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Hydroxyapatite Coatings on Titanium Alloy TNTZ using Electrophoretic Deposition

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Abstract. TNTZ is a β-type titanium alloy that designed for orthopedic implant application. This material has superiority in mechanical properties such as high strength to work on load bearing or dynamic bearing, elasticity that is close to the human bone, contained non-toxic materials, and biocompatible. However, the inertness of titanium made this material still have no bioactivity, so that it cannot trigger the bone tissue to grow faster and produce optimum osseointegration. Hydroxyapatite (HA) has chosen as the coating material for TNTZ since the biocompatibility and bioactivity of this ceramic material. So that, by combining mechanical properties of TNTZ and bioactivity of HA it can be expected that better orthopedic implant would be produced. Electrophoretic Deposition (EPD) has chosen as the coating method since the simplicity of the making, relatively low cost, and the ability to coat things with complicated design. In this method, electrical current is used trough cathode and anode within the HA suspension. The electrical potential (voltage) will transport the small particle of HA to be deposited on the surface of TNTZ until producing an even layer of HA coating. This coating process requires two major parameters that are voltage and coating times. The desired quality of HA coating that would produce can be achieved by adjusting these parameters. Voltages are in the range of 7, 10, and 13 volts while coating times are in the range of 7, 10, and 13 minutes. Based on the result it is known that the best HA coating that can be produced are on 10 minutes and 10 volts. This best result shows the good surface morphology, optimum value of mass growth, coating thickness, and surface coverage. Based on this research it can be concluded that increasing voltage and coating times will increase the coating thickness and surface coverage of HA coating. This result shows that the EPD can be used to produce TNTZ titanium implant that coated with HA for orthopedic application.

Keywords: TNTZ, Hydroxyapatite, EPD, Coating, Orthopaedic Implant

1. Introduction

TNTZ is a β-type titanium alloy that designed for orthopedic implant application[1], [2]. This material has superiority in mechanical properties such as high strength to work on load bearing or dynamic bearing, elasticity that is close to the human bone, contained non-toxic materials, and biocompatible[2]. However, the inertness of titanium made this material still have no bioactivity, so that it cannot trigger the bone tissue to grow faster and produce optimum osseointegration[3]. Besides that, some research revealed that using titanium implant for a long period can cause some adverse reaction, such as chronic inflammation, foreign body giant cell reaction, and aseptic loosening[4]–[6]. A series of this adverse reaction is caused by the debris from oxide layer and metal ions at the titanium surface that detached and enters the bone tissue since the corrosion of metal material in the body fluids[6]–[9].

To decrease the adverse effect of this debris particle and improve the bioactivity of the material, it needs additional material to coat the TNTZ[10]. Hydroxyapatite (HA) has chosen as the coating material for TNTZ since the biocompatibility and bioactivity of this ceramic material as we know that HA is one of the main compounds that build human bone along with the proteins, other minerals, and bone cells[11]. So that, by combining mechanical properties of TNTZ and bioactivity of HA it can be expected that better orthopedic implant would be produced[12]. Electrophoretic Deposition (EPD) has chosen as the coating method since the simplicity of the making, relatively low cost, and ability to coat things with the complicated design[13]–[15]. In this method, electrical current is used trough cathode and anode within the HA suspension. The electrical potential (voltage) will transport the small particle of HA to be deposited on the surface of TNTZ until producing an even layer of HA coating[16], [17]. This coating process requires two major parameters that are voltage and coating times. The desired quality of HA coating that would produce can be achieved by adjusting these parameters[18].

Many researchers have been conducted to understand the HA coating process on the titanium using EPD method[13], [19], [20]. These research usually use commercial pure titanium (CpTi) or titanium alloy (Ti6Al4V)[13], [21], [22]. HA particle that has been used also have variation, such as the microparticle or nanoparticle[23]–[25]. However, there are still wide ranges of parameters value in voltage and coating times that have been conducted on those researches. Because of that, it is necessary to research optimizing the parameters of EPD (voltage and coating times), especially on TNTZ material to know the optimum parameters.

