



# Mechanism of calcium phosphate deposition in a hydrothermal coating process



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## ABSTRACT

Hydrothermal process is a useful method for deposition of corrosion protective calcium–phosphate (Ca–P) coating on magnesium alloy (AZ31) substrate. Since the deposition mechanism determines the coating properties to a considerable extent, the present work studied the key steps in the formation of Ca–P during the hydrothermal process. Ca–P was deposited on four different metallic substrates: AZ31, zinc (Zn), titanium (Ti) and stainless steel (SS). The Ca–P coatings were studied by means of Raman spectroscopy, Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM) and energy dispersive spectroscopy (EDS) to determine the various steps in the coating formation and growth. The deposition of Ca–P layer was found to strongly depend on the substrate material. Little or no deposition took place on corrosion resistant SS and Ti substrates while thick layers formed on more reactive AZ31 and Zn substrates. The deposition mechanism changed with increasing temperature in the case of the AZ31 substrate. At lower temperature, the coatings consisted of tricalcium phosphate and monetite phases. Increase in deposition temperatures resulted in the formation of an additional thick magnesium hydroxide layer below a mixture of tricalcium phosphate and monetite layer when magnesium substrate was used.

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## 1. Introduction

Conventional metallic biomaterials such as Co–Cr alloys, stainless steel (SS 316L), pure Ti and Ti alloys possess a combination of good mechanical properties and high fracture toughness. These types of metals are widely used in load-bearing bio-medical applications. However, certain clinical limitations exist for these materials. For instance, stress shielding effect is induced due to the much higher elastic modulus of the metal in comparison with natural bone [1–7]. Bone, as a living tissue, constantly remodels and adapts to the stresses imposed upon it. This process of remodeling can lead to the phenomenon of stress shielding when an implant is present. If the implant carries a large fraction of the applied load compared to the surrounding bone, the bone experiences lower stresses resulting in reduced bone density. Conventional implant materials have significantly higher modulus of elasticity than bone causing the implant to carry a greater portion of the load and frequently causing stress shielding [5,6,8]. The stress shielding effect results in critical clinical issues such as an early implant loosening, hindering the healing process, and damaging adjacent anatomical structures and skeleton thickening [3,9,10].

Magnesium (Mg) alloys could be a good alternative for implant material due to its mechanical properties, non-toxic nature, biocompatibility, and biodegradability. The density and elastic modulus of Mg are close to that of the human bone, which avoids stress shielding effect [11–13]. However, from a corrosion perspective, Mg is one of the most reactive metals. Its poor corrosion resistance seriously limits the use of Mg and its alloys as metallic implants, but it is a good starting point to consider them for potential applications as bioresorbable implants [14–17]. The corrosion performance needs to be improved through surface modification in order to extend the Mg degradation time and to avoid too rapid production of hydrogen gas during the corrosion process, which may not be tolerated by host tissues due to bubble formation [18]. Mg surface can be modified by different methods such as electrodeposition [19,20], biomimetic [21], and fluoride conversion coatings [22,23] with some improvement in corrosion resistance. Besides these methods, the hydrothermal process has been found as a useful method for the deposition of compact and protective Ca–P coating with adequate corrosion resistance [24]. Onoki et al. used a double layered capsule hydrothermal hot-pressing technique for developing hydroxyapatite (HA) coating on Ti and Mg substrates with good adhesion properties (4–5.5 MPa) [25,26]. The hydrothermal process has been used for deposition of Ca–P on other metallic substrate as well.

Ban et al. [27] deposited Ca–P on Zn, Ti, SS, nickel (Ni) and iron (Fe) substrates by using hydrothermal–electrochemical process and,

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according to their results, relatively successful deposition of Ca–P coatings resulted in the presence of electric current.

Xiong et al. [28] reported deposition of nano-hydroxyapatite (nano-HA) coating on a titanium–niobium (TiNb) substrate by hydrothermal method at pH 7.4 at varied times and deposition temperatures (80 °C–200 °C). According to their results, a few scattered particles started to deposit on the TiNb alloy surface only after 5 h of deposition process at 160 °C, and the number of the particles increased by increasing the deposition temperature to 200 °C. Moreover, Calixto de Andrade et al. [29] reported the deposition of a very thin layer of HA under the hydrothermal process after 6 h on Ti substrate pre-treated with NaOH by using simulated body fluid as deposition solution. Fujishiro et al. [30] reported hydrothermal deposition of HA coating on Fe, aluminum (Al), copper (Cu) and Ti plates at 140–200 °C and pH 3.4–10.0. According to their results, deposition of HA films was only successful on the Fe surface while the other metallic substrates had only few crystals of HA on their surface. On the other hand, Liu et al. [31] reported deposition of a fairly uniform crystalline HA layer on different metallic substrates such as Ti, Al, Cu and SS by seeded hydrothermal deposition method. The process was done in two steps: deposition of a seed layer by means of electrochemical method which was followed by a hydrothermal process. They found that the seed layer improves the deposition of HA layer during the hydrothermal process. However, without a seed layer no uniform coating is observed on the metallic substrates after the hydrothermal deposition and only a few granular HA particles were deposited at the surfaces. Thus, based on literature reports, the hydrothermal process is a successful method for deposition of compact and protective calcium phosphate coating on some metals while it is unsuccessful for others [27,29–31]. In many of the reported deposition attempts it was not clear what caused the success or lack of deposition.

