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Hydroxyapatite Coating on Alloys CoCrMo-TiN with Sol-Gel Method

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Abstract

Hydroxyapatite is synthesized by precipitation-sonification using calcium from field snail shell and powder phosphorus from $(NH_4)_2HPO_4$. The calcium value was measured by atomic absorption spectrophotometer was 82.82%. The temperatures were varied on 600, 800, and 1000 °C to determine the best temperature of the coating. The best temperature was used to superimpose the HAp on the CoCrMo-TiN metal alloy using the modified sol-gel method. The layer on the metal alloy was identified with x-ray diffraction (XRD) and corrosion test. The XRD result showed that most of the CoCrMo-TiN metal alloy surface was coated by HAp. Beside HAp, there were several other phases such as calcium phosphate, carbonate apatite type A and type B. The best result of the corrosion test was showed in CoCrMo-TiN metal alloy coated with HAp with the smallest corrosion rate 0.0082 mpy.

Keywords: *hydroxyapatite, CoCrMo-TiN, precipitation-sonification, sol-gel modified*

Abstrak (Indonesian)

Hidroksiapatit (HAp) disintesis dengan metode presipitasi-sonikasi menggunakan sumber kalsium dari serbuk cangkang keong sawah dan sumber fosforus dari $(NH_4)_2HPO_4$. Kadar kalsium diukur menggunakan spektofotometer serapan atom sebesar 82.82%. Suhu diragamkan pada 600, 800, dan 1000 °C untuk menentukan suhu terbaik pelapisan. Suhu terbaik tersebut digunakan untuk melapiskan HAp pada paduan logam CoCrMo-TiN menggunakan metode sol-gel termodifikasi. Lapisan yang menempel pada paduan logam diidentifikasi dengan diffraksi sinar X (XRD) dan uji korosi. Hasil XRD menunjukkan sebagian besar permukaan paduan logam CoCrMo-TiN terlapisi oleh HAp. Selain HAp, terdapat fase lain seperti kalsium fosfat, apatit karbonat tipe A dan tipe B. Hasil uji korosi paling baik ditunjukkan pada paduan logam CoCrMo-TiN yang terlapisi HAp dengan laju korosi paling kecil, yaitu 0.0082 mpy.

Keywords: hidroksiapatit, paduan logam CoCrMo-TiN, presipitasi-sonikasi, sol-gel termodifikasi

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INTRODUCTION

Traffic violations by motorists often cause traffic accidents. This can lead to fractures that will affect the function of the body. Function of the body can be corrected as before by doing a bone implant. Hydroxyapatite (HAp) can be used as bone implants because it is biocompatible, bioactive, and the similarities in biological terms with bone tissue and non-toxic so that it can adjust to the bones in our bodies [1,2].

Synthesis of hydroxyapatite can be done by several methods, such as wet and dry methods. Wet method can be carried out through precipitation, while the dry method is done through high temperature and hydrothermal treatment. The method used in this research were wet through precipitation method because it involves a simple reaction between $Ca(OH)_2$ (calcium hydroxide) with phosphate salt $(NH_4)_2HPO_4$, cost of synthesis of HAp are relatively inexpensive, and has high purity. Sources of calcium in this study originated from paddy conch shell powder *(Bellamyâ javanica)*, so as to increase the selling value of the shell, and reduce waste in the environment. In addition, the content of Ca in snail shell powder rice so that it can be used as a source of calcium [3]. Phosphorus sources used can be derived from the ammonium hydrogen phosphate $(NH_4)_2HPO_4$, phosphoric acid (H_3PO_4) and pentaoksida phosphorus (P_2O_5). However, in this study using $(NH_4)_2HPO_4$ because of pH when mixing the calcium source will be more easily monitored [4].

Metal material that is commonly used as a means of implants, among others, metal titanium (Ti), cobalt-based alloy (Co) and stainless steel metal. Some of these materials have advantages and disadvantages of each. Metal Ti has biocompatibility and excellent corrosion resistance, but has a very high price so rarely used as implants. Stainless steel metal having a low biocompatibility allowing for corrosion inside the body when the implant. Therefore, the need for implant materials alternative as a tool, which is based metal alloys Co. The Co-based alloys have high levels of biocompatibility relatively better than stainless steel, although not as good as the Ti metal compatibility. To improve the corrosion resistance of the based metal alloys, Co must be coated using a titanium nitride (TiN). In addition, to improving corrosion resistance, TiN coating also prevents the release of ions making up the CoCrMo alloy. Sukaryo *et al.* [5] have superimposing CoCrMo alloys with TiN by looking at the effect of adding nitrogen after coating, stated that the addition of nitrogen 0.35% can increase the corrosion resistance of the alloy. This study uses CoCrMo alloys that have been coated with TiN, then the metal alloy to be coated with HAp using a modified sol-gel method.

