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Fabrication, characterisation and corrosion of HA coated AZ31B Mg implant material: Effect of electrodeposition current density

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Abstract:

Due to its biodegradability, Mg has recently been chosen as a potential temporary load bearing implant material. However the corrosion resistance of Mg must be improved to control its degradation rate matching with the bone healing process. One way to solve the issue is to deposit another bioactive and biocompatible hydroxyapatite (HA) coating on Mg implant via electrodeposition. With this motivation, the current paper explores how the current density, a crucial process parameter, influences the formation, characteristics and degradation of HA-coating. Electrodeposition at three different current densities (3, 6 and 13 mA/cm^2) was performed on AZ31B Mg substrate followed by an alkali treatment to ensure the complete HA deposition. Surface morphology, chemical composition, crystallinity and texture of the coating were evaluated, followed by a potentiodynamic corrosion tests to assess the degradation resistance of the coated samples. Characterisation results show that low current density of 3 mA/cm^2 results in a compact, dense and uniform coating layer as compared to 6 mA/cm^2 and 13 mA/cm^2. Accelerated H_2 gas evolution at Mg cathode and faster deposition at higher current density (of 13 mA/cm^2) cause the lack of integration and bonding of crystals, thus resulting in relatively porous, inhomogeneous and rough HA coating. HA coating deposited at low current density is shown to exhibit

the best corrosion protection compared to those at higher current density. The findings clearly indicate that the integrity of the coating layer is a crucial quality indicator. Higher current density can produce the coating thickness of as high as 50 µm with appropriate application of the current density followed by alkaline treatment. It is also demonstrated that the electrodeposition could be a promising viable method to fabricate HA-coated AZ31B implants with better and prolonged corrosion protection.

Keywords: Magnesium implant, biodegradation, electrodeposition, current density, HA coating, surface morphology, corrosion resistance

1. Introduction

Alternative to permanent implants, e.g. titanium, stainless steel and cobalt chromium alloy, biodegradable Mg alloys have recently attracted a significant attention as an orthopaedic implant [1]. This is mainly due to the fact that Mg alloys are biocompatible, has mechanical properties close to human bone and can be absorbed completely in physiological environment [2,3]. However, the major problem of Mg alloy is its fast degradation via corrosion process before the completion of bone healing, which deteriorates implant's performance, consequently limiting its clinical application for load bearing implants [4,5]. Therefore, it is expected that the degradation rate of Mg alloy must be adjusted to the healing rate of the affected surrounding tissues, and its degradation by-products must be within the body's acceptable absorption level. In the past, different mechanical surface treatment approaches including machining, peening and burnishing are used to improve mechanical and biological properties of Mg [6,7]. One way to resolve this is to modify the surface with biodegradable coating [8]. To this regard, among many, calcium phosphate (Ca-P) based hydroxyapatite (HA) ($Ca_{10}(PO_4)_6(OH)_2$) as a bioactive barrier coating is widely used for metallic substrates

to control the corrosion kinetics [9–12]. Further, HA is found to be a prime mineral component of human bones, thereby providing an excellent ability to create a stable bond chemically with natural bones, and hence promoting favourable osteointegration for implants.

Over the years, many techniques have been reported in literature to deposit HA coating. They include plasma spraying [13], thermal spray [14], ion implantation [10], radio frequency (RF) sputtering [15], PVD [16] , hydrothermal [17] and sol-gel process [18]. Among them, the electrodeposition has however been considered widely for Mg-based implants because the process involves low temperature, is simple, cost effective and able to deposit the coating on the complex shapes. The coating morphology, thickness and crystal orientations can be controlled by varying the deposition current density, potential, deposition time, temperature and electrolyte's composition. However, the synthesis of HA via the precipitation method causes the formation of agglomerate crystals whose size is often difficult to control. Therefore, to this end, a relatively unstable dicalcium phosphate dihydyrate (DCPD) or brushite ($CaHPO_4.2H_2O$) like coating is formed first followed by an alkali treatment for conversion of a more thermodynamically stable HA crystal phases. Alkali treatment temperature and time period also influence the formation of final morphology and structure of HA coating. The efficacy of HA over DCPD had overwhelmingly been confirmed by researchers [19]. However, the direct formation of HA coating is highly related with the electrodeposition parameters. Most importantly, research has shown that the current density largely affects the electrolyte pH around the cathode, thus impacting the equilibrium of the relative concentrations of $H_2PO_4^-$, HPO_4^{2-} and PO_4^{3-} and the equilibrium of Ca-P precipitation reaction [20]. For instance, Djosic et al. [21] studied Ca-P based DCPD (brushite) coating on the titanium (Ti) substrate at different

