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RESEARCH ARTICLE

Effect of Bilayer Nano-Micro Hydroxyapatite on the Surface Characteristics of Implanted Ti-6Al-4V ELI

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ABSTRACT - Ti-6Al-4V ELI is a well-known, popular medical-grade titanium alloy due to its biocompatibility and excellent mechanical properties. However, like other metal implants, it is less bioactive that affects tissue regeneration around the implant, and may lead to implant failure. So, a bioactive substance such as hydroxyapatite (HA) has usually been coated on metal implants to improve its bioactive properties. However, a single layer of HA was reported to be dissolved into body fluid after a long time of exposure in the human body. In this study, bilayer HA was deposited on the surface of screw-type implants made of Ti-6Al-4V ELI through electrophoretic deposition (EPD method. The bottom layer consists of micro-size of HA, and the second layer contains nano-size HA. The suspension contains each micro and nano size of HA powder was homogenized for 1 h followed by sonication for 2 h using a magnetic stirrer. The coating layer was subsequently sintered at 700°C for 1 h. The bilayer-coated screw implant was then implanted into the proximal tibia of health rattus novergicus under proper surgical procedures. Some screws without HA deposition were also implanted into rattus novergicus for comparison. The implanted screws were then taken out via surgery after 2, 3 and 4 weeks, and they were subsequently observed by optical microscope, SEM and XRF. The results showed that organic material is found on each coated specimen, and few HA layer is disintegrated from the surface of the screw. The disintegrated HA remained in the surface of the screw, and the amount of HA increased with increasing implantation time, which indicates the increase of osseointegration between the bone and HA layer. XRF showed a significant difference in Ti and titanium oxide contents on the surface of the coated samples and the non-coted ones, where it is only 0.66%Ti (0.39% TiO_2) on the surface of the screw with HA layer and 70%Ti (67% TiO2) for without HA. When TiO_2 is formed as a fast self-healing reaction while the screw is exposed to body fluid, the HA acts as an interface against body fluid that may contain aggressive ions. So, HA layer is not only effective against corrosion attack but also inhibits the formation of TiO_2 on the implant surface. The coated screws also revealed a strong bonding between the HA layer and the surface of the implant screw. Besides, the ratio between Ca and P elements on the screw surface is in the range of 0.58 – 2.04, which is in the range of bone characteristics.

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1.0 INTRODUCTION

There are many causes of metal implant surgery on human bones due to car accidents, work accidents, and osteoporosis. So far, stainless steel, cobalt alloys and titanium alloys have been used as implant material [1]. Ti-6Al-4V ELI is one of the most common biomaterials because of its high corrosion resistance, low elasticity modulus and high strength that is close to bone properties, good biocompatibility and excellent biomechanical properties [2,3]. Biocompatibility is important to make the sensory system presume implant as an integral part of the body [4]. However, there is another important requirement to have a better performance as biomaterial known as bioactive; that is, the ability to accelerate the regeneration of bone on the implant surface [5]. As for other metal implants, Ti-6Al-4V ELI is still lacking in this capability [6]. A previous study on a new type titanium alloy showed that the fibrosis layer interfacial between non-coated implants and bones [7]. It may trigger a corrosion process through electron transfer from the implant to body fluid. In the biomedical field, it could result in inflammation.

In order to decrease the possibility of such inflammation, introducing a coating layer from bioactive materials on the surface was developed. This coating layer covers an implant's surface, inhibiting the corrosion process or TiO_2 formation [8]. The biggest potential for bone substitution is Hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$, also known as HA. HA is a material that is close to human bone and teeth and is bioactive. HA is a calcium phosphate that contains hydroxide. The toughness of HA is about 1/40-1/70 of titanium alloys. In detail, HA can develop tight bonding with bone tissue, exhibits osteoconductive behavior, is stable toward resorption, and has no adverse effects on the human organism [9]. Regarding the above attributes, HA could form coating layers over the implant surface and attract calcium deposition over the bone and implant. So that, using HA deposition over implanted material could accelerate the healing time after bone surgery.

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However, HA does not have superior mechanical properties as well as titanium alloys. HA has a density of about 3.16 g/cm3 and a compressive strength of 100-200 MPa. HA resources are abundant, such as cow bone, fish, and shells. It is already commercial in the market for research grades. HA could be synthesized through combined calcium (Ca) and phosphor (P) with a wet or dry method. The wet method could be realized with precipitation and sol-gel. The dry method is realized with mixed Ca and P at high temperatures. The wet method commonly results in a higher purity of HA than the dry method. The Ca/P ratio to form HA is about 1.67.

