



Dual layer inorganic coating on magnesium for delaying the biodegradation for bone fixation implants



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ABSTRACT

In this study, a dual layer inorganic coating was formed on a pure magnesium metal using electrochemical methods to delay the biodegradation of the metal for potential bone fixation implant applications. Firstly, a layer of silicate-based coating was formed on the base metal using the plasma electrolytic oxidation (PEO) method. A second layer of calcium phosphate (CaP) was formed on the PEO coating using the electrodeposition method. *in vitro* electrochemical degradation testings showed that the double layer coating (PEO-CaP) has significantly improved the initial degradation resistance of the metal. Localized degradation was not evident on the PEO-CaP coated metal even after 72 h exposure to simulated body fluid (SBF).

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1. Introduction

Inorganic phosphate-based and silicate-based coatings have been widely studied for reducing the degradation rate of magnesium and its alloys for their potential applications in bone fixation implants [1–7]. Plasma electrolytic oxidation (PEO) and electrodeposition methods are the two common techniques used for the inorganic coatings [1–3,5–7].

In general, PEO technique produces a hard, thick and well adherent film on metallic materials [8]. Recent studies have shown that PEO coatings on magnesium and its alloys have improved their degradation resistance in simulated body fluid (SBF) [3,7]. However, due to the inherent porous nature of the PEO coatings, their performance for a relatively longer period of time in body fluid is questionable. In fact, Liang et al. [9] reported that a PEO coating on a magnesium alloy exhibited only short-term protection in chloride-containing solution. The aggressive chloride ions, present also in body fluid, penetrate through the pores and attack the inner compact layer, which is reported to be MgO [10]. A second coating layer to seal the PEO outer porous layer is necessary to produce implants with acceptable service life.

Calcium phosphate (CaP) has been widely used in biomedical applications due to its biocompatibility, osseointegration and low degradation [11]. Hence, this inorganic material could make a suitable sealing layer on the porous PEO coating. Recently, Liu et al.

[4] carried out chemical deposition of CaP on PEO coated pure magnesium. They observed that the morphology of the CaP coating consisted of two regions, i.e., flake-like and porous structures, which indicate incomplete sealing of the PEO pores. This could be due to the relatively slow coating method on a degrading material. Although the authors reported improvement in the degradation resistance, the corrosion current density (i_{corr}) (calculated based on the cathodic curves) suggests that the improvement is not highly significant (PEO coated = $10 \mu\text{A}/\text{cm}^2$ and PEO-CaP coated $5 \mu\text{A}/\text{cm}^2$). An electrodeposition method could be a more suitable technique to coat CaP on the PEO layer for achieving a complete coverage of the pores. In the electrodeposition method, the material is held at a cathodic potential and hence there will be less dissolution of magnesium as compared to that of the chemical method, during the coating process.

In this work, a silicate-based layer was coated on pure magnesium using the PEO method and then CaP was coated using the electrodeposition method. The *in vitro* degradation behaviour of the dual layer (PEO-CaP) coated material was tested using electrochemical methods in simulated body fluid.

2. Experimental procedure

Pure magnesium (99.9 wt%) was used as a base material in this study. PEO coating was carried out in an electrolyte containing 2 g/l KOH and 7 g/l Na_2SiO_3 . A pulsed constant-current method, i.e., 30 mA/cm², 2 ms/18 ms pulse on/off time, was applied for

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20 min with a final voltage of 483 ± 2 V. An electrodeposition method, i.e., pulsed potential (-3 V) with a duty cycle of 35% [6] for 60 min, was used to coat CaP on the PEO coated metal. The CaP coating solution consisted of 0.1 M $\text{Ca}(\text{NO}_3)_2$ and 0.06 M of $\text{NH}_4\text{H}_2\text{PO}_4$. The PEO and PEO-CaP coatings were characterized using scanning electron microscopy (SEM) and Fourier Transform Infrared (FTIR) Spectroscopy (PerkinElmer Spectrum 100). The coating thickness was measured using a DualScope[®] coating thickness gauge.

In vitro degradation studies were carried out in a simulated body fluid (SBF) maintained at a physiological pH value of 7.4 and temperature of 37 ± 0.5 °C. The SBF composition and the experimental set-up used in this study can be found elsewhere [12]. Electrochemical impedance spectroscopy (EIS) tests were performed at the open circuit potential with AC amplitude of 5 mV over the frequency range of 10^5 Hz to 10^{-2} Hz. Potentiodynamic polarization tests were performed at a scan rate of 0.5 mV/s.

