig. 5, it appears that the corrosion rate of all samples coated with HA in SBF solution is smaller than the corrosion rate control of cobalt alloy without coating. This means that the HA layer covering the surface of the cobalt alloy is able to reduce the corrosion rate of cobalt alloy. Cobalt alloy without HA coating has the corrosion rate of 0.288mpy = 0.0074mmpy [10], it is still below the standard tolerated by body which is 0.457 mpy = 0.012 mmpy [17].Thus, the use of cobalt alloys as the implant material will not harm the body because the corrosion rate is still far below European standards. The HA coating further reduce the corrosion rate of cobalt alloy, therefore it is qualified as the material of implant prosthesis.

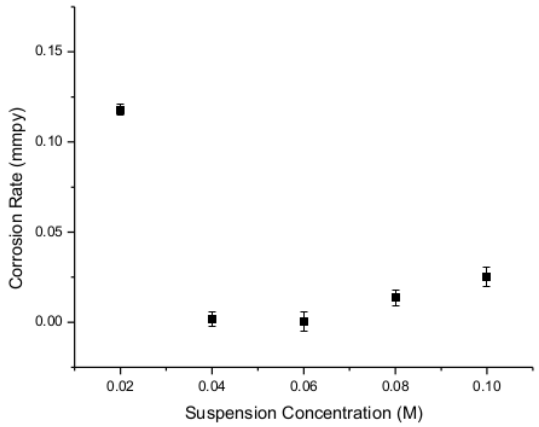

Fig. 5. The corrosion rate variation suspension concentration of HA

Based on Fig. 5, it can be seen that the corrosion rate decreases with the increase of HA suspension, especially at a concentration of 0.02 M – 0.08 M. This is due to the greater concentration the thicker layer resulted (Fig. 3). The presence of HA layer on the cobalt alloy inhibits the corrosion of cobalt alloy. Samples with suspension concentration HA-ethanol of 0.02M has the highest corrosion rate value compared to other samples, which is 0.1177 mmpy. This is because the sample of 0.02 M, HA which coated substrate was not distributed evenly. In the sample of the suspension concentration HA-ethanol of 0.04 M and 0.06 M, they have relatively low corrosion rate values compared to most other samples, which are 0.0018 and 0.0003 mmpy. In both samples, the HA layer covering the cobalt alloy substrate surface was distributed evenly. Therefore, the HA coating can protect the surface of the substrate, resulting in the low value of corrosion rate.

4. Conclusion

Suspension concentration of HA-ethanol 0.02 M to 0.1 M on cobalt alloy coating by using EPD method has effects on the thickness and adhesion strength of HA layer. The higher the suspension concentration of HA-ethanol, the thicker the layer of HA, but the value of the adhesion strength layer becomes lower. Suspension concentration of HA 0.04 M is the best concentration, with characteristics that qualified the standards of the bone implant prosthesis which are HA coating thickness of 199.93 ± 4.85 μm, the corrosion rate of 0.0018 mmpy and adhesion strength of 4.175 ± 0.716 MPa.

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