Hydroxyapatite Coating On 316L Stainless Steel Using Dip Coating Technique

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Abstract. 316L stainless steel is one of the metal biomaterials used in implant applications because it has excellent mechanical strength. To improve the biocompatibility and activity of metals, a coating on metal surfaces is required. 316L stainless steel is coated with hydroxyapatite using a dip coating technique. Firstly, the suspension was prepared by mixing 10 grams of hydroxyapatite, 1 gram of sago starch, with distilled water with certain weight which was then stirred at a speed of 250 rpm for 20 hours. The substrate then dipped 1 time with dipping time for 20 seconds. Coating hydroxyapatite was sintered at temperatures of 600°C, 700°C and 800°C for 1 hour. The results show that the thickness of the hydroxyapatite layer on the substrate has decreased with increasing amount of distilled water used. However, the thickness of the layer increases with increasing sintering temperature. The best value of shear strength was obtained in the addition of 16 grams of distilled water with sintering temperature of 800°C which is 11.78 MPa. Furthermore, the coating attached to all substrates is hydroxyapatite with an average composition of 99.37% as evidenced by the results of XRD analysis.

1. Introduction
Metallic biomaterials have been widely used for biomedical application such as orthopedic and dental applications [1]. For implant application, metallic biomaterials such as Ti and its alloy, Stainless Steel, and Cr-Co alloys are used for reconstructions of hard tissue as used mainly in orthopedics surgery [2, 3, 4].

Metal commonly has a good mechanical strength to support heavy part of body, but has a weak bond with bones and causes the release of harmful ions into body fluids if used for long periods. The differences composition between the original bone and metal implants causes ineffective ability to form new tissue between the two. The stability of an implant is achieved if the implant has a direct structural and functional relationship between bone tissue and the surface of the implant which involves optimum cellular and molecular interactions [5].

To reduce the negative impact above, bioactive coating is carried out on metal substrates using hydroxyapatite. Hydroxyapatite (Ca_{10}(PO_4)_6(OH)_2) has been used for the field of medicine and orthopedics due to its similarity of chemistry composition and structure of human bone tissue [6]. Hydroxyapatite is a crystalline molecule which is basically composed of phosphorous and calcium which occupy about 65% from mineral fraction in bone [7]. Metals that coated with hydroxyapatite
are not only intended to minimize direct contact between the substrate with body fluids, but also to increase bioactivity and biocompatibility for new bone formation. Coating using hydroxyapatite creates limits for the release of harmful ions from metal and reduces the coefficient of friction of the implant to the surrounding environment [8, 9].

There are several methods that have been used for the coating of hydroxyapatite on metal implants, including plasma spraying [10, 11], dip coating [12, 13, 14, 15], electrochemical deposition [16, 17], electrophoretic deposition [18, 19], and sol-gel [20, 21]. The hydroxyapatite coating process using the dip coating method is carried out by dipping the substrate into hydroxyapatite solution at a constant speed. After determining the length of time for immersing the substrate, then the metal substrate is withdrawn from the suspension solution [22].

The objective of this study is to coating hydroxyapatite on the surface of stainless steel 316L with variations in addition of distilled water in the suspension solution and the sintering temperature use dip coating technique.

2. Methodology

2.1. Substrate Preparation

The substrates used for this study was 316L stainless steel. Samples, 2 cm × 3 cm × 0.1 cm in size, were polished with #1200 SiC paper. Then they were immersed in acetone (Merck, Germany) for 15 minutes and then washed with distilled water (Brataco Chemica, Indonesia). After that, the substrates were dried at temperature 100°C for 10 minutes.

2.2. Suspension Preparation and Hydroxyapatite Coating

Preparation of hydroxyapatite suspension was started by adding 10 grams of hydroxyapatite (Lianyungan Kede Chemical Industry Co. Ltd, China) and 1 gram of sago starch (Puri Pangan Sejahtera, Indonesia) than followed by the addition of differences distilled water 16 grams, 18 grams, and 20 grams. Then the mixtures were stirred using magnetic stirrer for 20 hours at room temperature with stirring speed of 250 rpm.

For coating on the surface of substrate, all samples were dip-coated with hydroxyapatite suspension for 20 seconds with one time dipping. Finally, the substrates that coated with hydroxyapatite were sintered with furnace at three different temperatures 600°C, 700°C, and 800°C for 1 hour.

2.3. Characterization Technique

Sample characterization was determined using Scanning Electron Microscope (SEM) to observe the morphology of the sample and the thickness of the coating. X - Ray Diffraction (XRD) analysis aimed to see the chemical compounds contained in the sample and their composition. Autograph machine was used to measure the shear strength of the sample.