current density and concluded that the brushite coating with the smallest crystallite (of 15.6 nm) and the greatest porosity was obtained at high current density because the crystallite growth is suppressed by hydrogen evolution reaction. On the contrary, the less porous coatings with bigger crystallite were obtained at lower current densities because crystallite growth dominates over hydrogen evolution reaction. Using hydro-thermal-electrochemical process, Wang and Du [22] showed that the current density of as low as 1.25 mA/cm^2 was able to deposit a dense HA coating of 26 µm thickness on Ti6Al4V. He et al. [23] further used low current density in a range of 1.25 mA/cm^2 and 3.61 mA/cm^2 and demonstrated that thicker HA coating on Ti6Al4V via electrodeposition can be achieved at higher current density of 2.5 mA/cm^2..

Therefore, it can be said that the current density is a major parameter to influence the phase composition and microstructure of Ca-P species. Jamesh et al. [24] electrodeposited HA coating on commercially pure (CP) Mg alloy using 100 mV and demonstrated the viability of the technique. Effect of the relatively lower current density on DCPD coated Mg-Ca-Zn alloy was studied by Bakhsheshi-Rad et al. [25]. They reported that low current density (0.15-0.4 mA/cm^2) produces the needle-like finer crystallites and provides better corrosion resistance as opposed to rough, coarse plate-like morphology generated at high current density (of above 0.8 mA/cm^2). In addition to the current density, the electrodeposition voltage influences HA coating. An intermediate voltage of -1.8V is found to exhibit a uniform coating with fine crystallised HA [26]. The effect of voltage (between -3 and -5 V) on HA coating quality and formation is studied outlining the benefit of the lower voltage in electrodeposition [27]. Further work has investigated the effect of electrolyte pH and temperature in a pulsed electrodeposition of HA on Mg-Zn-Ca alloy, and showed that when the pH is higher than 6 and temperature about 80°C, the formation of HA is more favourable over

DCPD and octacalcium phosphate (OCP) [28,29,29]. Improved corrosion resistance and cell viability of Ca-P based HA deposited via chemical deposition was reported by Wang et al. [30]. However, the formation mechanism and corrosion resistance of HA coated AZ31B Mg alloy fabricated by electrodeposition was little studied. Further, the direct formation of HA coating would be related to crystal structure and surface properties of AZ31B Mg alloy. Moreover, AZ31B is considered as widely accepted Mg alloy material for potential biodegradable implants. Understanding the deposition mechanism and underlying corrosion behaviour for HA coating via electrodeposition is thus crucial for developing an improved AZ31B alloy based implant. In addition, past studies investigated HA deposition at relatively low current densities (0.15 – 1.2 mA/cm^2), which resulted in thin HA coating (<15 µm) on Mg substrate. Thinner coatings are found to be more prone to delamination induced damage and, as such, may not be able to provide the substrate better and longer protection from corrosion.

To this regard, this paper aims to present a comprehensive investigation into the influence of the current density on the quality, microstructure, topography, composition, thickness and corrosion behaviour of HA coated AZ31B alloy. During the electrodeposition, the current density was varied between 3 and 13 mA/cm^2. Our hypothesis is that whether high current density during electrodeposition will enable thicker HA deposition and better corrosion protection. For each coated sample prepared at different current density, the unstable DCPD coating was converted to the stable and dense crystallite Ca-P based HA coating via an alkali treatment. The final HA crystal growth, formation and structure was characterised while potentiodynamic corrosion tests were carried out to evaluate the corrosion resistance of HA coating.

2. Materials and method

2.1 AZ31B substrate preparation

Test specimens of 20 mm x 20 mm x 10 mm are cut from extruded AZ31B alloy cylindrical solid blocks of ø50 mm x 200 mm (purchased from Luoyang Magnesium Gurnee Metal Material Co. Ltd, Hunan, China). Each specimen is machined by face milling (VMC 480P3, Hardinge's Bridgeport 3-axis machining centre, USA) with a spindle speed of 4000 rpm, feedrate of 300 mm/min and depth of 0.5 mm to generate a semi-finished surface. Elemental composition of the alloy (% in weight) is 2.5-3.5% Al, 0.6-1.4% Zn, 0.2-1% Mn, <0.01% Fe, <0.08% Si, <0.01% Cu, <0.001% Ni, and Balance Mg. The substrate is further grounded with 1000-2000 grit SiC abrasive paper to ensure a uniform polished surface. Average surface roughness of specimens is maintained in the range of R_a 0.23 - 0.45 µm, with an aim of minimizing the effect of surface texture on the HA coating deposition quality and overall performance. Specimens are washed with deionised (DI) water, followed by a thorough ultrasonic cleaning with acetone and dried in air for 2 hours. Before the electrochemical deposition, all specimens were stored in an oven set at a temperature of 67 °C for 24 hours under air atmosphere to minimize further oxidation impacting elemental composition and surface topography.

