



# Improved corrosion protection of magnesium by hydrothermally deposited biodegradable calcium phosphate coating



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## HIGHLIGHTS

- The corrosion protection of hydrothermally deposited Ca–P coatings was studied.
- The Ca–P coatings improved the corrosion performance of Mg substrate up to 10,000-fold.
- The corrosion resistance improved by increasing deposition temperature.
- Deposition mechanism of coating changed by increasing deposition temperature.

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## ABSTRACT

The corrosion protection of hydrothermally deposited calcium phosphate coatings on AZ31 magnesium alloy were studied for their potential use in biocompatible and bioresorbable temporary implants. The coatings mainly consisted of calcium phosphate phases (monetite and tricalcium phosphate). Potentiodynamic and electrochemical impedance spectroscopy (EIS) confirmed that the coatings provided varying levels of corrosion protection depending on the coating deposition temperature and duration. EIS results showed that the size of capacitance loops and the absolute impedance value ( $|Z|$ ) increases by increasing the deposition temperature and corresponding growth in coating thickness. In agreement with the electrochemical experiments, immersion tests in simulated body fluid also indicated large improvement in corrosion protection as the mass loss was significantly reduced when coating was applied as compared to the bare metal. Using the thickest coating obtained at 190 °C deposition temperature, the corrosion current density of the coated magnesium was 10,000 fold lower compared to the bare metal. This result confirmed that the new hydrothermal coating is suitable to protect Mg implant against corrosion with further advantage of being bioactive and biodegradable.

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## 1. Introduction

The interest in using magnesium alloys has been steadily increasing [1–3] due to their low density and favorable mechanical properties. However, a significant obstacle of using magnesium in most applications is its rapid corrosion requiring corrosion protection measures. One of the emerging applications of magnesium is its use as biocompatible and biodegradable temporary implant material [2,4], when its corrosion is taken advantage of by allowing the magnesium metal to corrode and be absorbed by the body. Magnesium could provide significant advantage compared to

currently used implants made of titanium (Ti), stainless steel (S.S.), and cobalt–chromium (Co–Cr) alloys when used for temporary implantation since it does not require removal and associated second operation. Magnesium alloys are also advantageous in reducing the stress shielding effect due to the mismatch in mechanical properties between implant materials and bone tissue. The stress shielding phenomenon causes stress concentration at bone-implant interfaces and may result in critical clinical issues such as implant loosening, delay in healing process and consequently damaged bone growth. Ti, SS, and Co–Cr alloys have high Young's modulus (100–200 GPa) while magnesium alloys have lower modulus (41–45 GPa), close to that of human bone (10–30 GPa); therefore use of Mg avoids or minimizes stress shielding effect [2,4,5].

Despite the high potential of using magnesium alloys as

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temporary and biodegradable implants, applications are not widespread as the corrosion rate of Mg alloys is too high, resulting in excessive hydrogen evolution and local alkalization close to the surgery region, as well as premature degradation in the implant's mechanical integrity before sufficient bone healing can occur [3]. To put Mg to practical use, it is necessary to improve its corrosion performance through alloying or surface modification. Although the corrosion resistance of Mg can be enhanced by alloying elements with low toxicity such as zinc and calcium, as well as the potentially more harmful aluminum or rare earth metals, the amounts of these elements must be limited in order to maintain desired mechanical properties and reduce potential toxicity leading to insufficient improvement in corrosion properties. The alternative is surface modification and coating that could reduce the corrosion rate to a higher extent [6,7]. Anodizing, electrodeposition, fluoride conversion and biomimetic coatings have been used on Mg alloys. However, these coatings do not provide sufficient protection: Biomimetic and anodic coatings are reportedly rather permeable, exhibiting many cracks [1,8]. Relatively thin but dense coating can be made of magnesium fluoride ( $MgF_2$ ) as a conversion coating but it gradually dissolves when the sample is transferred to fluoride-free solutions; precluding long-term protection [1,8]. Thus, no suitable coating seems to exist for magnesium implant application and there is a need for a novel coating that is dense and able to provide superior corrosion protection. In addition, the coating must be biodegradable and biocompatible as the biological response of implant materials strongly depends on the implant's surface properties due to interactions between the cells and biomaterials taking place at the tissue–implant interface [9].

