

## THE IMPORTANCE OF CURRENT MODE ON THE PROPERTIES OF PEO COATINGS DEPOSITED ON THE SURFACE OF POWDER METALLURGY-PRODUCED MG SUBSTRATE

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### Abstract

Plasma electrolytic oxidation (PEO) technique is a process of surface treatment of light metallic materials such as magnesium alloy, to produce coatings increasing the corrosion resistance. In this work, the effect of direct or alternating current deposition mode on the structure and corrosion behavior of PEO coatings on Mg substrates prepared by powder metallurgy (PM) was studied. It was observed that during the deposition process of PEO coatings, the varying of current mode between alternating current (AC) and direct current (DC) led to significantly different surface modifications and coatings properties. In the case of DC PEO coatings, significantly higher thickness was achieved than in the case of AC PEO coatings. On the other hand, AC PEO coatings achieved smaller pore sizes compared to the DC PEO coatings. Considering the denser and less porous structure of AC PEO coating, significantly better electrochemical properties were observed using potentiodynamic measurements in Hank's solution. Compared to the uncoated PM Mg substrate, there was an order of magnitude decrease in the  $i_{\text{corr}}$  of PEO-coated Mg substrate. In the case of DC PEO coatings, the  $i_{\text{corr}}$  value was determined to be  $8.3 \mu\text{A}\cdot\text{cm}^{-2}$ , and in the case of AC PEO even  $3.4 \mu\text{A}\cdot\text{cm}^{-2}$ .

**Keywords:** Magnesium, powder metallurgy, PEO coating, corrosion, Hank's solution

### 1. INTRODUCTION

Magnesium and its alloys have many advantages over commonly used biodegradable materials, including that Mg is essential for human metabolism, is biocompatible and has good mechanical properties (specific strength, toughness) [1-3]. These properties have undoubtedly attracted much attention with respect to the applications of biodegradable implants [3-5]. Biodegradable implants, which include Mg, are of interest in medical applications [1,3,5]. They offer tissue repair and temporary support during tissue repair/healing and can be gradually dissolved and absorbed by the human body [3]. However, it is well known that Mg alloys as potential biomaterials are characterized by high corrosion rates and chemical reactivity [5-7]. This precludes their wider use where implant integrity could be lost or failure in the body could occur. The increase in local pH and release of hydrogen gas around the Mg implant during uncontrolled degradation can lead to tissue necrosis, reduced cell growth or unavailability of nutrients around the implant [3]. The use of implants prepared by powder metallurgy (PM) is advantageous for bioapplications because they improve integration with tissue during the healing process [2-4]. In addition, PM allows the combination of a wide range of materials, either metallic or metal matrix composites (MMC) containing ceramic filler, mainly hydroxyapatite. These above undesirable behaviors of Mg can be rescued by applying a suitable ceramic coating to the Mg surface to facilitate smoother degradation and reduced corrosion of the Mg implant. A wide range of such potential coatings is currently available. These include the application of calcium phosphate-based coatings and hydroxyapatite prepared by various techniques such as solution deposition, sol-gel method, hydrothermal synthesis, thermal spraying, etc. [8-9]. It also includes coatings like PEO [10]. PEO coatings have been shown to have good biocompatibility and adhesion. The advantage of PEO coatings is their easy and environmentally acceptable production, good

osseointegration support, which promotes the healing process. The actual biodegradation process and the degree of corrosion resistance are then determined by the structure and phase composition of PEO coatings.

In this study, PEO-based coatings will be applied to the surface of PM Mg samples by DC and AC electrolytic oxidation. The aim of this work is to develop PM Mg material and improve the corrosion properties of PM Mg surfaces using PEO coatings, which will enable their use in biomedical applications.

