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LETTER

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

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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. [11] have recently reported a cathodic hydroxyapatite deposition procedure on magnesium alloys. 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 PEO process was carried out using a pulsed DC electrical source with a pulse ratio of $t_{on}:t_{off} = 2:20$ ms in two alkaline electrolytes viz., (a) 2 g/L KOH + 10 g/L Na_3PO_4 and (b) 2 g/L $Ca(OH)_2$ + 10 g/L Na_3PO_4. The coatings were obtained at a constant current density of 30 mA cm^{-2} for 15 min. 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 setup. 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.

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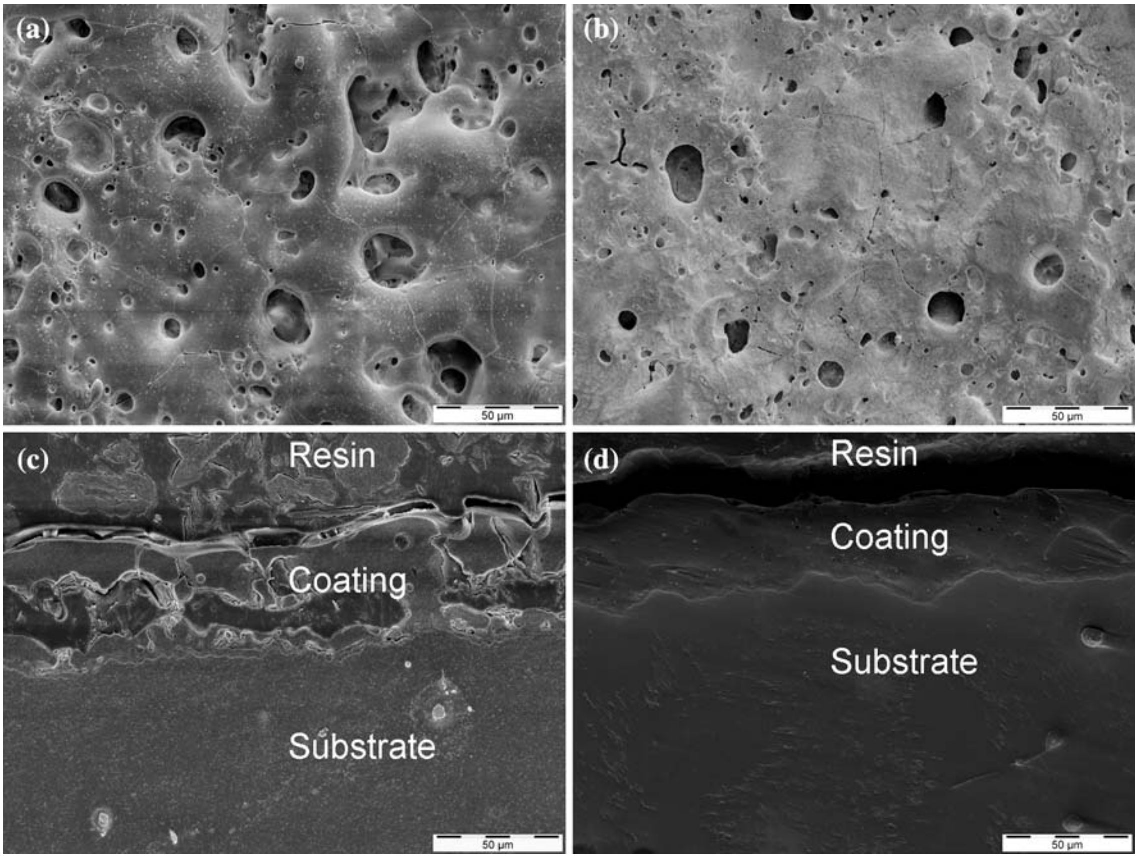


Fig. 1 Scanning electron micrographs showing the surface morphology and cross-section of PEO coatings obtained from **a**, **c** KOH electrolyte and **b**, **d** $Ca(OH)_2$ electrolyte