We previously reported the deposition of a uniform and protective Ca–P layer on AZ31 magnesium substrate [24]. However, the deposition mechanism of Ca–P coating during the hydrothermal process was not elucidated in that study. Therefore, the aim of this paper is to present a more thorough understanding of the deposition mechanism of Ca–P layer on the AZ31 substrate during the hydrothermal process by means of comparing deposition under different conditions, especially by comparing deposition among various metal substrates. Raman spectroscopy analysis, X-ray diffraction, FTIR and cross sectional analysis were used to characterize the coating layers and determine aspects of coating deposition mechanism.

## 2. Experimental procedures

The hydrothermal coating deposition method has been reported in our previous study [24]. Briefly, a mixed aqueous solution containing 0.1 M  $\text{Ca}(\text{NO}_3)_2$  (99.98% purity, Alfa Aesar) and 0.06 M  $\text{NH}_4\text{H}_2\text{PO}_4$  (98% purity, Alfa Aesar) was prepared for the hydrothermal process. The pH of solution was adjusted to 3.9–4.0 by using ammonia. AZ31 magnesium alloy was used as substrate for the coating process. Disks were cut into 25 mm diameter and 2 mm thickness from commercial AZ31 rod. Hydrothermal deposition was carried out at varied temperatures (100 °C, 130 °C, 160 °C and 190 °C) for 3 h, so the samples henceforth were named as HE100 °C–3 hr and HE130 °C–3 hr, HE160 °C–3 hr and HE190 °C–3 hr, respectively.

Ca–P coating was also deposited on Ti, SS and Zn substrates at 160 °C for 3 h for comparison. These substrates were polished with 2400 grit abrasive paper, and then ultrasonically cleaned in acetone for 20 min. The samples were named as Ti substrate, SS substrate and Zn substrate, respectively.

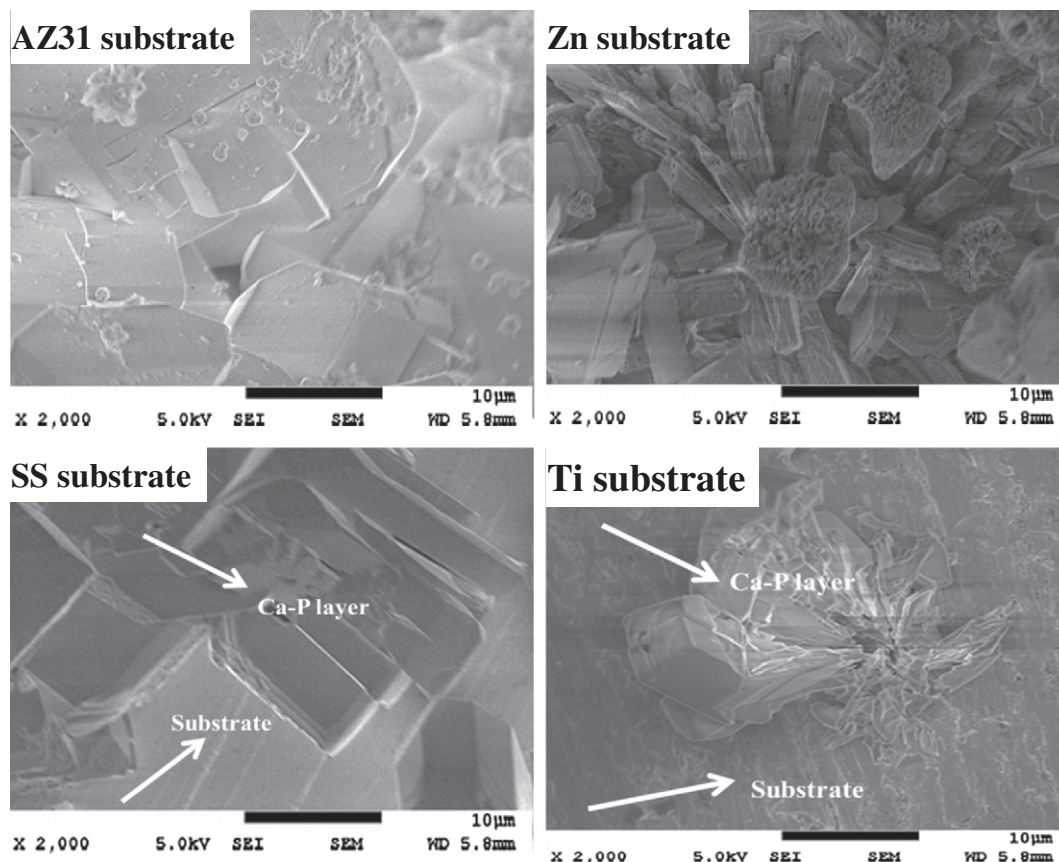


Fig. 1. SEM micrograph of coating on different substrates.

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