Synthesis and Process Evaluation of Calcium Phosphate Coatings Depositions on Pure Magnesium via Simple Chemical Conversion Method

Mohd Amin Farhan Zaludin[1,2]*, Zul Azhar Zahid Jamal[1], Mohd Nazree Derman[1,2,3], Mohd Zaheruddin Kasmuin [1,2] and Azmi Rahmat[2]

[1]Centre of Excellence (COE) Frontier Materials Research, School of Materials Engineering, No 66-68, Blok B, Taman Pertiwi Indah, Universiti Malaysia Perlis (UniMAP), 01000, Kangar, Perlis, Malaysia.
[2]School of Materials Engineering, Universiti Malaysia Perlis (UniMAP), Taman Muhibbah, 02600, Arau, Perlis, Malaysia.
[3]Institute of Nano Electronic Engineering, Taman Pertiwi Indah, Universiti Malaysia Perlis (UniMAP), 01000, Kangar, Perlis, Malaysia.

ABSTRACT

Simple chemical conversion has been employed in order to coat calcium phosphates (CaP) on magnesium (Mg) substrate. The Mg substrates were coated in a primary phosphating bath before secondary treated with an alkaline solution of sodium hydroxide, NaOH. In this paper, the fabrication process of the coatings via simple chemical conversion method were discussed and evaluated in terms of electrochemical, phase analysis, and microstructural aspects. XRD diffractogram confirmed that the primary coating composed of dicalcium phosphate dehydrates (DCPD) and after the secondary treatment, the DCPD transformed into more stable hydroxyapatite, HA. The microstructural observations show that the coating is composed of flower-like shape crystallites. Besides, the potential-time curves of both primary and secondary coated samples suggests that the minimum deposition time for better coverage of the coatings is 30 minutes.

Keywords: Calcium phosphate coating, conversion coating, hydroxyapatite, magnesium

1. INTRODUCTION

Mg exhibit comparable properties with natural bones which make them suitable to be applied as implant materials [1]. However, due to its electrochemical reactive behaviour, Mg is prone to corrosion from exposure to surrounding fluids. Calcium phosphate (CaP) based coatings became one of the best bioactive and biodegradable coating candidates for Mg alloys. One of CaP phases, hydroxyapatite (HA) possessed similar mineral component to human skeletal system [2]. Numerous deposition methods have been utilized in order to coats CaP into Mg substrate surface [3][4]. The chemical conversion coating possesses advantages from several aspects such as relative ease of setup and fabrication, effective, and low cost [3]. Chemical conversion is a utilization process of metal implant surface in converting it to a thin coat of metal oxides and/or other compounds via chemical or electrochemical process [5]. Several studies have been done to coat CaP on Mg alloys by employing chemical conversion coating process [3][4][6][7][8]. However, most of the studies focused on the performance of the coatings inside the corrosion media. This paper intended to evaluate and discussed in details about the formation and process of the CaP coating via a chemical conversion method on Mg substrate.

2. METHODOLOGY

2.1 Coatings Preparations

99.9% purity of Mg will be used as substrate materials. The samples were cut from the ingot and ground according to metallography procedure up to 1200 grit. Prior to coating processes, the

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*aminzaludin90@yahoo.com

samples were cleansed by using deionized water (DI). The samples will be coated by using a simple chemical conversion method. The coating procedure will employ the steps as described previously by Chen et al. [4]. The selection of this procedure is because of its simplicity and ease of coating fabrications on the substrate. The coating procedure will be divided into two steps, which is primary (phosphating) and secondary (alkaline treatment) coating process. The primary coating process conducted in order to coat the metal surfaces with CaP compounds. The latter secondary coating process is carried out in order to convert any CaP phases obtained after primary coating into a more stable HA. The primary coating bath consists of calcium nitrate tetrahydrate, $Ca(NO_3)_2.4H_2O$, sodium phosphate, Na_3PO_4 and nitric acid, HNO_3 were used to adjust the bath pH to 2.6. The amount or concentration of the calcium ion and phosphate ions sources that will be selected are $[Ca^{2+}]/[PO_4^{3-}]$ = 0.30M/0.18M. The Mg substrate will be primary coated at 40°C for 10, 20, 30 and 60 minutes. For secondary coating, the Mg substrate will be primary coated for 60 minutes before undergoes the secondary coating treatment inside 1M NaOH solutions. The secondary coating will be conducted at 80°C for 10, 20, 30 and 60 minutes.