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2. Materials and Method

2.1. Sample Preparation

Titanium TNTZ in bar shapes with 400 mm long and 5 mm in diameter providing by IMR Tohoku University Japan was cut using grinder until 50 mm long and 5 mm in diameter. After that, titanium samples were cleaned using sandpaper with size 800, 1000, 1500, and 2000. Then, solution treatment was conducted to the samples in the temperature about 700^{o}C and holding for 2 hours. After that, samples were cleaned using sandpaper until really clean. Then, pre-treatment was conducted by submerging the samples in the ethanol 96% and acetone within ultrasonic cleaner for 15 minutes, respectively. After that, samples remained in HNO3 15% for 15 minutes and then followed by submerging in the NaOH 1 mol for one hour.

2.2. Hydroxyapatite (HA) Suspension Preparation

Hydroxyapatite (HA) suspension was made by mixing the 4 gram of commercial HA particles from SIGMA Aldrich with the particle size 10 µm within 100 ml of ethanol 96%. The suspension was stirred up by using hotplate magnetic stirrer with the velocity of 100 rpm for one hour (homogenization).

2.3. HA coating using EPD method

Series of EPD tools consisted of a power supply for adjusting the voltage, a pair of cathode and anode that immersed in the HA suspension that stirred up using hotplate magnetic stirrer. The cathode was a carbon bar, and the anode was the samples. The parameters that used in this research were 7, 10, and 13 volts and 7, 10, and 13 minutes.

2.4. Sample Characterization

Image of surface morphology of each sample will be captured by using the optical microscope and scanning electron microscopy (SEM). Mass growth of each sample will be measured by using digital scales. The coating thickness of the HA layer will be measured by coating thickness gauges. Surface coverage value will be measured by imaging software ImageJ using the image from the optical microscope.

3. Result and Discussion

3.1. Surface Morphology of HA coating on TNTZ

Figure 1. and Figure 2. shows the image surface morphology of HA coating on the TNTZ surface that captured by the optical microscope. Based on the figures it can be seen that the samples from voltage and coating times' treatment have been coated finely by HA particles. There was a very little empty spot that can be seen from these figures, but on each treatment can be seen that HA coating that produced have a different coating thickness and particle distribution.

7v 10v 13v

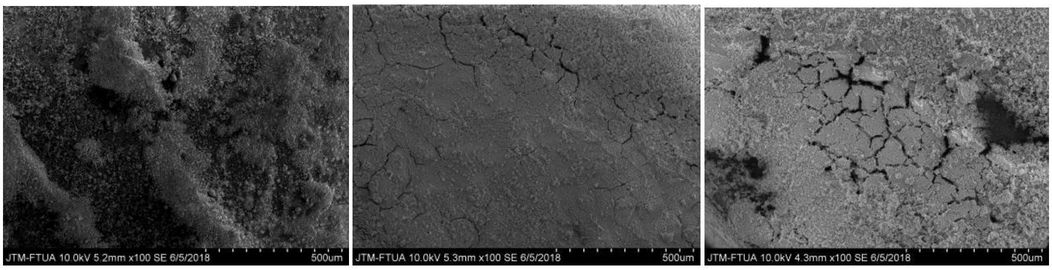
Figure 1. Surface morphology of HA coating on TNTZ at different voltage

7 min 10 min 13 min

Figure 2. Surface morphology of HA coating on TNTZ at different coating times

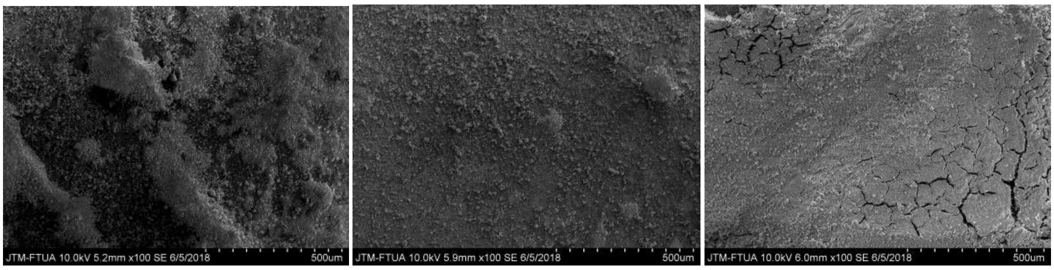
The result that can be seen on the figures shows that increasing of voltage will increase the surface coverage and thickness of HA coating. This pattern also found on the samples from coating times treatment. However, increasing the value of voltage and coating times at some point will produce HA coating that has the crack. Samples from 13 volts and 13 minutes treatment show the HA coating that has the most crack. These results indicate that increasing of coating thickness will decrease the bonding strength between HA particles that would easily produce the crack.