Deposition HA over the surface implanted material such as Ti-6Al-4V ELI could eliminate the lack of bioactive aspect of the Ti-6Al-4V ELI. HA reacts with human body fluid, but there is no rejection regarding the biocompatibility of HA. HA surface dissolves till equilibrium among physiologic fluid, and HA surface is attained. The attractive force between positive and negative ions leads to new bone formation [10]. It is recommended that the suitable thickness of an inorganic coating layer such as HA for biomedical applications is in the range of 50-200 µm.

There are many ways to deposit the HA layer on the surface of the implant, such as thermal spraying, dip coating, electrophoretic deposition (EPD) [11], or investment casting [12]. Investment casting is a special casting technique that can produce a close-tolerance product with a competitive cost compared to other casting methods. SS 316 L is coated with HA by dipping directly into HA slurry, resulting in easy-to-control and consistent HA coating thickness applicable to small and complex shapes [12]. However, this method has a critical weakness. To increase the bonding between metal and HA, an elevated thermal treatment known as sintering should be introduced. This treatment can promote cracks on the HA coating layers. Development of the deposition method should be taken care of to prevent cracking.

Among the methods, EPD has some interesting features, i.e. uniform thin layer, close tolerance, low cost, simplicity, ability to do at low temperature, settable thickness, and good bonding strength. EPD process deposits inorganic colloid particles in the dispersion solution on the metal surface using electric current [13]. Deposit particles have a physical bond with the metal surface. EPD mechanism could be divided into two stages: (1) electrical current between the negative and positive electrode leads HA ions to move to the electrode with the opposite charge sign, known as electrophoresis, (2) HA ions are deposited on the surface of the electrode, form a homogenous film. However, like other methods, a sintering procedure is also required after the EPD process.

Some work has been recently conducted to find the best parameter of EPD to coat titanium using micro/nano size HA [14-18]. The best parameter, for instance, the usage of micro size HA on the sample with a diameter of 10 mm and thickness of 4 mm; the potential of 5, 8, and 11V provided the thickness of HA layer of 70.9, 95, and 114.5 mm, respectively. When the potential was kept at 8 V, increasing EPD time from 5, 8 and 11 minutes increased the thickness (73.3, 88.4, and 120 mm, respectively). The HA coverage area is in the range of 70-90% [14]. When introduced into body tissue, a single layer of HA deposition on the implant surface had partly dissolved into body fluid after long-term use [19]. Some cracks were also found on a single layer of HA. Implanted Ti-6Al-4V ELI on white rabbit bone for 2 to 12 weeks showed an increase in TiO2 formation on the surface of an implant caused by body fluid attack [20]. It may lead to corrosion. So, multilayers of HA might be proposed to overcome the weakness of a single layer mentioned above.

A schematic of multilayer deposition can be seen in Figure 1. The HA layer is almost covered with bigger size HA particles. The particle shape is almost circular geometry. The geometry of particles, however, forms space near the interface among the particles. These particles get continuity after sintering cause of local melting at the interface. However, space size might promote small cracks, as mentioned above. To cover these empty spaces, it is emphasized that some smaller size particles could be introduced into the space. We prepare micro and nano-size HA for this purpose. Big enough different sizes among these HA particles might enable a higher level of HA layer continuity.

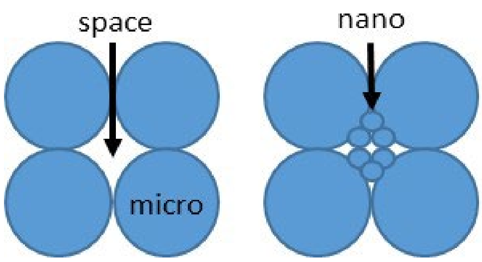


Figure 1. Idea of the HA multilayer deposition

In this study, micro-nano HA layers were deposited on the Ti-6Al-4V ELI screw through the EPD process. Then the screw was sintered at 700 °C for an hour to gain better adhesion between the screw and HA layers. The screw was then implanted on the proximal tibia of a healthy Rattus Novergicus. The implant was also done with a non-HA deposited screw. In this paper, the result of the screw surfaces observation before and after implantation is reported.

