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Preparation, scratch adhesion and anti-corrosion performance of TiO₂-MgO-BHA coating on Ti6Al4V implant by plasma electrolytic oxidation technique

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ABSTRACT

Bovine hydroxyapatite (BHA) (from cortical bone), was selected as the main electrolyte for plasma electrolytic oxidation (PEO) on Ti6Al4V implant. The prepared PEO coatings were examined by X-ray diffraction, field emission scanning electron microscope and energy-dispersive X-ray spectroscopy. The surface roughness, adhesion strength, wettability, surface energy and corrosion behaviour of the film were also investigated. The results show that the oxide layer (26 μm) formation on the Ti6Al4V was rough and porous. The micro-pores were filled with anatase TiO₂, cubic MgO and hexagonal BHA particles. The porous structures and the compound particles were mainly composed of Mg, O, Ca, P, Ti, Na and Al. Unlike previous coatings produced from calcium and phosphorus inorganic solutions, the coating formation from a newly developed bovine bone-derived HA electrolyte revealed an additional MgO phase in the coating layer. Moreover, higher amount of single phase hexagonal crystalline BHA phase with a Ca/P ratio of 1.1 was achieved with a single PEO process. A film-to-substrate adhesion strength of 1862.24 mN and scratch hardness of about 4.1 GPa was achieved from this method. The TiO₂/MgO/BHA film exhibited better wettability, higher surface energy and superior corrosion resistance compared to the bare Ti6Al4V substrate.

1. Introduction

Titanium and its alloys (Ti) have been widely employed as bone implants because of its excellent strength, good corrosion resistance, zero allergic problems and low density. However, it is far from being an ideal material from a medical standpoint due to its insufficient bioactivity when implanted in the human body [1]. To enhance its bioactivity, several surface electrochemical treatments have been used such as electrophoretic deposition (EPD), sol-gel and plasma electrolytic oxidation (PEO) etc. Plasma electrolytic oxidation, or also known as...
anodic spark deposition (ASD), has been gaining a wider acceptance as a novel technique for the formation of adherent and microporous oxide layer on light materials (Ti, Mg, Zr and their alloys). It has been established that the PEO method offers unique advantages in terms of uniform coating, adhesion strength, anti-corrosion and more environmentally friendly compared to other conventional techniques [2]. As reported in the literature, the surface features of the PEO coatings on titanium alloy implants are greatly dependent on the concentration and composition of the electrolyte. Currently, the inorganic calcium and phosphate-based electrolytes are still the most widely used electrolyte as a source of bioactive elements [3]. Owing to the fact that natural bone is a composite of organic and inorganic material, there has been an increasing demand to develop coatings with unique phase/elemental composition and structural resemblance to hard bone tissues in recent years [4,5]. Moreover, it is very meaningful to develop the PEO coatings with superior biocompatibility especially for biomedical applications. In order to further enhance the biocompatibility of Ti and mimic the biological portion of human bone, the correct selection of naturally occurring hydroxyapatite (HA), which is structurally similar to natural bone tissues especially bovine material origin as electrolyte solution for PEO is very important.

Bovine bone or also known as xenogeneic bone materials are naturally bioactive substance with similar physio-chemical properties to natural bone. The non-vital bone materials from cows are processed at high temperature to fabricate a material medically safe for humans. The bovine bone is a typical combination of organic and inorganic composites. The organic portion are mainly collagen and proteins, while the inorganic portion are mainly hydroxyapatite (HA) with a trace amount of magnesium, sodium and carbonate incorporated in the structure [6]. The presence of magnesium is important for biological activity, bone growth and enhanced mechanical properties of the coating [7]. Therefore, bovine bone-derived HA has great potential to further improve the biocompatibility of Ti implant. Bovine bones are found in abundance, easy to process and at a relatively low cost. In view of the aforementioned structure and composition, bovine bone derived HA could be used as electrolytes in the coating of titanium alloys by the PEO method. Furthermore, there are no reports on this type of bioactive coating. In the present study, the surface properties of PEO coatings developed on Ti6Al4V substrate were characterized by FESEM, EDS, XRD, profilometer, scratch tester and contact angle measurement. Moreover, the anti-corrosion performance of the coating was evaluated by potentiodynamic polarization test in Ringer’s solution. The work reported in this paper is part of the on-going investigation to improve the bioactivity of Ti6Al4V substrate with natural bovine bone via the PEO treatment.