2.2 HA coating deposition

HA coating was deposited on the prepared substrate surface via an electrochemical process. The electrolytes are a mixture of solution of 0.042 mol/l $Ca(No_3)_2$, 0.025 mol/l $NH_4H_2PO_4$, 0.1 mol/l $NaNO_3$, 20 ml/l H_2O_2 in DI water. The solution pH was adjusted to about 5 by adding HNO_3 (if the initial pH is less greater than 5) or $(CH_2OH)_3CNH_2$ (if the initial pH is less than 5) as the smaller pH of 5 or slightly acidic electrolyte favours

the formation of dense and platelet-like HA crystals [31]. In addition, the pH value of about 5 is selected because it is known that the pH in the proximal area of the surgical incision of the implant can drop to as low as 4 (acidic), mainly due to the biomaterial associated infection, or can be caused by the surgical insertion itself, which can be a very traumatic experience for the human body [32]. The chemicals used in preparing the solution were all analytical grade, ensuring purity and quality of the reagents. $Ca(NO_3)_2$, $NaNO_3$, H_2O_2 and $NH_4H_2PO_4$ were purchased from Chem-Supply, Australia, while HNO_3 and $(CH_2OH)_3CNH_2$ were from Sigma-Aldrich Australia.

The target specimen surface was placed into a dedicated beaker containing the prepared electrolytic solution. A standard galvanostat/potentiostat workstation (PGZ100, VoltaLab 10, running on VoltaMaster 4 software) equipped with three electrode configuration was employed to facilitate the electrodeposition to occur. Figure 1 shows the schematic diagram of the electrochemical setup. Specimens (substrates) were used as the working electrode (cathode), while a graphite/carbon rod served as the counter electrode (anode) and Ag /AgCl as the reference electrode. As can be seen in Fig. 1, the coating was deposited on the bottom surface with an area of 15 mm x 10 mm. The other faces of the sample were covered with a yellow gel tape. HA coated samples were prepared at three different current density of 3 mA/cm^2, 6 mA/cm^2 and 13 mA/cm^2 for 2 hour at a room temperature of 23°C. The deposition potentials were measured and recorded with respect to the reference electrode. In order to ensure uniform and homogenous electrolytic solution and consequently, the coating deposition, a magnetic stirrer rotating at 300 rpm mixed solution during the whole deposition period. As-deposited sample was then immersed into 0.25 M of aqueous alkali (NaOH) solution for 4 hours at 60°C. This converted the bi-phasic HA coating comprising of calcium-deficient HA (CDHA) and DCPD into a

single CDHA coating. After the coating conversion, the sample was rinsed with DI water a few times and dried in air for 2-4 hours for further characterisation and assessment.

[Insert Fig. 1]

2.3 Characterisations of HA coatings

Surface topography, structure and elemental compositions of HA coating at different current density were characterised and analysed using a scanning electron microscope (SEM) equipped with an energy dispersive spectroscopy (EDS) (Merlin, Carl Zeiss Co., Oberkochen, Germany), operated at 2 kV and 80 pA (for SEM) and 8 kV and 2 nA (for EDS). Atomic weight (in %) of Ca and P within HA coating was estimated from EDS spectra obtained across the coated surface of the interest. Total percentage weight of Ca + P and Ca:P ratio were determined to evaluate the degree of HA deposition at different current density.

X-ray diffraction (XRD) (Scintag ARL X'TRA, Ecublens, Switzerland) observation using Cu X-ray at 40kV and 30 mA was performed to evaluate the presence of crystal phases formed within the HA coating. The XRD spectra pattern was obtained at a low incidence angel of 5° and step size of 0.02°. Three dimensional (3D) surface feature and roughness of the coating was observed and measured using a laser scanning digital microscope (LEXT OLS4100, Olympus) with a capacity of measuring features of 10 nm resolution). Coating roughness was measured using an optical profilometer (Wyko NT110, Veeco, USA).