2.0 METHODOLOGY

The as-received sample is a commercial Ti-6Al-4V ELI rod with 6 mm in diameter. The rod was cut with a sewing machine and was then machined to make a screw. The screw head has a diameter of 4.5 mm and a head length of 2 mm.

The screw length is 3 mm with a dimension of M3×0.5 (diameter×pitch). The chemical composition check of the Ti-6Al-4V ELI screw shows that the amount of Al and V is about 6 and 4%. Extra-low interstitial elements are also fulfilled with the composition. The appearance of a screw made from Ti-6Al-4V ELI, a specimen in this study, can be seen in Figure 2. The screw, after the EPD process, here is marked as an EPD-ed screw.

The screw was smoothened with the abrasive paper mesh of #800, #1000, and #1500 consequently. The screw surface was purposely mirror-like surface. Then screw was ultrasonically cleaned in methanol for 15 minutes. The surface was observed under a stereo microscope to ensure no scratches were traced. When scratches were revealed, the screw was carefully smoothed again with abrasive papers. Then screw was immersed for about 30 minutes in ethanol 70% (pH 7.33), acetone, and nitric acid 25%, respectively. The specimen was then ultrasonic cleaned in distilled water for 15 minutes and immersed in NaOH 1 mol for 60 minutes.

HA suspension is made from HA powders (1 g of micro-size and 1 g of nano-size) and ethanol. Ethanol is used as a solution cause of its better performance than other solutions such as water and butanol. Water has poor dispersion stability and butanol low-grade evaporation that leads to hot cracking during sintering. The HA powders were poured into a 100 ml ethanol and mixed. Mixing was performed on a hot stirring plate till suspension formed; it was about 60 minutes for a homogenous suspension. Some HNO_3 was added during mixing into suspension till pH 4 was attained. Finally, the suspension was sonicated in an ultrasonic bath for 120 minutes [21, 22].

In the EPD process, the screw is used as a cathode, while graphite is used as an anode. These two electrodes were separated by about 15 mm. A power supply with a digital display was used to provide a direct current. There are four schemes of bilayer EPD-ed, i.e. (1) the first layer of nano-size deposition was performed with a voltage of 2V for 2 minutes, with the second layer done with a voltage of 5V for 2 minutes, (2) the first layer of nano-size deposition was performed with a voltage of 3V for 2 minutes, continue with the second layer that done with a voltage of 10V for 2 minutes; (3) the first layer of nano-size deposition was performed with a voltage of 2V for 3 minutes, continue with the second layer that done with a voltage of 5V for 5 minutes; (4) the first layer of nano-size deposition was performed with a voltage of 3V for 3 minutes, continue with the second layer that done with a voltage of 10V for 5 minutes. After the EPD process finished, the screw was pulled out and air-dried.

Because the bonding strength of HA layers was still low, the screw was sintered properly. The sintering procedure could be explained as follows: heated to 700 °C at a speed of 1 °C/min, held at 700 °C for 1 hour, and annealed. The heating speed is kept at 1 °C/min to prevent hot cracking due to the big difference in dry conditions between the interface of screw-HA and the outer surface of the HA layer [17]. The temperature of 700 °C is believed that local melting at the interface among particles has occurred [14]. The sintering was performed in a high-temperature vacuum tube furnace GSL-1100. The EPD-ed screw was put on the white porcelain in the furnace.

(a) (b) (c)

Figure 2. Ti-6Al-4V ELI screw appearances; (a) design, (b) before, and (c) and after the EPD process

On the other hand, some white mice (*Rattus Norvegicus Wistar)* were prepared for the implant experiment. These mice were supplied from the pharmacy laboratory of Andalas University. The condition of mice should fulfill standards for animal testing, both inclusion and exclusion. Mice should be acclimated for one week to the experimental environment in a plastic cage, with routine cleaning and ad libitum feeding every day. The inclusion criteria are male animal, health, free of physical defect, age of 4-6 months, and body weight of 200-300 g. During the experiment, mice should fulfill exclusion criteria, i.e. be ill, get weight loss, and die at the end of the experiment.

