



Short communication

Fabrication and characterization of hydrophobic microarc oxidation/poly-lactic acid duplex coating on biodegradable Mg–Ca alloy for corrosion protection



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ABSTRACT

A double layer coating was prepared on biodegradable Mg–Ca alloy by microarc oxidation (MAO) followed by dip coating process. The results showed that hydrophobic poly-lactic acid (PLA) as a top layer with thickness of 37–40 μm provides significantly higher corrosion resistance in terms of corrosion current and charge transfer resistance, while the MAO coating alone (8–10 μm) exhibits lower corrosion resistance. However, both coating scenarios demonstrate better corrosion resistance compared with the uncoated Mg–1.34wt% Ca alloy. Contact angle (CA) measurements showed that the double layer MAO/PLA coated sample presented hydrophobic properties with a CA of 95.30° which is higher than that of MAO coating (CA = 22.90°). The results also exhibit that hydrophobic PLA is effectively seals the porosities of the MAO layer providing effective protection for the biodegradable Mg alloy in the simulated body fluid (SBF) environment and improving the corrosion protection capacity of the MAO surface treatment.

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Biomedical applications (such as orthopedic, cardiovascular and tissue engineering) of magnesium and its alloys are hindered by their poor corrosion resistance compared to other metals such as titanium alloys, cobalt chromium alloys and stainless steels [1]. Coatings are considered as an effective method to enhance the poor corrosion resistance and to control the degradation rate of Mg alloys in physiological environments. Typical surface modification techniques include electrodeposition (ED), physical vapour deposition (PVD) [2], laser cladding, dip coating [2], ion implantation [3] and chemical conversion coatings [4]. Micro-arc oxidation (MAO) is a chemical conversion process and is one of the most appropriate method for Mg alloys owing to its excellent abrasive resistance, enhanced corrosion resistance and high bonding strength to the

substrate [3,5–7]. However, MAO coating is not able to provide long term corrosion protection for Mg alloys in physiological environment owing to its porous structure [5,8]. Therefore, polymer coating have been employed to seal the pores of the MAO coating on the surface of Mg alloys [3]. In this view, dip coating which is a suitable and relatively simple technique is used in this work for applying the poly-lactic acid (PLA) coating as an overlayer to seal the pores and cracks of the MAO layer and to prevent its premature failure. PLA is a naturally biodegradable material with biological properties suitable for the production of bioabsorbable orthopedic implants and micro-devices for intravenous controlled release of drugs [9,10]. Thus, in the present study, a combination of MAO and PLA polymer coating was applied to provide a double-layer coating in order to improve the coating adhesion to the substrate and to enhance the corrosion resistance of the Mg–Ca alloy in physiological conditions. Therefore, samples of Mg–1.34wt% Ca alloy with dimensions of 15 mm \times 10 mm \times 10 mm were used as substrates. For MAO coating, a sodium aluminate-based aqueous solution consisted of 3 g/L KF and 10 g/L NaAlO₂ was employed as an

