Corrosion behavior of Ti6Al4V ELI coated by bioceramic HA in artificial saliva at fluctuating temperatures

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Abstract. Titanium and titanium alloy have been used widely in both orthopedic and orthodontic applications. Dental implant in orthodontic is utilized to replace the missing teeth through implanting them into the human jaw as a teeth root. Ti6Al4V is one of a titanium alloy that has been developed as a dental implant due to its mechanical strength, corrosion resistance, and bio-compatibility. Hydroxyapatite is applied as the coating material is significantly a solution to overcome the inert properties of Ti6Al4V and becomes bioactive. The study goal is to determine the corrosion rate of Ti6Al4V ELI coated nano-sized hydroxyapatite using electrophoretic deposition (EPD) method applying the 5 V voltage and in 5 minutes. The implant was soaked in a solution of artificial saliva for six weeks at fluctuated temperature, 20°C and 60°C. The results showed that the corrosion rate decreased from 1.1413 mpy to 0.4236 mpy because of hydroxyapatite coating. By the hardness properties also decreased from 318 HVN into 203 HVN. This indicated that the nano-hydroxyapatite might inhibit corrosion behavior and during corrosion process occurred the implant was not able to maintain its mechanical properties.

1. Introduction

Public awareness of the importance of oral and dental health is increasing [1]. One of the dental care improvements is the use of dental implant functioning to replace missing tooth and caries so that mastication and aesthetic function, as well as comfort for its users, can be obtained [2].

Commonly used materials for the dental implant are titanium and its alloys [3-5]. It is due to its advantage of having osseointegration properties, compatibility, corrosion resistance, the excellent and inert ability to withstand mechanical loads when chewing [6]. However, this titanium has a disadvantage that is susceptible to corrosion aggressiveness of the body fluids. It results in the side effects on surrounding tissues and makes it less bioactive [3]. To increase the bioactivity, then this
Titanium is coated with hydroxyapatite used as a barrier to the release of metal ions of the body's tissues [4].

Coating method applied is Electro Phoretic Deposition (EPD) method with better coating result, simple instrumentation and short formation time [4].

Previous studies conducted micro hydroxyapatite coatings corrosion using EPD method on Ti6Al4V material corroded with Hanks solution at room temperature (37°C) for four weeks. The increased the coating layer bioactivity with the formation of ten μm coating thickness with fracture free [4]. Meanwhile, other studies corroded the nanoscale hydroxyapatite layer using EPD method on Ti-CaP material and soaked with SBF solution at 37°C, and resulted in reduced corrosion rate [7]. However, since dental implants functioned in fluctuating temperatures, it is necessary to test the behavior of implanted corrosion in these fluctuating temperatures.

Bioceramics are used as raw materials on surgical implants that have biocompatible properties and are important parts of biomaterials [8]. One of the most commonly used types of ceramics is hydroxyapatite [HA; Ca10[PO4]6[OH]2] which has excellent bioactive, bioactivity, biocompatibility and osteoconductivity [3,5]. Hydroxyapatite-coated implants greatly affect osteoblast differentiation, induce some osteogenic markers and increase osteogenesis [9].

This present study uses nano-size HA at it has high dissolubility rate and is more resorbable [10]. The particle size of nano-HA can produce layers with flatter, homogeneous and quite thick structure [11]. The nanoparticles may cause interactions with certain serum proteins that will increase the adhesion of osteoblasts on the material surface [12].

The components of human bone apatite are composed of calcium phosphate nanocrystals and the nanostructures of hydroxyapatite crystals, which are similar to the inorganic components of human bone tissues [13]. Crystal nano molecules can interact with specific molecules of the body such as proteins and nucleic acids like DNA. These functionalities are invisible in micro size hydroxyapatites [14].

None the less, HA deficiency is low on its mechanical properties and susceptible to corrosive [3,4]. One way to improve the nature of HA is by coating. The chosen coating method in this study is the electrophoresis deposition method due to its excellent coating results, simple in instrumentation, and short formation time [4]. EPD method is an affordable alternative method that can produce layers with the right composition, good adhesion strength and varied thickness started from 1-50 μm [15].

HA coating by EPD method was performed with a 5 minute test time and a 5 V voltage to avoid cracking. Small particle deposition is preferable to using low voltage to avoid cracking [16]. Sintering is conducted to improve the quality of the layer. Before sintering, the 1 x 24 hours specimen was held in abeyance to stabilize the aggregate size of the particles within a narrow size range to improve the coating stability [16]. The purpose of sintering is to strengthen the bond between HA and Ti6Al4V ELI so that the layer is not easily loosed. In this study, sintering was performed at a temperature of 800°C with 1-hour heating 100°C/h and 100°C/h cooling rate [4].
2. Research methods

2.1. Specimens Preparation

Ti6Al4V ELI specimens were cut to a size of 1.5 mm x 1 mm and then sanded to smooth the surface of the specimen. After that further cleaning was performed by using an ultrasonic cleaning machine to remove impurities particles attached to the specimen. Then the coating was done.

2.2. Testing Procedure

The coating was carried out by electrophoresis deposition method in which the nano-HA and ethanol were mixed to form HA solution with a pH of 7, 5 V voltage and 5 minutes. After being coated, it was laid for 1 x 24 hours, and then being sintered in the temperature of 800°C. Further, it was soaked by weight loss method using saliva solution medium and corroded for 6 weeks by varying the frequency of heat-cold cycle on the specimen. The utilized hot-cold cycle was fluctuation temperature of 20°C and 60°C where the specimen was heated to 60°C and then cooled to 20°C.