2.4 Corrosion test

In order to evaluate the degradation resistance of HA coating, short term corrosion behaviour was studied through potentiodynamic tests performed in 5% (wt) NaCl (purchased from Chem-Supply Australia) solution at 37°C using a three electrode system. Slightly higher NaCl concentration was selected to evaluate the efficacy of the corrosion protection by HA coating from relatively aggressive media. Moreover, past researchers used 5% NaCl aqueous solution for corrosion testing of HA coating on Mg alloys as well [33,34]. The same potentiostat (PGZ100, VoltaLab 10, USA) employed during electrodeposition of HA coating was used for the galvanic corrosion tests. Coated AZ31B sample with an exposed HA coated area of 4 cm^2 within the electrolytic NaCl solution act as a working electrode, while a graphite/carbon rod acted as a counter electrode and a saturated Ag/AgCl as the reference electrode. The rest of surface area of the sample was covered with sol-gel yellow tape. Figure 2 shows the corrosion test setup. Open circuit potential was monitored for 30 minutes to stabilize the solution, which allowed an equilibrium state to be reached. Following this, linear sweep voltammetry (LSV) experiments were carried out by applying an electrical potential from -1.7 V to -1.3 V at a scan rate of 1 mV/s. The corrosion potential E_{corr}, corrosion current density I_{corr}, corrosion resistance R_p and corrosion rate were estimated by using standard Tafel extrapolation technique from the experimental potentiodynamic polarization plot. s. Corroded surface topography was observed under a laser scanning microscope (LEXT OLS4100, Olympus).

[Insert Fig. 2]

3. Results

3.1 Surface morphology and chemical composition

Figure 3 illustrates SEM images and EDS spectrums of HA coating prepared at the three different current density. For all current densities, regular plate-like HA crystal

structures were observed (Fig. 3a, b and c). Platelets may correspond to the orientation of [121] plane of pseudo-hexagonal crystal system [35]. When the current density is low, up to 6 mA/cm^2, the crystals seem more regular and oriented and lapped closely on each other, creating a micro-porous structure. As the current density increases to 13 mA/cm^2, the crystal size increases and their distribution is more randomized. This may potentially make a more macro-porous structure.

Figures 3d, e and f show EDS spectra illustrating elemental composition of a selected area of HA coating. As expected, along with O, predominantly the main elements – Ca, P, Mg are present in HA coating.

Figure 4 shows that as the current density increases from 3 to 6 mA/cm^2, the percentage weight of Ca+P increases rapidly. However, when the current density increases further to 13 mA/cm^2, the rate of increase of HA deposition is not significant. The same trend of Ca:P ratio within HA coating is observed. For the current density of 3 mA/cm^2, Ca:P ratio is about 1.98 which is closest to the desired ratio of 1.76 generally expected within HA coating to be formed. Further the presence of Ca is found to be higher as compared to P when the current density increases further up to 13 mA/cm^2. This perhaps indicates the formation of unstable and unbalanced deposition of Ca-P based crystals with high proportion of Ca ions.

Due to its flaky and soft crystal structural nature and fluctuation in inherent kinetics of the electrodeposition process and alkali treatment, the HA coatings deposited are not always uniformly distributed on the substrate. As such, we would have observed the coating with variable thickness or even no coating in some areas of the coated surface. Figure 5 shows representative magnified SEM images of damaged HA coating areas for different current density. Cracks and damaged areas were observed. When the

current density is 3 mA/cm^2, the damage area is small (Fig. 5a). However, the extent of damage is becoming large as the current density increases, exposing a significantly thinner layer of coating and/or Mg substrate surface (Fig. 5b). In particular, when the current density is 13 mA/cm^2, a layer of damaged particles is observed, indicating little or no deposition of coating (Fig. 5c). Figs. 5d and e illustrate a representative EDS spectra of a damaged area, showing the presence of more Mg and O as compared to Ca and P. Therefore, the above results clearly show that higher current density causes a depletion of HA coating deposition in some areas. In other words, a heterogeneous surface morphology of HA coating is likely to occur at high current density in electrodeposition.

