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Research Article

Addition of Zirconium Oxide for Reduction of Hydroxyapatite Layer Cracks in Ti-6Al-4V ELI Implant Materials for Improved Osseointegration

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ABSTRACT

The hydroxyapatite (HA) layer on the surface of the implant material tends to crack during the sintering process for layer densification. This causes the process of implant union with bone (osseointegration) does not function perfectly in the human body. This study aims to reduce cracking by increasing the adhesion of the HA layer on the surface of the Ti-6Al-4V Extra Low Intertitial (ELI) implant material. The research used the dip coating method to get a thin and even layer. To strengthen the adhesion of the coating, Zirconium Oxide (ZrO_2) was added to commercial HA suspension. The test specimens were heated at sintering temperatures of 800 ^{0}C, 900 ^{0}C and 950 ^{0}C with a heating rate of 5 ^{0}C /minute. Layer morphology and cracks were examined using an optical microscope. The percentage of layer cracks will be measured using ImageJ software. The addition of ZrO_2 results in cracks reduction in the HA layer of the surface of the test specimen. The percentage of cracks decrease with the increasing of ZrO_2 addition (17% and 20% weight) to the suspension of the HA layer. These result is certainly appropriate for increasing osseointegration in the human body.

1. INTRODUCTION

Ti-6Al-4V *Extra Low Intertitial* (ELI), a type of titanium alloy that is widely used for implant materials, especially for dental and orthopedic implants [1]. This titanium has better physical and mechanical properties than stainless steel and pure titanium, which is lighter, more ductile, stronger, lower modulus of elasticity, and having good biocompatibility in the body.

However, the drawback is that titanium has less bioactive properties [2]. Therefore, Ti-6Al-4V ELI needs to be coated in order to obtain a good osseointegration process in the area around the implant. One of coating substrate that can be sufficient is hydroxyapatite (HA). However, the results of several studies indicate that there are still many cracks found on the surface layer of HA [3-8]. These cracks will later lead to implant failure.

Cracks occur due to the lack of strong adhesion of the HA layer on the surface of the implant material. The lack of strong adhesion of this layer is due to the brittle nature of HA ceramics when heated during the sintering process to solidify the layer. When heated, the metal has a large strain, while HA

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has a small strain. This condition causes thermal stresses that encourage cracks [3].

There are two HA coating processes that are often used, namely the Electro Phoretic Deposition (EPD) method and the Dip Coating method. These two methods were chosen because they are cheap and easy to implement for coating [3,4].

A number of studies have stated that coating Ti-6Al-4V ELI with nano commercial HA through the EPD method, producing an even layer over the entire surface. However, there are also found layers that are not evenly distributed. This is due to the accumulation of HA or agglomeration in some areas of the surface layer. This condition causes cracks on the surface of the coating during the sintering process [4]. The more agglomeration occurs, the more cracks are found in the layer.

Cracks during the sintering process are generally caused by differences in the thermal coefficient of the material and HA. Ti-6Al-4V ELI has a lower thermal coefficient (~10.3μm/mK) than HA (~14 K/mK). This difference in thermal coefficient affects the difference in expansion and shrinkage between the HA layer and the material during heating and cooling as well as during the sintering process, resulting in thermal stress. This condition causes thermal stresses that encourage cracks [5].

Subsequent research, coating HA microparticles on Ti-6Al-4V with the EPD method, obtained the best layer morphology at a voltage of 8 volts and a time of 8 minutes. However, the coating is brittle and has many cracks on the surface [6]. To improve the adhesion of the coating, the implant material Ti-6Al-4V was coated with commercial HA plus P_2O_5, Na_2Co_3 and KH_2PO_4 additive solvents. As a result, no cracks were found when the sintering temperature was 800 ^{0}C. However, when heated at a sintering temperature of 900 ^{0}C, cracks were found on the surface of the coating [7].

In addition to using commercial HA, there are also a number of studies that use natural HA for HA coating suspensions. This is because natural HA is easier to obtain and the price is not too expensive [8]. However, the result is also the same. Ti-6Al-4V coating using beef bone HA suspension, cracks were found when heated at a sintering temperature of 900 ^{0}C.

In addition to the difference in thermal coefficients, this crack is also caused by the lack of strong adhesion between the HA layer and the Ti-6Al-4V material during the sintering process. The larger the HA particle size, the greater the cavity (porosity) between the particles. Because the HA particles of bovine bone of 125 m are quite large, the amount of ethanol used as a solvent for HA, trapped in the cavities formed in the HA coating process, that is also quite large. This condition will cause cracks on the surface of the coating during the sintering process, due to the trapped ethanol evaporates quickly [8].