## 2. EXPERIMENTAL PART

Atomized Mg powder (99.8% Mg; Goodfellow, Huntingdon, UK) with a maximum particle size of 50  $\mu\text{m}$  was used for the preparation of the substrates. For the experiment, 2.5 g of Mg powder was filled into the steel dies. Then, Mg powder was compacted in two ways – cold-pressed and hot-pressed. In the case of cold-pressed (CP) samples, the pressing was performed using an Instron 5984 series universal testing system (Instron, Norwood, MA, USA) as follows: speed 2  $\text{mm}\cdot\text{min}^{-1}$ , maximum stress 400 MPa with a dwell time of 60 s. For the hot-pressed (HP) samples, the pressing was performed as follows: preload 5 MPa at 350 °C for 15 min, loading 20  $\text{MPa}\cdot\text{min}^{-1}$ , maximum stress 400 MPa with a dwell time of 60 s. The cooling of the samples in closed dies was carried out slowly in the air. After they reached laboratory temperature, the samples were extruded and ground using #4000 SiC paper.

PEO coating deposition was carried out in an alkaline electrolyte composed of 10  $\text{g}\cdot\text{l}^{-1}$   $\text{Na}_3\text{PO}_4\cdot 12\text{H}_2\text{O}$  and 1  $\text{g}\cdot\text{l}^{-1}$  KOH. The pH value of electrolyte was set at 12.4 using 1M KOH solution. Coatings have been fabricated using two techniques – DC and AC current technique. Deposition was performed in the two-electrode system with PM Mg samples employed as an anode and 304 stainless steel plate as a cathode. After the deposition, all coated samples have been finally rinsed with distilled water, alcohol, and air-dried.

To investigate the morphology and microstructure of the deposited PEO coatings, the Zeiss EVO LS-10 scanning electron microscope (SEM) (Carl Zeiss Ltd., Cambridge, UK) equipped with an Oxford Instruments Xmax 80  $\text{mm}^2$  energy dispersive spectrometer (EDS) (Oxford Instruments plc, Abingdon, UK) was used. The corrosion behavior of PM Mg samples and PEO-coated samples was evaluated by potentiodynamic measurements performed using a potentiostat/galvanostat Bio-Logic VSP-300 (BioLogic, Seyssinet-Pariset, France) in Hank's solution (HS) (GE Healthcare; PAA Laboratories GmbH, Austria) at room temperature. A typical three-electrode cell with a sample as the working electrode, a saturated Ag/AgCl electrode as the reference electrode, and a platinum mesh as the counter electrode was used. The corroded area of the sample was approx. 1  $\text{cm}^2$ . The open circuit potential (OCP) was stabilized at 60 min and the potential ranged from -200 mV to +500 mV vs. OCP. The scan rate was 1  $\text{mV}\cdot\text{s}^{-1}$ .