3. Results and Discussion

3.1. Result on Visually Analysis

Based on the results of the study, 9 samples coated with hydroxyapatite were obtained with variations in the addition of distilled water and sintering temperatures. The part observed in this case was the layer deposited on the substrate. The observation is shown in Table 1.
Table 1. Observation visually results.

| Sample | Mass of distilled water (gram) | Sintering temperature (ºC) | Results                      |
|--------|--------------------------------|----------------------------|------------------------------|
| S1     | 16                             | 600                        | No cracks on deposition layer|
| S2     | 18                             | 600                        | No cracks on deposition layer|
| S3     | 20                             | 600                        | No cracks on deposition layer|
| S4     | 16                             | 700                        | No cracks on deposition layer|
| S5     | 18                             | 700                        | No cracks on deposition layer|
| S6     | 20                             | 700                        | No cracks on deposition layer|
| S7     | 16                             | 800                        | No cracks on deposition layer|
| S8     | 18                             | 800                        | Cracks on deposition layer   |
| S9     | 20                             | 800                        | Cracks on deposition layer   |

From Table 1, it is known that the hydroxyapatite layer cracks in samples S8 and S9 occurred after going through the sintering process. Cracks occurs because the influence of volume shrinking process during crystallization and phase transformation [23]. When the hydroxyapatite coating is too thin and sintered at high temperatures, the possibility of cracks will be greater than the thick hydroxyapatite coating layer.

3.2. SEM Analysis

The thickness and morphology of hydroxyapatite on 316L stainless steel surfaces can be seen using SEM. The results of sample observations were carried out using 150, 500 and 1000 times magnification. Further, to know the thickness of the sample were carried out using 200 times magnification.

Figure 1 shows the coating of hydroxyapatite on the 316L stainless steel substrate using a 500 and 1000 times magnification at sintering temperature 700ºC.

![SEM image of coating hydroxyapatite on a 316L stainless steel substrate with difference amounts of distilled water](image-url)
In the variation of the amount of distilled water 18 and 20 grams (Figure 1) it can be seen that the size of the deposited hydroxyapatite particles is not too different. This is caused hydroxyapatite coating has not been fully sintered due to the low temperature of 700°C. Figure 2 and 3 shows SEM cross section images of hydroxyapatite coating.

![Figure 2](image1)

**Figure 2.** SEM cross section image of hydroxyapatite coating layer with different amounts of distilled water (a) 20 grams, (b) 18 grams and (c) 16 grams at 700°C.

![Figure 3](image2)

**Figure 3.** SEM cross section image of hydroxyapatite coating layer with different sintering temperatures (a) 600°C, (b) 700°C and (c) 800°C with 16 grams of distilled water.

Based on Figure 2, for addition of 20 grams of distilled water the thickness of the hydroxyapatite layer is 42 μm, then it increase to 58 μm and 114 μm when distilled water amount decrease from 18 grams to 16 grams. More distilled water added to the suspension, the thickness of hydroxyapatite layer attached to the 316L stainless steel metal surface decreases. This indicates that the addition of distilled water is inversely proportional to the viscosity and viscosity directly proportional to the thickness of the hydroxyapatite layer on the metal surface.

In a study conducted [24] regarding hydroxyapatite dip coating on cobalt alloys, it was found that the higher concentration of hydroxyapatite suspension, the greater of thickness the hydroxyapatite coating on the substrate surface. When more distilled water is used, the less hydroxyapatite has been successfully deposited, causing its thickness to decrease. Different from the previous results, the difference in sintering temperature (Figure 3) did not result in a significant change in the thickness of the hydroxyapatite layer. At sintering temperature 600°C, the thickness of the layer is 113 μm and 114 μm for 700°C and 800°C respectively.

In addition, sintering temperature will affect the surface morphology of the hydroxyapatite layer deposited on the 316L stainless steel surface. Surface morphology of hydroxyapatite coating using 16 grams of distilled water at three different sintered temperatures is shown in Figure 4 and 5.
Figure 4. SEM image of hydroxyapatite coating at different sintering temperature (a) 600°C, (b) 700°C and (c) 800°C with magnification 150 times.

Figure 5. SEM image of hydroxyapatite coating at different sintering temperature (a) 600°C, (b) 700°C and (c) 800°C with magnification 1000 times.

In Figure 5 (a) hydroxyapatite coating layer has not completely sintered due to the low temperature and the presence of a number of pores on the coating surface. In Figure 5 (b) the hydroxyapatite particles have started to solidify, but the pores on the surface of the coating are enlarging. Than in Figure 5 (c) with increasing sintering temperature, it can be seen that the hydroxyapatite particles have a denser structure and reduced pores.