HAp coating on the metal alloy TiN coated CoCrMo already done with a modified sol-gel method. Definition of modified sol-gel method in this study is the use of gel coat result sonication for CoCrMo-TiN metal alloys, because in general are used to coat the metal alloys, namely the supernatant by Dip-Coating technique [6]. After coating, the HAp coating on CoCrMo-TiN metal alloys will be tested further, the XRD test and corrosion test. This study aims to coat the metal alloy CoCrMo-TiN using hydroxyapatite with modified sol-gel method.

EXPERIMENTAL SECTION

The materials used were freshwater snail shell, alloys CoCrMo-TiN distilled water, deionized water, HCl 37%, $(NH_4)_2PO_4$.

Procedure

$Ca(OH)_2$ suspension from snail shell was added with 0.3M $(NH_4)_2HPO_4$ solution drop at 40±2°C temperature for 1 hour while stirred using a magnetic stirrer. The formed mixture was then sonicated to obtain a uniform HAp particle size. Sonication time was 6 hours. Sonication resulting solution was decanted for 24 hours at room temperature. Furthermore, centrifuged at 4500 rpm for 15 minutes to get gel. Gel results of centrifuge is then used to coat the metal alloy CoCrMo-TiN.

This coating uses a modified sol-gel method. Coating using a modified sol-gel method includes several stages of the process of growing a thin layer and process heating. In a modified sol-gel method, the gel was separated by centrifugation from the soles. The gel has formed then coated manually with a spatula to a metal alloy CoCrMo-TiN, then put in a furnace at a temperature variation of 600, 800, and 1000°C for 2 hours. Temperature variations that have been done have been the best temperature for coating. The best temperature is determined using an optical microscope. Then the gel that has been coated on CoCrMo-TiN metal alloy was analysed using X-Ray Diffraction (XRD) and corrosion test.

RESULT AND DISCUSSION

This study uses the wet method through the principle of precipitation in the synthesis of HAp. The advantage of this method, which is simple reaction, a by-product is water, the possibility of contamination during processing of low and low processing costs. Synthesis of HAp carried out by react a source of calcium and phosphate sources. Calcium sources used in this study, namely $Ca(OH)_2$ which is derived from the shells of snails fields, while phosphate source used is $(NH_4)_2HPO_4$. Before powder $Ca(OH)_2$ is reacted with $(NH_4)_2HPO_4$, powder $Ca(OH)_2$ suspension first made by adding deionized water. After the powder $Ca(OH)_2$ into a suspension with a concentration of 0.5 M, then a solution of $(NH_4)_2HPO_4$ 0.3 M was added to the suspension of $Ca(OH)_2$ with a speed of 6 mL / min. This is done so that a solution of $(NH_4)_2HPO_4$ reacts completely with the suspension of $Ca(OH)_2$. Synthesis of HAp is performed at a temperature 38-40°C with the aim of increasing the reaction kinetics of HAp formation and increase the dissolution of $Ca(OH)_2$ [3]. Solution of $(NH_4)_2HPO_4$ was added to the suspension of $Ca(OH)_2$ slowly until the pH of the solution after mixed into a 9, because HAp stable at a pH greater than 4.2 [7] . The reaction between the suspension of $Ca(OH)_2$ 0.5M with a solution of $(NH_4)_2HPO_4$ 0.3 M produce byproducts that are not harmful to the environment, namely H_2O and $(NH_4)OH$. Here is a synthesis reaction HAp:

$$10Ca(OH)_{2(Susp)}+6(NH_4)_2.HPO_{4(aq)} \rightarrow Ca_{10}(PO_4)_6(OH)_{2(s)} +6H_2O_{(aq)} +12NH_4OH_{(aq)}$$

After the pH of the mixed solution reach 9, and then it was decanted for 24 hours. This is done so that decantation suspension mixture of $Ca(OH)_2$ 0.5M with a solution of $(NH_4)_2HPO_4$ 0.3M sedimentation at room temperature. The next stage is sonication for 6 hours. Riyanto [8] have done this with a stage sonication time variation of 2, 4 and 6 hours. Sonication with a time of 6 hours showed a dominant HAp with the highest peak at 2θ angle 31.8316° and homogeneity of the sample is higher than the sample HAp with sonication time 2 and 4 hours. Crystal size was obtained by 41.9583 nm.