## 3. RESULTS AND DISCUSSION

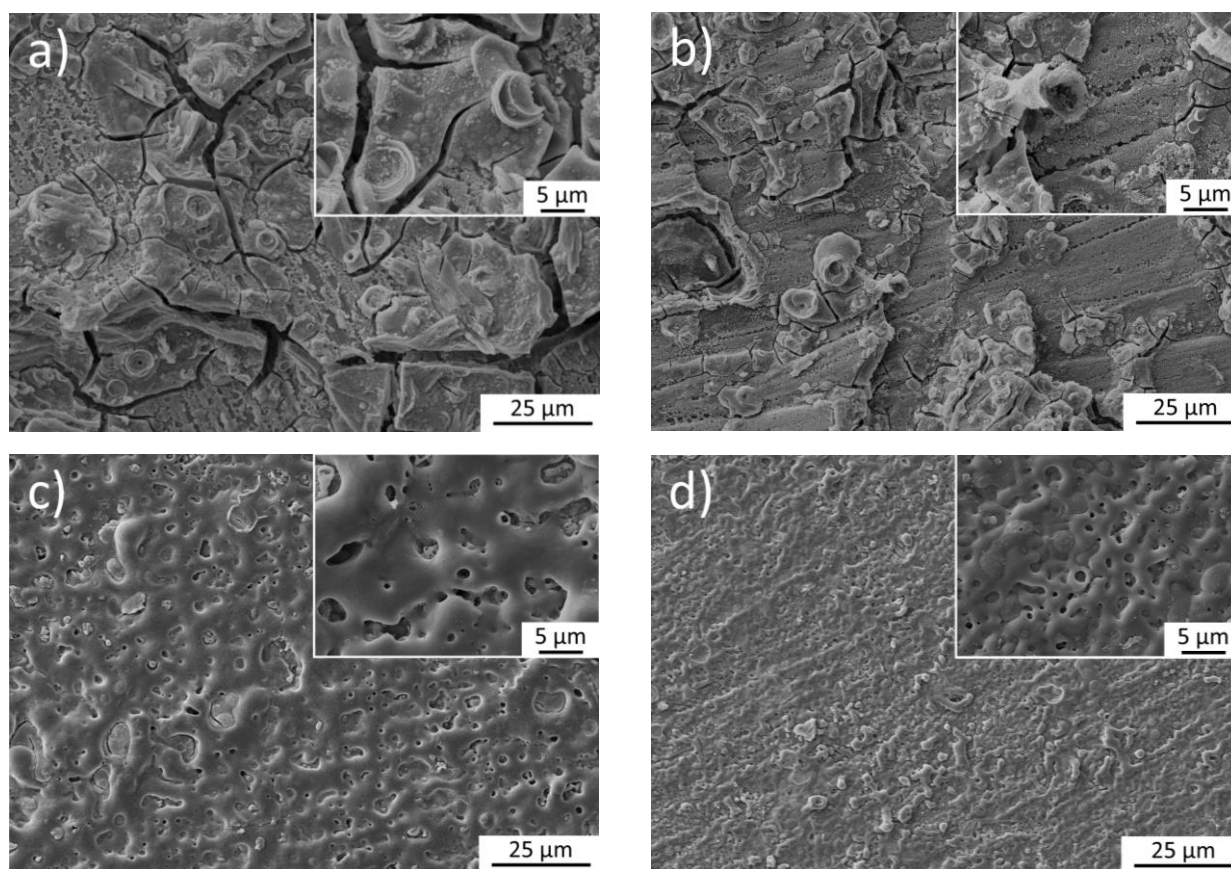
### 3.1 Structural analysis

The deposition of PEO coatings was carried out on both cold and hot pressed PM Mg samples (**Figure 1**). As can be seen from (**Figure 1a** and **Figure 1b**), no continuous PEO layer was deposited on the surface of the cold-pressed PM Mg substrates using either DC or AC current mode. The PEO coatings were defective and were severely cracked. As shown in (**Figure 2a** and **2b**), it was clear from the perpendicular cuts that the PEO coatings were not uniform and there was Mg substrate degradation in the surface layer under deposited PEO coatings. From the metallographic section, it is clear that the thickness of DC PEO coating is approximately twice that of AC PEO.

As shown by elemental EDS analyses (**Figure 2a** and **2b**), higher oxygen concentrations were also detected in the degraded surface layer of the PM Mg substrate. Therefore, it can be assumed that it was  $\text{Mg}(\text{OH})_2$ . This can be attributed to the lower cohesion of cold-pressed Mg substrates. During the deposition, the coating bath/medium may have predominantly permeated between the Mg powder particles and this may have caused

the corrosion attack of the PM Mg substrate along with partial deposition of the PEO coating. The  $Mg(OH)_2$  present led to local increase in volume, which could have led to stresses in the surface layer, crack formation and consequently degradation of the PM Mg with PEO coating [8,11].