3. Results and discussion

The thickness of the PEO coating was measured to be 24 ± 3 μm . After the electrochemical deposition of CaP, the dual layer coating thickness was 37 ± 4 μm . The SEM micrographs of the PEO and PEO-CaP coatings are shown in Fig. 1(a–d). The PEO coating exhibited a rough surface (Fig. 1a). A higher magnification of the coating revealed porous structures (Fig. 1b). However, the PEO-CaP coating showed a flat morphology with some CaP particles protruding outside the surface (Fig. 1c). A higher magnification revealed aggregation of thin flat CaP particles (Fig. 1d). There was no evidence of the underneath porous PEO layer, which suggests complete coverage by CaP coating. Fig. 2 shows the FTIR spectra of PEO and PEO-CaP coated samples. The PEO coating exhibited strong peaks at 970 and 870 cm^{-1} corresponding to silicate [13,14], and the PEO-CaP coating showed strong peaks at 1130,

1150 and 980 cm^{-1} corresponding to phosphate [15]. The absence of silicate peaks for the PEO-CaP coated samples further confirms the dense coating of CaP. Based on our previous work [2], it can be suggested that the CaP coated formed is dicalcium phosphate dihydrate ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$).

The Nyquist plots of the bare metal and the coated samples after 2 h exposure to SBF are shown in Fig. 3a. As expected, the pure magnesium, which is prone to general and localized degradation, showed two capacitance loops (one at high frequency and another at a mid-frequency – suggesting partial protection) and an inductive loop at low frequency (indicating pitting corrosion) [16,17]. Both the coated samples (PEO and PEO-CaP), however, exhibited a large single capacitive loop suggesting a better performance of the coatings in SBF. Importantly, there was no sign of inductive loop for both the coated samples indicating that the samples did not undergo localized degradation. The

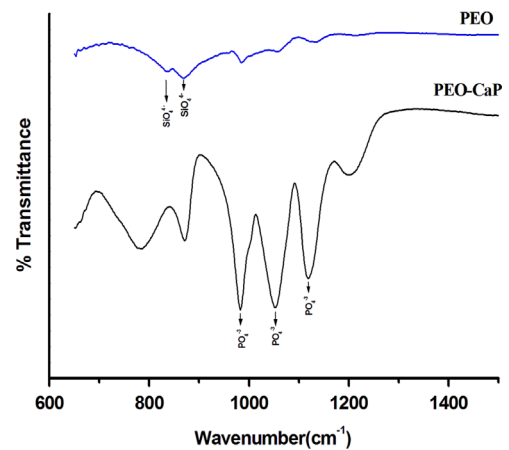


Fig. 2. FTIR spectra of PEO and PEO-CaP coatings on pure magnesium.

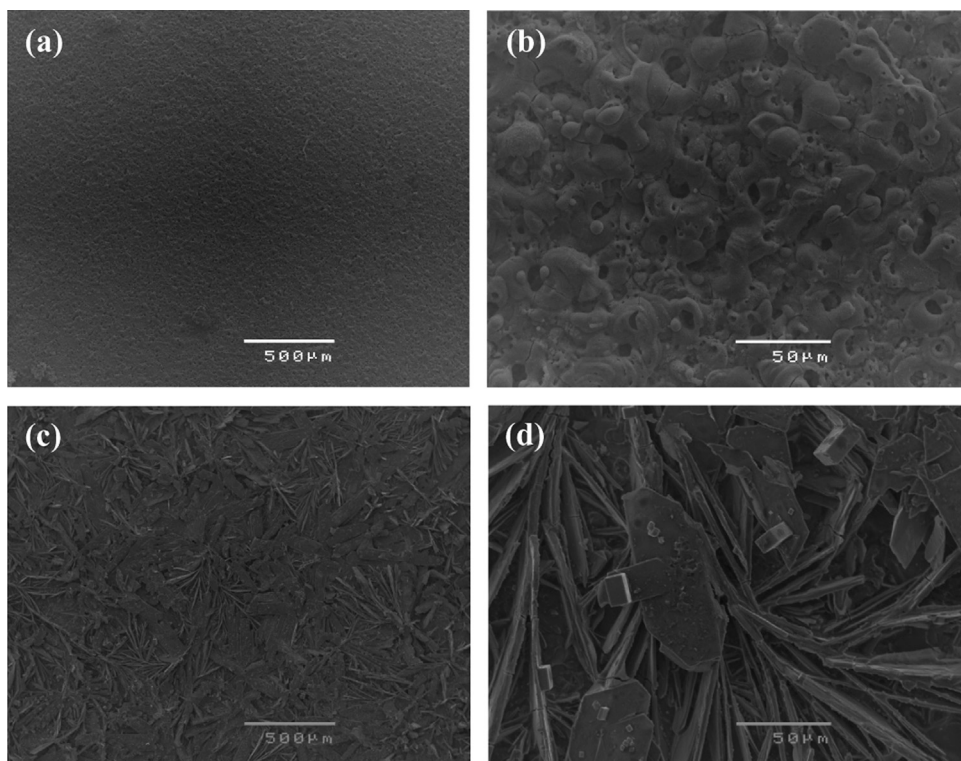


Fig. 1. SEM micrographs of the coatings on pure magnesium: (a and b) PEO coating, and (c and d) PEO-CaP coating.

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