Hidroxyapatite coating on CoCrMo alloy titanium nitride coated using biomimetic method

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Abstract. Bone implants is a way to cure broken bones which is being developed. The implants can be made of metals, ceramics and polymers. Metallic materials commonly used are titanium (Ti), stainless steel, and metal alloys. This study used Co-based alloys, i.e. CoCrMo coated with titanium nitride (TiN) which was then coated on hidroxyapatite (HAp). The HAp coating on the surface of CoCrMo alloy was done by biomimetic methods, first by soaking the metal alloys in simulated body fluid (SBF) solution for 18, 24, and 36 hours. The immersion in the SBF solution produced white coat on the surface of the metal alloy. The layers formed were analyzed by scanning electron microscope (SEM) and characterized by x-ray diffractometer (XRD). Based on the SEM results of 36 hours treatment, the morphology of apatite crystal formed fine grains. According to XRD result, there were HAp peaks at angles 2θ 31.86, 32.25, dan 39.48. However, there were also CaCO₃ peaks at angles 2θ 29.46, 36.04, and 46.79. It indicated the pure HAp is not yet formed.

1. Introduction
Orthopedic field becomes very important because the number of accidents in Indonesia that resulted in fractures is increasing every year. Bone implants is one way of healing a fracture that continues to grow. Implants can be made from metals, ceramics and polymers. Metallic materials used for implants are titanium (Ti), stainless steel and metal alloys. Metal Ti has the highest biocompatibility and has better corrosion resistance, but its price makes this metal began to reduced usage. Similarly, Stainless steel, although the price is cheaper but does not have good corrosion resistance. The use of cobalt-based alloys (Co) as a substrate bone implants continue to be developed in line with human needs. Co-based alloys have a lower level of biocompatibility of Ti, but it is better than stainless steel. Another advantage of the use of Co-based alloys is the price is relatively cheaper and has better mechanical properties compared to Ti alloy [1]. In addition, the Ti metal alloys, namely Ti6Al4V still contains ions of Al and V ions are harmful to the body. NiTi alloys are also often used as an implant material, because it has the corrosion resistance and good biocompatibility. However, the content of Ni is relatively high, reaching 50% make use of metal alloys is reduced because it can cause allergies or even poisoning the human body. Coating of hydroxyapatite (HAp) on metal surfaces can improve the biocompatibility properties of the metal and accelerate bone growth. HAp has been recognized as a bone substitute material and teeth as it has in terms of their biological similarity to human hard bone tissue [2]. This study will use the Co-based alloys, which are coated CoCrMo titanium nitride (TiN). Based on the standard European medical applications, the rate of corrosion for metal implants should be less than 1 mpy. TiN coated CoCrMo alloy has a corrosion rate of 0.0424 mpy. This shows the TiN coated CoCrMo alloys can be used for medical applications. Alloy surfaces TiN coated CoCrMo metal (CoCrMo-TiN) will be coated with HAp, so that the biocompatibility of CoCrMo alloy is getting better and can accelerate bone growth when implanted into the body. CoCrMo alloy coating with HAp-TiN performed using biomimetic methods. The method is a biomimetic coating method that mimics biological systems in the body. The advantages of this method compared with other methods, such as plasma spraying, electrophoretic deposition, and sol-gel is made of apatite crystals have high bioactivity and resorption properties are good, and can accelerate bone growth. Coating by biomimetic
method performed by immersion in a solution of simulated body fluid (SBF) [3]. Research Habibovic et al. (2002)[4] reported that HAp can be formed in a solution of 5x SBF with low intensity. After the coating will be performed morphological analysis by scanning electron microscope (SEM) and characterization by x-ray diffractometer (XRD).

2. Experimental Method
Research procedure consists of preparation of metal alloys with a base treatment process, the metal alloy coating CoCrMo-TiN with hydroxyapatite using biomimetic methods, and characterization by SEM and XRD. TiN metal alloys and CoCrMo-CoCrMo soaked in alcohol, and then sonicated for 1 hour and drying. TiN metal alloys and CoCrMo-CoCrMo alloys immersed for 15 minutes in a solution of NaOH 5 M. After that, the metal alloy is dried in an oven at 70°C. CoCrMo alloy and CoCrMo-TiN then coated with HAp. Coating CoCrMo alloy and CoCrMo-TiN done by dipping metal alloy into a beaker containing a solution of 5x SBF placed on a hot plate. Soaking is done for 18, 24, and 36 hours, and the temperature is kept constant at 37°C. After 18, 24, and 36 hours of metal removed and dried, then viewed a layer that is formed by optical microscopy and morphological analysis by SEM and XRD characterization.