In this research, ZrO_2 will be added to the HA suspension on Ti-6Al-4V ELI coating through the Dip Coating method. The goal is to obtain a strong adhesion so that the surface layer is not easily cracked later during the sintering process. The addition of ZrO_2 is expected to increase the adhesion of the HA layer. ZrO_2 has fracture resistance and high flexural strength. Beside, it has the property of absorbing energy during the transformation from a tetragonal atomic arrangement to a monoclinic atomic arrangement [9, 10].

In addition, ZrO_2 can also conduct good heat to Ti-6Al-4V ELI because the thermal expansion coefficient of ZrO_2 (9.6×10^{-6}/°C) is close to the coefficient of thermal expansion of Ti-6Al-4V ELI (8.6×10^{-6}/°C). The ZrO_2 phase bond in the HA layer becomes a diffusion barrier against the decomposition of the material (substrate) to protect the cracks in the layer. In this case, ZrO_2 serves as a barrier so that the adhesion bonds on the material and the HA suspension are not pulled during the heating process. With the surface layer that is not easily cracked, it will trigger good osseointegration or implants in the body [11].

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2. METHODOLOGY

2.1. *Material*

This study used 9 of Ti-6Al-4V ELI test specimens (square plate shape), with dimensions of 10 mm x 10 mm x 4 mm. After the specimens were cut, they were sanded using silicon carbide sandpaper with a mesh size of 800-1500, then polished using alumina powder [12]. Furthermore, the specimens were cleaned with a solution of acetone, 70% ethanol, 25% nitric acid with pH 7.3 conditions and washed with pure water for 30 minutes [12]. Then the specimen was immersed for 1 hour in 1 mol NaOH solution [13]. The final cleaning used a multi-frequency ultrasonic bath and dried with a stirring hot plate for 5 minutes at a temperature of 50 ^{0}C [13].

For the suspension layer, commercial nano size (200 nm) HA (Sigma Aldrich, USA) and ZrO_2 (XFNANO brand) were used, model number XFI01-3, 95% purity. The suspension consisted of 4 grams of HA powder plus 0.8 grams of ZrO_2 (17 wt%) and 4 grams of HA powder plus 1.0 grams of ZrO_2 (20 wt%) which were mixed in 100 ml of ethanol solution at pH 4.0 using the addition of HNO_3 solution [14]. After that, homogenization of the solution was carried out with a magnetic stirrer for 1 hour, followed by sonication in an ultrasonic bath for 2 hours. The HA which had been attached to the surface of the test specimen was dried for 24 hours at room temperature.

2.2. *Methodology*

HA coating using the dip coating method. This method was chosen because it is easy to do and the cost is not expensive [15]. Immersion was carried out with a withdrawal speed of 4 mm/s, referring to the results of an even layer of HA in previous studies [15-19]. Furthermore, the resulting layer will be compacted by a sintering process using the Vacuum Tube Furnace GSL-1100. The sintering process is carried out with temperature variations of 800 ^{0}C, 900 ^{0}C and 950 ^{0}C, heating rate of 50 ^{0}C/minute. After being heated, it is held for 2 hours so that the temperature is evenly distributed in the test specimen, followed by annealing for 24 hours [3-5].

Then, the thickness of the coating was measured using the Sanfix Thickness Gauge (μm), GM 280 series, followed by measuring the surface coverage of the layer using ImageJ software [17]. The Olympus LG-PS2 Stereo optical microscope was used to observe the morphological and cracking characteristics of the coating. To get the percentage of layer cracks, ImageJ software is also used. Then the percentage of crack reduction in the test specimen layer without the addition of ZrO_2 with the addition of ZrO_2 will be compared at each sintering temperature of 800 ^{0}C, 900 ^{0}C, and 950 ^{0}C.

3. RESULTS AND DISCUSSION

3.1. *Coating Thickness and Surface Coverage*

One of the factors of good HA coating adhesion is that the coating has a thin and uniform thickness over the entire surface [3]. Therefore, in this study, the Dip Coating method is used. For the suspension, commercial nano size HA is used. In general, it can be seen that the test specimens have been coated with HA evenly almost all over the surface. From the calculation of the ImageJ software, the results of the thickness and surface coverage of the HA layer on the Ti-6Al-4V ELI implant material are obtained as given in Table 1.

Table 1. HA Coating Thickness and Surface Coverage on Ti-6Al-4V ELI.

No.	**Sintering Temp.** *(°C)*	**ZrO_2** (*wt%*)	**Thickness** (*μm*)	***Surface Coverage (%)***
1.	800	17	89.7	88.92
2.		20	87.4	88.93
3.		0	85.6	89.05
4.	900	17	92.5	91.14
5.		20	93.8	87.32
6.		0	86.1	90.27
7.	950	17	95.3	87.48
8.		20	91.2	90.57
9.		0	88.4	86.85

In Table 1, it can be seen that the HA layer obtained is a thin layer with a layer thickness of 87.4 - 95.3 m. This is in accordance with the results of several previous studies, namely the standard thickness of a thin HA layer of 50-100 m [3-5]. The surface coverage layer obtained is also good, in accordance with the standard surface coverage layer, which is > 90 percent [6-8]. The best value obtained in this study, is namely the addition of 20% ZrO_2 with a surface coverage value of 89.58 ± 2.00.

