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A preliminary study of calcium containing plasma electrolytic oxidation coatings on AM50 magnesium alloy

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Abstract

Plasma electrolytic oxidation coatings were produced from potassium hydroxide (KOH) and calcium hydroxide (Ca(OH)₂) based electrolytes containing sodium phosphate (Na₃PO₄) under identical processing conditions on AM50 magnesium alloy. The coating obtained from the Ca(OH)₂ electrolyte was relatively thin and was having a smooth surface compared to the coating from the KOH electrolyte. XRD analyses showed that both the coatings were constituted with magnesium phosphate and magnesium oxide. However, the EDS studies revealed that the coating obtained from the (Ca(OH)₂) electrolyte contained calcium in the order of 10 at.%. Corrosion behaviour assessment by electrochemical impedance spectroscopy showed that the calcium containing PEO coating offered a better corrosion resistance than the coating obtained from KOH electrolyte in the long term tests performed in 0.1 M NaCl solution. The better corrosion resistance and higher stability of the calcium containing coating is attributed to its microstructural morphology and phase composition. The results suggest that this calcium-containing coating can be useful for bio-medical applications and further detailed investigations are in progress.

Magnesium alloys owing to their light weight, excellent castability and good mechanical properties are employed for applications in automotive and electronic industries [1]. Bio-degradable nature of magnesium alloys makes them an attractive candidate for implant materials [2]. The corrosion resistance of magnesium alloys is of concern and a variety of surface modification technologies is contemplated for enhancing their service life and durability, especially in aggressive environments [3-5]. In recent times, plasma electrolytic oxidation (PEO) has been the most preferred process for the treatment of magnesium alloys [6]. The majority of the research papers published on the PEO coating of magnesium alloys are based on either ammonium hydroxide or potassium hydroxide electrolytes [7-10]. For the bio-medical applications, it is significant to prepare the coating containing Ca and P, which provides better biological compatibility and biological activity. Wen et al., have recently reported a cathodic hydroxyapatite deposition procedure on magnesium alloys [11]. As the PEO coatings offer a much superior corrosion resistance than the conversion coatings or cathodically deposited coatings, in the current work we have made an attempt to produce a PEO coating containing calcium and/or calcium compounds from a calcium hydroxide (Ca(OH)₂) based electrolyte on an AM50 magnesium alloy and compare the corrosion performance with that of a coating obtained from a conventional KOH based electrolyte with the same level of phosphate ions under identical processing conditions. A successful development of a calcium containing coating in this preliminary investigation shall lead us to explore this coating further on the bio-degradable magnesium alloys for implant applications.

Specimens of size 15 mm × 15 mm × 4 mm of a cast AM50 magnesium alloy were used as substrate for the PEO processing. They were ground successively with 500, 800, 1200 and 2500 grit emery sheets and cleaned with acetone before the PEO treatment. The plasma electrolytic oxidation process was carried out using a pulsed DC electrical source with a pulse ratio of $t_{on} : t_{off} = 2 \text{ ms} : 20 \text{ ms}$ in two alkaline electrolytes viz., (a) 2 g/L KOH + 10 g/L Na₃PO₄ and (b) 2 g/L Ca(OH)₂ + 10 g/L Na₃PO₄. The coatings were obtained at a constant current density of 30 mA·cm⁻² for 15 minutes. The temperature of the electrolytes was always kept at 10 ± 2°C by a water cooling system. The surface morphology of the PEO coated specimens was examined in a Cambridge stereoscan scanning electron microscope (SEM), and X-ray diffraction (XRD) was performed using a Bruker X-ray diffractometer with Cu-Kα radiation to determine the phase composition. The elemental composition of the PEO coated specimens was assessed in a Zeiss Ultra 55 scanning electron microscope equipped with an energy dispersive X-ray spectrometer (EDS).