Before the surgical operation, EPD-ed screws and surgical tools were sterilized in an autoclave. The operation room was also sterilized. The prospective area around the implant (mice leg) was cleaned; Leg hair was shaved and then cleaned with disinfectant (betadine and alcohol 70%). EPD-en screw was put at the proximal tibia with a drilling procedure of 3 mm diameter and 200 rpm, under excess cool sterile saline flow 0.9%. Open bleeding during surgery was sterilized and treated. Bleed closing was done by sewing with a surgical string of chromic 4.0 adsorbable in muscle and silk 2.0 on the derm. Then the area was covered with a bandage to prevent contamination. Analgesic drug (paracetamol) was orally drunk after the mice woke up, and disinfectant betadine treatment on the scar. A proper medical treatment procedure was done for three days and good care for two weeks with an ad libitum diet was done for the mice [23]. All the operation procedures and post-treatment were fully done with the help of biomedical students. Appearances during and after surgical operations on mice's legs can be seen in Figure 3.

After a certain duration of post-implant, namely 2, 3, and 4 weeks. All screw was taken out from the implanted area. The screw was observed under a stereo microscope Olympus LG-PS2 and an SEM Hitachi S3400 for more detailed observation. Stereo microscope observation means checking the appearance of HA layer morphology on the screw after being implanted. Before observation, dust or improperly attached powder should be removed with an air blow. The screw was attached to double tape above the specimen holder of the SEM. Observation magnification was 3.2 times the objective lens at a stereo microscope and 100 times at 8 kV at SEM. The surface covered with HA layers was evaluated with ImageJ software. HA layer's thickness was measured with Sanfix thickness gauge series GF-280. The presence of chemical compounds was checked with EDX and XRF epsilon 3. Due to body fluid and HA-deposited reactions, some changes in the chemical compound might occur on the HA layer.

(a) (b)

Figure 3. Ti-6Al-4V ELI screw was implantation (a) before and (b) after the EPD process

3.0 RESULTS AND DISCUSSION

3.1 Screw Appearance Before Implanted

The change in appearance of the screw before implant can be seen in Figure 4. It is a clear change in the colour between before EPD-ed and after the first layer that indicated HA deposition. The white colour seemed continuous and thin. The second layer with the micro size of HA provided a white colour with a higher magnitude of roughness. The micro-size layer covers the nanolayer size. It confirmed that EPD had successfully deposited a bilayer of HA with different-sized particles. It is a quite simple, easy and cheap technique to do on the implant material such as screw.

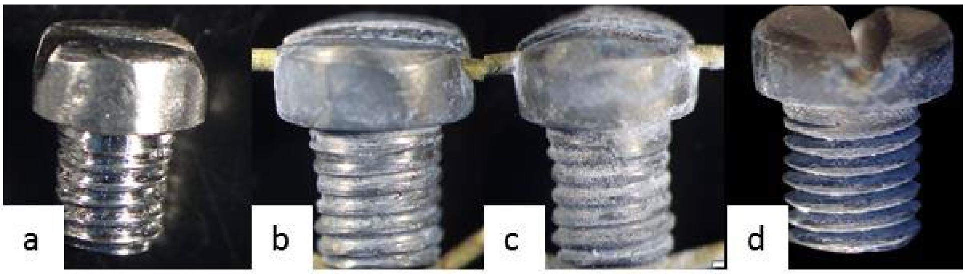
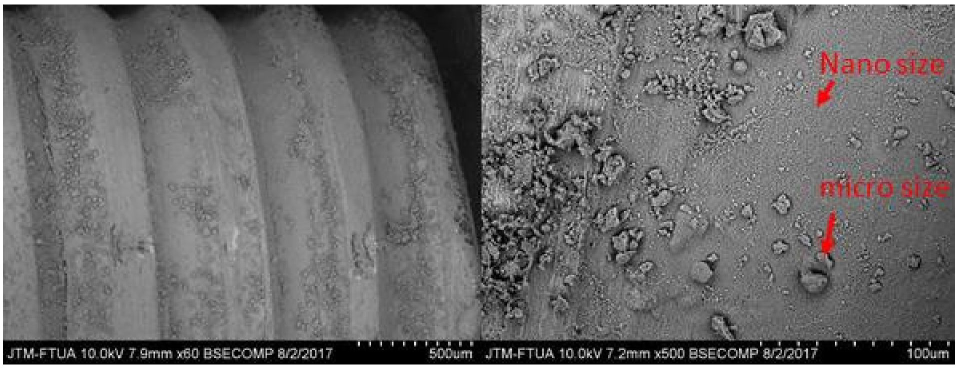


Figure 4. Change of appearance of Ti6Al4V ELI EPD-ed screw at 5V for 5 minutes (a) before EPD-ed, (b) with first layer, (c) with second layer, and (d) after sintering

Figure 5 revealed that the first layer of nano-size had properly and uniformly covered the surface. However, the second layer with microsize seemed to pile up at some sites on the surface. This happened because HA micro size is not easy to attach to nano size. It might imply that the smaller particles' size made it easier for deposition to form a coating layer with stronger bonding among them and properly attached to the surface. Bigger particle sizes lead to a higher surface roughness with cavities around the interface bounding, prefer to form some stacks then easier to separate off the surface.