The micrographs showing the surface morphology of the specimens PEO coated in the KOH and $Ca(OH)_2$ electrolytes are presented in Fig. 1a 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 ($Ra = 3.7 \pm 0.3$ μm) compared to the coating obtained from $Ca(OH)_2$ electrolyte ($Ra = 2.9 \pm 0.2$ μm). Thickness measurements with an eddy current probe showed values of 56 ± 6 μm for the coatings obtained from KOH electrolyte and 38 ± 5 μm 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 Fig. 1c and 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-min treatment in both the electrolytes was around 490 V, despite the fact that the breakdown voltages were slightly different with values of 245 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 Fig. 2. It can be observed that both the KOH electrolyte coating (Fig. 2a) and the $Ca(OH)_2$ electrolyte coating (Fig. 2b), were constituted with MgO and $Mg_3(PO_4)_2$ 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 $Ca(OH)_2$ electrolytes are shown in Fig. 3a and b, respectively. The oxygen and phosphorous contents in both the coatings were

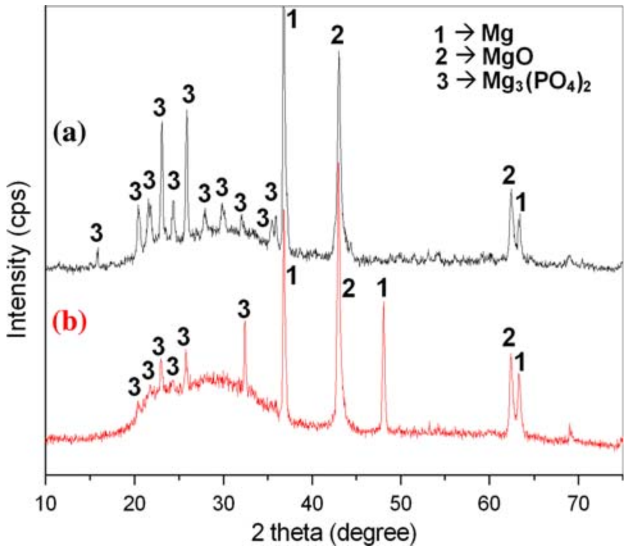
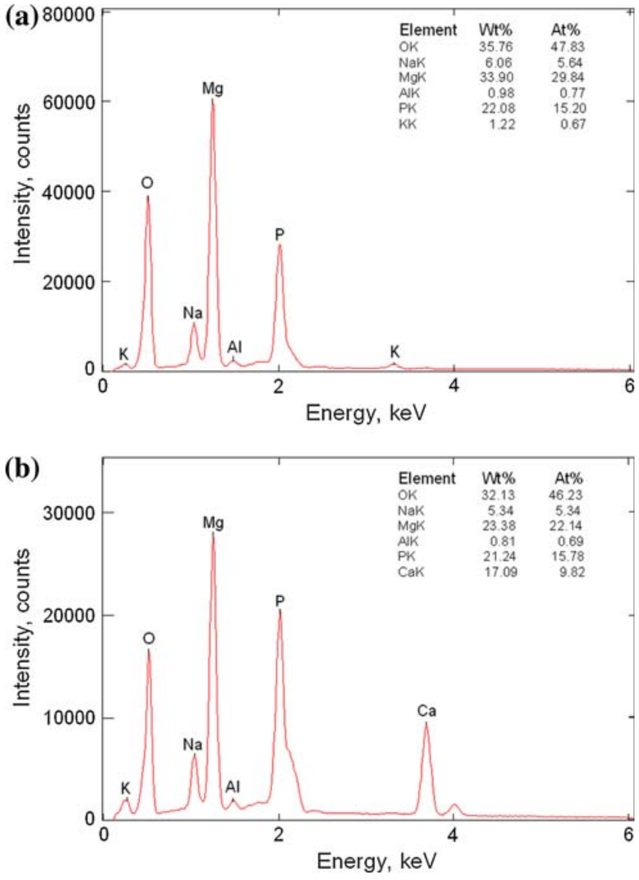


Fig. 2 X-ray diffraction spectra of PEO coatings obtained from (*a*) KOH electrolyte (*b*) $Ca(OH)_2$ electrolyte