Electrochemical impedance spectroscopy (EIS) tests were carried out using a Gill AC potentiostat/frequency response analyser with a three electrode cell set-up. The measurements were performed at open circuit potential with an AC amplitude of 10 mV over a frequency range of 0.01 Hz to 30 kHz on the PEO coated specimens exposed to 0.1 M NaCl solution for different durations viz., 0.5, 2, 5, 10, 25 and 50 h. As the calcium hydroxide coating survived the 50 h EIS test, the test was extended up to 150 h to understand its long term stability in this corrosive environment.

The micrographs showing the surface morphology of the specimens PEO coated in the KOH and Ca(OH)₂ electrolytes are presented in **Figures 1(a) and (b)**, respectively. Typical porous structure, characteristic of PEO coatings, is evident in both these specimens. The pore diameters were in the range of 1 – 10 μm in both the coatings. However, the coating from the KOH electrolyte seemed to have a higher pore density compared to the coating from the Ca(OH)₂ electrolyte. Further, the KOH coating had a higher roughness value ($R_a = 3.7 \pm 0.3 \mu\text{m}$) compared to the coating obtained from Ca(OH)₂ electrolyte ($R_a = 2.9 \pm 0.2 \mu\text{m}$). Thickness measurements with an eddy current probe showed values of $56 \pm 6 \mu\text{m}$ for the coatings obtained from KOH electrolyte and $38 \pm 5 \mu\text{m}$ for the coatings produced from Ca(OH)₂ electrolyte. The scanning electron micrographs showing the cross-section of coatings from KOH and Ca(OH)₂ electrolytes in **Figures 1(c) and 1(d)**, respectively, corroborate the eddy current probe measurements. The KOH coating was found to contain numerous cracks in the cross-section, whilst the Ca(OH)₂ coating was observed to have a relatively more compact structure. It is pertinent to point out that the final voltage at the end of the 15 minutes treatment in both the electrolytes was around 490 V, despite the fact that the breakdown voltages were slightly different with values of 245 V and 260 V in the KOH and Ca(OH)₂ electrolytes, respectively. The voltages in the PEO processing is governed by the composition of electrolyte, pH, conductivity, the thickness of the layer that is grown on the surface of magnesium substrate and its compactness. Thus, even though the coating obtained from the Ca(OH)₂ is relatively thinner, this specimen registered the same voltage as the KOH coated specimen, on account of the lower conductivity of the Ca(OH)₂ electrolyte and also due to the more compact coating.

The XRD spectra of the two coatings are presented in **Figure 2**. It can be observed that both the KOH electrolyte coating (Figure 2a) and the Ca(OH)₂ electrolyte coating (Figure 2b), were constituted with MgO and Mg₃(PO₄)₂ phases. Characteristic peaks corresponding to the magnesium substrate were also observed in both the cases, as the measurements were made in incident mode. EDS analysis was performed on both

the coated specimens to assess the elemental distribution in the coated surface. The EDS spectra of the specimens produced from KOH and $\text{Ca}(\text{OH})_2$ electrolytes are shown in **Figures 3a and 3b**, respectively. The oxygen and phosphorous contents in both the coatings were nearly the same. However, the magnesium content was lower in the coating obtained from $\text{Ca}(\text{OH})_2$ electrolyte, and further this coating contained close to 10 at.% calcium. It should be pointed out that in both the coated specimens a broad region was observed in the range $2\theta = 20$ to 35° in the XRD spectra, and interestingly no calcium containing compounds could be identified in the coating obtained from $\text{Ca}(\text{OH})_2$ electrolyte. The observation that there was an appreciable amount of calcium in the coating as revealed by EDS analysis, suggesting the possibility of the presence of calcium containing phase(s), possibly $\text{CaH}(\text{PO}_4)$ and/or CaO in amorphous form. The other possibility is that the replacement Mg with Ca in the lattice might have resulted in $\text{Mg}_2\text{Ca}(\text{PO}_4)_2$ phase in this coating. However, it could not be ascertained by XRD measurements at this juncture. Yao et al., have reported similar observations in their attempt to produce calcium containing PEO coatings in an electrolyte containing sodium hydroxide, sodium hexametaphosphate and calcium hypophosphite [12].