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electrolyte. A flat stainless-steel plate and the Mg-1.34Ca alloy sample were used as a counter electrode and working electrode, respectively. MAO was performed at a constant current density of 5 A/cm² at 15 °C for 60 min using a DC pulse power supply and a stirring and cooling systems. A pulse frequency was fixed at 100 Hz and the duty cycle (the ratio between pulse width and pulse repetition time) was 6%. Prior to the dipping of MAO coated sample, 6 wt.% PLA pellets ($M_w = 148,000$ g/mol, Minneapolis, MN) were dissolved in dichloromethane (DCM; CH₂Cl₂, Sigma–Aldrich, UK) by stirring for 2 h at room temperature. The samples were dipped for 3 times and withdrawn at a constant speed of 40 mm/min to form a uniform coating and then dried at room temperature. X-ray diffractometry (Siemens-D500) was used for phase identification using Cu-K α radiation generated at 40 kV and 35 mA. Microstructural observation was performed using a scanning electron microscope (SEM; JEOL JSM-6380LA). The details of the bonding strength tests and bio-corrosion experiments can be found in our previous paper [11]. A three-electrode cell was used for potentiodynamic polarization (PARSTAT 2263) and electrochemical impedance spectroscopy (EIS) tests in simulated body fluid (SBF) solution according to [11]. The SEM micrographs and EDX analysis in (Fig. 1a,d) show the presence of a eutectic lamellar structure composed of Mg₂Ca and α -Mg at the grain boundaries of the Mg–Ca alloy which is consistent with the Mg–Ca phase diagram [12]. The microstructure of the MAO coating is presented in Fig. 1b,e and shows a great amount of porosity and micro-cracks resulting in a rough surface. Formation of such porosity is attributed to the sparking discharge and gas bubbles at the surface of the anode. While crack formation can be related to the thermal stresses resulting from the rapid re-solidification of the molten surface oxide [13]. These pores and micro cracks adsorb corrosion species which deems the coating not very resistant to corrosion. However, after PLA polymer coating, the porous structure of the MAO layer is sealed with a uniform polymeric layer (Fig. 1c,d) to improve the corrosion resistance of the MAO coating. The EDX analysis of the MAO coating showed that it is porous and contains Al, Na, Si, O, and Mg. The high intensity Al element comes from the electrolyte. It reacts with Mg and O to form the MgAl₂O₄ (spinel) porous outer layer. The EDX analysis of the PLA overlayer showed the presence of C and O.

Cross section microstructure shows that the thickness of MAO coating is around 8–10 μ m. This coating was bonded with the Mg–Ca alloy via sintered interlocking. The MAO layer indicated a

bi-layered structure which is consisted of an outer porous layer and a dense inner layer (Fig. 2a). This peculiar structure is a result of the fact that the oxide grows in the MAO treatment in both inwards and outwards directions from the original Mg alloy surface. There is a good agreement between this finding and typical structure of the MAO coatings [13]. In MAO/PLA coating, two-layer structure can be observed which contains a PLA layer with a thickness of 30–35 μ m as the top layer and MAO layer as the underlayer (Fig. 2b). It is also obvious that the PLA uniformly covers and seals the surface of the MAO coating. In this regard, there is a good adhesion between the substrate/coating and no obvious micro-cracks could be detected at the interface of MAO/PLA. The results of bonding strength tests showed that the mono MAO layer presented good bonding strength (23.5 MPa), while, the MAO/PLA coating exhibited lower bonding strength (14.7 MPa). However, compared to the direct PLA coating on the surface of Mg alloy, i.e. without MAO treatment, that had a bonding strength of 2.5 MPa only [14], the bi-layer MAO/PLA coating demonstrated significantly higher bonding strength. This is because the intermediate MAO layer provides good bonding through mechanical interlocking effect.

The XRD patterns of the uncoated sample confirms the SEM/EDS microstructural observations regarding the formation of the Mg₂Ca compound besides α -Mg (Fig. 3a) which is in agreement with the Mg–Ca phase diagram [12]. The pattern of the MAO coated Mg–Ca alloy depicts that this layer consists of MgO and MgAl₂O₄ phases along with α -Mg. The presence of α -Mg peaks in the MAO XRD pattern is due to the porous structure of the MAO layer resulting in the X-rays reaching the Mg alloy surface. However, the presence of MgAl₂O₄ is attributed to the presence of aluminate ions (AlO²⁻ or Al₂O₄⁻) in the electrolyte which react with Mg²⁺ ions at the oxide/electrolyte interface, leading to the formation of MgAl₂O₄ [15]. The duplex coating MAO/PLA samples consist of two intense peaks at $2\theta = 16.68^\circ$ and $2\theta = 18.96^\circ$ which is in agreement with the results of Sacchetin et al. [9]. The contact angle of the uncoated and coated samples showed that the uncoated Mg–Ca sample has a hydrophilic surface with contact angle (CA) of 42.30° (Fig. 3b). However, MAO coating is even more hydrophilic (CA = 22.90°), as the water droplet easily wets and spreads out over the MAO film and quickly penetrate into the sample. In contrast, the double layer MAO/PLA coated sample presents hydrophobic properties with a CA of 95.30°, indicating that the polymer coating over MAO layer can effectively diminish its contact area with the corrosive aqueous