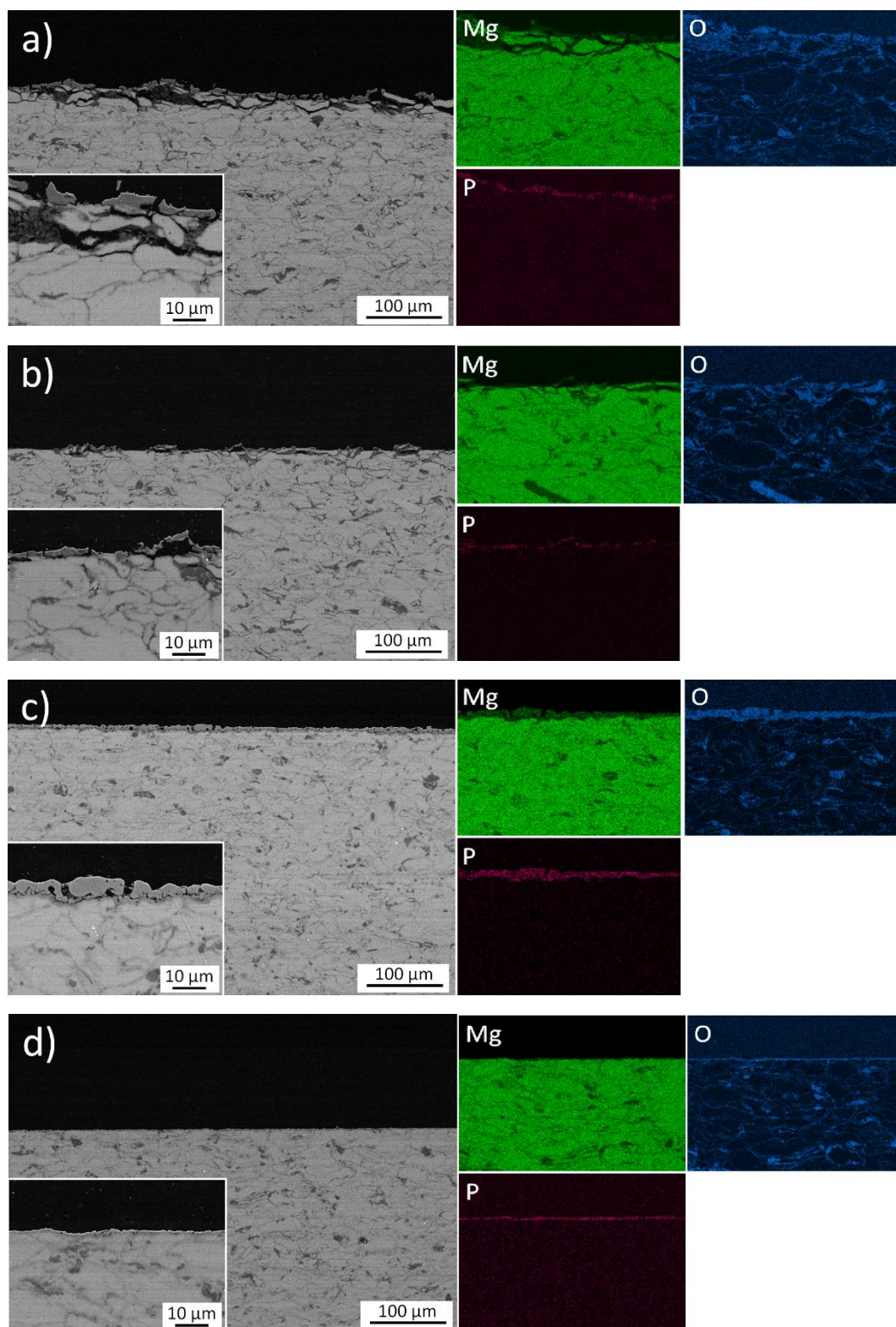
The PEO coatings that were deposited on the surface of the hot-pressed PM Mg substrates did not show the presence of undesirable structural defects and surface cracks (**Figure 1c** and **1d**). PEO coatings showed their typical structure. From (**Figure 1c** and **1d**), it can be noticed that in the case of the sample with deposited PEO using AC current mode (ACHP), the pore size on the surface of the PEO coatings is lower and the structure was denser than that of the sample with deposited PEO using DC current mode (DCHP). This could positively affect the corrosion behavior [12].



**Figure 1** Surface morphology of deposited PEO coatings, a) DCCP, b) ACCP, c) DCHP, d) ACHP

As shown in (**Figure 2c**), the PEO coating deposited by the DC technique on the hot-pressed Mg substrate was continuous along its entire length and had a thickness of approximately 8  $\mu m$ . In the case of PEO coatings applied by the AC (ACHP) technique, the thickness was around 2-3  $\mu m$  (**Figure 2d**).

Hot pressing of PM Mg substrates probably resulted in a more compact and dense structure, which better resisted the penetration of the coating bath into its volume and did not undergo corrosion attack and degradation, and the PEO layer was preferentially formed.