The electrochemical corrosion behaviour of the magnesium alloy substrate PEO coated in the KOH and $\text{Ca}(\text{OH})_2$ electrolytes was assessed by EIS tests in 0.1 M NaCl solution, and the results are presented in the form of Bode plots in **Figures 4a and 4b**, respectively. It can be observed in Figure 4a that the corrosion resistance of the specimen coated in KOH electrolyte dropped from an initial value of $6 \times 10^5 \Omega\cdot\text{cm}^2$ (after 0.5 h of exposure) to around $5 \times 10^4 \Omega\cdot\text{cm}^2$ (after 5 h of exposure), and remained stable at this value up to 10 h of exposure. However, upon further exposure, the coating was found to fail as evidenced by the drop in the resistance value to around $6 \times 10^3 \Omega\cdot\text{cm}^2$ after 25 h and further down to $5 \times 10^3 \Omega\cdot\text{cm}^2$ after 50 h of exposure. The Optical macrograph of the 50 h EIS tested specimen shown in **Figure 5(a)** reveals the localized damage on the coated surface, and the higher magnification SEM micrograph presented in **Figure 5(b)** demonstrates the pit morphology and also the extent of corrosion damage. The phenomenon of this localized damage after 25 h of exposure was also brought out in the EIS plots which showed inductive loops in the Nyquist plots.

In the case of the specimen coated in $\text{Ca}(\text{OH})_2$ electrolyte the corrosion behaviour in the initial stages of exposure was similar to that observed for the specimen coated in KOH electrolyte, but with a slightly higher initial corrosion resistance values viz., $8 \times 10^5 \Omega\cdot\text{cm}^2$ after 0.5 h and $4 \times 10^5 \Omega\cdot\text{cm}^2$ after 5 h of exposures. Further, in the tests after prolonged exposures viz., 5, 10, 25 and 50 h, the rate of degradation was much slower, and the specimens remained stable without showing any signs of significant electrochemical degradation. From the Bode plots, it was found that this specimen had a resistance of around $1.5 \times 10^5 \Omega\cdot\text{cm}^2$ even after 50 h of exposure, and the surface of the specimen was found to be intact without any corrosion damage in the SEM observations. As this coating survived 50 h of EIS test without any significant degradation, EIS tests were performed after 100 h and 150 h of exposures. Even though there was a drop in the corrosion resistance values to around $6 \times 10^4 \Omega\cdot\text{cm}^2$, the coating was found to remain stable even after 150 h of exposure in this corrosive environment. There was no macroscopic corrosion damage on the surface even after 150 h of exposure to the corrosive environment, as can be observed from the optical macrograph in **Figure 5c**. The higher magnification scanning electron micrograph shown in **Figure 5d** reveals that there was some degradation on the surface and also inside the pores. In summary, the PEO coating obtained from the $\text{Ca}(\text{OH})_2$ electrolyte, despite being thinner than the KOH coating, remained very stable in the corrosive environment, which is attributed to the compact microstructural features. In addition, the

chemical/phase composition of this coating viz., the calcium containing compounds, could have also contributed to the higher corrosion resistance and stability of this coating. Further work is underway for a better understanding of this phenomenon and it extended to bio-degradable magnesium alloys for potential bio-medical applications.

