EFFECT OF SURFACE PRETREATMENT ON THE FORMATION AND PROTECTIVENESS OF PEO LAYERS ON PURE MAGNESIUM AND WE43 ALLOY

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Abstract

Plasma electrolytic oxidation (PEO) has emerged as a promising surface modification technique to enhance corrosion resistance of magnesium alloys. This study investigates the influence of different surface pretreatments: polishing, grinding, and shot-peening, on the formation and performance of PEO coatings on pure magnesium and WE43 (Mg-4Y-3RE) alloy. SEM analysis was used to characterise the coating morphology, while electrochemical impedance spectroscopy was employed to monitor corrosion behaviour over 168-hour period. The results reveal that PEO significantly improves corrosion resistance in both materials, with polished samples exhibiting the highest initial polarisation resistance. Interestingly, shot-peening had a detrimental effect on corrosion resistance in pure magnesium after longer immersion period but resulted in improved performance for WE43, attributed to the beneficial interaction between deformation-induced lattice defects and rare earth elements. These findings highlight the complex relationship between alloy composition, surface preparation, and corrosion behaviour.

Keywords: Magnesium; plasma electrode oxidation, surface treatment; corrosion

1. INTRODUCTION

Rapid development of magnesium alloys during the last decades was significantly motivated by various industries, including automotive, electronics and biomedicine. Biocompatibility and biodegradability of magnesium make it a very interesting material for temporary implants, some of which are already being commercially produced [1, 2]. A lot of work has been done to improve the corrosion resistance of the magnesium alloys, which is still one of the decisive factors which negatively affect the wider utilisation of this material in medicine. The common approach was to tailor composition, microstructure and/or surface to increase the corrosion resistance [3–5]. Among the surface treatments, plasma electrolytic oxidation (PEO), also known as micro-arc oxidation, has emerged as a promising method for enhancing surface properties.

PEO is an electrochemical surface treatment process that forms a ceramic-like oxide coating on metals such as aluminium, titanium, and magnesium through high-voltage anodic oxidation in electrolytic solutions. In the case of magnesium, the process leads to the formation of relatively thick, adherent, and corrosion-resistant oxide layers that significantly improve the material's corrosion and wear resistance [6]. Recent studies have demonstrated the effectiveness of PEO in enhancing the corrosion behaviour of various magnesium alloys, including AZ-, ZK-, WE-type alloys, etc. [7–9]. In addition to alloy selection, pre-treatment of the substrate surface can significantly affect the morphology, thickness, and protective properties of the resulting PEO coating [10].

This study compares PEO coatings formed on pure magnesium and the WE43 (Mg-4Y-3RE) alloy, emphasising the influence of different surface pretreatments: polishing, grinding, and shot-peening. The motivation of this work is to provide insight into optimising surface preparation strategies for PEO treatment.

2. MATERIALS AND METHODS

Two materials were used in this study – pure magnesium and commercial WE43 alloy (Mg-4Y-3RE-0.4Zr). Pure magnesium was supplied in the cast form and the WE43 alloy as an as-extruded bar. In order to reveal any residual stresses and dissolve secondary particles in WE43, both materials were annealed at 530 °C for 16h and subsequently quenched in water. Set of samples having dimensions of 15 ×15 × 4 mm^3 were cut from both materials for subsequent surface treatment. One set of samples was ground on #1200 emery paper and the second set of samples was ground and polished with a decreasing particle size down to 1 μm, followed by electrochemical polishing by Struers Lectrolol and Struers AC2 solution. Plates having size of 5 × 5 cm^2 of both materials were cut and ground by #1000 emery paper. Subsequently, one surface was shot-peened by AZB100 ceramic shots with coverage and Almen intensity set to 100 % and 6 N, respectively. Finally, samples of 15 ×15 × 4 mm^3 were cut for the surface treatment.

Plasma electrolytic oxidation was performed using N8762A DC power source and electrolyte consisting of 12 g/L $Na_3PO_4 \cdot 12H_2O$ and 1 g/L KOH. A magnesium sample served as an anode and steel sheet as a cathode. A constant current density of 50 μA/cm^2 was applied for 10 min and the solution was stirred during the process to ensure a good homogeneity.

The resulting PEO layers were studied by scanning electron microscope (SEM) ZEISS Auriga compact equipped with EDAX energy-dispersive X-ray spectroscope (EDS). The samples for cross-section analysis were embedded in conductive epoxy resin, cut approximately in the middle, ground, and polished with decreasing particle size down to 50 nm.