2. Experimental

2.1. Materials and method

Ti6Al4V alloy plate was used as the substrate. Before the PEO process, the samples were cut in the sizes of 20 × 10 × 2 mm³. The titanium surfaces were ground using SiC paper with grids of 600, 800, 1200, 1500 and 2000. Then, the samples were cleaned by acetone, rinsed with distilled water and dried in a hot air stream. The PEO solution contained 4 g/L Na₃PO₄ and 1.5 g/L high quality bovine hydroxyapatite (BHA) particles (Gadjah Mada University, Yogyakarta, Indonesia). A DC power supply unit (Keysight Technologies Deutschland
A high-voltage DC power source (Micro Materials Ltd; Wrexham, UK) of 1500 V/30 A capacity was used for the PEO treatment. The titanium substrate was used as the anode, while a stainless steel container was the cathode. The electrolyte bath temperature was maintained at 30–35 °C by stirring and a cooling system. The PEO process parameters of the TiO2-MgO-BHA thin-film coating on the Ti6Al4V substrate are presented in Table 1.

The surface characterization and cross-sectional morphologies of the PEO coated samples were observed using a FEI Quanta 450 FEG FE-SEM. The elemental coating compositions and distributions were determined by the energy dispersive X-ray spectroscopy (EDS) attached to the FE-SEM. The phase composition of the bovine powder and the PEO-coated sample were analysed by the grazing incidence X-ray diffraction technique using a PANanalytical X’Pert High score Empyrean, 45 kV and 40 mA with a Cu Kα radiation at a scanning speed of 1°/min. The average surface roughness of the Ti6Al4V and TiO2-MgO-BHA PEO film was measured using SJ-Mitutoyo surftest SJ-201 profilometer.

The film to substrate adhesion was measured by a scratch tester machine (Micro Materials Ltd; Wrexham, UK). The measurements were performed by the lateral movement of the indenter tip (radius = 25 μm) across the coated sample over a distance of 1000 μm. The test was carried out at a maximum load of 2500 N. The critical load value was confirmed by the scratch track. Afterwards, the scratch track was observed using FESEM and optical microscope, to analyse the damage and changes of the as-deposited coatings. In order to determine the magnitude of the damages, the critical load, frictional curve and penetration depth as a function of critical load were also studied.

The surface wettability was analysed by sessile Easy DROP instrument (OCA 15EC; DataPhysics Instruments GmbH; Germany). The drop image was stored by a video-based optical contact angle measuring instrument and the contact angle value was used to calculate the surface energy. The liquid volume was kept constant (5 μl) throughout the sample contact angle measurement, while the drop-in velocity was 2 μl sec⁻¹.

The in vitro corrosion measurements of the samples were carried out by a potentiodynamic polarization method using a potentiostat/galvanostat/frequency response analyser from Metrohm (Model: AutoLab PG STAT30). The polarization behaviour was recorded during immersion in Ringer’s solution (8.6 g/L NaCl, 0.3 g/L KCl and 0.33 g/L CaCl2) for 3 days using a three-electrode cell. The sample, a platinum wire and a saturated calomel electrode (SCE) were the working, counter and reference electrodes, respectively. The corrosion potential and corrosion current density were obtained from the Tafel plots with the scan rate of 2 mV/s. The polarization resistance \( (R_p) \) values were evaluated using the following equation: \[ I_{corr} = \frac{\beta}{R_p} \] where \( \beta \) is a constant calculated by the following equation:

### Table 1. Deposition parameters for PEO TiO2-MgO-BHA coating.

<table>
<thead>
<tr>
<th>Coating</th>
<th>Bovine-derived HA (g)</th>
<th>Na(_3)PO(_4) (g/L)</th>
<th>Voltage (V)</th>
<th>Treatment time (min)</th>
<th>Current density (mA/cm(^{-2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO2-MgO-BHA</td>
<td>1.5</td>
<td>4.0</td>
<td>275</td>
<td>10</td>
<td>5</td>
</tr>
</tbody>
</table>
\[ \beta = \frac{\beta_a \beta_c}{2.3 I_{corr} \left( \beta_a + \beta_c \right)} \]  

where \( \beta_a \) is the anodic Tafel slope while \( \beta_c \) is the cathodic Tafel slope, and \( R_p(\Omega) \) the polarization resistance. The protection efficiency of the TiO\(_2\)-MgO-BHA film was obtained from \( R_p \) value using the formula [9]:

\[
\text{Protection efficiency} = \frac{R_p(\text{PEO film}) - R_p(\text{bare \ Ti})}{R_p(\text{PEO film})} \times 100
\]

3. Results and discussions

3.1. Surface characterization

Figure 1 shows the XRD patterns of the BHA powder and BHA-PEO coated sample. It can be observed that the PEO-coatings differed considerably from the prepared BHA powder material that was essentially pure and crystalline (Figure 1(a)). The PEO coating consists mainly of anatase TiO\(_2\), cubic MgO (periclase) and BHA phases. The peaks of BHA are more intense than those of the anatase TiO\(_2\), suggesting a greater presence of BHA in the coating. The relatively weak and broad peaks at 2\( \theta \) ranging from 31.70° to 34.4° on the BHA-PEO pattern indicates the presence of a single-phase hexagonal crystalline BHA in the coating. The Bragg peaks at 37°, 41.5°, 43°, and 62.5° observed for the cubic MgO are due to the thermochemical reaction of the Mg element from BHA powder and hydroxide ion (OH\(^-\)) during the PEO process.

Unlike the coatings produced from the Ca and P inorganic solutions, [10] the phase composition analysis confirms the presence of an additional MgO phase when a natural bovine bone was used as the electrolyte solution. MgO is a mineral supplement used for

Figure 1. XRD patterns of the BHA powder and BHA-PEO coating obtained under current density 5 mA cm\(^{-2}\), deposition time 10 min, and voltage 275 V (a) the standard bovine bone data and (b) BHA-PEO coating.
the treatment and prevention of Mg deficiency in the blood. It is especially vital for healthy muscles and bones, improving biocompatibility and eliminating the effect of stress shielding. It is worth mentioning here that this is the first study which reports the formation of MgO on titanium alloy substrate.

The surface morphology of BHA coating and composition formed on the Ti6Al4V substrate by PEO is shown in Figure 2. The coating exhibits a typically rough $2.21 \pm 0.07 \, \mu m$ and microporous (10.5 \, \mu m) structure (Figure 2(a)). The surface roughness ($R_s$) of the TiO$_2$-MgO-BHA film is significantly higher than the bare Ti6Al4V substrate (0.16 $\pm$ 0.01). The greater surface roughness is due to the chemical reaction of Ti6Al4V and electrolyte borne ingredients, and the subsequent formation of the complex layer on the Ti6Al4V surface. A preferentially growth of wool-like BHA structure is seen in the coating as depicted by the inset of Figure 2(b). The tiny micropores appear to be well separated and distributed over the entire film surface.

The pores are formed by the dissolution of Ti (substrate), and gas effervescence from micro-arc discharge channel. During the PEO process, high temperature ensued the appearance of micro-sparking on the Ti6Al4V substrate, then the localized melting of Ti6Al4V occurs followed by the immediate melt quench of the molten spots. This haphazard process occurred over the substrate and resulted in the formation of a porous coating. Figure 3 shows the elemental composition of the BHA-PEO coatings obtained on the surface of the Figure 2(a) and from Inset, it can be observed that the elements of Al, P, Na, Ti, O, Ca, and Mg were incorporated into the coating during the PEO process.