Calcium–phosphate (Ca–P) coatings are preferred for biomedical applications since Ca–P is the main inorganic constituent of natural bone and it can speed up bone growth. Producing Ca–P crystals by hydrothermal process has a successful history [10–14]. However, there are only a few publications regarding deposition of Ca–P crystals directly on metal substrate. Liu et al. reported deposition of a fairly uniform crystalline hydroxyapatite (HA) layer on metal substrates by seeded hydrothermal deposition method in two steps: Deposition of a seed layer by means of electrochemical method which was followed by hydrothermal process. They found that the seed layer improves the deposition of HA layer during hydrothermal process. However, they did not investigate the corrosion performance of the obtained coatings [15]. Onoki et al. used a double layered capsule hydrothermal hot-pressing technique for developing HA coating on Ti and Mg substrates with good adhesion properties (4–5.5 MPa) [16,17]. Hiromoto et al. [18] used hydrothermal method to deposit HA in a wide range of pH (6.3, 7.3, 11.3) at 8 h and 24 h deposition times. Longer deposition time and near neutral pH enhanced the coating performance and they reported a tenfold improvement in the corrosion rate reduction of Mg substrate based on corrosion current densities. However, this improvement is not fully adequate for protecting magnesium implants in applications where the healing may take several months as there is potential for rapid loss of mechanical integrity of the metal through corrosion. Ng et al. [19] and Zhu et al. [20] developed a thick magnesium hydroxide layer,  $Mg(OH)_2$ , by means of hydrothermal process for surface modification of Mg. Gupta et al. developed compact and pore-free  $Mg(OH)_2$  layer which improved corrosion performance of Mg substrate in phosphate buffer saline (PBS) solution [21]. Although,  $Mg(OH)_2$  layer can improve the corrosion performance of Mg substrate it is not preferred in biomedical application unlike the biodegradable and biocompatible Ca–P coatings. Apart from biocompatibility requirement, the deposited coating layer must be dense and adherent. Thus, a hydrothermal deposition method was selected in the present work to grow bioresorbable Ca–P coating in such a way that most of the

coating defects would undergo self-healing during the deposition and thus provide high corrosion resistance at least for the initial healing period when mechanical support is needed.

The hydrothermally deposited Ca–P coating was successfully prepared and partially characterized for its morphology, thickness, composition and mechanical properties as reported separately [22]. According to this report, XRD analysis showed that the deposits obtained from hydrothermal process were mainly a mixture of monetite ( $CaHPO_4$ ) and tricalcium phosphate with small amount of magnesium substitution [ $Ca_{2.86}Mg_{0.14}(PO_4)_2$ , also known as whitlockite]. Similarly, the FTIR spectra for Ca–P coating layers deposited showed vibration bands corresponding to monetite and tricalcium phosphate phases. Moreover, the coating thickness was found to increase steadily by increasing the deposition temperature from 100 °C to 160 °C with 3 h deposition time (20  $\mu m$  at 100 °C, 48  $\mu m$  at 130 °C, 61  $\mu m$  at 160 °C) followed by a sharp increase to 389  $\mu m$  at 190 °C. With the increase in coating thickness, the coating adhesion dropped from 5.8 MPa (sample coated at 160 °C) to 3.1 MPa (sample coated at 190 °C). The investigation of corrosion behavior of the coated magnesium alloy by electrochemical methods is reported in this work.

## 2. Experimental details

### 2.1. Materials

The hydrothermal coating deposition method was reported elsewhere [22], using analytical grade  $Ca(NO_3)_2$  (99.98% purity) and  $NH_4H_2PO_4$  (98% purity), obtained from Alfa Aesar. AZ31 magnesium alloy was used as substrate for the coating process. Disks were prepared with 25 mm diameter and 2 mm thickness from commercial AZ31 rod. Prior to coating process, AZ31 substrate was prepared with up to 2400 grit abrasive paper, and then ultrasonically cleaned in acetone for 20 min prior to coating. The coated samples were named as HE100 °C-3hr and HE130 °C-3hr, HE160 °C-3hr and HE190 °C-3hr respectively, referring to the deposition temperature and duration. For the 190 °C hydrothermal process, heating durations of 1 and 2 h were used as well.

### 2.2. Characterization of coatings

The electrochemical behavior of uncoated and coated samples was investigated on duplicate samples. Potentiodynamic polarization tests were done using a Solarton potentiostat (Model SI 1287) conducted in simulated body fluid solution (SBF) according to a reported procedure [23] at pH 7.2–7.4. For the electrochemical tests, a three-electrode cell was used with the sample as working electrode, SCE (sat. KCl) was used as the reference, and graphite as the counter electrode. An area of 1  $cm^2$  of the working electrode was exposed to the solution. A 1  $mVs^{-1}$  scanning rate was applied during the potentiodynamic polarization test. Prior to the polarization test, samples were equilibrated in SBF solution for 30 min.

Electrochemical impedance spectroscopy (EIS) test was performed in order to investigate the corrosion behavior of coatings in SBF solution using a Solarton potentiostat (Model SI 1260). The EIS tests were conducted at the open circuit potential (OCP) in the frequency range of 100 kHz to 10 mHz, using 10 mV amplitude of signal's perturbation.

Immersion tests were conducted in SBF standard solution for up to 28 days in order to assess the early corrosion performance. Each sample with an exposure area of 4.9  $cm^2$  was immersed in 50 ml of the SBF solution at 37 °C. The exposure area was controlled by covering the rest of the sample surface with a polymer resin. After each immersion time, the samples were extracted and the corrosion products were removed by using chromic acid and silver

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