3. Results and Discussion
After immersion, the surface of the metal alloy CoCrMo-TiN becomes black, because titanium oxide layer on the surface of a metal alloy reacts with ions in the NaOH solution to form a hydrogel titanate, while metal alloy CoCrMo unchanged. Furthermore, the two metal alloys dried in an oven for 30 minutes to dehydrate the hydrogel layer to form crystalline sodium titanate titanate (Na$_2$Ti$_6$O$_{13}$) stable.

The reaction that occurs in the process of treatment with a base are as follows:

\[
\text{Ti} + 3 \text{ OH}^- \rightarrow \text{Ti(OH)}_3^+ + 4e^- \\
\text{Ti(OH)}_3^+ + e^- \rightarrow \text{TiO}_2\text{H}_2\text{O} + \frac{1}{2} \text{H}_2\text{(g)} \\
\text{Ti(OH)}_3^+ + \text{OH}^- \leftrightarrow \text{Ti(OH)}_4 \\
\text{TiO}_2\text{H}_2\text{O} + \text{OH}^- \leftrightarrow \text{HTiO}_3^-.\text{H}_2\text{O}
\]

The method is a biomimetic coating method that mimics biological systems in the body, with this method HAp layer formed naturally on the surface of the sample through immersion in SBF solution. According Colovic et al. (2011)[5], excess biomimetic method compared to other coating methods are that the HAp coating structure and morphology characterization similar to those formed in the body. Coating by biomimetic method performed on CoCrMo alloys with and without treatment with a base first, to see the effect of this treatment on the coating to the surface of a metal alloy. The results of the two alloy coating to the metal (Figure 1) with immersion in SBF solution for 36 hours that preceded the treatment with a white base layer is formed on the surface, whereas the untreated alloy CoCrMo coated with a base yet. The formation of a white layer on the metal alloys given treatment with alkaline ions caused metal alloy constituent, namely Co, Cr, Mo regardless, so it reacts with NaOH and accelerate the coating on the surface of a metal alloy. Widya (2014)[6] reported, on the surface of CoCrMo alloys by immersion in a solution of 5x SBF for 48 h to form a white layer. Based on these results, treatment with a base that is first performed before the coating can accelerate the coating on the metal surface.

![Figure 1 Results of the metal alloy coating CoCrMo](a) With Alkali Treatment (b) Without Alkali Treatment
The coating also performed on CoCrMo-alloy with TiN treatment process with a base. Metal alloy coating is done with the variation of time 18, 24, and 36 hours. Results CoCrMo-alloy coating of TiN (Figure 2) for 18, 24, and 36 hours by immersion in SBF solution had formed a thin layer of white on the surface. Coating for 36 hours resulted in an increasingly white coating evenly. This suggests immersion in the SBF solution the longer it will create a layer that is formed on the metal surface evenly. Furthermore, the white layer formed on the metal alloy CoCrMo-TiN morphology analysis by SEM.

![Figure 2](image)

(a) 18 hours               (b) 24 hours                    (c) 36 hours

Figure 2  Results of HAp coating on CoCrMo alloy-TiN

Based on the results of SEM images (Figure 3) is not visible compound apatite crystal morphology of the coating for 18 and 24 hours with a magnification of 1500x. This shows, on immersion for 18 and 24 hours a metal alloy surface is not coated HAp. The results of SEM images for the coating for 36 hours with a magnification of 1500x already appeared several compounds apatite crystal morphology assembled and refined grains are still few. Based on these results, the immersion for 36 hours had already been formed HAp on the surface of a metal alloy CoCrMo-TiN. After that, the characterization by XRD on the white layer formed on the surface of a metal alloy CoCrMo-TiN with immersion in SBF solution for 36 hours.