Element	Wt%	At%
OK	35.76	47.83
NaK	6.06	5.64
MgK	33.90	29.84
AlK	0.98	0.77
PK	22.08	15.20
KK	1.22	0.67

Element	Wt%	At%
OK	32.13	46.23
NaK	5.34	5.34
MgK	23.38	22.14
AlK	0.81	0.69
PK	21.24	15.78
CaK	17.09	9.82

Fig. 3 Energy dispersive spectra of the PEO coatings obtained from **a** KOH electrolyte and **b** $Ca(OH)_2$ electrolyte

nearly the same. However, the magnesium content was lower in the coating obtained from $Ca(OH)_2$ 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 $2\varphi = 20°$ to 35° in the XRD spectra, and interestingly no calcium containing compounds could be identified in the coating obtained from $Ca(OH)_2$ electrolyte. The observation that there was an appreciable amount of calcium in the coating as revealed by EDS analysis suggested the possibility of the presence of calcium containing phase(s), possibly $CaH(PO_4)$ and/or CaO in amorphous form. The other possibility is that the replacement Mg with Ca in the lattice might have resulted in $Mg_2Ca(PO_4)_2$ phase in this coating. However, it could not be ascertained by XRD measurements at this juncture. Yao et al. [12] have reported similar observations in their attempt to produce calcium containing PEO coatings in an electrolyte containing sodium hydroxide, sodium hexametaphosphate and calcium hypophosphite.

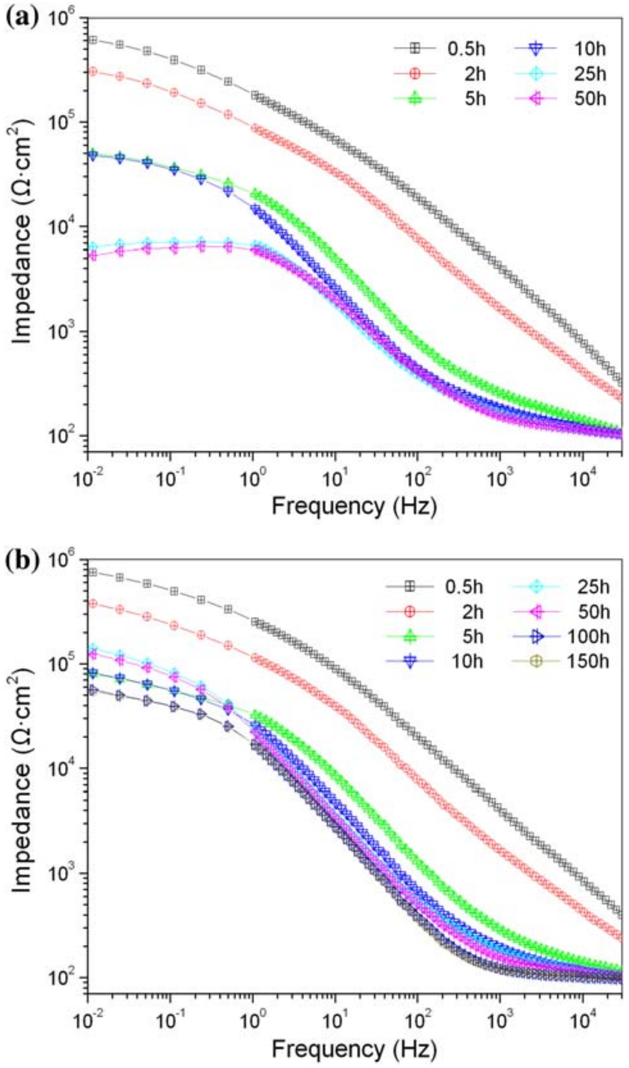


Fig. 4 Electrochemical impedance behaviour of magnesium alloy specimens PEO coated in **a** KOH electrolyte and **b** $Ca(OH)_2$ electrolyte (test environment: 0.1 M NaCl solution)