Overall, all samples have a thin thickness and even surface coverage. The surface of this thin and even layer is good for the compaction process (densification), especially to minimize cracks during the sintering process later. The comparison of the thickness and surface coverage of this layer can also be seen in Figure 1.

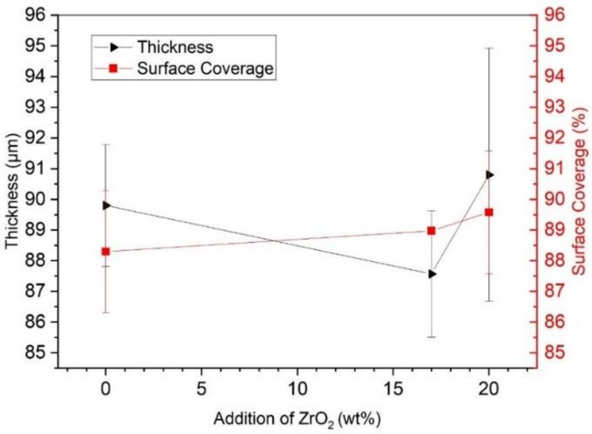


Figure 1. The value of thickness and surface coverage of the HA layer on variations in the addition of ZrO_2 mass.

From Figure 1, it can be seen that the surface coverage of the HA layer increases with the addition of ZrO_2. This indicates that ZrO_2 has good adhesion properties. so that the bond of the HA suspension with the Ti-6AL-4V ELI material becomes strong. The more addition of ZrO_2, the better the adhesion bond between the suspension and the substrate. As for the thickness, the thin thickness value was obtained at the addition of 17% ZrO_2 (87.57 ± 2.06 m). However, the addition of 0 and 20% ZrO_2 also had good thickness values, namely 89.80 ± 1.98 m and 90.80 ± 4.12 m. This indicates that the Dip Coating method is able to produce a thin and even layer.

3.2. Observation of Coating Crack

After measuring the thickness and surface coverage of the layer, then inspection of the layer cracks is carried out by observing the morphological characteristics of the test specimens as shown in Figure 2. In line with that, the results of the percentage of HA layer cracks in each test specimen can also be seen in Table 2. The percentage of this HA layer crack was measured using ImageJ software.

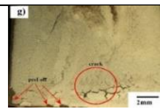
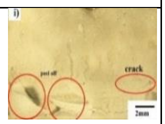
Temp Sintering (°C)	0 % ZrO_2	17% ZrO_2	20% ZrO_2
800			
900			
950			

Figure 2. Observation of the layer morphology on each test specimen on the variation of T sintering and the addition of ZrO_2 mass.

In Figure 2, it can be seen, at a sintering temperature of 800 ^{0}C, layer crack are not found in all test specimens, whether with or without ZrO_2 addition [2a-c]. Besides being caused by a thin and even layer, the absence of cracks is also due to the sintering temperature of 800 ^{0}C which is the optimum temperature that affects the chemical properties of the HA coating to be stable (i.e. HA does not change the structure) because it has good adhesion to the surface of the material. At this sintering temperature of 800 ^{0}C, there is no degradation of Ti-6Al-4V ELI and also no metal-induced decomposition of HA.

In contrast, at T sintering 900 ^{0}C, new cracks is found in the test specimens coated with HA without the addition of ZrO_2 [2d]. The crack is initiated by a

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number of layers peeling off, which results in a void layer and debonding of the bond at the interface, then the layer has micro-cracks [4].

Ahas been known, sintering is required for layer compaction. However, the disadvantage is that high sintering temperatures can also cause the HA surface to crack, due to the brittle nature of HA plus the difference in the coefficient of thermal expansion between HA and the material during the sintering process, which results in thermal stress leading to cracking.

In addition, cracks are also caused by differences in the coefficient of thermal expansion [4,5]. During sintering, the coefficient of thermal expansion of hydroxyapatite (15.2 × 10^{-6}/ °C) is lower than that of Ti-6Al-4V ELI (8.6 × 10^{-6}/ °C). Because HA has a low coefficient of thermal expansion compared to metals, it does not conduct heat well to Ti-6Al-4V ELI. The difference in expansion and shrinkage between the HA and Ti-6Al-4V ELI layers also produces thermal stresses and residual tensile stresses that will encourage cracking [11].

Table 2. Percentage of cracks in the HA layer in each test specimen on the variation of T sintering and the addition of ZrO_2 mass.