![Figure 3](image)

(a)Coating for 18 hours          (b)Coating for 24 hours              (c)Coating for 36 hours

Figure 3  SEM photos CoCrMo-alloy coating TiN 1500x magnification

Characterization by XRD performed to identify the crystalline phase layer attached to the metal alloy CoCrMo-TiN by matching the data 20 diffractogram and the scattering intensity of the JCPDS database. If there are at least 3 highest peaks are identical to the database then allegedly phase equal to the standard. Based on the results diffractogram (Figure 4) and has been matched with JCPDS there HAp peaks at 20 angle of 31.86, 32.25, and 39.48. In addition, there are also peaks at angles 20 CaCO$_3$ 29.46, 36.04, and 46.79 with a higher intensity compared with HAp. This indicates that the pure HAp formed yet. Based on the results of characterization by XRD, there are peaks of HAp which indicates that the results are consistent with the SEM images showing the morphology of the apatite compounds in the form of fine grains. CaCO$_3$ sharper peaks of HAp shows the degree of crystallinity owned CaCO$_3$ higher than HAp. HAp does not have a high degree of crystallinity because when its synthesis does not use such a high temperature synthesis of HAp in general. Purnama et al (2006)[7] reported that high temperatures can increase the degree of crystallinity of HAp. These results are consistent with the
results reported Habibovic et al. (2002)[4], the HAp formed on the metal surface by immersion in a solution of 5x SBF with low intensity.

![Diffractogram HAp coating on TiN coated CoCrMo alloys](image)

Figure 4 Diffractogram HAp coating on TiN coated CoCrMo alloys

On immersion in SBF solution, sodium titanate formed on the surface of the TiN coated CoCrMo alloy after treatment with a base react with ions in the SBF solution. Sodium ions from the sodium titanate dissolved and replaced by H$_3$O$^+$ ions from SBF, then OH$^-$ of interesting metal hydroxy cations Ca$^{2+}$ of the SBF solution and drawn by cation anion PO$_4^{3-}$ previously been deposited [8]. The mechanism that occurs when metal alloy CoCrMo-TiN soaked in SBF solution can be seen in Figure 5 [8]. HAp formation reactions that occur on immersion in SBF solution are as follows:

\[
\text{Ca}^{2+} + 2\text{OH}^- \rightarrow \text{Ca(OH)}_2
\]

\[
10\text{Ca(OH)}_2 + 6\text{PO}_4^{3-} \rightarrow \text{Ca}_{10}\text{(PO}_4\text{)}_6\text{(OH)}_2 + 18\text{OH}^-
\]

![Mechanism of chemical reactions in solution while soaking in SBF](image)

Figure 5 Mechanism of chemical reactions in solution while soaking in SBF

HAp coating on the surface of a metal alloy not only can be done with just a biomimetic method. There are several methods of coating used, the electrophoretic deposition. Electrophoretic deposition method is a method of coating with the aid of an electric field. The advantages of this method is to have high strength coating, coating evenly, and quickly. Prihantoko (2011)[9] reported that HAp-chitosan coating on the surface of a metal alloy CoCrMo-TiN using electrophoretic deposition method produces a thin and fragile layer. Results coating by biomimetic method in this study is more powerful than the stick EPD method is still fragile. Coating by electrophoretic deposition method is also need to synthesize HAp first. However, the method of biomimetic HAp is formed naturally in the process so that more efisisen HAp coating to the surface of the metal alloy.
HAp has the molecular formula Ca$_{10}$(PO$_4$)$_6$(OH)$_2$ and has the properties of biocompatible, bioactive, and not toxic. Biocompatible is the ability of a material to adjust to the situation in the body. While the bioactive is the ability of a material to stimulate new bone growth around the implant. It can be seen from the phenomenon of interface between HAp with the cell body which shows the surface of HAp dissolution occurred after implant into the body. Dissolution of the HAp surface occurs until equilibrium is reached between the saline condition with HAp surface. After that, the case of adsorption of proteins and bioorganic compounds then occurs until finally the cell adhesion of cells to form new bone [10].

4. Conclusion
Layer of HAp with low intensity managed to form on the surface of the TiN coated CoCrMo alloys by treatment with alkaline process using a biomimetic method by soaking for 36 hours in a solution of 5x SBF. Based on the results of SEM images on the coating for 36 hours, it looks crystal morphology of apatite compounds such as fine grains. Based on the characterization results and there has been matched with JCPDS HAp peaks at 20 angle of 31.86, 32.25, and 39.48, but other than HAp peaks are also peaks at angles 20 CaCO$_3$ 29.46, 36.04, and 46.79. This shows pure HAp formed yet.

5. References
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