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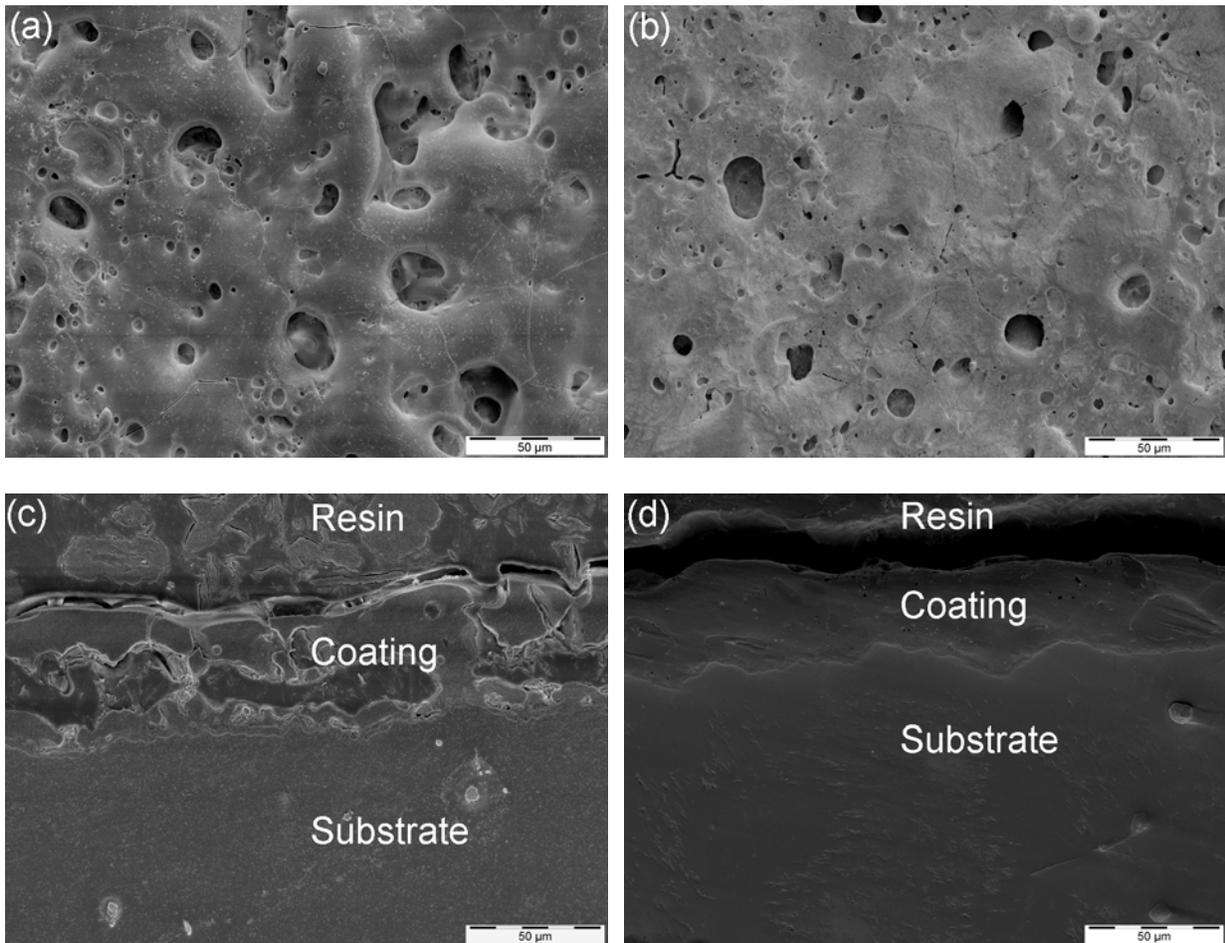


Figure 1 Scanning electron micrographs showing the surface morphology and cross section of PEO coatings obtained from (a) & (c) KOH electrolyte (b) & (d) $\text{Ca}(\text{OH})_2$ electrolyte