2.2 *Characterization of the coatings*

The formations of CaP coatings via simple chemical conversion method were evaluated from electrochemical, phase and microstructural aspects. For electrochemical aspects, the potential-time test was conducted in parallel with the primary and secondary coating process. The samples (working electrode) having an exposed area of 1 cm^2. The reference electrode for primary bath was saturated calomel electrode (SCE, +0.242 V vs SHE) and for the secondary bath was mercury/mercury oxide electrode (Hg/HgO, -0.101 V vs SHE). The selection of difference reference electrode for each bath is because of high concentration of OH^- and corrosiveness of the NaOH solutions. The potential readings during the coating process were recorded by using Ultra DMM V2.0.0.17498 software attached with a digital multimeter (Model: Pro'sKit Mt-1820). The phase analyses of the coated samples were executed by X-Ray Diffraction (Model: Bruker D2 Phaser). The scanning range 2θ was set from 10° to 50°. The microstructure analyses were conducted by Scanning Electron Microscope (Model: JEOL JSM-6460LA).

3. RESULTS & DISCUSSIONS

3.1 *Primary coating (Phosphating process)*

The phosphating is one of electrochemical coating process [9]. During the immersion of Mg substrate into the primary phosphating bath, there will be anodic and cathodic reactions occur on the substrate surface. The reactions are described by equations (1) and (2) [6].

Anodic: $Mg \rightarrow Mg^{2+} + 2e^-$ (1)
Cathodic: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ (2)

The resultant OH^- from equation (2) will raise the pH at the interface of Mg-phosphating bath solutions. The increment of pH value will stimulate the precipitation of CaP phase on the substrate when their solubility limits have been surpassed [6] [7]. The source of calcium in the phosphating bath, $Ca(NO_3)_2.4H_2O$ will react with phosphoric acid (originated from the dissolution of Na_3PO_4) to produce brushite or dicalcium phosphate dehydrate, $CaHPO_4.4H_2O$ (denoted by equation (3)).

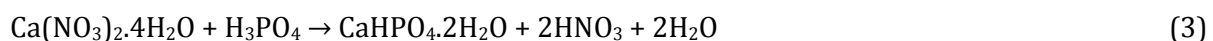$Ca(NO_3)_2.4H_2O + H_3PO_4 \rightarrow CaHPO_4.2H_2O + 2HNO_3 + 2H_2O$ (3)

Figure 1 shows the potential-time curves of Mg substrate inside the phosphating bath for primary coating. Theoretically, the phosphating process could be classified into 5 distinct stages. The stages are (i) electrochemical attack on the substrate, (ii) amorphous precipitation, (iii) dissolution of the base metal, (iv) crystallization and growth, and (v) crystal reorganization [10]. From Figure 1, it could be observed that in the early stage of immersion (0-3 minutes), the potential experience sudden increment and decrement in value before steadily increase and become stable around 10 minutes of immersion. The instability of potential value in the early minutes of immersion may be subjected to the surface activation along with the exfoliation of loose oxide film on the Mg substrate [7] [8]. The shift of potential in a negative direction is due to the depletion of H^+ ions at the interface of Mg-phosphating bath solutions that is by cause anodic and cathodic reactions described by equations (1) and (2) [9]. Then, the shift of potential towards positive direction is due to deposition of the DCPD into the Mg substrate (equation (3)). In the later stage, the potential-time curve becomes stable and it is suggested that the coating becoming more complete throughout the Mg substrate surface.
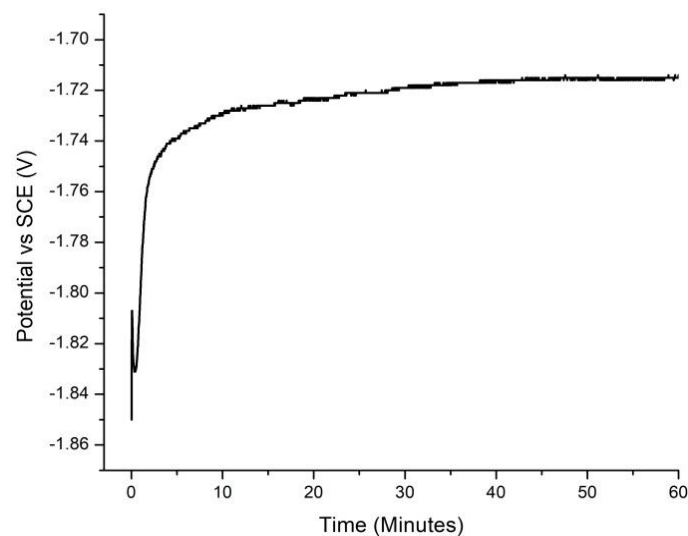