Samples from 10 volts and 10 minutes treatment show the best HA coating layer. HA coating layer that produces on these samples are more even than the other samples, and there is a very small amount of crack that can be found. In addition to, samples from 7 volt and 7 minutes treatment still showing non-even coating layer and there are so many spots that not coated yet. These results indicate that there is an optimal value of voltage and coating times that should be considered to produce better HA coating using the EPD process. Based on the figures it can be concluded that the samples from 10 volts and 10 minutes treatment are the samples that have the best HA coating. Other researches also have the same result with this current research. Enhancement of voltage and coating times will always be made a positive linear correlation. It indicates that energy that produces from potential differences between cathode and anode (voltage) is the most important factor to produce HA coating on the surface of the TNTZ using EPD process. Meanwhile, coating times will affect the amount of deposited HA particle on the surface of TNTZ, longer times for coating will increase the amount of HA particle that deposited[13], [16], [26], [27].



7v 10v 13v

Figure 3. SEM imaging of HA coating on TNTZ at different voltage



7 min 10 min 13 min

Figure 4. SEM imaging of HA coating on TNTZ at different coating times

The results of SEM imaging also have the same pattern with optical microscope result and inclined to support each other. Based on the SEM imaging it can be seen that the samples from 7 volts and 7 minutes have non-even HA coating layer and there are many stacks of HA particles. Samples from 10 volts and 10 minutes treatment show the HA coating layer that more even than other samples and HA particles distribution is homogeneous, beside that there is a very little area that shows crack. Samples from 13 volts and 13 minutes treatment show thicker HA coating layer than other samples and show many areas that have the crack. Based on this result, it can be concluded that samples from 13 volts and 13 minutes cannot be used for orthopedic implant application because HA coating that produces is not appropriate with the desired one. Another research also has the same result with this current research[15], [22], [28].

3.2. Mass Growth of TNTZ samples

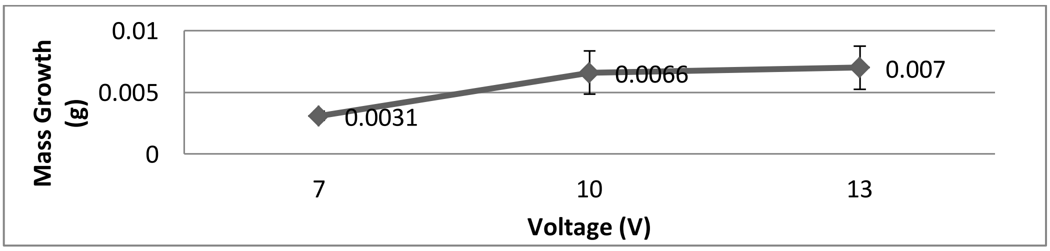


Figure 5. Samples mass growth at a different voltage.

Figure 5. shows the graphic of correlation between the mass growth of samples at the different voltage. Based on the graphic it can be seen that increasing voltage will increase the mass growth. It means that a higher voltage will increase the amount of particle that can be deposited on the TNTZ surface. Mass growth from samples of 7-volt treatment until 10-volt treatment is pretty significant. But, mass growth from samples of 10 volts until 13-volt treatment seems not significant. This result shows that there is an optimum value of the voltage that able to give enough energy for depositing HA particles on TNTZ surface. Based on the theory, particle in small size inclined more easily to deposited and require smaller voltage[13], [25], [29].