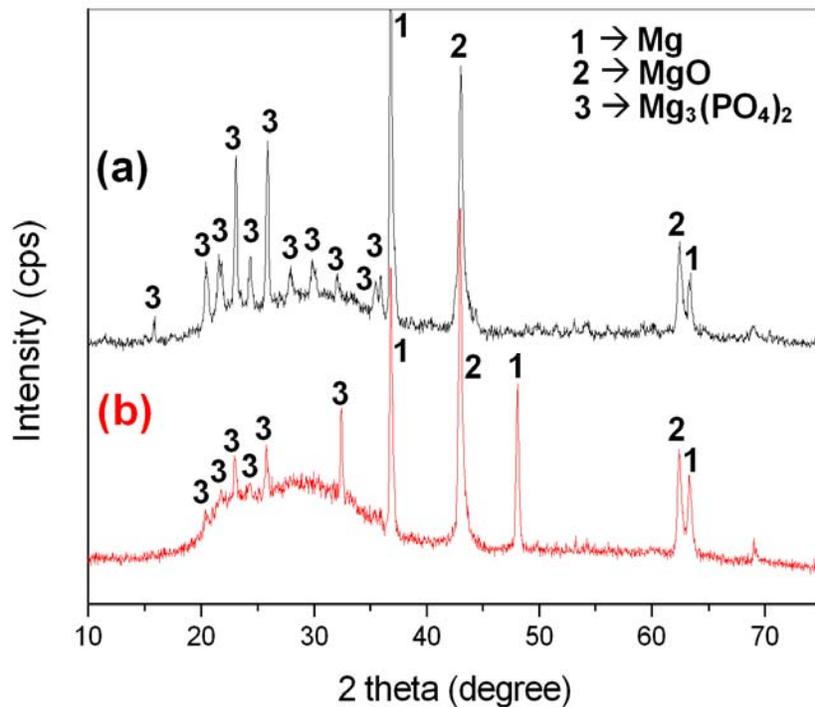


Figure 2 X-ray diffraction spectra of PEO coatings obtained from (a) KOH electrolyte (b) $\text{Ca}(\text{OH})_2$ electrolyte

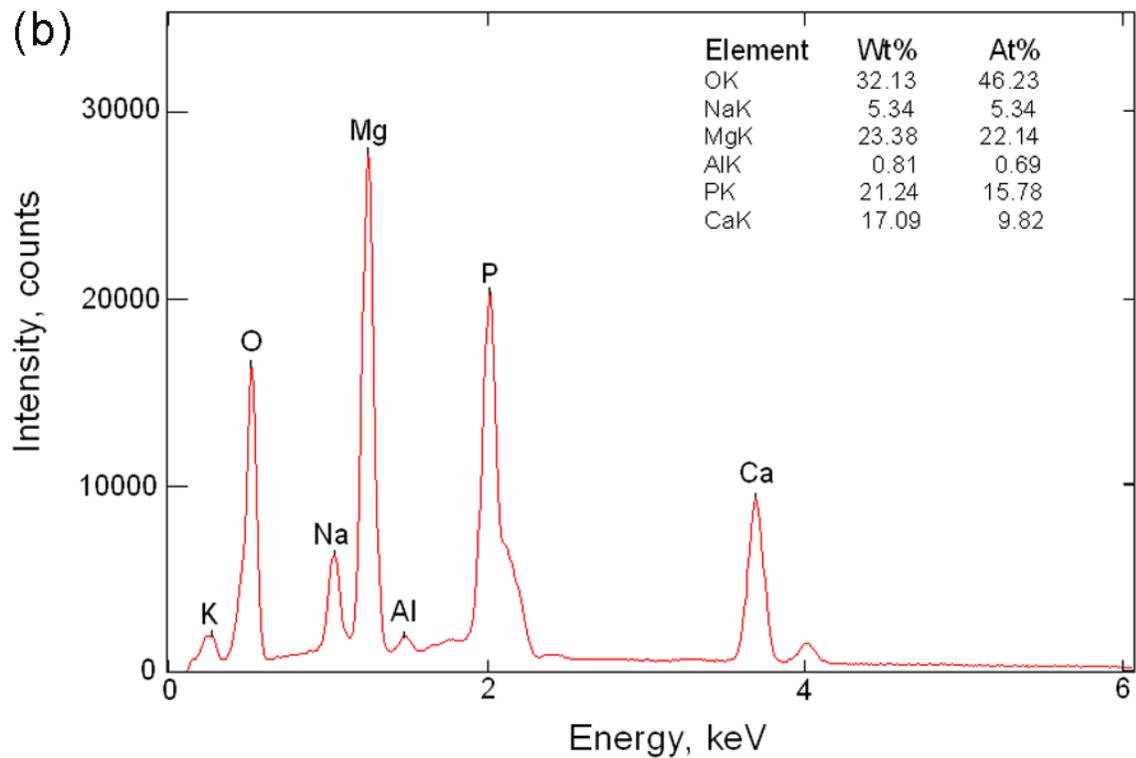
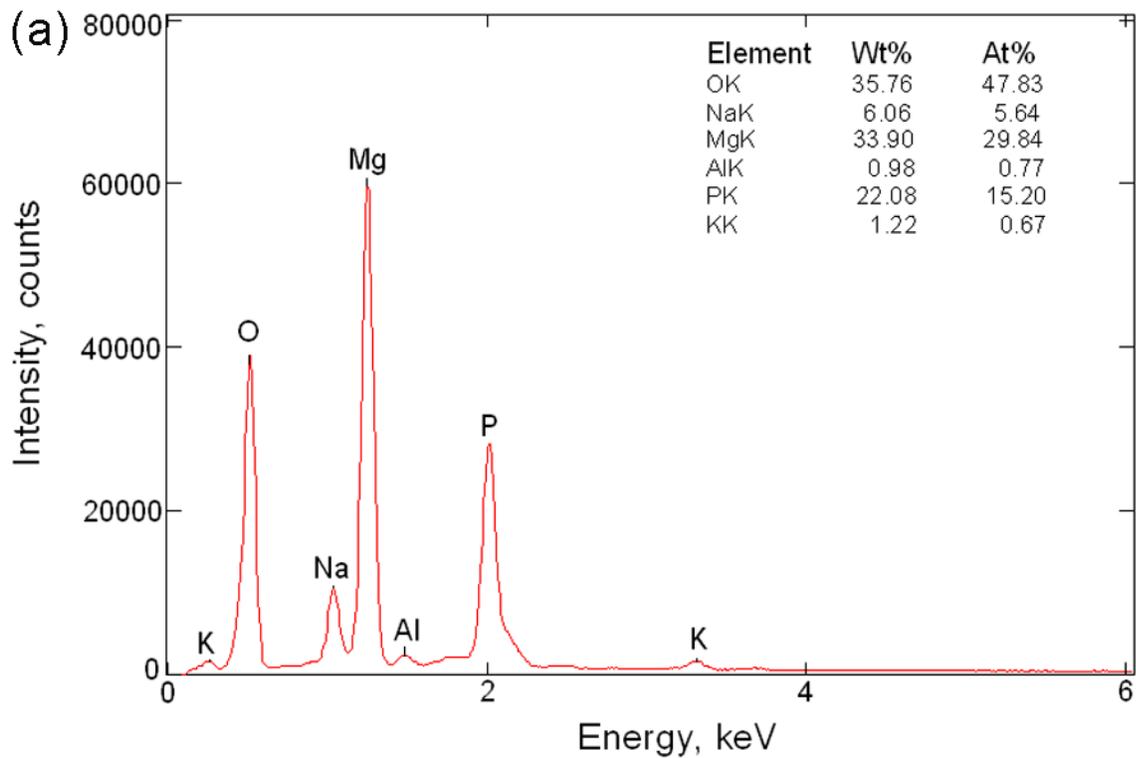