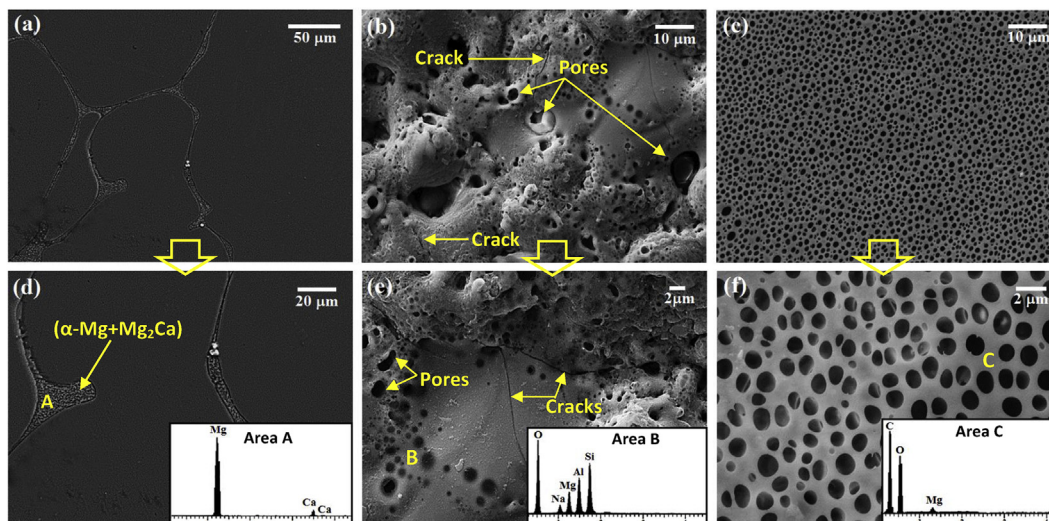


Fig. 1. Surface morphology of (a,d) uncoated Mg–Ca alloy, (b,e) mono-layer MAO coating and (c,f) bi-layer MAO/PLA coating.

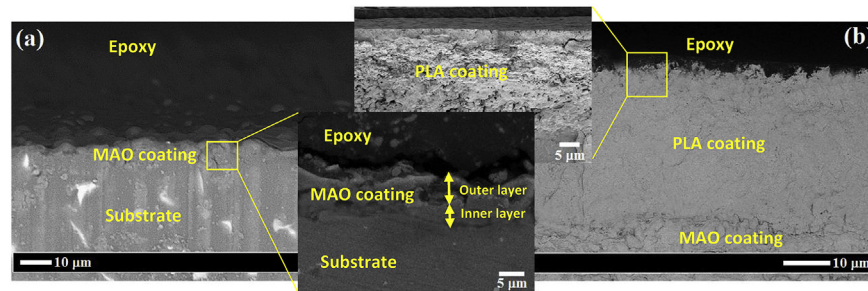


Fig. 2. Cross sectional SEM micrographs of (a) mono-layer MAO coating and (b) bi-layer MAO/PLA coating.