Figure 1. Potential-time curves of Mg substrate in primary coating bath.

Figure 2 shows the XRD diffraction pattern of the primary phosphating coated samples. The diffractogram confirmed that the samples composed of Mg [PDF 03-065-3365] and DCPD phases [PDF 01-072-0713]. This is evidenced by the occurrence of the major planes of DCPD such as (0 2 0), (1 2 $\bar{1}$), (0 4 0), and (1 1 $\bar{2}$) at 2θ value of 11°, 21°, 24° and 29°. As we go from 10 to 60 minutes, the intensity of DCPD (0 2 0) peaks is increasing which shows the maturation and increase crystallinity of DCPD phases [11] and the main Mg peak such as peak (1 0 1) at angle 37° slightly decrease, which shows the enhancement of DCPD coating coverage on the substrates.
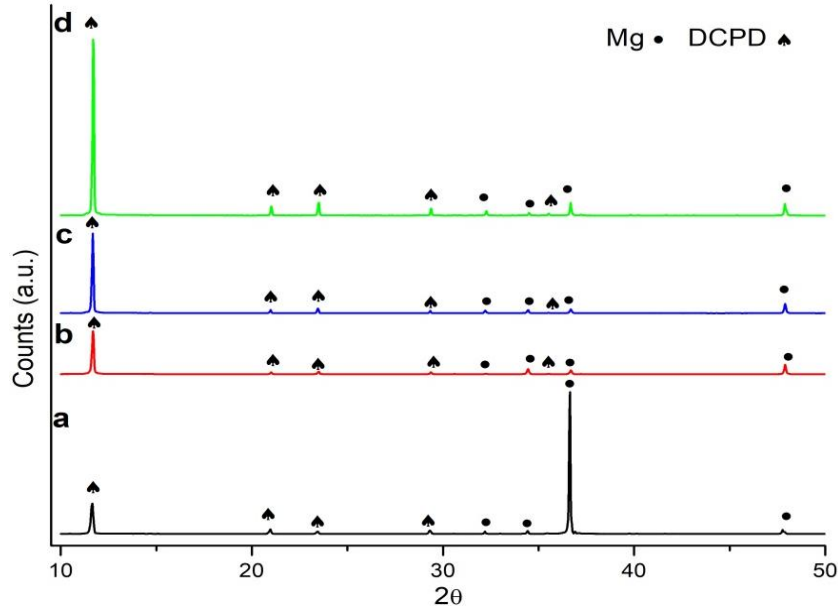
Figure 2. XRD diffractogram of primary coated samples inside phosphating bath for (a) 10 (b) 20 (c) 30 and (d) 60 minutes.