According Delmifiana and Astuti [9], the longer sonication time it will improve the homogeneity of the sample HAp. The sonication was performed to refine a large granules into granules and smaller again until the nanoscale. This proves that the sonication affect the crystal size, because the samples were synthesized using sonication method has a smaller size than without using sonication. After sonication process is done, the next sample in a centrifuge at 4500 rpm for 15 minutes. Stages centrifuge performed at 4500 rpm for 15 minutes, because the optimum conditions. If this condition is done under or above the optimum conditions for the separation of the supernatant was precipitated with imperfect due to the presence of sediment that are still in the supernatant. The purpose is to obtain a gel centrifuge. The resulting gel at this stage is white. Then the gel was added to a glass vial and put in the refrigerator to retard bacterial growth.

There are several coating techniques commonly used in the sol-gel method, the dip coating, spin coating and electrophoretic deposition. The principle of sol-gel are generally used to synthesize inorganic compounds through chemical reactions in solution at low temperatures, this is done for the synthesis of HAp. The principle of using the sol-gel that becomes solid solution. The technique is often used for coating using sol-gel principle, namely dip coating, and spin coating and electrophoretic deposition. Dip coating is a coating technique which consists of a substrate wherein the substrate is normally drawn vertically from the solution at a certain speed. Solution that attaches to flow downward due to gravity and the solvent evaporates, and accompanied by a condensation reaction, so that the results obtained in the form of a solid film layer. Spin coating is a coating technique to deposit a thin layer by spreading the solution onto the substrate in advance. Then the substrate is rotated at a constant speed in order to obtain certain deposition of thin layers on a substrate, or method of acceleration solution on the substrate is rotated. Coating by spin-coating technique is done by means of coater at high speed (rpm) in the period. Electrophoretic deposition (EPD) is a coating technique that uses the principle of separation of components or charged molecules based on differences in levels of migration in an electric field [10]. The third technique is the coating of HAp coating on CoCrMo-TiN metal alloys must be synthesized in advance. This seems inefficient that need a more efficient coating technique that is used modified sol-gel method.

Generally, the sol-gel method is used to coat metal alloys, namely in the supernatant phase or sol, but in this study were used to coat that is in the gel phase. Gel results manually centrifuge then superimposed on CoCrMo-TiN metal alloys [6]. Modification of the sol-gel method is done, due to coat metal alloy CoCrMo-TiN with HAp using techniques dip coating, spin coating, and Electrophoretic deposition (EPD) is relatively requires longer stages must synthesize HAp due prior to becoming a solid [11]. After becoming solid, then HAp characterization using XRD to prove the results are synthesized HAp. Dissolved hydroxyapatite synthesized using alcohol, after it's done on a metal alloy coating. The next stage, the coating on the metal alloy in the back using XRD characterization to prove gel that coats the metal alloy is HAp or other compounds. This requires too many steps, the cost is relatively expensive, but still got a thin layer, so that the necessary steps to metal alloy coating is more efficient, cost is relatively cheaper and get a thicker layer produced.

Previous TiN coating on a metal alloy CoCrMo aims to prevent the corrosion of metal alloy CoCrMo with the release of constituent ions CoCrMo alloys for titanium nitride has a trait that is very hard or has good wear resistance. While HAp coating on the metal alloy CoCrMo-TiN aims to increase the growth of bone tissue. This coating is done at a temperature variation of 600, 800, and 1000°C for 2 hours. The purpose of the various temperatures is to see the best coating results. Metal alloy coating CoCrMo-TiN at temperature variation of 600, 800, and 1000°C for 2 hours using an optical microscope can be seen in Figure 1.

Based on observations using an optical microscope in Figure 1, white precipitate that coats the metal alloy CoCrMo-TiN is relatively flat but still fragile as indicated by the presence of cracks in the coating. Landless heating causes deposition attached to the metal alloy CoCrMo-TiN become brittle. In order for the deposition on the surface coated with a strong metal alloy composite material needs to be added such as chitosan. In addition, there needs to be a colloidal stabilizer such as DEA (diethanolamine) in order to form a more stable colloidal. Based on the temperature variations are used, it turns out the temperature 1000ºC coating produces a coating on a metal alloy that is better than the temperature of 600ºC and 800ºC.