The Mg element in the coating originates from the electrolyte, which shows that the bovine bone particles take part in the coating. A high Ca/P ratio of around 1.1 was obtained using a single PEO process.

The spatial distribution of the Ca, P, Ti, O, Na, Al and Mg elements in the BHA-PEO coating is shown in the elemental mapping images in Figure 4. From Figure 4, it can be seen that the Mg, Ca and P are uniformly present over the surface of the coating.

Figure 5 shows a typical cross-sectional FESEM image of the PEO-coated sample. No distinct separation and voids were observed between the Ti6Al4V alloy substrate and the
coating layer, indicating a good metallurgical bonding between the coating and the substrate. Even though some mild defects were noticed in the coating, the major part of the coating was relatively compact and uniform. From the top cross-sectional surface, a tiny crack was observed. Further, it was seen that the crack propagated down to the centre cross-sectional region, where it was arrested close to the interface layer. The intrinsic growth stress developed by the rapid melting/solidification and precipitation of the compound...
layers are thought to be the main causes of cracking. An average coating thickness of about 26 ± 0.32 μm as obtained by this method. The high energy input accompanied by the high intensity spark is thought to be responsible for the thick layer formation during the PEO process.
3.2. Adhesive strength of TiO$_2$-MgO-BHA coatings

Figure 6 presents the adhesive strength of the BHA-PEO coatings. Figure 6(a) shows the residual scratch track and the failure point of the BHA coated sample, together with the graph of depth, load and frictional force vs. scratch length, in the scratch force analysis. It can be seen from Figure 6(a) that as the normal load increases progressively, delamination starts to occur intermittently along the scratch length. The commencement of chipping at both trackside surface (Figure 6(a)) signifies the removal of the film from the substrate. The scratch length, load and failure point are 640.94 μm, 1862.24 mN and 640.94 μm, respectively. At a scratch length of about 359.06 μm which corresponds to a high load of 1862.4 mN, a sudden change in the frictional and depth penetration curves takes place, followed by the fluctuation of these curves. This behaviour indicates the total complete failure of the coating.

The average width of the scratch track was determined using the optical microscope, and the scratch hardness number, was determined using the formula below:

\[ H_{sp} = \frac{8P}{\pi w^2} \]  

\( \text{(4)} \)

Figure 5. Cross-sectional FESEM micrographs of BHA-PEO coating obtained at current density 5 mA cm$^{-2}$, deposition time 10 min, and voltage 275 V.

Figure 6. The load, depth and friction vs. scratch length as well as the failure point of as prepared TiO$_2$-MgO-BHA.
where $H_{\text{sp}}$ is the scratch hardness number, $P$ is the normal force (N) and $w$ is the scratch width (m). A maximum scratch hardness of about 4.1 GPa was obtained for the coating. The higher adhesive strength and hardness are due to the proper combination of higher thickness and compact structure. The chemical interaction, which occurs at the Ti6Al4V alloy substrate/coating interface, enhanced the mechanical bonding and consequently improved the adhesive strength of the coatings.

### 3.3. Wettability and surface free energy analysis

The contact angle measurements of the bare Ti6Al4V alloy and BHA-PEO coating are shown in Figure 7. From Figure 7, it can be observed that the TiO$_2$-MgO-BHA PEO film shows good wettability compared to the bare Ti6Al4V alloy. The contact angle of the bare Ti6Al4V and PEO film are 57.1° and 35.2°, respectively.

The free surface energy, $E_s$ was calculated from the contact angles using the equation below: [12]

$$E_s = E_{vl} \cos \theta$$  \hspace{1cm} (5)

where $E_{vl}$ is the free surface energy between water and air under ambient condition, 72.8 mJ/m$^2$ for pure water and $\theta$ the static contact angle. The BHA-PEO coatings have higher free surface energy (59.5 mJ/m$^2$) than the bare Ti6Al4V (39.5mJ/m$^2$). The lower contact angle and higher surface energy of the PEO treated Ti6Al4V is due to the formation of the TiO$_2$/MgO/BHA layer on its surface. It was reported that the behaviour and interaction of proteins on the surface of implants are dependent on the surface free energy, especially on the adsorption of water and cellular adhesion strength [13,14]. Thus, the presence of the TiO$_2$/MgO/BHA composite films on Ti6Al4V by the PEO method with high free surface energy is expected to improve the osseointegration of the implants.