Figure 3 shows the microstructure observations for primary phosphating coated samples. After immersion for 10 min, some flower-like shape DCPD crystallite about 500µm in diameter was observed. There are also some cracks that could be found adjacent to the DCPD crystallite. The cracks were suggested to be composed of magnesium hydroxide, $Mg(OH)_2$. As the coating time prolonged, the crystallite size increased and by the coating time about 30 minutes, the substrate was fully covered with DCPD crystallite. At 60 minutes of coating process, the DCPD crystallite size is comparable with the previous one. The microstructure obtained in Figure 3 match and in the same argument with the potential-time curves and shows that the coating begin to cover most of the substrate surface at an immersion time of 30 minutes onwards.
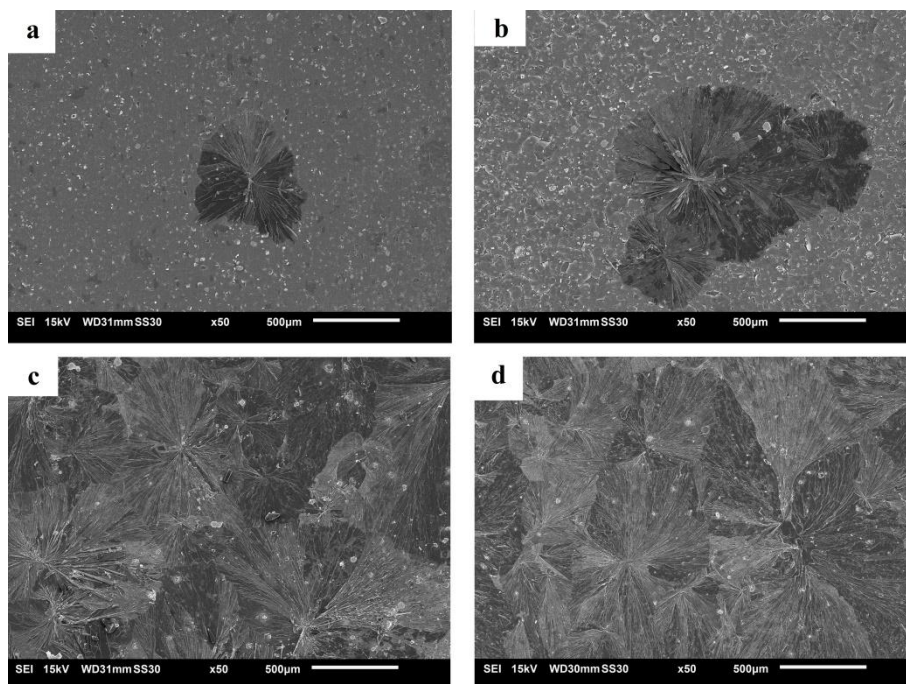
Figure 3. Microstructure observations of primary coated samples inside phosphating bath for (a) 10 (b) 20 (c) 30 and (d) 60 minutes

3.2   Secondary coating (Alkaline Treatment)

The samples of primary phosphating coated for 60 minutes that composed of DCPD phase were alkaline treated at 80°C for 10, 20, 30 and 60 minutes inside 1M NaOH solutions. Figure 4 shows the potential-time curves of the alkaline treated samples. The DCPD transformed to HA in accordance with equation (4):