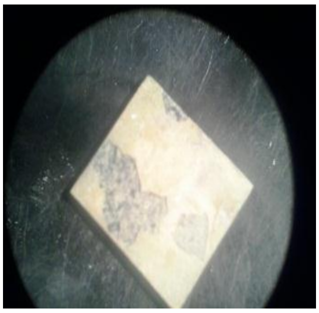

Figure 1. CoCrMo-TiN coating on the temperature 1000ºC for 2 hours

Based on these results, the possibility of heating at a temperature of 600ºC and 800ºC are not enough to make such a metal alloy coating deposition at a temperature of 1000ºC. After determine the optimum temperature for the coating, the gel centrifugation product will be superimposed on CoCrMo-TiN metal alloys manually. Referring to Prasetyanti [12] and Pudjiastuti [13], turns temperature 1000ºC showed the formation of HAp, so that the modified sol-gel method is expected to be more efficient in the HAp coating on the metal alloy. The higher of the temperature while allowing HAp coating the coating on the metal alloy, the better HAp compaction occurs at temperatures between 1000-1500ºC.

The nature of the coating is associated with several aspects, one of which is the adhesion between the coating and the metal alloy CoCrMo-TiN. Good adhesion between the layers of the base metal on the type of metal layers in the form of alloys. Metal alloys in this study, namely CoCrMo-TiN. Selection of metal alloys cause the atoms in the metal alloys follow the lattice arrangement of the base metal atoms that are in good contact. Adhesion properties of this layer becomes very important because it can lead alloy layer attached to the metal becomes brittle. Therefore, the metal alloy surface must be clean of dirt (crust, grease, oxides, etc.). In addition to the metal alloy surfaces must be clean, surface area and depth profiles are also a factor that is important so that the layer can be attached more strongly on CoCrMo-TiN metal alloys. Actually depth profiles can be done by sanding the metal surface to become rough. Stainless steel metal sanding to improve the surface roughness of the metal and removes the natural oxide layer which is owned metals such as chromium oxide layer. CoCrMo-TiN metal alloys in this study was not done sanding, because it was feared TiN which serves to prevent corrosion of the alloy will be separated, resulting in the release of CoCrMo alloy constituent time of implant. The nature of the metal alloy layer is also affected by the non-equilibrium conditions. Non-equilibrium condition is caused by the temperature is not enough to diffuse well occupy lattice. Therefore do variations in temperature to determine the temperature optimum for coating [14].

The gel solidifies and coat the metal alloy CoCrMo-TiN, then analyzed using XRD. Based on X-ray diffraction pattern in Figure 2, which has been matched with the data obtained JCPDS 2θ angle of 27.63º, 33.26º, 54,51º is owned HAp peaks. While the 2θ angle of 36.26º, and 47.67º is owned AKA peak, and AKB. The existence of AKA and AKB on the X-ray diffractogram not be harmful to the human body, because of AKA and AKB is a type of HAp composites were included into the category of $Ca_3(PO_4)_2$ (calcium phosphate) that appears at an angle 2θ 41.41º. Based on the profile of the X-ray diffractogram, the regular arrangement of atoms in the sample makes the higher the level crystalinity. This showed with higher intensity and narrower half-peak width. HAp intensity higher than AKB and AKA. Hydroxyapatite also appear on other minor peaks, among others in the region 2θ 24.93º, 56.82º, 59.31º, 62.94º, and 64.23º. HAp lattice parameters a = b = 9418, c = 6884. Lattice parameters obtained in the gel solidifies and coat the metal alloy CoCrMo-TiN at a = 12.5788 Angstrom, c = 9.2068 Angstroms. Lattice parameters were obtained away from HAp lattice parameters but still within the range of multiples of the HAp parameters. It is influenced by temperature, duration of sonication and heating [9,12]. Crystal size obtained in the HAp coating of metal alloy CoCrMo-TiN reached around 43.9595 nm. Crystal size will affect the size of the pore [8]. The larger the pore size of the crystals formed will be small, so that will accelerate the growth of new bone tissue. Diffractogram HAp coating the metal alloy CoCrMo-TiN can be seen in Figure 2.