[Insert Fig. 3]

[Insert Fig. 4]

[Insert Fig. 5]

3.2 XRD and XPS observations

Figure 6 depicts the XRD patterns of HA coating deposited at different current densities. Significant peaks corresponding to HA crystal phases along with Mg covering the substrate surface were observed. As the current density increases, the distribution of crystal phases and the extent of their presence remain the same. However, the peak intensity of HA crystal phases has changed. For instance, for HA crystal phase at peak of 27°, the intensity decreases slightly when the current density increases from 3 to 6 mA/cm^2. However, at the same location, the peak intensity has increased again when the current intensity increases to 13 mA/cm^2. The similar effect is observed at a lower peak angle of 12°. The presence of Mg peaks also suggests that HA coating is not able to completely mask the underlying substrate due to regions

of poor surface coverage. Such phenomenon is supported by damaged or cracked coating areas shown in Fig. 5. In addition, XRD patterns for all current densities do not reveal any crystal phases of DCPD (brushite) coating, confirming that the coating has been fully converted to HA after alkali treatment.

Figure 7a shows the representative XPS spectra of the crystal phases of bare and HA coating deposited at 3 mA/cm^2. Ca and P elemental sharp peaks (Fig. 7b, c) are clearly observed on HA coating, while no such peaks are noticed on bare AZ31B surface. This is further evidence of a successful HA coating deposition. Mg elemental peaks were observed on both bare and HA coated surface. However, Mg peak intensity for HA coating (Fig. 8d) is relatively very small. These results suggest that HA coating contains some amount of porosity (or thin areas) even it is deposited at a low current density of 3 mA/cm^2. The amount of delaminated coating area may be higher at a higher current density. However, it is always expected that with an appropriate design and consideration of current density and deposition time, porosity can be minimised to ensure a more compact and uniform coating topography for potential corrosion protection.

[Insert Fig. 6]

[Insert Fig. 7]

3.3 Coating roughness

Figure 8 shows surface topography in terms of average roughness R_a and maximum peak to valley R_t of HA coating deposited at different current density. Both R_a and R_t values increase with the increase of current density. This is due to the fact that higher current density causes HA coating surface texture evolve to be rougher, non-uniform, and irregular. For example, when the current density is 3 mA/cm^2, R_a and R_t are 4.15

μm and 40.14 μm, respectively. However, they increase respectively by 20% and 64% when the current density is at 6 mA/cm^2, and by 43% and 121% when the current density reaches to 13 mA/cm^2, suggesting a significant increase of roughness at higher current density. Higher roughness is potentially due to higher rate of H_2 gas generation at the cathode surface resulting in more porosity in coating. Also the high rate of PO_4 ions generation and as such, relatively coarse particles deposition might contribute to the increase in coating surface roughness. Further increase of the current density might cause fall-off of coarse particles, hence accelerating generation of even rougher and non-uniform coating surface. The error bars depicted in Fig. 8 shows standard deviation (SD) and the extent of spread of roughness values measured on the underlying surface. It can be seen that at higher current density, for instance, at 6 and 13 mA/cm^2, R_a and R_t are widely spread from the mean value, indicating a relatively more irregular, porous coating topography across the surface. For instance, as compared to R_a = 4.15 ± SD 0.68 and R_t = 40.14 ± SD 10.27 μm at 3 mA/cm^2, roughness values with higher SD of R_a = 5.96 ± SD 0.71 μm and R_t = 88.92 ± 35.78 μm are observed at 13 mA/cm^2. Note that roughness values are the average of roughness measurements taken along at least five profiles on the coating surface area of 0.65mm x 0.65mm. Therefore, it is clear that lower current density produces a compact and regular HA crystals with smooth surface topography, which are expected to increase the corrosion resistance. These results are consistent with SEM and EDS spectra as discussed earlier.

[Insert Fig. 8]

3.4 Coating thickness

Figure 9 illustrates SEM image of cross-sectional view of HA coating deposited at the three current densities. It can be seen that there is a transition layer between HA coating layer and Mg substrate. HA coating layer consisting of Ca and P is more dense and compact when the current density is low (of 3 and 6 mA/cm^2) (Figs. 9 and b). On the other hand, the coating appears rough and porous, and the crystal platelets are relatively large when the current density increases to 13 mA/cm^2. It is also observed that the thickness of HA coating is about 40, 46 and 50 μm, respectively at a current density of 3, 6 and 13 mA/cm^2. The intermediate uniform transition layer thickness is always found to be lower than HA coating thickness. This result again confirms the sheer influence of the current density on HA coating thickness and porosity. The transition layer would compose of $Mg(OH)_2$ and/or MgO which would enable the formation of interfacial chemical and mechanical bonding between HA coating and Mg substrate [27]. The cross-sectional growth of Ca-P coating with the effect of the current density and deposition time is studied by other researchers. For instance, Wang et al. reported a relatively dense transition layer between Ca-def HA coating and Mg-Zn-Ca substrate, which is expected to be beneficial for improvement of interfacial strength of the coating [28]. In other work, Bakhsheshi-Rad et al. reported DPCD coating with some cracks in places of the layer when the current density is higher [25]. The coating layer thickness observed by different researchers is however sparse. This can be mainly attributed to the difference in the deposition time and absolute value of the current density considered in those specific studies. Along the cross-section of the top layer of the coated samples, at different current density, we did not observe any chemical compositional change and the Ca:P ratio is found to remain very close to 1.67 of stoichiometric HA, except slightly higher ratio for HA at higher current density (of 13 mA/cm^2).