Corrosion resistance was measured using electrochemical impedance spectroscopy by Biologic VSP-300 potentiostat in a tree-electrode configuration. The measurement was performed in the solution of 0.9% NaCl, at room temperature and in the frequency range 100 kHz-20 mHz with amplitude of 10mV. The samples were measured in the selected time periods up to 188 hours.

3. RESULTS AND DISCUSSION

Plasma electrolytic oxidation of all samples resulted in the formation of a porous ceramic-like oxide layer on the samples' surface. The previous study revealed that the layer is formed primarily by $Mg_3(PO_4)_2$ and MgO [11]. **Figure 1** shows the topography of the individual samples. It is clear that there is, on one hand, a systematic difference between the pure magnesium and the WE43 alloy, and on the other hand, the difference between the pre-treatments is almost negligible. Pure magnesium exhibits a much higher density of large pores having a size of more than 10 μm, encircled by distinct ridges. The WE43 alloy showed formation of larger pores only occasionally in the case of the polished sample, while a slight increase in density was observed in the ground and shot-peened sample, as shown in **Figure 1**. The observed topography is typical for this type of surface treatment and was repeatedly reported for various alloys [10–13].

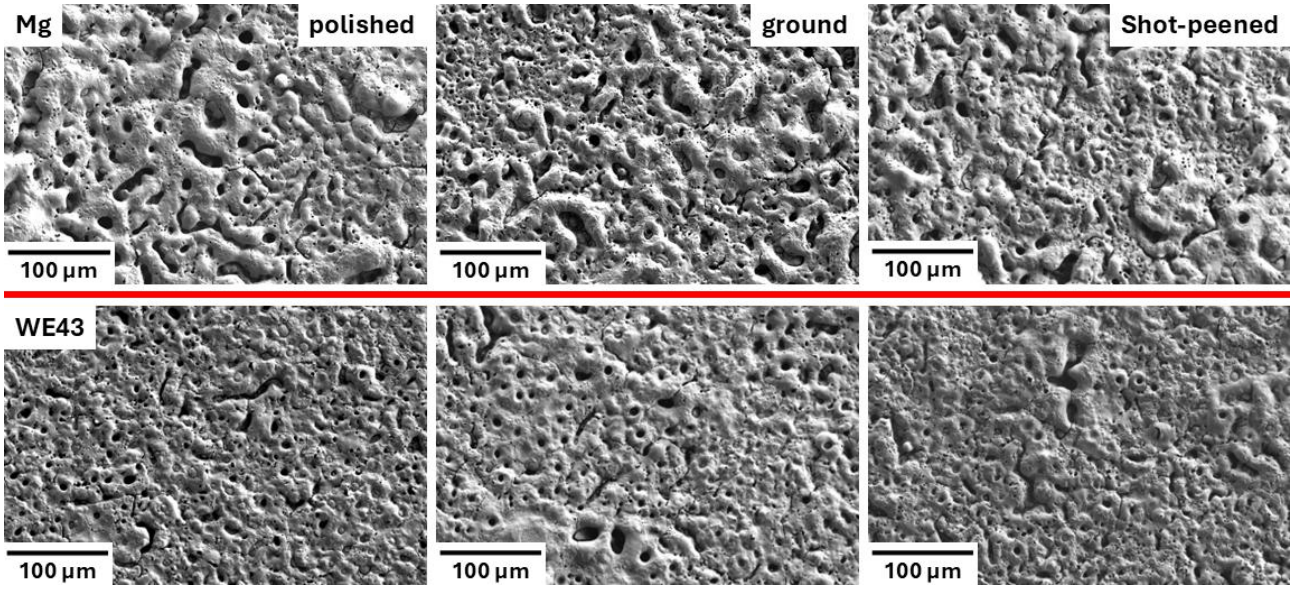


Figure 1 Topography of PEO developed on the investigated samples

Figure 2 shows the cross-sectional cut through the PEO layer of the pure magnesium samples. The average thickness of the layer in all samples was comparable and exceeded 20 µm. However, the layers exhibited a high porosity, especially between the dense inner layer attached to the sample surface and the outer layer. Note that the dense inner layer is the most important for the resulting corrosion resistance [14]. The detail of the PEO microstructure formed on the polished Mg sample is shown in **Figure 3**. The SEM analysis revealed that the layer is formed by submicron crystals of various sizes. Nevertheless, the individual crystals in the large areas of the layer cannot be distinguished by SEM because of the resolution limit. Therefore, these parts of the layer are potentially nanocrystalline or even amorphous, but an additional investigation is needed in this regard to draw some conclusions. Note that the results of the WE43 alloy were systematically comparable, and, therefore, they are not shown in this paper.