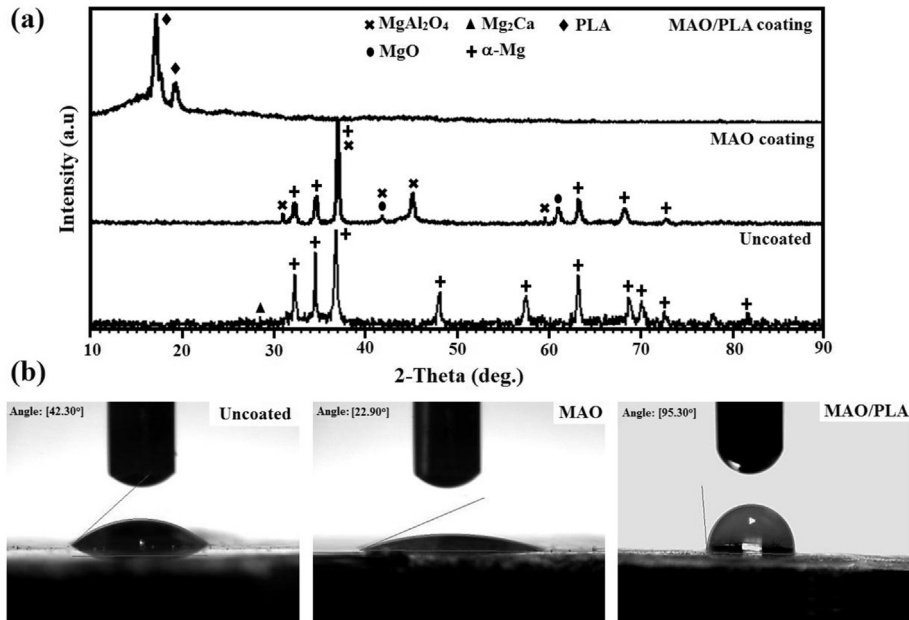


Fig. 3. (a) X-ray diffraction patterns and (b) Images of water contact angle of uncoated, MAO coating and MAO/PLA coating Mg–Ca alloy.

solution, which would result in significant improvement in corrosion resistance.

The electrochemical polarization curves in Fig. 4a show that the corrosion potential (E_{corr}) of the MAO/PLA coated Mg–Ca alloy is $-1530 \text{ mV}_{\text{SCE}}$ which is approximately $256 \text{ mV}_{\text{SCE}}$ higher than that of the uncoated sample ($-1786 \text{ mV}_{\text{SCE}}$). It is also found that the E_{corr} of the MAO coated Mg–Ca alloy is $-1576 \text{ mV}_{\text{SCE}}$, indicating that both coated samples have more positive E_{corr} than that of the uncoated samples. In addition, a significant decrease in the i_{corr} to $7.3 \mu\text{A}/\text{cm}^2$ from $241.5 \mu\text{A}/\text{cm}^2$ was observed after the MAO coating. The presence of non-interconnected micro-defects in the relatively thick MAO layer can slow the transportation of the electrolyte and reduce i_{corr} of the coated sample [16,17]. Note that MAO/PLA coating underwent lowest i_{corr} of $0.03 \mu\text{A}/\text{cm}^2$ which can be attributed to the sealing of porosities and microcracks of the MAO coating and thus interrupting the penetration of the corrosive species to the Mg substrate.

The EIS spectra of uncoated and coated samples demonstrated capacitive depressed semicircles in the high frequency region (Fig. 4b). After single layer and double layer coating, the capacitive loop of uncoated Mg alloy is evidently enlarged, indicating that the corrosion resistance is extremely increased. The EIS spectra of uncoated and coated samples can be fitted well using a simple equivalent circuit to characterize the samples (Fig. 4b) where R_e represents the solution resistance, C_c is the coating capacitance and

R_{ct} is the charge transfer resistance. As can be observed in the graph the charge transfer resistance (R_{ct}) of uncoated, MAO and MAO/PLA coating were 1.49 , 6.58 and $2591.3 \text{ k}\Omega\text{cm}^2$ respectively, indicating difficulty in charge transfer and good corrosion protection ability of the double-layer coated sample. The polarization test and EIS study revealed that a high level of corrosion protection of the Mg substrate can be provided by MAO/PLA coating through sealing of the MAO porosities and blocking the ionic transport in the MAO coating, including, e.g., chloride ion penetration through pores and subsequently the formation of a galvanic cell [13,16,18]. Based on these observations, the following mechanism is proposed to elucidate the corrosion process. First, when the electrolyte reaches the MAO coating/Mg alloy interface via pores in the coating, the corrosion starts by forming magnesium hydroxide at the interface, accompanied with its dissolution and re-formation at the freshly exposed surface (Fig. 4c). Replacing OH^- by Cl^- leads to the formation of more soluble magnesium chloride compound, which results in localized dissolution of the surface film and exposing bare surface to re-attack [12]. Next, the Mg alloy begins to dissolve accompanied with hydrogen evolution. Hydrogen exerts pressure on the MAO coating causing forming cracks and rupture [19–21]. However, after PLA coating, the surface of the MAO layer is homogeneously covered, thus transportation of corrosive ions (Cl^-) and electrolyte was largely hindered. Therefore, it can be stated that the MAO/PLA double-layer coating provides reasonable corrosion

