PREPARATION OF ZEOLITIC IMIDAZOLATE FRAMEWORK-8 (ZIF-8) PARTICLES ON PLASMA ELECTROLYTIC OXIDATION (PEO) COATING UNDER LABORATORY CONDITIONS

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Abstract

Magnesium Mg and its alloys are attractive materials in industries such as automotive and aerospace. However, their use is often limited by their susceptibility to corrosion. One way to improve the corrosion resistance of these materials is to apply protective coatings. In this work, we focus on the preparation of plasma electrolytic oxidation (PEO) with zeolitic imidazolate framework-8 (ZIF-8) particles on AZ31 magnesium alloy. ZIF-8 particles were prepared by in-situ method on PEO coating at different times under laboratory temperature. The presence of ZIF-8 particles was characterized by scanning electron microscopy with an energy dispersive spectrometer (SEM-EDS). The corrosion properties were characterized by potentiodynamic polarization in 0.9% NaCl. The results showed that ZIF-8 particles were successfully prepared and their uniform distribution on PEO coating increased with time. The preparation of ZIF-8 particles improved the corrosion properties of PEO coating, and the best corrosion resistance was observed when the particles grew for 48 h.

Keywords: ZIF-8 particles, PEO coating, AZ31 alloy, corrosion, 0.9% NaCl

1. INTRODUCTION

Magnesium and its alloys have garnered significant attention in recent years due to their exceptional properties, including low density, high specific strength, vibration damping capacity, effective electromagnetic shielding, biodegradability, and biocompatibility. Thanks to this combination of attributes, Mg alloys find broad applications in sectors such as the automotive industry, high-speed railways, aerospace, and increasingly in biomedicine [1]. In medicine, they have shown promise as materials for biodegradable implants, for instance, temporary orthopaedic fixations (screws, splints, pins) or coronary stents [2].

However, a crucial limitation for the wider use of magnesium and its alloys is their susceptibility to rapid and uncontrolled corrosion in aqueous environments [3]. To overcome this issue, various surface treatments are being intensively investigated, e.g. superhydrophobic coatings, fluoride coatings [4,5]. One effective method is plasma electrolytic oxidation (PEO), which creates a protective oxide layer on the alloy surface, significantly improving its corrosion resistance [6].

Despite the proven effectiveness of PEO coatings, their typical microstructure often exhibits a certain degree of porosity, which can provide pathways for corrosive solutions to reach the underlying material. Therefore, research is focused on further modifications of PEO layers with the aim of minimizing their defects and thus enhancing their barrier properties. Among the promising approaches is the use of metal-organic frameworks (MOFs) for pore sealing and further functionalization of the surface [7].

In this work, we focused on the application of zeolitic imidazolate framework-8 (ZIF-8), a prominent representative of MOFs, on a PEO coating formed on a magnesium alloy. ZIF-8 stands out due to its high specific surface area, acceptable chemical stability, and and carrier of corrosion inhibitors [7,8]. Recent studies have reported the optimization of the preparation conditions of ZIF-8 particles on PEO layer under different conditions and observed that the combination of MOF coatings and PEO coatings leads to an increase in the corrosion protection of magnesium alloys [9,10].

The aim of this work is to prepare ZIF-8 particles on AZ31 magnesium alloy pretreated with PEO coating. The particles will be obtained by in situ method and grown on the surface of PEO coating at laboratory temperature at different time intervals. The formation of ZIF-8 particles will be characterized by SEM-EDS and corrosion properties by PDP method.

2. EXPERIMENTAL

AZ31 alloy

AZ31 magnesium alloy samples (20 × 20 × 6 mm) were used for corrosion tests. The alloy chemical composition was determined using Glow-Discharge Optical Emission Spectroscopy (GDOES); 3.60 Al, 1.34 Zn, 0.28 Mn, 0.03 Si, 0.002 Fe, 0.01 Sn (in wt%). The samples of AZ31 alloy were ground using 320 and 1200 SiC grit abrasive papers, washed in distilled water and isopropyl alcohol and then dried by hot air.

Preparation of PEO coating

PEO coating deposition was carried out in an alkaline electrolyte composed of $Na_3PO_4 \cdot 12\ H_2O$ and KOH. The pH value of electrolyte was set at 12.4 using KOH solution. Coatings have been fabricated using direct current. Deposition was performed in the two-electrode system with AZ31 alloy 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. The constant current density of 50 $mA \cdot cm^{-2}$ was applied to the sample for 10 min.