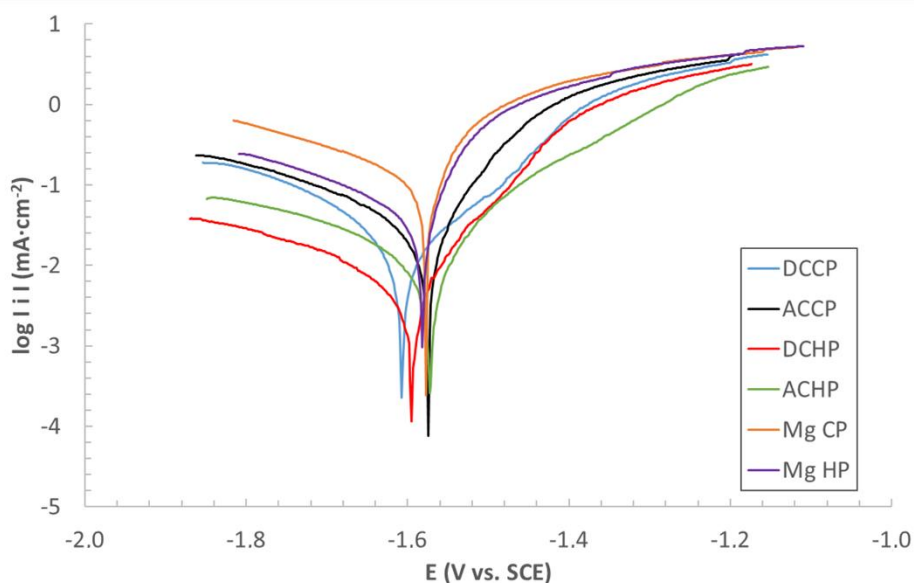


**Figure 2** SEM micrographs of cross section of PEO coatings, a) DCCP, b) ACCP, c) DCHP, d) ACHP

### 3.2 Potentiodynamic measurements

From the results of the potentiodynamic measurements in Hank's solution (HS), it can be seen from the results (**Figure 3**) that the worst corrosion results were achieved in the case of uncoated Mg substrates. As the results

**Table 1** show, the  $i_{corr}$  value of hot-pressed PM Mg substrates was lower than the cold-pressed PM Mg substrates. This may be due to their more compact structure. Deposition of PEO coatings on cold-pressed Mg did not lead to a significant improvement in corrosion resistance. Better corrosion results were achieved in the case of PEO-coated hot-pressed (ACHP and DCHP) samples, when  $i_{corr}$  decreased at least by one order of magnitude compared to uncoated Mg substrates. Better corrosion resistance is due to the absence of structural defects in PEO coatings [12]. The best corrosion results were obtained in the case of the ACHP sample. Even though the PEO coatings applied in the AC mode reached lower thickness, due to their denser structure and lower porosity compared to the coatings applied in the DC mode, there was a worse penetration of the corrosion medium through the PEO layer to the Mg substrate [11-14].



**Figure 3** Potentiodynamic polarization curves of Mg substrates and PEO-coated Mg substrates

**Table 1** Results of potentiodynamic measurements

Sample	$E_{corr}$ (mV)	$i_{corr}$ ( $\mu\text{A}\cdot\text{cm}^{-2}$ )
CP Mg substrate	-1577	95.6
HP Mg substrate	-1580	41.1
DCCP	-1605	19.9
ACCP	-1572	23.8
DCHP	-1594	3.4
ACHP	-1572	8.3

#### 4. CONCLUSION

The results showed that the application of PEO coatings led to an increase in the corrosion resistance of the PM Mg substrate. A more suitable mode for the deposition of PEO coatings appears to be altering current (AC), when PEO coatings achieve a denser structure with a smaller pore size and thus achieve better corrosion resistance in Hank's solution. Application of PEO coatings led to the decrease of corrosion current density  $i_{corr}$ , where in the case of DC PEO coatings, the  $i_{corr}$  value was determined to be  $8.3 \mu\text{A}\cdot\text{cm}^{-2}$ , and in the case of AC PEO even  $3.4 \mu\text{A}\cdot\text{cm}^{-2}$ . Also, it was found that PM Mg substrates prepared by cold pressing are not suitable, as they do not show sufficient cohesion, their degradation occurs during the deposition of PEO coatings, and the deposited PEO coatings achieve poor quality.

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