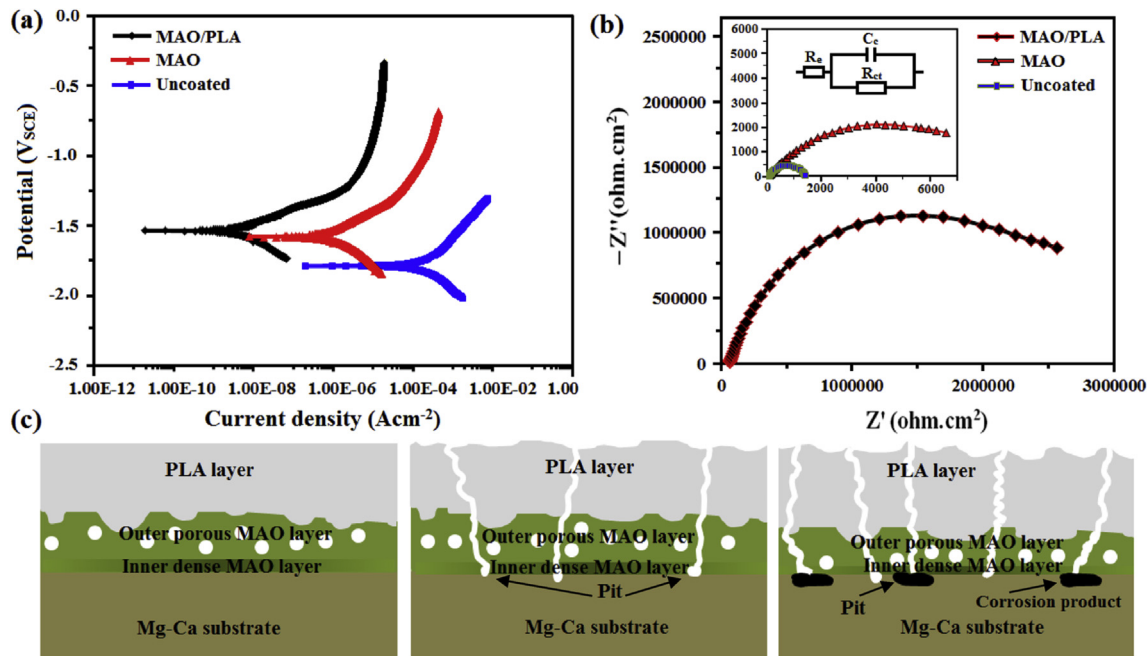


Fig. 4. (a) Potentiodynamic polarization curves, (b) Electrochemical impedance spectroscopy measurements and (c) Schematic illustration of electrochemical corrosion mechanism of MAO/PLA coating in the SBF solution.

barrier for the Mg–Ca alloy in the SBF environment. However, upon increasing the immersion time, it is expected that corrosive species will reach the interface with Mg alloy and hydrogen gas will be released that may cause bursting or delamination of the coating layer.

The results of the present study show that a PLA layer can be prepared on a MAO-coated Mg–Ca alloy via relatively simple method. This results in significant increase in contact angle from 42.30° , for the uncoated alloy to 95.30° for the duplex coating. The adhesive strength of MAO/PLA coating is 14.7 MPa which is lower compared to the MAO coating (23.4 MPa). In comparison with the single layer MAO coating, the double layer MAO/PLA coating demonstrates considerably lower corrosion current density ($0.03 \mu\text{A}/\text{cm}^2$) and higher charge transfer resistance ($2591.3 \text{ k}\Omega\text{cm}^2$). The results also exhibit that sealing the porous MAO layer by PLA polymer coating considerably enhances the corrosion resistance of the Mg alloy in the SBF physiological environment and demonstrates the potential of the MAO treatment for biomedical applications.

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