$$10CaHPO_4.2H_2O + 12NaOH \rightarrow Ca_{10}(PO_4)_6(OH)_2 + 4Na_3PO_4 + 30H_2O \qquad (4)$$
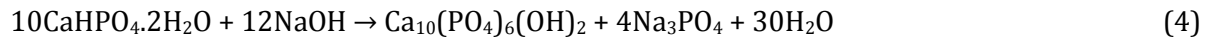
From literature, the transformation of HA from DCPD composed of 3 stages which is; (i) acidic CaP phase dissolution, (ii) phase transformation, and (iii) HA formation [12]. From Figure 4, the potential curves show sudden shifts towards positive and negative value immediately after immersing inside NaOH solutions. This positive shifting may be subjected to surface activation of the substrate while negative shifting is due to the phase dissolutions of DCPD inside the NaOH solutions. Besides, it is known that NaOH solutions are alkaline and very corrosive in nature. Then, about 1 minutes of immersion, the curve shifts towards positive directions, indicating that the phase transformations and HA formation stages are taking place. The excess OH- ions supplied by the alkaline solutions enhanced the phase transformations of the DCPD to HA, in accordance with equation (4). The fluctuations of potentials in the curves from 1-4 minutes of alkaline treatment could be subjected to the nature of the conversion process of the DCPD into HA. It is stated that the phase transformations of DCPD into HA is a fast solid-solid phase transitions that occurs very quickly at high liquid-to-solid ratio, generally 100:1[11][13]. So, the fluctuations of potential-time curves are anticipated. Besides, the potential fluctuations may also occur because micro-dissolutions of the coatings towards the formation of stable HA along with the filling effect of pores and gaps on the coating-substrate interface. As the alkaline treatment time prolonged, the potential curve steadily increases and stable, indicating the progressive HA coating formations.
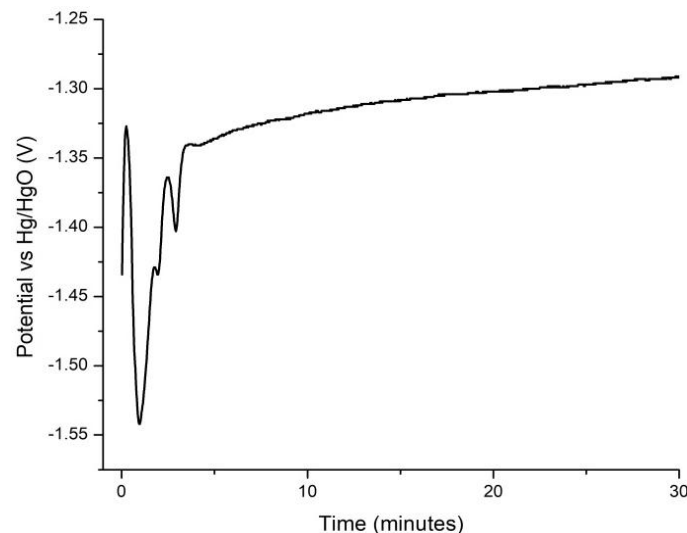

Figure 4. Potential-time curves of DCPD coated substrate in NaOH bath at 80°C.

Figure 5 shows the XRD diffraction pattern of the alkaline treated phosphating coated samples. The diffractogram confirmed that the samples composed of Mg [PDF 03-065-3365], DCPD (PDF 01-072-0713) and HA phases (PDF 01-074-7564). For 10 minutes alkaline treated samples, the (0 2 0) DCPD peaks still traceable, which means that at the moment, phase transformations of DCPD into HA still progressing. As the alkaline treatment time prolonged, the DCPD phase peaks

disappear. The HA (0 0 2) peak could be observed at 26° angle, which conforms the reaction in equation 4. It should be noted that the Mg peaks intensities are increased compared to the primary coated samples diffractogram as in Figure 2. The increment of the Mg peaks intensities could be subjected to the porous nature of the coating and the erosion process impart by the secondary coating treatment towards the sample [8].
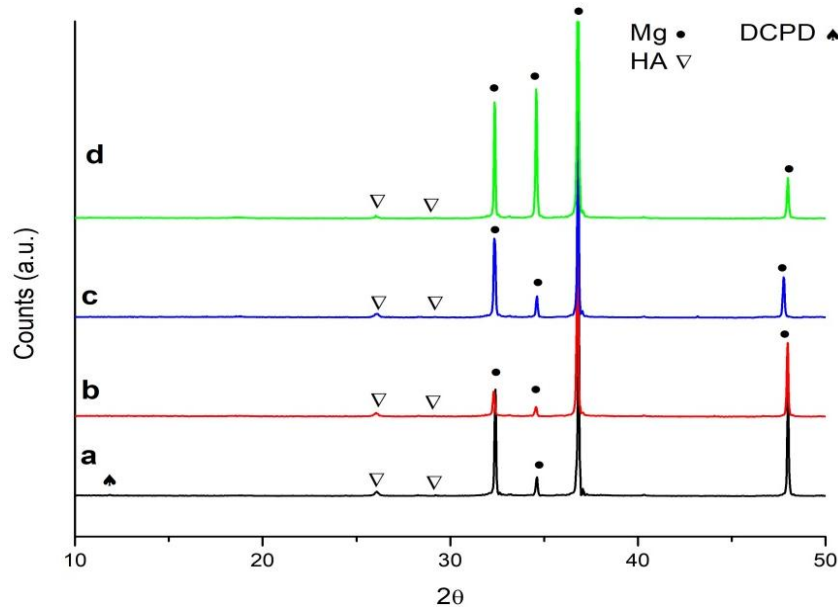