Figure 3 Energy dispersive spectra of the PEO coatings obtained from (a) KOH electrolyte (b) $\text{Ca}(\text{OH})_2$ electrolyte

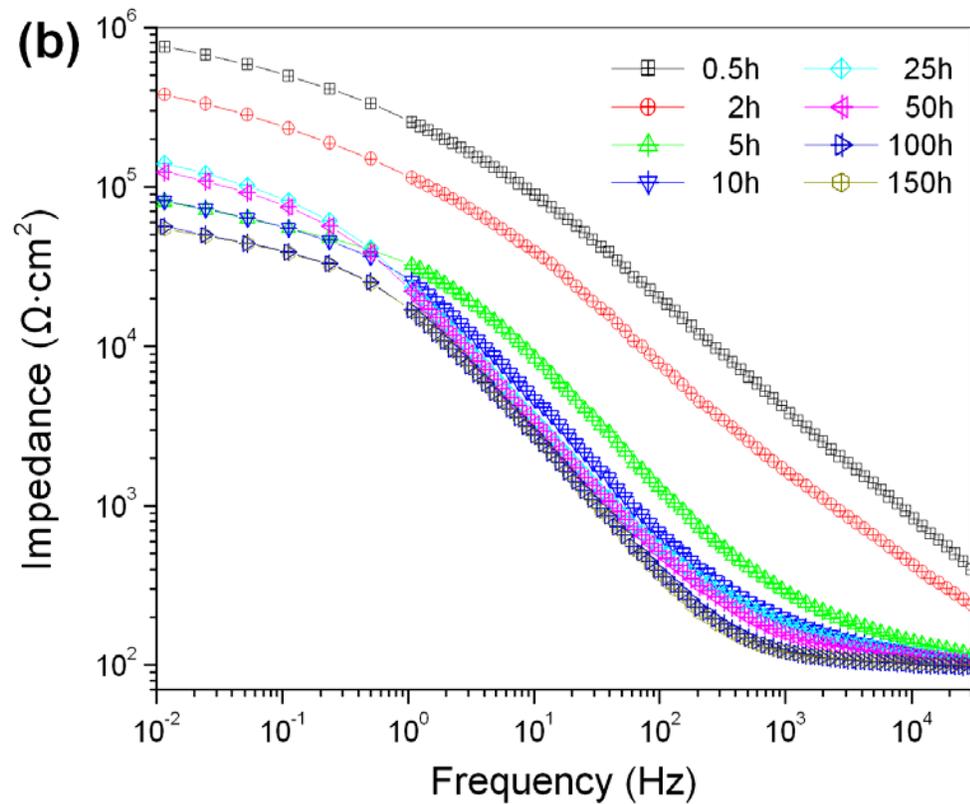
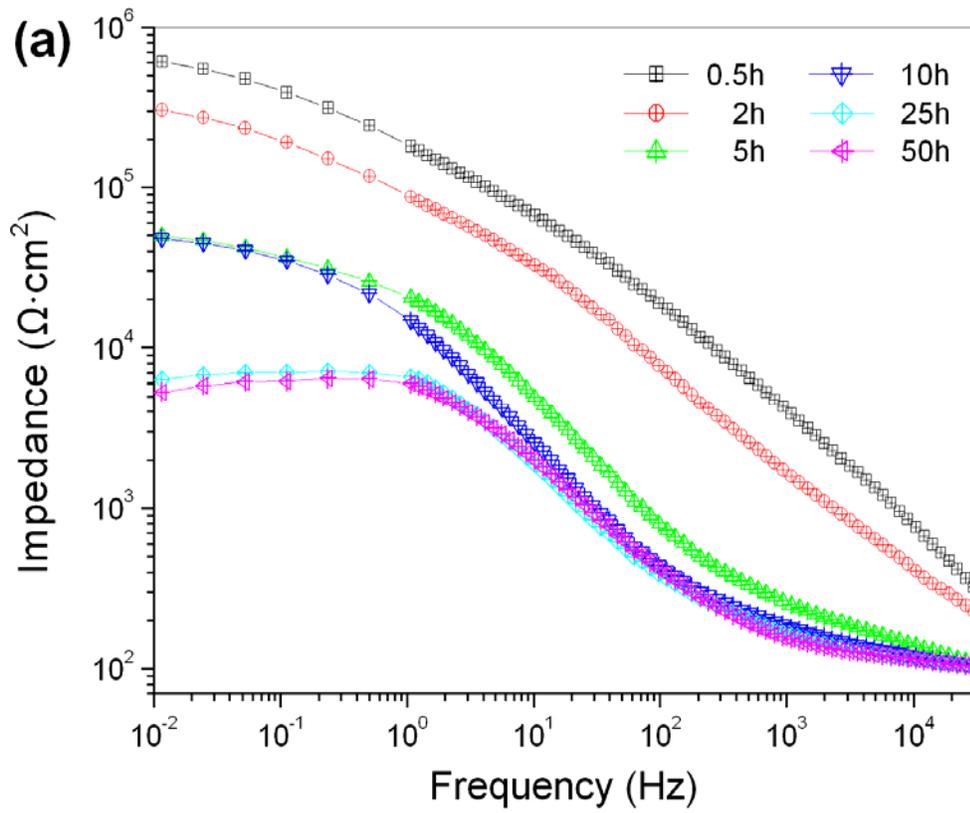