However, samples from coating times treatment show the different mass growth pattern (Figure 6.). Mass growth value is decreased from sample 7 minutes until 10 minutes treatment, then increase again on the samples from 13 minutes treatment. It can be assumed that this result is caused by electrical voltages that not stable during the coating process that is resulting non-linear mass growth data. Lack of data can be another reason for such phenomena like this since a small amount of data will produce larger deviation value. Based on the theory, it can be known that increasing of coating times value will increase the amount of HA particle that deposited on titanium surface[30]–[32].

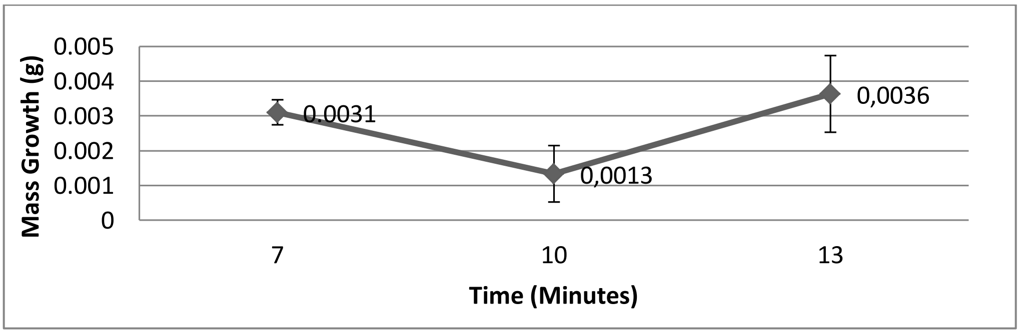


Figure 6. Graphic of samples mass growth at different coating times

3.3. Coating Thickness of HA on TNTZ

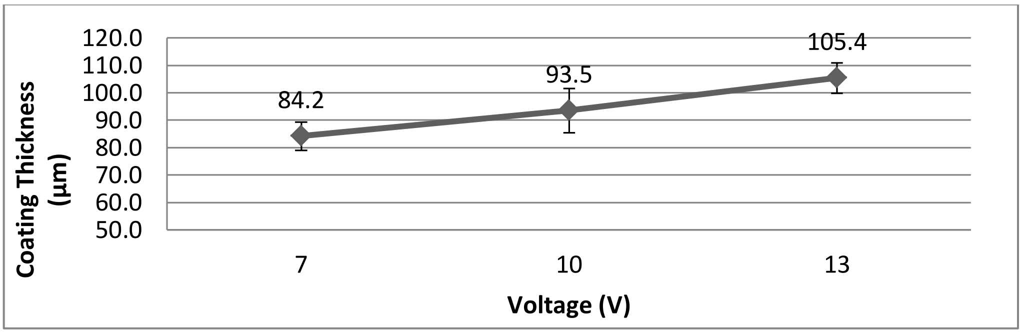


Figure 7. Graphic of HA coating thickness at different voltage

Figure 7. shows the graphic of correlation between HA coating thickness at the different voltage. Based on the graphic it can be seen that increasing voltage will increase the thickness value of the HA

coating. This result has a similar pattern with the result from optical microscope imaging and mass growth measurement. However, the result from coating times treatment shows a different pattern but similar to the result from mass growth measurement from the same treatment (coating times treatment) (Figure 8.). Other research also revealed the same result with current research. Based on the result, it can be seen that the value of HA coating thickness that produces on this research have been fulfilled the desired coating thickness that can be used for orthopedic implant application (50-100 μm)[33]–[35].