2.3. Characteristic of surface

After the corroded for six weeks, then the corrosion rate was calculated using weight loss method, continued to measure the hardness of specimen using Vicker test instrument, and conducted observation using SEM to see specimen surface morphology.

3. Result and discussion

3.1. Analysis of corrosion rate

Seen in Figure 1 that there is a decrease in corrosion rate in each sample in line with the increase of test time in the sample. The highest corrosion rate has occurred in the HA-coated Ti6Al4V ELI specimens for two cycles, and the lowest occur in the HA 6-cylinder Ti6Al4V ELI specimens for six cycles.
In the previous studies, TNTZ was coated with coronated synovial fluid collagen for six weeks for joints. It resulted in an increased corrosion rate [17]. The comparison result of the corrosion rate is shown in Figure 2.

In Figure 2, the corrosion rate of the material without coating is increasing, in contrast to the material with HA coating that is decreasing. Consequently, HA can inhibit the corrosion rate on the surface of Ti6Al4V ELI.
3.2. Mechanical properties (Hardness)

Meanwhile, the testing of the mechanical properties can be seen in Figure 3. The picture present that the hardness value decreases after being corrected by HA-coated Ti6Al4V ELI specimen which is lower than the uncoated Ti6Al4V ELI specimen. This shows the accordance with time immersion of Ti6Al4V ELI specimen in saliva solution. The hardness of both coated and uncoated specimens of Ti6Al4V ELI declines.

![Result of hardness of sample](image)

**Figure 3.** Graphic of sample hardness result

Based on the result of previous studies, Ti6Al4V ELI was soaked in a solution of Artificial Saliva pH five within 1000 hours resulted in a declining hardness value [18]. Whereas in other studies, Ti-12Cr and CPTi were immersed in a solution of Artificial Saliva pH five within three weeks with a constant temperature of 37°C resulted in a decreasing hardness [19]. Similarly, the research conducted [17] also resulted in decreased hardness values.

3.3. Examination of the microstructure

Based on the observation result utilizing SEM in Figure 4 it can be highlighted that the Ti6Al4V ELI specimen at two weeks immersion for two cycles (a) and (b) the HA layer is starting to crack and to peel slightly. At four weeks immersion time for 4 cycles (c) and (d) the HA layer begins to exfoliate and display titanium. At 6 weeks immersion time for 6 cycles (e) and (f) the HA layer begins to fall
even though there is no corrosion yet. It determines that HA serves to inhibit corrosion of Ti6Al4V ELI and makes the HA specimens not easily falling out.

![Figure 4. The observation result of HA encapsulated Ti6Al4V ELI specimen after soaking with saliva solution for 6 weeks, with 200X magnification (a) and (b) samples for 2 cycles (c) and (d) samples for 4 cycles (e) and (f) samples for 6 cycles.](image)

### 3.4. Chemical composition of corroded artificial saliva solution

The testing of corroded artificial saliva solution composition can be seen in Table 1. The composition shows the elements contained in the artificial saliva solution. It was because before being corroded, the highest element was at Mg equal to 55.851% and the lowest at Ti equal to 0.027%. After experiencing the corrosion for 2 cycles, the highest element was obtained at Cl equal to 39.388% and the lowest at V equal to 0.023%. Hence, for 6 cycles, the highest element was obtained at Cl equal to 35.105% and the lowest at Ti equal to 0.027%. The results indicates that an increase of an element followed by the decrease of the other elements due to the percentage of solubility where it should be 100%. The reduction of these elements occurred because of the reaction between these elements with HA.
**Table 1** Chemical Composition of Artificial Saliva Solution

| No. | Element | Mass Weight (%) |
|-----|---------|-----------------|
|     |         | Before Corrosion | 2 cycles/ | 6 cycles/The |
|     |         |                  | The highest | Lowest       |
| 1   | Na      | 0.15             | 0.71       | 1.47         |
| 2   | Mg      | 55.85            | 1.37       | 0            |
| 3   | Al      | 17.98            | 4.69       | 2.66         |
| 4   | Si      | 13.85            | 5.68       | 3.72         |
| 5   | P       | 6.08             | 13.42      | 18.67        |
| 6   | Cl      | 0.09             | 39.38      | 35.11        |
| 7   | K       | 0                | 17.35      | 16.31        |
| 8   | Ca      | 0                | 11.24      | 13.8         |
| 9   | Ti      | 0.03             | 0.31       | 0.02         |
| 10  | V       | 0.09             | 0.02       | 0.06         |
| 11  | Fe      | 0.07             | 0.94       | 0.26         |
| 12  | Ag      | 3.9              | 4.86       | 6.71         |
| 13  | Ru      | 1.89             | 0          | 1.52         |

4. Conclusion

By this present study result, it can be concluded that the occurring corrosion rate in each test sample is influenced by the fluctuations frequencies in the temperature. The higher the frequency of temperature fluctuations, the more the corrosion rate decreases. Also, the corrosion rate of Ti6Al4V ELI coated HA is 0.7514 mpy which is smaller than that of non-coated Ti6Al4V ELI of 0.8106 mpy.

The corrosion rate gives effect to the hardness value of the sample: the more the corrosion rate declines, the more the hardness values of the sample decrease. The highest hardness value occurred in the Ti6Al4V ELI sample without HA coating for two cycles of 281.8 HVN and the lowest on the HA-Ti6Al4V ELI coated sample for 6 cycles of 203.2 HVN.
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