A micrograph after sintering on the bilayer EPD-ed screw can be seen in Figure 6. Figure 6(a) shows that the nanolayer is well covered on the surface and some spots with micro size HA. It implied that the first EPD-ed with 2V for 2 minutes (scheme 1) is able to deposit nano HA over the surface, but the second EPD-ed with 5V for 2 minutes failed to deposit micro HA. Increasing the potential to 3V for 2 minutes in the first EPD-ed increases the covered area with nano HA. However, increasing the potential to 10 V for 2 minutes seemed to have a minor effect on the extended deposition of micro HA. Higher energy seems needed to deposit bigger (micro) size particles. Figure 6(c) shows that a uniform nanolayer was covered with more massive and better distribution of micro-size HA particles. It seems that 5V and 5 minutes result in a bigger energy than 10 V for 2 minutes. Further, the increased time of the second EPD-ed in Figure 6(d) provided degradation quality of the deposition. According to the morphology of the bilayer after sintering, the best combination of EPD-ed is with the first layer of 3V for 2 minutes (nano) and the second layer of 5V for 5 minutes (micro).



(a) (b)

Figure 5. Micrograph of a screw sample with the first layer of nano size (2V, 2 minutes) and a second layer of micro size (5V, 2 minutes) at (a) 60× and (b) 500× magnification

The calculation of the covered surface of HA layer containing the first layer of nano-size and the second layer of nano-size shows that both voltage and time will produce higher energy to cover the surface with the micro size of HA. It might indicate that the energy of 5V for 5 minutes 3 is higher than that of 10V for 2 minutes. Energy is more dependent on the time. Smaller energy is needed to deposit the nano size of HA; a small amount of energy is produced from 2V for 3 minutes to get a fully covered surface with nano HA. The smallest energy from 2V 2 minutes can cover 95.26% of the surface with nano HA, and a few surfaces (about 4.7%) remained uncovered. Potentials of less than 5V make it difficult to deposit micro-size HA uniformly. Potentials of more than 10V tend to make agglomerated HA and undistributed deposition. It is agreed with the previous report that the optimum EPD potential is in the range of 5 to 10V [24].

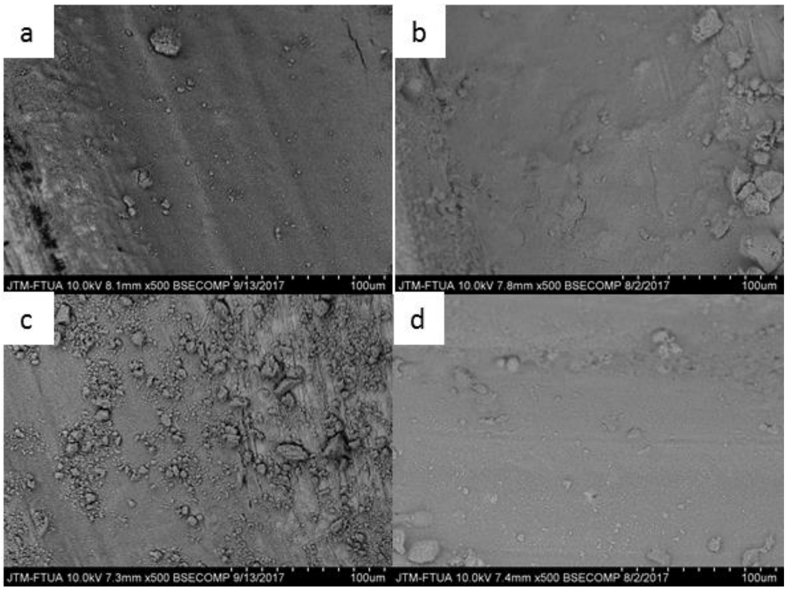


Figure 6. Micrograph after sintering on the bilayer EPd-ed screw at; (a) 2V for 2’, (b) 5V for 2’ (scheme 2), (c) 5V for 5’ (scheme 3), (d) 10V for 5’ (scheme 4)