Figure 4 Electrochemical impedance behaviour of magnesium alloy specimens PEO coated in (a) KOH electrolyte and (b) $\text{Ca}(\text{OH})_2$ electrolyte. Test environment: 0.1 M NaCl solution

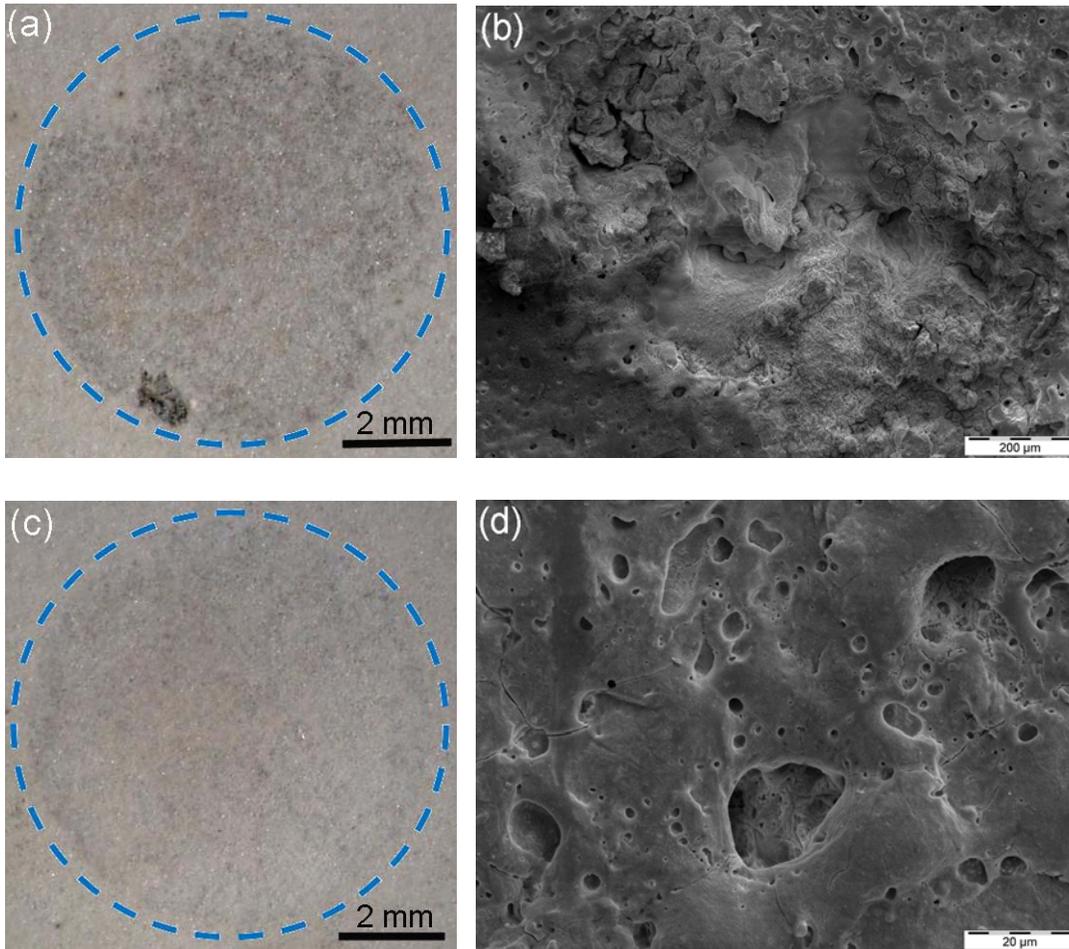


Figure 5 Optical macrographs and scanning electron micrographs of the EIS tested PEO coated specimens

(a)-(b) – Specimen coated in KOH electrolyte – after 50 h of EIS testing

(c)-(d) – Specimen coated in $\text{Ca}(\text{OH})_2$ electrolyte – after 150 h of EIS testing