The electrochemical corrosion behaviour of the magnesium alloy substrate PEO coated in the KOH and $Ca(OH)_2$ electrolytes was assessed by EIS tests in 0.1 M NaCl solution, and the results are presented in the form of Bode plots in Fig. 4a and b, respectively. It can be observed in Fig. 4a that the corrosion resistance of the specimen coated in KOH electrolyte dropped from an initial value of 6×10^5 Ω cm^2 (after 0.5 h of exposure) to around 5×10^4 Ω 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 6×10^3 Ω cm^2 after 25 h and further down to 5×10^3 Ω cm^2 after 50 h of exposure. The optical macrograph of the 50-h EIS-tested specimen shown in Fig. 5a reveals the localised damage on the coated surface, and the higher magnification SEM micrograph presented in Fig. 5b demonstrates the pit morphology and also the extent of corrosion damage. The phenomenon of this localised 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 $Ca(OH)_2$ 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., 8×10^5 Ω cm^2 after 0.5 h and 4×10^5 Ω 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 1.5×10^5 Ω 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 and 150 h of exposures. Even though there was a drop in the corrosion resistance values to around 6×10^4 Ω 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 Fig. 5c. The higher magnification scanning electron micrograph shown in Fig. 5d reveals that there was some degradation on the surface and also inside the pores. In summary, the PEO coating obtained from the $Ca(OH)_2$ 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

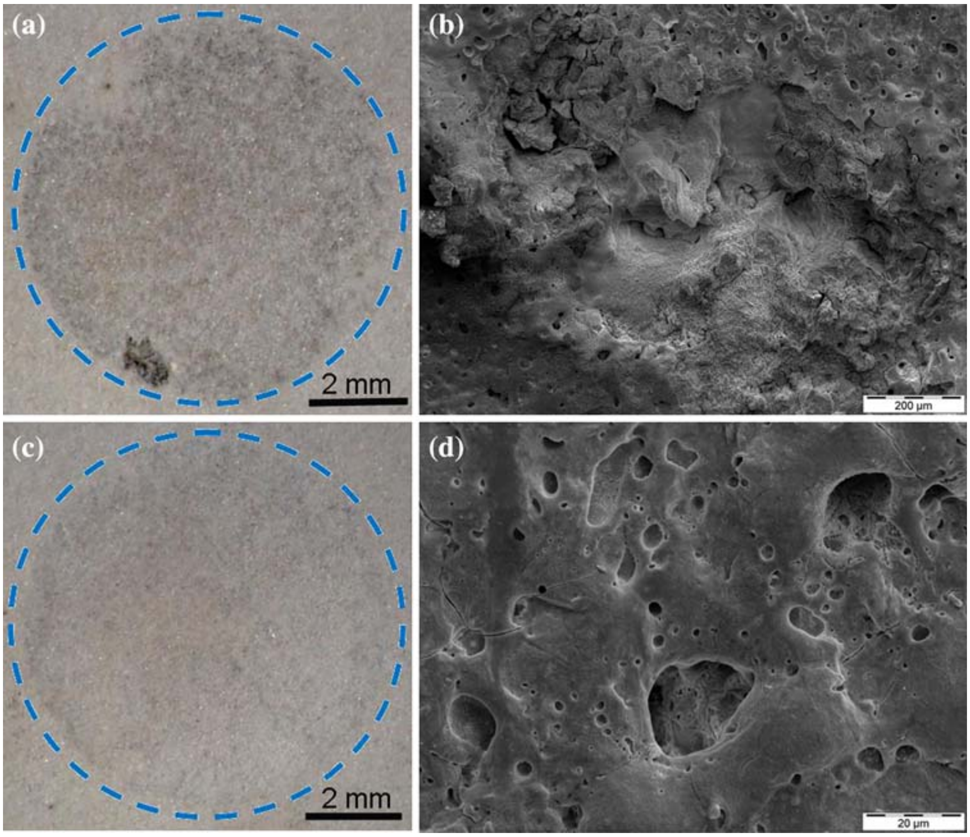


Fig. 5 Optical macrographs and scanning electron micrographs of the EIS-tested PEO-coated specimens. **a**, **b** Specimen coated in KOH electrolyte—after 50 h of EIS testing. **c**, **d** Specimen coated in $Ca(OH)_2$ electrolyte—after 150 h EIS testing

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 is extended to bio-degradable magnesium alloys for potential bio-medical applications.

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