The coating thickness of the sample with 5V for 5 minutes shows that this scheme fulfilled the thickness requirement of coating surface (50-100 μm). Thickness might be closely related to the amount and distribution of HA micro-size deposited on the surface. Thickness increases with increasing voltage up to 5V. However, a higher potential of 10 V for 5 minutes reduces the thickness of the coating. Electric field, electrode resistance, and suspension conductivity are used to determine a non-linear connection between potential and thickness. High potential leads to polarization change on the electrode earlier than conductivity change of suspension [24]. So, the saturated condition of the solution is achieved, and HA layers bonding is weakened, which may lead to HA releasing from the surface.

3.2 Screw Appearance at Post-Implantation

By using the optimum condition of bilayer coating production (scheme 3), the coated screw was implanted in some white mice (*Rattus norvegicus Wistar)*. The white mice were conditioned to be dead after the implanted duration for 2, 3, and 4 weeks. A re-surgical operation was conducted on the dead mice. The implanted site was opened again to release the implanted screw. This second surgical operation was done by the same biomedical students. A photograph of the screw’s appearance after being implanted for 2, 3, and 4 weeks can be seen in Figure 7. Organic materials could be seen as marked as a red dot. Organic materials were found in all specimens. They had stuck on the surface because of direct contact between the screw and surrounding environments, such as soft tissue, body fluid, and bone. The presence of these materials is related to the web bone regeneration process or osseointegration. Silver metallic colors in Figures 8(a), 8(b), and 8(c) are directly related to the titanium material of the screw. The white area in Figures 8(d), 8(e), and 8(f) are HA bilayers that covered the screw. Longer implantation times made some parts of HA layers fall out. This fall-out was followed by the presence of a red dot on titanium, which means HA had made bounding with the bone, which means the osseointegration is also improved. A good confirmation of the condition in Figure 7 is found in Figure 8. Thicker layers were found on the EPD-ed screw-in Figures 8(d), 8(e), and 8(f) related to the HA bilayer and organic materials. However, a red arrow pointed to numerous cracks in Figure 8(d). This crack may relate to the break out of HA layers, which might continue to its fall-out, as revealed in Figure 7.

3.3 Elemental and Compound Distribution

XRF examination results on the surface of the screw as shown in Table 1. It is shown that as the main indicator of bone healing, -a higher content of calcium was found on the EPD-ed screw. It was almost two times higher than a non-EPD screw. It is indicated that the significance of HA bioactive on Ca deposition. Another main constituent of bone is phosphor. The number of P was significantly higher on the EPD-ed screw than on the non-EPD one. It was almost five times higher. The content of Ca had significantly increased with implanted time, while P content decreased. The number of Ti was extremely reduced with the HA layer's existence. It is indicated that the excellent effectiveness of HA covers titanium alloys. Almost 60% of Ti was exposed after two weeks of implantation, while only 0.4% of Ti was found after four weeks of the implant. Aluminum was exposed in big enough numbers during the implant. And a few numbers of vanadium were exposed on the EPD-ed screw. It might indicate that possibility inflammation reaction could be suppressed with EPD-ed.

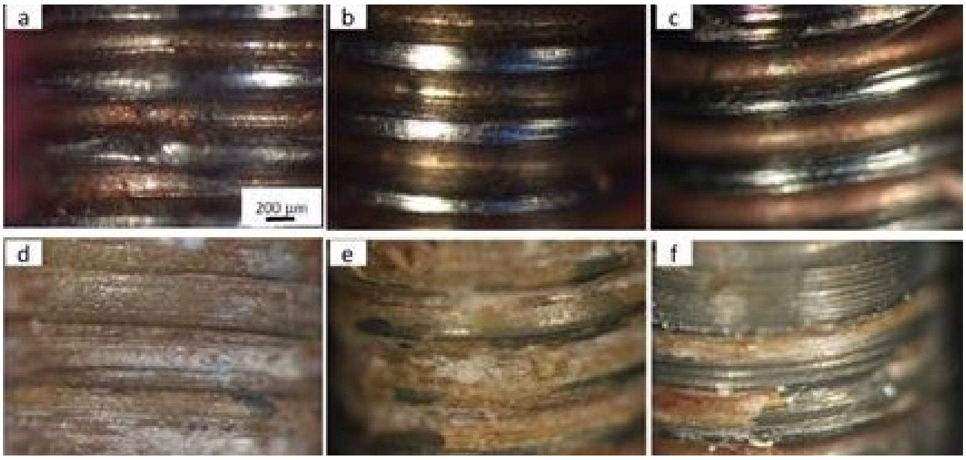


Figure 7. Ti-6Al-4V ELI screw appearance by optical microscope after implantation of (a), (b), (c) non-EPD screw and (d), (e), (f) EPD-ed screw at 2, 3 and 4 weeks of implantation