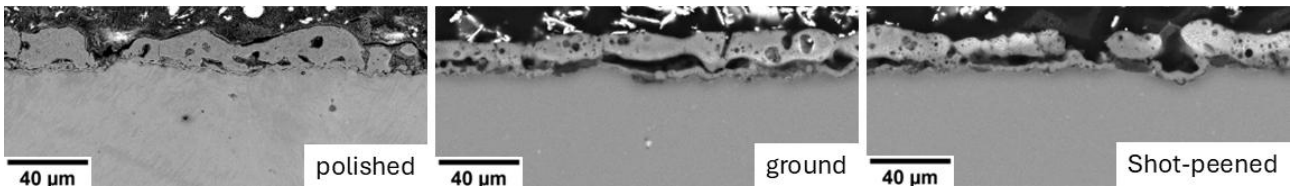


Figure 2 Cross-section of magnesium samples with various pre-treatment

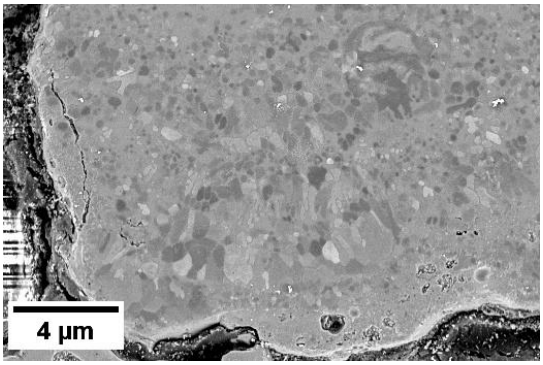


Figure 3 Detail of the PEO layer cross-section

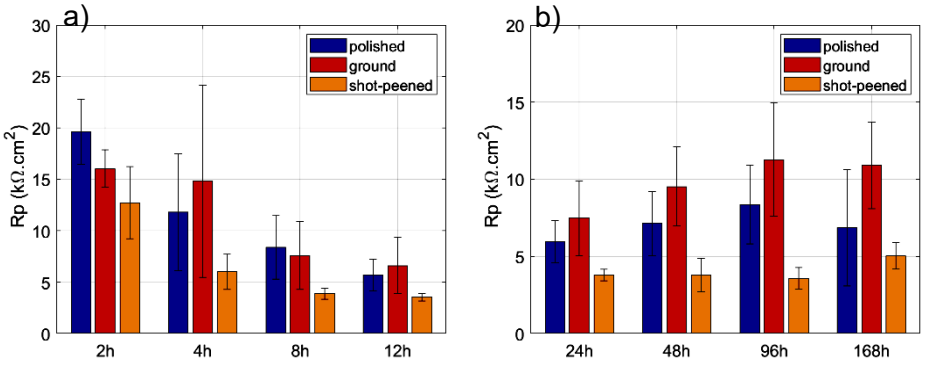
The effect of the PEO layer formation on the corrosion resistance of all investigated samples was continually analysed for a one-week period. The results of polarisation resistance evaluated from the electrochemical impedance spectroscopy are shown in **Figure 4**. The PEO-free samples exhibited polarisation resistance highly dependent on the pretreatment, and the results of the measurement performed after 2 hours of immersion are shown in **Table 1**. Pure magnesium showed systematically lower values of the polarisation resistance than the WE43 alloy. The other important observation is that the polished samples have approximately double the polarisation resistance of the ground ones in the case of both materials, and the polarisation resistance of the shot-peened samples was extremely low, independent of the material. These results are in a good agreement with the fact that the surface roughness has a negative effect on the corrosion resistance [15, 16]. Consequently, the ground samples exhibited higher reactivity. The shot-peening introduces to the material not only significant change in topography, but the high deformation and a consequent residual strain as well [17]. All these factors significantly negatively affect the corrosion resistance, and, therefore, the resistance of shot-peened sample to corrosion was extremely low.

Table 1 polarization resistance of the PEO-free samples after 2 hours of exposure

	Pure Mg			**WE43**		
	polished	**ground**	**Shot-peened**	**polished**	**ground**	**Shot-peened**
Rp (kΩ·cm²)	0.82 ± 0.02	0.31 ± 0.02	~0.02	4.7 ± 0.2	2.83 ± 0.16	~0.02

The PEO formation on the samples' surface resulted in a significant increase in the corrosion resistance of all investigated samples, as shown in **Figure 4**. Interestingly, the highest increase was measured for the polished samples. The subsequent increase in the immersion time resulted in a gradual decrease in the polarisation resistance of all samples. A much higher drop was found in the case of all WE43 samples. However, this is given by 2-3 times higher polarisation resistance measured for the 2-hour immersion time. The decrease in the corrosion resistance was completed approximately after 12 hours of immersion, and afterwards, a small but continuous growth of the corrosion resistance was measured for almost all samples. The only exception was the shot-peened Mg sample, for which the polarisation resistance did not change with immersion time.