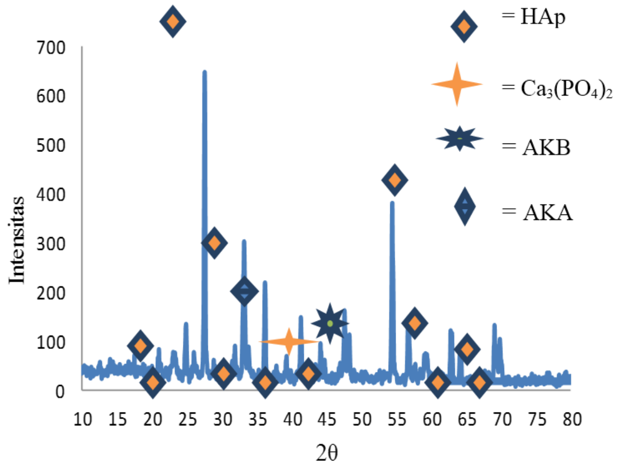

Figure 2. Diffratogram of HAp coating on metal alloy CoCrMo-TiN

The rate of corrosion

Events corrosion is a process of degradation or release of a component material into a lasting ion gradually due to electrochemical attack occurs when a metal is placed in the opposite electrolytic environment. The rate of corrosion can be done by several methods, namely polarization measurement and weight lost method. Polarization measurement method can be performed by Tafel extrapolation technique and polarization resistance technique. Corrosion test in this study used the method of measurement of polarization as named Polarization Resistance Technique (PRT). Mechanical linear polarization resistance observed patterns cathode or anode polarization curves between -10 mV to 10 mV at local anodic and cathodic curves meeting. Corrosion test in this study was the corrosion rate (mpy) held by a metal. Of this corrosion conducted using a set potentiostat 273. The results of this test will get the value of test, is expected to get a small value of corrosion rate. The smaller the value of the rate of corrosion of a metal, the metal will have good corrosion resistance. Corrosion test results obtained on CoCrMo alloy corrosion rate of 0.0149 mpy. Based on the results of corrosion tests in this study, CoCrMo-TiN metal alloy corrosion rate of 0.0424 obtained mpy. Corrosion test results on CoCrMo-TiN metal alloy that has been coated with HAp obtained corrosion rate of 0.0082 mpy. Corrosion test results of CoCrMo alloy can be seen in Figure 3.

Based on the results of corrosion tests in Figure 3, the corrosion rate is highest in the sample CoCrMo-TiN metal alloys of 0.0424 mpy. This is possible because of the element nitrogen is less pure Ti metal coating, this causes the conductivity increases and resulting in increased corrosion. This suggests that the presence of TiN coating corrosion rate obtained is getting smaller when compared to the rate of corrosion of metals Ti, therefore, with the expected resilience TiN coating corrosion on the metal alloy will Co, is getting better. With the decrease in corrosion rate is quite large, meaning the presence of nitrogen can increase corrosion resistance. The rate of corrosion on the metal alloy samples CoCrMo better when compared with samples CoCrMo-TiN metal alloys. It can be seen from the corrosion rate in each sample. The rate of corrosion which is owned by CoCrMo alloy samples of 0.0149 mpy smaller when compared to the rate of corrosion which is owned by the sample-TiN CoCrMo alloys.

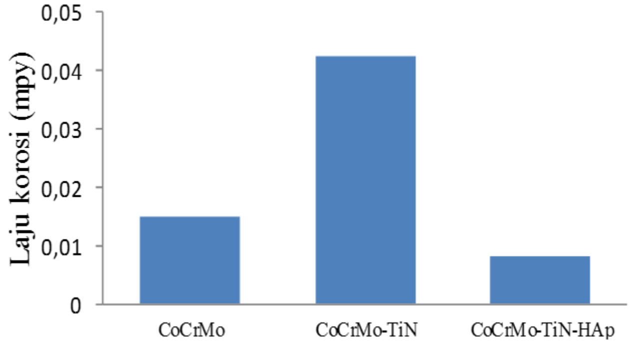

Figure 3. The results of corrotion test

These conditions indicate that a decline in the rate of corrosion which is identified by a decrease in the corrosion rate of a metal alloy has better corrosion resistance. The decline in the rate of corrosion is possible presence of elements of Cr (chromium) and Mo (molybdenum) that acts as a passive oxide layer to improve the corrosion resistance alloys Co. The decline in the rate of corrosion or corrosion resistance is influenced by the composition of the alloy and the environment corrosion. Elemental composition of high Cr expected to act as a protective coating to prevent corrosion occurring [15]. The most excellent corrosion resistance shown by samples CoCrMo alloy-TiN coated HAp with the smallest corrosion rate when compared with other metal alloy samples, amounting to 0.0082 mpy. It is caused by HAp coated on metal alloys. The thickness is an important factor in corrosion resistance. Increasingly thicker layer will increasingly provide protection against corrosion of metal alloys, but with HAp without any other composite added it would be easier brittle layer. Based on European standard medical application level positions corrosion rate should be less than 1 mpy, while the corrosion rate standard for medical applications must be less than 0457 mpy. Corrosion test results of the three samples in this study showed resilience three samples have good corrosion and can be used for medical applications.

CONCLUSION

Hydroxyapatite can be deposited on the metal alloy CoCrMo-TiN with a modified sol-gel method, but still fragile. XRD results showed that there AKA, AKB, and calcium phosphate besides HAp. Corrosion test results show CoCrMo alloy-TiN with HAp coating has good corrosion resistance because it has a low corrosion rate.

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