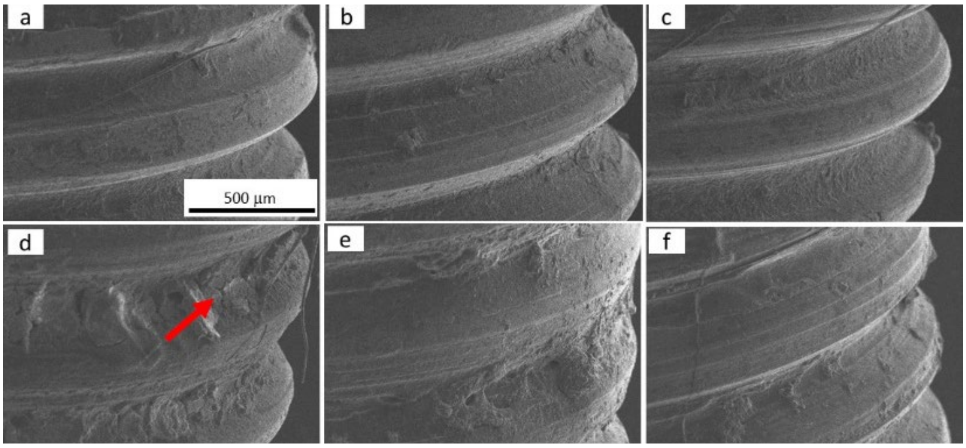


Figure 8. Ti-6Al-4V ELI screw appearance by SEM after implantation of (a), (b), (c) non-EPD screw, and (d), (e), (f) EPD-ed screw at 2, 3 and 4 weeks of implantation

Table 1 shows an elemental ratio of Ca to P. When the original TiO2 layer gets scratched or broken, Ti tries to form a new TiO2 layer that is also able to absorb surrounding ions including Ca and P [25]. So that even the non-EPD-ed screw shows Ca and P elements, as shown in Table 2. When Ca and P contents change during implantation, their ratio also automatically changes. The ratio of Ca/P increased with implantation time. The EPD-ed screws have a lower ratio (0.59-1.03) than screws without HA layer (1.12 - 2.02). In comparison, the bone has a ratio Ca/P of 0.58-2.34, with an ideal value of 1.67 [26]. Simultaneously increasing Ca and P had kept the ratio of Ca/P along with the range. All the ratios were in the range of bone.

Table 1. Elemental distribution over screw after implanted

Element (%)	Non-EPD-ed screw			EPD-ed screw		
	Duration (weeks)					
	2	3	4	2	3	4
Al	8.389	1.518	1.506	4.316	7.532	3.505
P	10.479	9.533	6.793	38.701	32.802	31.355
Si	6.985	0.753	2.237	33.163	21.868	18.741
Cl	0.725	2.892	0.281	1.513	1.161	1.707
Ca	11.704	18.416	13.721	21.599	29.803	32.44
Ti	60.439	60.516	71.962	0.352	0.66	0.448
V	0.269	2.461	2.593	0.034	0.107	0.036
Cr	0.034	3.658	0.185	0.064	5.44	0.036
Fe	0.232	0.128	0.119	0.193	0.178	0.124
Bal.	0.594	0.304	0.6	0.054	0.448	0.074

Table 2. The ratio of Ca/P on screw surface after implanted

Duration (weeks)	2	3	4
Non-EPD-ed screw	1.12	1.93	2.02
EPD-ed screw	0.59	0.91	1.03

Table 3 shows the compound distribution on the surface of the screw. The presence of HA layers on the EPD-ed screw effectively decreased TiO_2 content by an enormous magnitude. It was reduced from about 60% to 0.3 %. TiO_2 was formed soon after titanium alloys were exposed to human body fluid. HA layer prohibited this reaction. TiO_2 is a natural product of corrosion reaction on titanium. Low TiO_2 content is directly connected to the improvement of corrosion resistance that might relate to the biocompatibility of the implant. Other metal oxides such as Al_2O_3 and V_2O_5 might be responsible for inflammation reaction after implant. The Al_2O_3 content is comparable among screw conditions. However, the EPD screw has significantly less amount of V_2O_5 than the non-EPD screw.