### 3.4. Electrochemical corrosion analyses

Corrosion monitoring is vitally important to determine the biological behaviour of the implant metal in an aggressive environment. Corrosion usually occurs when the metallic component of the alloy is oxidized and releases a substantial amount of ions. In this study,
the electrochemical behaviour of the bare Ti6Al4V and TiO\textsubscript{2}-MgO-BHA PEO layer was studied using potentiodynamic polarization measurement in Ringer’s solution. The polarization curves of the bare Ti6Al4V and coated layer are depicted in Figure 8 and the kinetic parameters obtained from the Tafel plots are reported in Table 2. As can be seen in Figure 8 and Table 2, the corrosion current density $I_{\text{corr}}$ revealed a significant decrease from 5.8 to 0.1 $\mu$A/cm$^{-2}$, when bovine-derived HA is formed on the Ti6Al4V surface. It is interesting to note that the corrosion potential ($E_{\text{corr}}$) of TiO\textsubscript{2}-MgO-BHA film (−0.204 V) shifts towards positive (noble) region compared to the bare Ti6Al4V. The shift of $E_{\text{corr}}$ is strongly dependent on the presence of the MgO phase, and to the Ca and P containing compounds in the TiO\textsubscript{2}-PEO coatings. Similar observation was also reported elsewhere [15].

In addition, the film shows higher resistance to corrosion over a potential range of −400 to +900 mV, which indicates that the TiO\textsubscript{2}-MgO-BHA film deposited on Ti6Al4V is less vulnerable to corrosion in the Ringer’s solution. The lower corrosion rate (CR) value observed for the film shows a stronger ability in resisting the corrosion process. The improved performance in the corrosion resistance of the PEO-coated layer is due to the formation of a compact complex TiO\textsubscript{2}-MgO-BHA film, which acts as a protective layer against Cl$^{-}$ transfer at the Ti6Al4V/coating interface. Studies have shown that the formation of a dense structure and thicker layer is beneficial for increasing the corrosion resistance in simulated body fluid (SBF) [16]. From the FESEM-cross-sectional micrograph (Figure 5), a 26 ± 0.32 $\mu$m thick and well adhered layer with fine pore size is formed on the Ti6Al4V surface. Consequently, the composite film formed on Ti6Al4V surface shows higher protection efficiency (PE) against aggressive ions in the physiological environment. The PE of the TiO\textsubscript{2}-MgO-BHA coating calculated from Equation (3) is 92. Therefore, from the $I_{\text{corr}}$, $R_p$, $E_{\text{corr}}$ and CR values of the
bare Ti6Al4V and PEO-composite layer, the PEO-composite layer shows higher corrosion resistance in the Ringer’s salt solution.

4. Conclusions

Coatings incorporating anatase TiO_2, MgO and BHA phases were successfully formed on Ti6Al4V alloy surface using bovine bone derived-HA via the PEO method. The formation of an additional phase, cubic MgO coating is due to the use of natural bovine derived HA electrolyte. The thickness of the coating was estimated as 26 μm, with a rough and microporous structure. A higher degree of a single-phase hexagonal BHA crystallinity was obtained with a Ca/P ratio of 1.1. The adhesion and scratch hardness of the PEO-coated sample is enhanced to a greater extent. Moreover, the formation of the TiO_2/MgO/BHA film gave good wettability, high surface energy and superior corrosion resistance compared to the bare Ti6Al4V substrate. The present work successfully demonstrates the use of naturally occurring bovine bone-derived HA to enhance the surface properties of the Ti6Al4V alloy.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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