Figure 5. XRD diffractogram of phosphating coated samples and alkaline treated for (a) 10 (b) 20 (c) 30 and (d) 60 minutes.

Figure 6 shows the microstructural observations of alkaline treated samples inside NaOH at 80°C. There is no significant change in the microstructural features of the HA coated samples. However, as the alkaline treatment time increase, it could observe that the coatings becoming denser. Besides, the flower-like HA crystallite possessed some micro-cracking on the edge of it. This could be attributed to the dissolution process of the DCPD into HA.
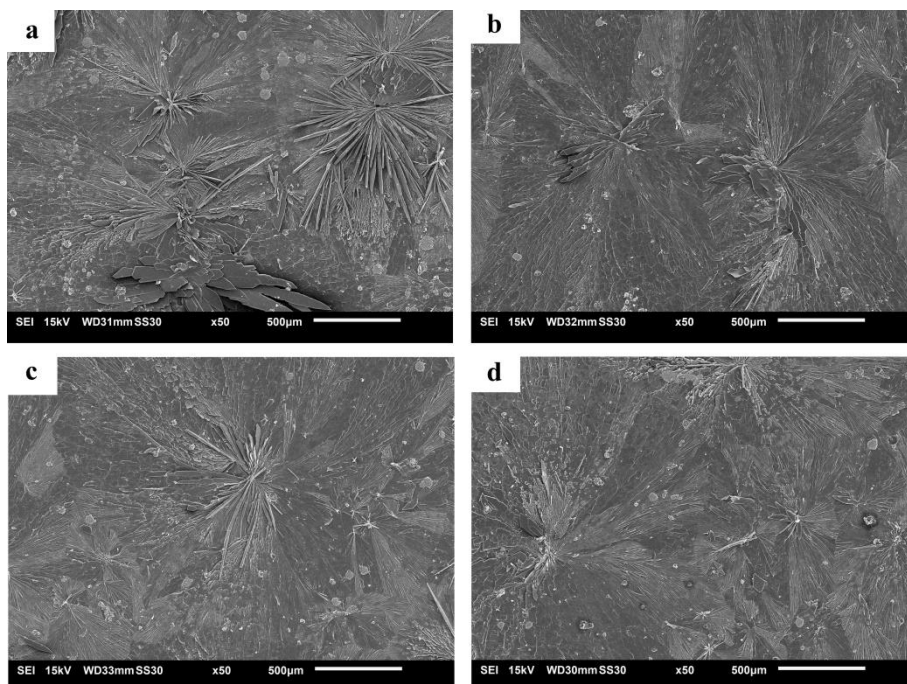
Figure 6. Microstructure observations of phosphating coated for 60 minutes and alkaline treated for (a) 10 (b) 20 (c) 30 and (d) 60 minutes.

4. CONCLUSIONS

The CaP coatings have been fabricated on pure Mg substrate. The formations of CaP coating by simple chemical conversion method composed of primary coating (deposition of DCPD from phosphating bath) and secondary coating (transformation of DCPD to HA phase). Both of the coating process possessed chemical reactions specifically to produce HA coatings. From the current work, it could be concluded that minimum deposition time for both coating processes is 30 minutes. As the coating process prolonged beyond 30 minutes, the potential-time curves become stable and the microstructural shows thorough and complete coating coverage. Both coating processes produced flower-like crystallites on the substrate surface. XRD confirmed the DCPD and HA phase occurrence. For future works, the coating process durations by this method should at least be conducted for 30 minutes. This is to ensure the coatings are complete and could provide the protections needed by the Mg substrates.

ACKNOWLEDGEMENTS

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