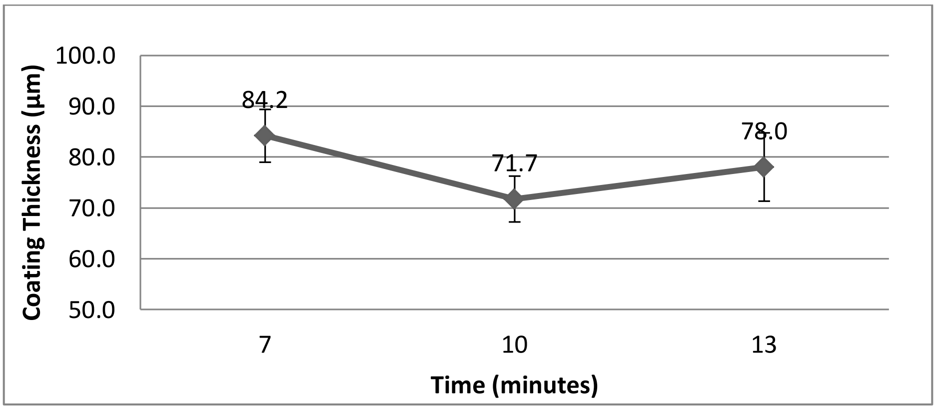


Figure 8. Graphic of HA coating thickness at different coating times

3.4. Surface Coverage of HA coating on TNTZ

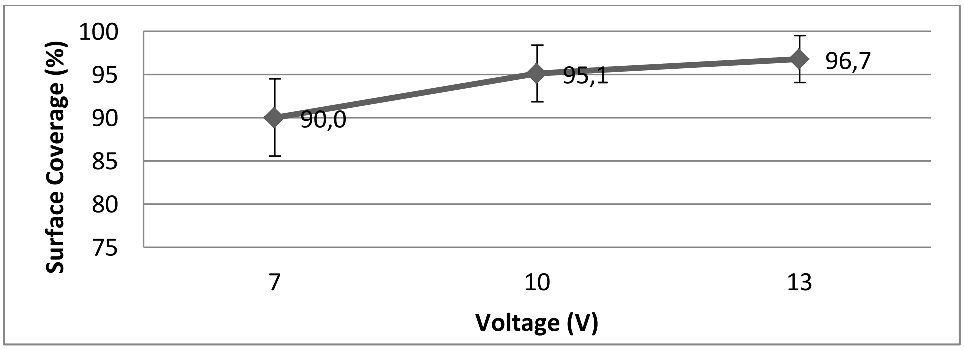


Figure 9. Graphic of HA surface coverage at different voltages

Figure 9. shows the graphic of correlation between surface coverage at the different voltage. Based on the graphic it can be seen that increasing voltage will increase the value of surface coverage by HA particles. Based on this result it can be assumed that voltage is the most important parameters that have a major role in the EPD process[18], [36]–[39]. Voltage can affect the whole coating variables, such as the mass growth of samples, coating thickness, and surface coverage. However, coating times also have a great effect on the EPD process but produces smaller value on coating variables (Figure 10.). Surface coverage that produces in this research relatively above 90% that indicated the coating process that conducted using EPD method is successfully produce desired HA coating on TNTZ surface.

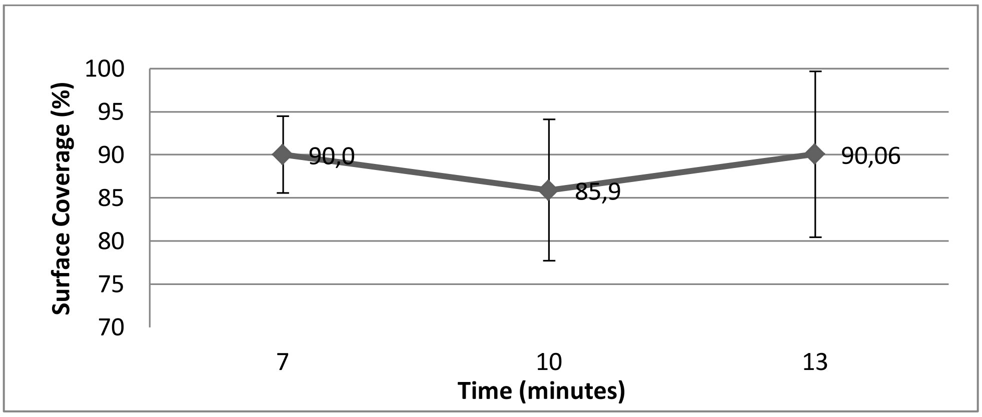


Figure 10. Graphic of HA surface coverage at different coating times

4. Conclusion

1. Voltage and Coating Times are the most important parameter on Electrophoretic Deposition process.

2. Increasing voltage and coating times will increase mass growth, coating thickness, and surface coverage of the samples.

3. The optimum parameters that produce the better quality of HA coating are 10 volt and 10 minutes treatment.

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