Table 3. Compounds distribution over screw after implanted

Compound (%)	Non-EPD-ed screw			EPD-ed screw		
	Duration (weeks)					
	2	3	4	2	3	4
Al_2O_3	10.661	2.149	2.143	5.555	9.478	4.49
P_2O_5	13.229	15.883	11.477	46.246	38.425	36.635
SiO_2	8.819	0.907	3.989	35.891	26.162	26.675
CaO	6.971	15.605	12.021	11.338	16.934	31.183
TiO_2	59.425	55.279	67.044	0.2	0.393	0.25
V_2O_5	0.176	2.31	2.453	0.021	0.068	0.021
Cr_2O_3	0.018	2.722	0.14	0.032	6.948	0.017
Fe_2O_3	0.12	0.093	0.087	0.093	0.089	0.058
BaO	0.243	0.209	0.426	0.021	0.175	0.029
Cl	0.336	5.052	0.22	0	0.507	0.646

3.4 Confirmation of Coating Effectiveness

The screws were washed with alcohol, then continued with acetone to ensure the effectiveness of layer coating. This procedure was done to remove organic materials. Differences in appearance before and after washing can be seen in Figure 9.

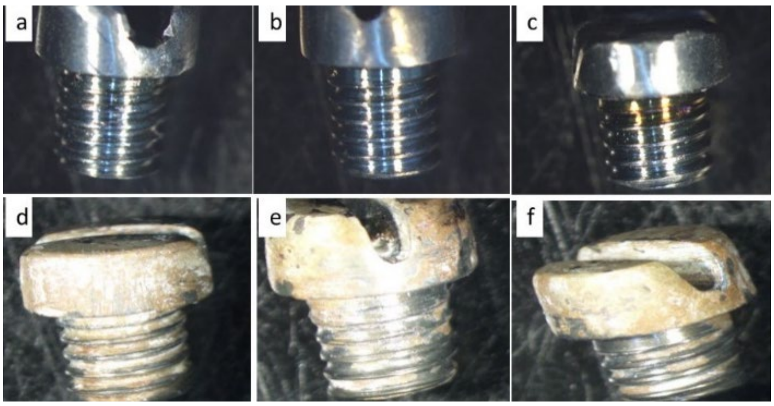


Figure 9. Implanted Ti-6Al-4V ELI screw appearance after washing with alcohol and acetone: (a), (b), (c) non-EPD screw, (d), (e), (f) EPD-ed screw at 2, 3 and 4 weeks of implantation

All non-EPD-ed screws showed organic material-free and excellent corrosion resistance of Ti-6Al-4V with a bright and light appearance. Advantages of EPD on the screw were revealed; (1) namely effectiveness of the HA layer, and (2) strong bonding between Ti-6Al-4V screw and HA layers.

4.0 CONCLUSIONS

HA bilayers of the nano layer and the microlayer had successfully deposited on the surface of the Ti6Al-4V screw. Some interesting things were drawn from this study. The nanolayer had easily and fully formed at a potential less than 5V. The microlayer needed higher energy to be deposited on the surface. The 5V 5 minutes successfully deposited micro HA in an enormous amount and was well distributed. Among the four alternative schemes, scheme 3 is the most effective to cover the screw surface and fulfills the thickness requirement of biomaterials.

The EPD-ed screw was mainly characterized by a higher deposition of Ca (about two times) and P (about 3-5 times), a lower ratio of Ca/P than the non-EPD-ed screw. The ratio of Ca/P typically increases with time. All ratios of Ca/P were in the bone characteristic range. Micro-nano HA coating layers also offered better performance against corrosion, in which a greatly reduced number of TiO2 on the screw. It is good news that the possibility of inflammation by the new formation of TiO2 could also be greatly minimized. A strong bond between micro-nano HA layers and the screw was attained through the EPD procedure. The Ti-6Al-4V screw showed excellent corrosion resistance during the implantation. The procedure of EPD is promising and has the potential to be applied to biomaterial implants. However, a longer-term observation of implants might be needed.

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