Synthesis of ZIF-8 on PEO coating

Firstly, 90 mmol of 2-methylimidazole (2-mIm) was dissolved in 30 mL of methanol to form the solution A. Then, 9 mmol of $Zn(NO_3)_2 \cdot 6\ H_2O$ (Aladdin, China, 99 wt%) was dissolved in 30 mL of methanol to form the solution B. Afterwards, the solution B was slowly added into the solution A and reacted under stirring at room temperature for 3, 8, 24 and 48 h. A PEO-coated AZ31 sample was introduced into solution A. The modified AZ31 alloy surface with PEO coating was pulled out, rinsed with methanol, water, dried and placed in an oven at 60 °C for 24 h.

Characterization of samples and PDP test

The morphology and microstructure of the PEO coatings and ZIF-8 coatings were investigated using s scanning electron microscope (SEM) equipped with an energy dispersive spectrometer (EDS). The corrosion behaviour of AZ31 alloy, PEO coatings and ZIF-8 coatings was evaluated by potentiodynamic polarization (PDP) measurements performed using a potentiostat in 200 mL 0.9% NaCl water solution at room temperature. Prepared samples as working electrode, reference saturated calomel (SCE) and auxiliary platinum plate electrodes were assembled into three electrode setup for the measurements. The corroded area of the sample was approx. 1 cm^2. The open circuit potential (OCP) was stabilized at 60 min and the potential ranged from -150 mV to +400 mV vs. OCP. The scan rate was 1 $mV \cdot s^{-1}$.

3. RESULTS AND DISCUSSION

The prepared PEO coating on AZ31 alloy had a typical porous structure (not presented) on which ZIF-8 particles were deposited by in situ method for different times (3, 8, 24 and 48 h) at laboratory temperature. Based on the literature search [8,9], a suitable concentration of precursors was selected for the preparation of ZIF-8 particles, which are zinc-based particles from the Metal Organic Framework (MOF) particle family. The experiments were conducted at laboratory temperature and an attempt was made to prepare ZIF-8 particles in situ on the PEO coating surface (**Figure 1**). The shortest reaction time used (3 h) was found to be clearly insufficient. The ZIF-8 crystals had just started to grow, therefore the coverage of the PEO coating was minimal. The longer reaction time (8 h) resulted in greater coverage of the PEO coating with ZIF-8 particles, but these particles had different size distributions, which is undesirable in terms of corrosion resistance. Moreover, the surface coverage was not always optimal when the experiments were repeated. A reaction time of 24 h led to the formation of crystals with relatively uniform size, but the surface of the PEO coating was not sufficiently covered. A reaction time of 48 h provided ZIF-8 particles and satisfactory coverage of the PEO coating, therefore corrosion experiments were performed with this reaction time. However, further research needs to focus on the preparation of ZIF-8 particles with shorter reaction time and uniform size distribution.