[Insert Fig. 9]

3.5 Corrosion results

Figure 10 depicts the polarization curves performed in 5% NaCl solution of uncoated or bare AZ31B and HA coated AZ31B deposited at different current density. The values of the electrochemical parameters in terms of E_{corr} (mV), i_{corr} (mA/cm^2), R_p (ohm.cm^2) and corrosion rate (mm/year), obtained from the polarization curves are summarised in Table 1. From Fig. 10, it is seen that corrosion potential (E_{corr}) for HA coating at low current density of 3 and 6 mA/cm^2 has shifted towards positive potential as compared to that for uncoated AZ31B. In other words, E_{corr} at 3 and 6 mA/cm^2 shows one-fold increase as compared to uncoated AZ31B. On the other hand, E_{corr} for high current density of 13 mA/cm^2 shifts towards more negative potential. This indicates that low current density up to 6 mA/cm^2 results in a more stable and corrosion resistive barrier layer of HA coating which resists the onset of corrosion. Corrosion current (I_{corr}) for HA coating at 3 mA/cm^2 is shown to be the lowest (0.069 mA/cm^2). For instance, as compared to uncoated AZ31B, I_{corr} for HA coating deposited at 3 mA/cm^2 decreases by about 92% from 0.923 mA/cm^2 to 0.069 mA/cm^2, while the same for HA coating deposited at 6 and 13 mA/cm^2 shows a comparable decrease by about 86% from 0.923 mA/cm^2 to 0.124 mA/cm^2. These results outline that HA coating deposited at all current density studied is able to resist corrosion by providing a barrier layer protecting AZ31B from penetrating water and chlorine through coating and retarding the underlying chemical reactions. It is also shown that HA coating at higher current density is more susceptible to corrosion kinetics accelerating potential degradation. This is due to more porous, non-uniform and rough coating topography resulted from rapid generation of H_2 bubbles and rate of deposition at higher current density. Therefore, at a given deposition time, low current density would be preferred.

Polarization resistance (R_p) for HA at 3 mA/cm^2 is the highest. For instance, as compared to uncoated sample (19.99 ohm.cm^2), the R_p increase is about 8.5, 4.8 and 4.26-fold, respectively for 3, 6 and 13 mA/cm^2. Furthermore, the corrosion rate (mm/year) for 3 mA/cm^2 is the lowest (1.56 mm/year) and shows a significant reduction of corrosion by 92% compared to that for uncoated sample. Current density of 6 and 13 mA/cm^2 however shows a comparable corrosion rate (2.77-2.78 mm/year) which is about 86% (maximum) lower that for the uncoated sample.

Similar observations for DCPD coating are reported by Bakhsheshi-Rad et al. and concluded that DCPD coated Mg-Ca-Zn alloy with a low current density (of 0.4 mA/cm^2) has the best corrosion resistance compared to that with 0.8 and 1.2 mA/cm^2 [25] Thinner coating layer due to the presence of less amount of porosity and micro-voids is shown to give a better shielding of the substrate from corrosive medium of NaCl solution.

Figure 11 shows the surface topography of corroded products of HA coating at different current densities after pitting corrosion tests. The dark green coloured zone is an indicative of non-corroded surface, while dark blue coloured zone indicates the corroded areas. As is obvious, the uncoated sample shows a larger area of corrosion (Fig. 11a). HA topographic surfaces for low current density (of 3 mA/cm^2) shows the least amount of corrosion pits (Fig. 11b,c). On the other hand, the pitting area increases with the increase of current density. In particular, 13 mA/cm^2 causes significantly an extended area of pitting, indicating severe corrosion occurred across the surface (Fig. 11d). This result is consistent with our earlier observations, outlining that a porous, rough and non-uniform coating produced at high current density is responsible for high corrosion rate and degradation of AZ31B alloy. In other words,

lower current density would be suitable to create a stable corrosion resistant barrier layer for preventing potential degradation of Mg in medium like human body fluid.