After 168 hours of immersion, the difference between the ground and polished sample was very small for the pure magnesium – the error bars overlapped especially because of a relatively high data scatter of the polished sample. In the case of the WE43 alloy, the difference between ground and polished sample was negligible. More interesting results were found for the shot-peening pre-treatment. The shot-peened samples exhibited notable lower corrosion resistance for the pure magnesium, while an increased one for the WE43 alloy. Therefore, the effect of shot-peening prior to the PEO formation is not straightforward and is composition-dependant.



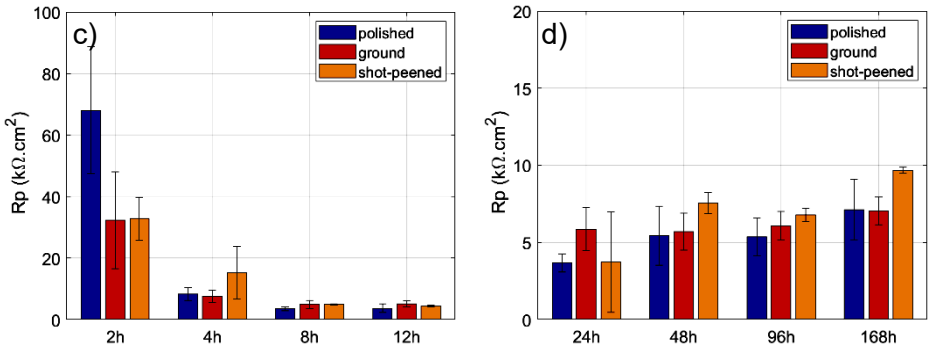


Figure 4 Evolution of the corrosion resistance of a-b) pure Mg, c-d) WE43, note the different scales.

The highest increase in the polarisation resistance due to PEO measured after 2-hour immersion for the polished samples was surprising with respect to our previous work on the AZ31 alloy, in which shot-peening exhibited the best performance as pre-treatment [10]. The subsequent decrease in the corrosion resistance within 12 hours can be directly associated with the dissolution of the dense inner layer, which is exposed to the corrosive media particularly at the bottom of the pores. Subsequently, corrosion properties of the underlying matrix start to play a significant role. Once the corrosion the magnesium matrix begins, the difference between the grinding and polishing smears away and the results are quite comparable. The reason is that the formation of PEO is associated with the dissolution of the magnesium matrix and grinding by #1200 emery paper does not cause too deep alternation if its properties. Therefore, once the dense inner layer is broke, the corrosion response is comparable, because the matrix properties are comparable. On the other hand, the effect of shot-peening is much deeper and only part of the affected matrix dissolves during the PEO preparation. Consequently, once the bare matrix is exposed to the corrosive media, the higher volume fraction of lattice defects causes increase in the corrosion rate of the pure magnesium. Interestingly, the increase in the corrosion resistance in shot-peened WE43 alloy can be explained by the same effect. The higher density of lattice defects accelerates the corrosion rate, but the occurrence of yttrium and rare earth metals in the matrix causes formation of stronger and more protective corrosion layer, which more effectively prevents further corrosion. This interrelation between density of lattice defects, alloy chemistry, and corrosion resistance was repeatedly shown especially after a substantial grain refinement [18–20]. Note that this effect was not observed in the case of the PEO-free shot-peened samples, because the deformation and roughness was too high, and therefore, the corrosion rate was dominated mostly by the defects and not the chemistry.

4. CONCLUSIONS

This study was focused on the effect of surface pre-treatment on the formation of PEO layer and subsequent corrosion resistance of the material. Pure magnesium and WE43 (Mg-4T-3RE-0.4Zr) were used as an experimental material. The results of this study confirmed that the formation of the PEO layer has a substantial effect on the corrosion resistance of the magnesium alloys and the effectiveness of the PEO layer is dependant on the surface pre-treatment. It was showed that difference between polishing and grinding was apparent only at the beginning of the corrosion process, while it was only minor after 12 hours of immersion. On the other hand, shot-peening as a pre-treatment has a positive effect on the long-term corrosion resistance in the case of the WE43 alloy, while a negative one for pure magnesium. The demonstrated composition-dependent response to surface pretreatment underlines the necessity for alloy-specific surface engineering strategies to optimise corrosion resistance of the magnesium alloys.

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