Also in a study [25], it was reported that the surface morphology of hydroxyapatite coating at sintering temperatures of 750°C and 800°C, the hydroxyapatite coating particles had begun to solidify but there were a large number of pores. Furthermore, the sintering temperature of 850°C reduces the pores and the coating layer is denser. In this case, the denser layer structure as a result of increasing the sintering temperature will improve the mechanical strength of the material [26, 27].

3.3. Shear Strength Analysis
Shear strength analysis is used to determine how the strange of layer hydroxyapatite stick to the substrate surface. Figure 6 shows the shear strength values with different amounts of distilled water. Namely 16 grams, 18 grams and 20 grams at 600°C sintering temperatures, respectively 11.38 MPa, 10.01 MPa, and 10.30 MPa. Based on the data, the shear strength value at adding distilled water 18 grams and 20 grams is not significant change. This can occur because the use of 20 grams of distilled water, hydroxyapatite layer is not successfully deposited evenly on the entire surface of substrate.

The influence of sintering temperature on the value of shear strength can be seen in the graph in Figure 7.
Figure 6. Shear strength value of coated hydroxyapatite on 316L stainless steel with different amounts of distilled water variations at 600°C.

Figure 7. Shear strength value of coated hydroxyapatite on 316L stainless steel at different sintered temperature with addition 16 grams and 20 grams distilled water.

Figure 7 shown that, the best shear strength value is 11.78 MPa for sample with amount of 16 grams of distilled water with a sintering temperature of 800°C. In addition, the graph shows that the value of shear strength in samples with addition of 16 grams and 20 grams of distilled water at sintering temperature of 700°C has decreased. The decrease in shear strength between hydroxyapatite layer and substrate deposition is due to the presence of a number of pores formed during the sintering process.

In their research [23] showed that there was a decrease in bonding strength of 46% at a heat treatment temperature of 700°C due to the presence of a number of pores on the substrate surface. These results are in accordance with the results of the SEM test shown in Figure 5 (b). Where the surface morphology of the hydroxyapatite layer on the substrate is characterized by enlarged pores after the sintering temperature is increased from 600°C to 700°C.

3.4. XRD Analysis

XRD analysis is done to know the chemical compound in the sample and its composition. The results of 316L stainless steel that coated with hydroxyapatite using 16 grams of distilled water at sintered temperature variations 600°C, 700°C, and 800°C can be seen in Figure 8.
Figure 8 shows that the majority of the products formed are hydroxyapatite. From the figure, overall peak value of hydroxyapatite having a hkl value similar to the characteristic pattern of the results of the standard XRD hydroxyapatite analysis from JCPDS (Joint Committee on Powder Diffraction Standards) data with No. 09-432 i.e. (002), (112) and (300) with an angle 2θ 25.887°; 32.196° and 32.902°. The peak of hydroxyapatite at the sintering temperature 600°C is with hkl (002); (112) and (300) at an angle 2θ 25.983°; 32.292° and 32.940°. At sintering temperature 700°C is with hkl (002), (112) and (300) at an angle 2θ 25.887°; 32.191° and 32.906°. While at sintering temperature 800°C, with hkl (002), (112) and (300) at an angle 2θ 25.887°; 32.274° and 33.157°.

From the XRD analysis results, it can also be seen that the composition of the compounds contained in the hydroxyapatite deposition layer can be seen in Table 2.
Table 2. Composition of compounds contained in the hydroxyapatite layer using 16 grams of distilled water.

| Component   | Sintering Temperature 600°C | Sintering Temperature 700°C | Sintering Temperature 800°C |
|-------------|-------------------------------|-------------------------------|-------------------------------|
| Hydroxyapatite | 99.6                          | 99.3                          | 99.2                          |
| Portline     | 0.4                           | 0.3                           | 0.4                           |
| Lime         | 0.0                           | 0.4                           | 0.4                           |

Based on the results of the XRD analysis it can be concluded that in this study, the dominant product contained in the deposited layer was hydroxyapatite with a percentage of 99.37%.

4. Conclusion
The difference in sintering temperature and the amount of addition of distilled water into the mixture, affects the thickness of the hydroxyapatite layer deposited on 316L stainless steel. The thickness of the hydroxyapatite layer obtained by adding 16 grams of distilled water at different sintering temperatures of 600°C, 700°C, and 800°C were 113 μm, 114 μm, and 117 μm. Meanwhile, the coating thickness at sintering temperature at 700°C with variations the amount of distilled water 16 grams, 18 grams and 20 grams decreased from 114 μm to 59 μm and then decreased again to 42 μm. This indicates that the more distilled water is used, the thickness of the hydroxyapatite layer will decrease, while the layer will increase with increasing sintering temperature. Furthermore, the highest shear strength value in this study was 11.78 MPa, namely at sintering temperature of 800°C and 16 grams of distilled water.

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