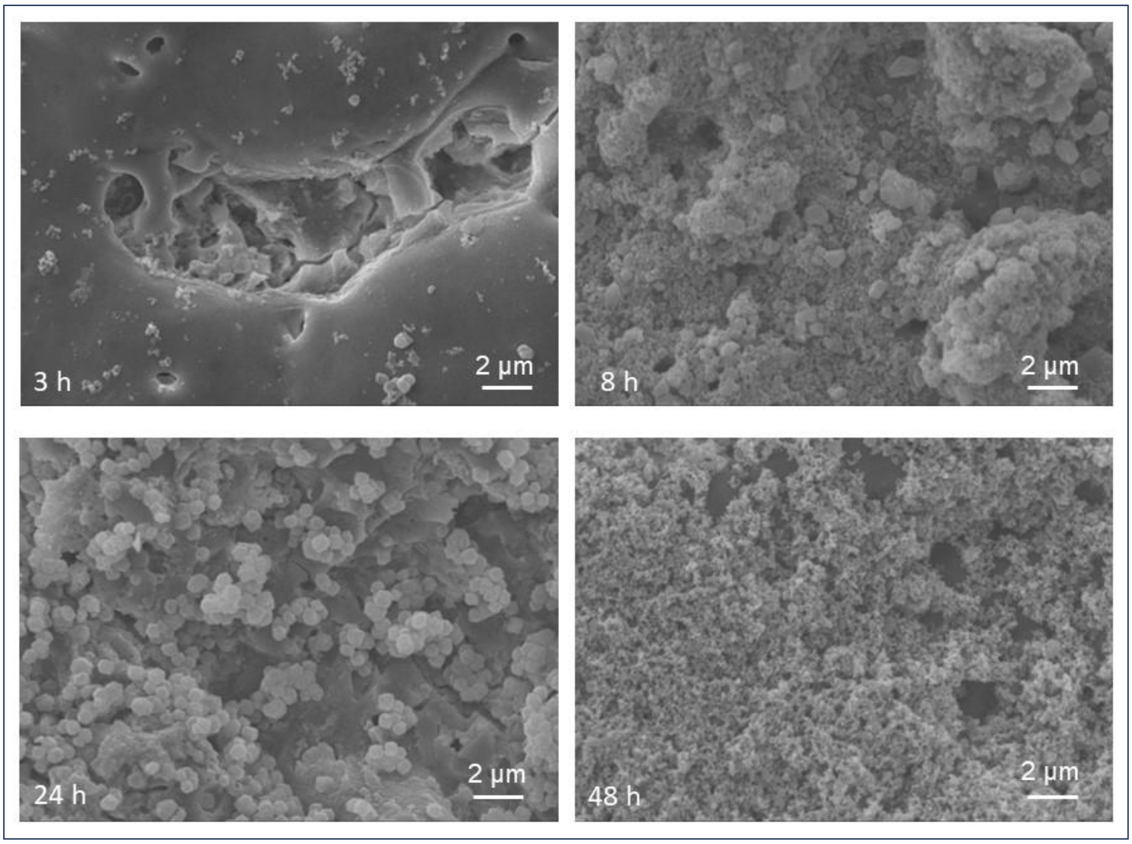

Figure 1 Morphology of ZIF-8 particles prepared at different reaction times (3, 8, 24 and 48 h) at laboratory temperature on PEO coating on AZ31 alloy

Table 1 Elemental composition of ZIF-8 coating prepared on AZ31 alloy with PEO coating

Element	Atomic%
C	47.4
N	12.7
O	25.7
Mg	4.4
Al	2.4
P	3.8
Zn	3.6

The detail of ZIF-8 crystals with a size of about 1 μm is shown in **Figure 2**. The elemental analysis of all ZIF-8 coatings prepared on PEO coatings corresponds to ZIF-8 particles (**Table 1**). The presence of magnesium and phosphorus corresponds to the PEO coating, which is composed of magnesium oxide (the predominant component of the PEO coating) and magnesium phosphate. Further, the shape of the crystals corresponds to ZIF-8 as described in the literature [11]. Unfortunately, the small particles and their low abundance compared to the PEO coating did not allow XRD identification.

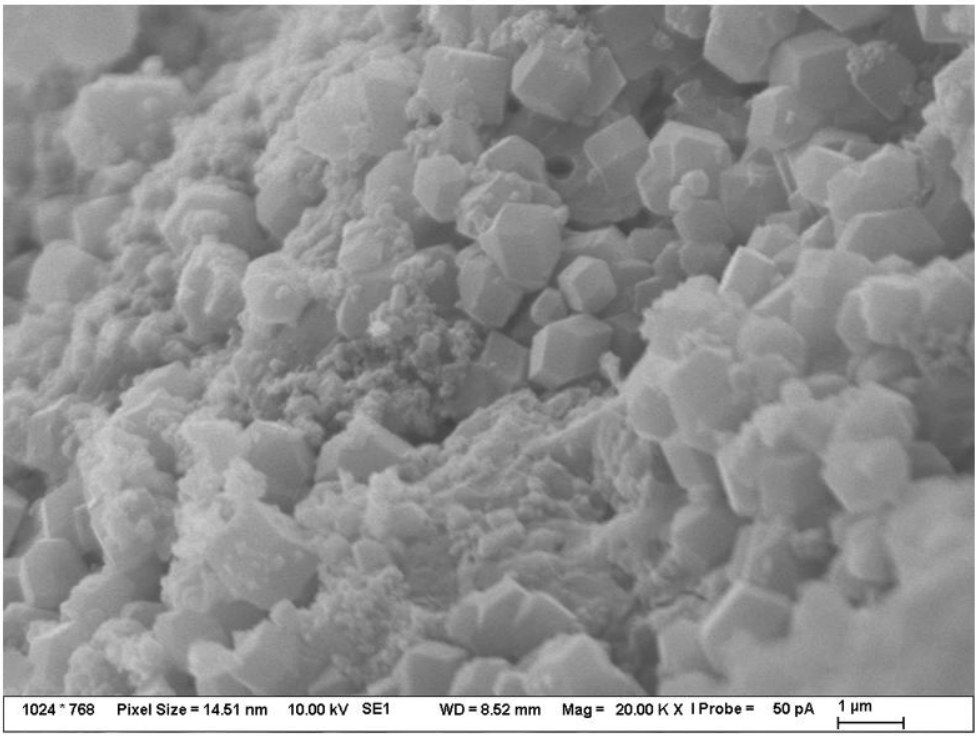

Figure 2 Detail of ZIF-8 particles prepared with a reaction time of 48 h at laboratory temperature on PEO coatings on AZ31 alloy

ZIF-8 coating prepared with a reaction time of 48 h and PEO coating were subjected to potentiodynamic polarization method in 200 mL 0.9% NaCl water solution (**Figure 3**). The potentiodynamic curves and electrochemical parameters obtained by fitting these curves (**Table 2**) showed that ZIF-8 coating improved the corrosion resistance as the corrosion current density decreased significantly compared to PEO coating. The corrosion current density for ZIF-8 was 0.04 μA/cm^2, while that for PEO coating was 0.26 μA/cm^2. The significant improvement in corrosion resistance was particularly evident when compared to AZ31 alloy, which had a much higher corrosion current density of 19.8 μA/cm^2. The anodic region shows the passivation region, but the extent is not affected by the ZIF-8 coating.