[Insert Fig. 10]

[Insert Table 1]

[Insert Fig. 11]

4 Discussion

CaP-based HA coating via electrodeposition is a complex and heterogeneous process. The underlying mechanism of Ca-P crystallite formation has been studied using the classical crystallization theory, in which, the influence of hydroxyl ions and pH in the electrolytic system on the thermodynamic driving force and the nucleation rate of Ca-P precipitation is emphasized [36]. Ca-P coating may include DCPD, OCP and HA. However, with appropriate control of bath composition, current density, pH and temperature, a favourable HA is predominantly formed. In other words, during electrodeposition, Ca-P precipitation is only HA when the initial electrolyte pH is between 5 and 6. This has been consistent to HA coating fabricated in this study, where a solution pH of 5 is maintained. However, HA coating morphology and quality at different current density can be affected by a slight variation of pH values of the final electrolyte at the end of electrodeposition [27,37].

It is reported that DCPD may contain crystals of planes [020] (*lathe-like*) and [121] (*flower-like*). However, a significant transformation of plate-like (or *flower-like*) crystals

of [121] plane to HA has occurred during alkaline treatment [38]. The thickness of the plates ranged from 0.5 µm to 2 µm. Such transformation was observed by other researchers [19,25], concluding that compared to the current density, alkali treatment temperature and time duration predominantly impacts transformation of DCPD to HA crystal phases. In our study, alkali treatment conditions remained constant, and thus we expected little or no influence on HA morphology and structures. In other words, overall, a consistent flower-like HA crystal structures was observed at three current densities, as shown in Fig. 3. This also clearly evidenced the formation of HA coating on AZ31B substrate studied.

Our results indicate that the quality of HA coating is highly undermined by higher current density. The mechanism for this can be explained by the underlying chemical kinetics between Mg substrate and electrolytic solution in forming Ca-P based HA coating [28,39], as shown in Fig.12. Primarily, continuous H_2 gas bubbles are generated at the cathode while an intermediate unstable layer of $Mg(OH)_2$ crystals is deposited on the substrate, as per the chemical reactions shown in Eqs. (1-3). At the same time, Ca^+ and HPO_4^- ions of electrolyte react with OH^- ions, forming Ca-P ($Ca_{10}(PO_4)_6(OH)_2$) crystals (Eq. 4). Simultaneous dynamic interaction between H_2 gas bubbles and Ca and phosphate precipitation at the cathode surface dictates HA coating formation.

Anodic reaction: $Mg \rightarrow Mg^{2+} + 2e^-$ (1)

Cathodic reaction: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ (2)

Overall reaction: $Mg + 2H_2O \rightarrow Mg(OH)_2 \downarrow + H_2 \uparrow$ (3)

Ca-P formation: $Ca^{2+} + HPO_4^{2-} + 12OH^- \rightarrow Ca_{10}(PO_4)_6(OH)_2 + 4PO_4^{3-} + 12H_2O$ (4)

[Insert Fig. 12]

Therefore, it is clear that when the current density is increased, the rate of H_2 gas generation increases, leading to more hydrogen bubbles accumulating on the cathode surface [24]. In other words, this forces more Ca and PO_4 ions to reach the cathode surface, hence depositing more mass of Ca and P within HA coating. At the same time, higher accelerated H_2 gas bubble generation decreases phosphate precipitation at the cathode surface when the current density increases further [35]. Due to this, higher current density is likely to cause deposition of coarse crystal particles. Consequently the lack of integration and bonding between crystals is pronounced, resulting in coating breakdown and delamination, as can be seen in Fig. 5c. Similar phenomenon behind HA coating formation mechanism including precipitation and crystallization process is reported in other research work [25].

As Mg substrate and HA coating have similar crystal structure, the interfacial tension due to their lattice mismatch is expected to be reduced to a minimum, and their chemical bonding thus decreases the system entropy, which may contribute to HA preferential nucleation on the AZ31B substrate. For instance, the crystal structure of HA is hexagonal and its plane spacing of (1 1 2) is very close to that of (1 0 0) of α-Mg, which are 2778 Å and 2779 Å, respectively. They might provide indigenous structural conditions conducive to HA precipitation on Mg substrate [28]. At high current density, the deposition process is predominantly the regime of kinetic control, leading to a pseudo-hexagonal crystal growing on a [1 2 1] planes other than the thermodynamically stable [0 2 0] plane. With the high rate of deposition, a secondary nucleation begins resulting in a faster growth of stacks of such crystallites. This eventually leads to more porous and/or unstable coating on the substrate and potentially can cause spallation or fall-off in some areas of the coated samples. Further