No.	ZrO_2 (wt %)	T Sintering (°C)	Coating Crack (%)
1.	0	800	0
2.	17	800	0
3.	20	800	0
4.	0	900	12.09
5.	17	900	0
6.	20	900	0
7.	0	950	17.39
8.	17	950	16.44
9.	20	950	14.30

Furthermore, cracks are also caused by an imperfect compaction process, namely the occurrence of temperature changes that are too fast when heating (thermal shock) [2, 10]. The ethanol element used as the HA solvent is trapped in the cavity formed in the coating process. This will cause cracks on the surface of the layer, because the trapped ethanol evaporates quickly [11, 21]. However, at T sintering 900 ^{0}C, cracks are not found in the test specimens coated with HA with the addition of ZrO_2 (17% and 20% wt). This indicates the effect of the addition of ZrO_2 to increase the adhesion of the coating obvious. In Table 2 it can also be seen, there is no layer crack (0%).

In this case, ZrO_2 becomes a good heat conductor to Ti-6Al-4V ELI because the thermal expansion coefficient of ZrO_2 (9.6 × 10^{-6}/°C) is close to the coefficient of thermal expansion of Ti-6Al-4V ELI (8.6 × 10^{-6}/°C). The ZrO_2 phase bond in the HA layer becomes a diffusion barrier against the decomposition of the material (substrate) to protect the cracks in the layer. ZrO_2 serves as a barrier so that the adhesion bonds on the material and the HA suspension are not attracted during the heating process. This result is better than the previous study which discussed nano-size (200 nm) commercial HA coating on Ti-6Al-4V ELI using the EPD method. In this study, cracks were found when the test specimen was heated at a sintering temperature of 900 ^{0}C [3-5].

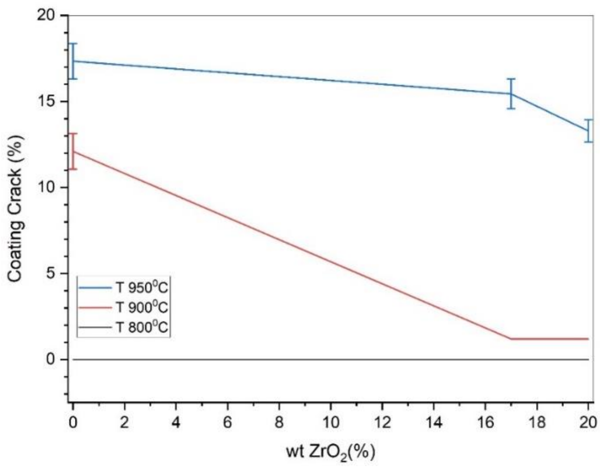

Figure 3. Percentage of coating crack to variations the addition of ZrO_2 and sintering temperature.

Furthermore, at T sintering 950 ^{0}C, cracks are found in all test specimens. However, what is interesting here is that there is a percentage of crack reduction measured by ImageJ software, as shown in Table 2. In the specimen without the addition of ZrO_2, the layer crack percentage is 17.39 %. The percentage of cracks continued to decrease to 16.44 % (17% wt ZrO_2) and 14.30 % (20% wt ZrO_2), more details can be seen in Figure 3. This reduction in cracks indicates that the addition of ZrO_2 to the HA suspension is able to increase the adhesion layer [20].

In Figure 3 it can be seen, the addition of ZrO_2 can reduce or eliminate cracks in the HA coating when T sintering is 900 ^{0}C and 950 ^{0}C. At T sintering 950 ^{0}C, the test specimen without the addition of ZrO_2, obtained a layer crack percentage of 17.39 %. The percentage of cracks continued to decrease to 16.44 % (17% wt ZrO_2) and 14.30 % (20% wt ZrO_2). Meanwhile, at T sintering 900 ^{0}C, there is no layer crack (0%) at the addition of 17% and 20% ZrO_2.

In this case, ZrO_2 has fracture resistance, because it has the property of absorbing energy during the transformation from a tetragonal atomic arrangement to a monoclinic atomic arrangement [9,20]. With the surface layer that is not easily cracked, it will trigger good osseointegration during implant placement in the body. This is because ZrO_2 also has micromorphological properties that can cause initial adhesion phenomena to produce collagen and mineral networks on the implant surface. This is what causes the process of bone union with implant material (osseointegration) which is good in the body [11, 21].

4. CONCLUSION

The Dip Coating method is able to produce a thin and even layer of HA on the entire surface of Ti-6Al-4V ELI. The addition of ZrO_2 is able to increase the adhesion and reduce the cracking of the HA layer on the Ti-6Al-4V ELI surface. The greater the addition of ZrO_2 mass to the HA suspension, the cracking layer becomes significantly reduced. It is hoped that the minimally cracked HA layer on the Ti-6Al-4V ELI surface can improve osseointegration in implant applications in the body.

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