Table 2 Potential (E) and corrosion current density (i) obtained from potentiodynamic polarization measurements

Sample	**E (V)**	**i (μA/cm^2)**
AZ31	-1.45	19.8
PEO/AZ31	-1.51	0.26
ZIF-8/PEO/AZ31	-1.60	0.04

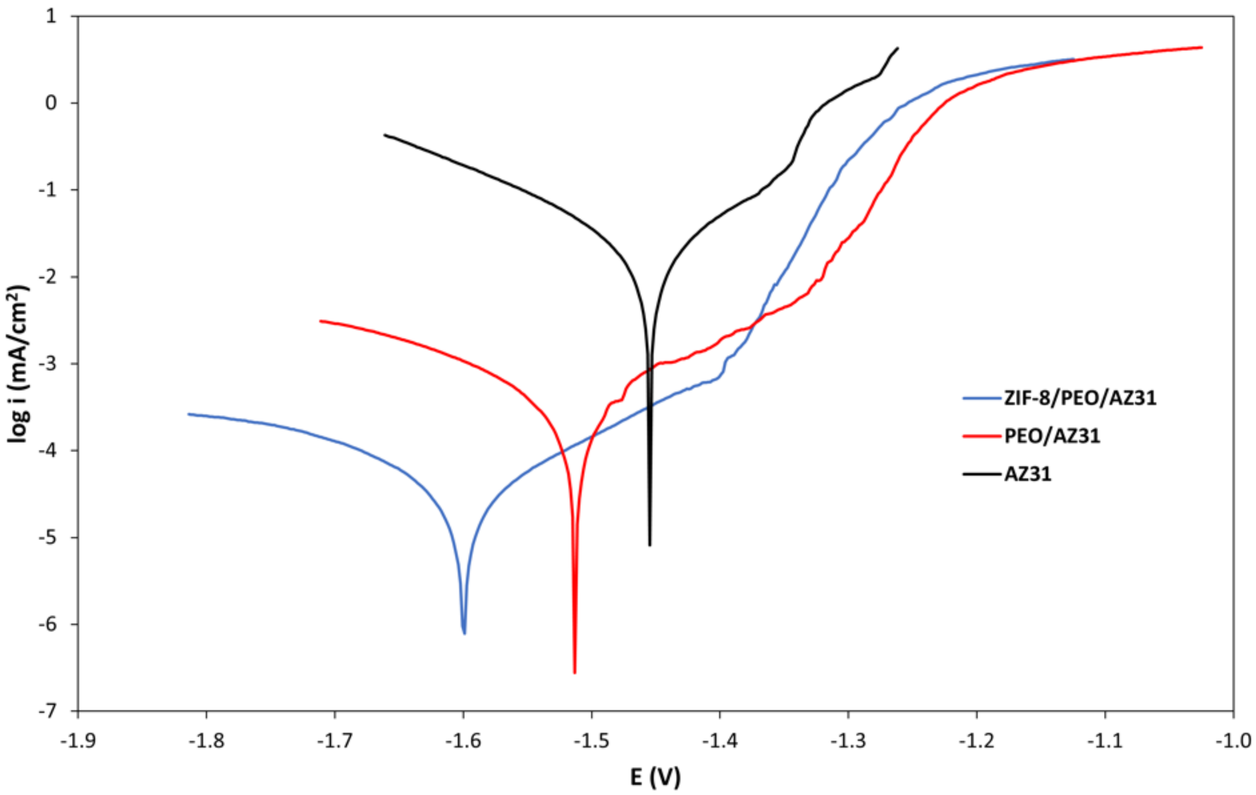

Figure 3 Potentiodynamic curves of the ZIF-8 coating (blue curve), the PEO coating (red curve) and AZ31 alloy (black curve). The graph expresses the dependence of current density (i) on the potential (E), which is related to the saturated calomel electrode (SCE)

4. CONCLUSION

ZIF-8 particles were prepared by in situ method on the surface of PEO coating under laboratory conditions at different times. The PEO coating surface was covered with ZIF-8 particles after a time of 48 h, and the particles had a size of about 1 μm. The formation of ZIF-8 particles on the surface improved the corrosion behaviour as indicated by PDP measurements in 0.9% NaCl. These results suggest a promising route for the preparation of MOF particles. Future work will target the preparation of ZIF-8 coatings with uniform particle size and improved PEO surface coverage under shorter time conditions.

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