alkaline treatment causes dissolution of associated oxide/hydroxide (e.g. CaO, $Mg(OH)_2$) within the exposed crater area, thus reducing the overall coating thickness at higher current density. This phenomenon is in agreement and consistent with our results and observations on cross-sectional morphology (see Fig. 9) where the change of the coating thickness with the increase of the current density (3 -13 mA/cm^2) seems to be not pronounced, i.e. the thickness only varies between 40 µm and 50 µm. However, the thickness of HA coating obtained from our study is found to be higher than that (maximum 21.8 µm) obtained at lower current density (1.25 - 3.61 mA/cm^2) used in literature, e.g. [23]. It is also imperative to say that higher current density may produce thicker and denser coating with appropriate combination and control of other parameters such as bath temperature, electrolyte pH and composition, and deposition time.

As a general observation, it is expected that the higher coating thickness due to the higher current density will provide higher corrosion protection and low corrosion rate in a corrosive medium. However, it is imperative to say that the integrity of the coating layer would perhaps be considered the most important factor that significantly affects the corrosion performance of HA coated sample. Our corrosion results indicate that while all HA coated samples offer an enhanced corrosion resistance as compared to the uncoated AZ31B, HA coating at low current density of 3 mA/cm^2 outperforms in terms of the corrosion resistance (i.e. higher I_{corr} and lower corrosion rate as outlined in Table 1) as compared to those at 6 and 13 mA/cm^2. This could primarily be due to the presence of a relatively dense, less porous and micro-voids even within a thin coating layer produced, thus offering a better protection in preventing Mg substrate from further pitting and degradation acceleration.

The overwhelming advantage of relatively thin but compact and uniform HA coating is outlined elsewhere [25], and thus confirms the efficacy of the present study. Recent research shows that reverse pulse current density is found to be an alternative approach for stable HA coating formation [28]. The appropriate cut-off of the current density weakens the generation of H_2 gas due to the reduction of H_2O, and hence supplements the consumed Mg and phosphate ions around the cathode rapidly, which promotes building a compact Ca-deficient HA coating on the Mg substrate. In this regard, Kolmas et al. [40] further reported that at a proper current density, the electrodeposition of HA coating doping with Na^+, Mg^+ and CO_3^{2-} ions reduces the grain size and crystallinity, hence increasing the bonding strength between the coating and the substrate. Thus it is clear that, with the appropriate control of the current density, the kinetics of the electrochemical reactions and ions formation can be adjusted, which will enable the nucleation and precipitation of HA crystals with the desired morphology, quality and corrosion resistance. It is to be noted that the corrosion results presented in this study are based on short term potentiodynamic tests in NaCl medium. However, further long-term immersion tests in simulated body fluid (SBF) are still required to investigate the sustained degradation behaviour in terms of H_2 gas, Mg ion and mass loss in more details to develop a comprehensive understanding on the effect of the current density on electrodeposited HA coating [41].

5 Conclusions

A deeper understanding of the influence of the coating formation parameters on the properties of electrodeposited Ca-P based HA coating is critical to better design a tailored biodegradable coating for Mg implants. This study has demonstrated the topography, crystal phases, thickness and corrosion performance of a cathodically electrodeposited HA coatings on Mg can be altered by controlling the current density

followed by an alkaline treatment. Electrodeposition at all three current densities resulted in HA coating with the same chemical composition and platelike structure corresponding to the pseudo-hexagonal crystal system. Despite the presence of the extent of cracks and fall-off of coating, the low current density (of 3-6 mA/cm^2) results in a uniform, compact and stable HA coating as opposed to porous, irregular and cragged coating at high current density, as they are evidenced from SEM, XRD and XPS analyses of top and cross-sectional coating surfaces. As such, the low current density (of 3-6 mA/cm^2) is found to generate a more smooth coating topography with lower surface roughness. Potentiodynamic and corrosion results show that HA coating at a low current density exhibits better corrosion protection for AZ31B in terms of higher corrosion potential, increased corrosion current and polarization resistance, with the presence of less damage on the corroded area. The findings clearly imply that the current density in electrodeposition of HA coating plays a critical role in controlling the coating characteristics, formation and degradation performance. In this regard, a low current density would be preferred to develop a tailored corrosion resistive barrier layer for a biodegradable Mg implant.

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