PREPARATION OF PEO COATINGS ON AZ31 MAGNESIUM ALLOY IN THE PRESENCE OF HUMIC ACID

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Abstract

Magnesium materials are desirable for surface treatment because of their low corrosion resistance. The preparation of coatings on AZ31 alloy by plasma electrolytic oxidation (PEO) in a bath with and without humic acid was investigated. The coatings were characterized using a scanning electron microscope (SEM) with energy dispersive X-ray spectroscopy (EDS) and Fourier transform infrared spectroscopy (FTIR). The corrosion properties were tested using the potentiodynamic polarization method in 0.15 M NaCl. The results show that the PEO coatings had significantly higher corrosion resistance than the AZ31 alloy. The PEO coating prepared in the presence of 5 mg/l humic acid (10 min deposition) appeared to have slightly better corrosion resistance than the PEO coating prepared in the absence of humic acid.

Keywords: Magnesium alloys, humic acid, applications, corrosion

1.   INTRODUCTION

Magnesium and its alloys have good mechanical properties such as good machinability and low density. A negative feature of these alloys is their low corrosion resistance. For this reason, various methods of surface treatment (e. g. superhydrophobic coatings, High Velocity Oxygen Fuel (HVOF) coating, Ni-P coating) are being investigated to improve their corrosion resistance [1].

One of these surface treatments can be plasma electrolytic oxidation (PEO). In this process, a coating of PEO is applied from the electrolytic bath to the surface of the sample under the influence of voltage and current. The magnesium alloy treated in this way provides higher corrosion resistance than an untreated surface. The electrolytic bath is usually composed of alkali metal hydroxides (NaOH, KOH) and simple inorganic substances such as phosphates, silicates, borate etc [2]. Organic additives (e.g. glycerol, phytic acid, 8-hydroxyquinoline, tannic acid) are also used to modify PEO electrolytes. Pan et al. [3] reported that the introduction of glycerol into the bath resulted in a denser coating with more uniform pores. Zhang et al. [4] found that the addition of 8-hydroxyquinoline (HQ) to the PEO bath caused the formation of insoluble $Mg(HQ)_2$ compound and reduced the pore size. Echeverry-Rendom et. al. [5] investigated the effect of hexamethylentetramine and mannitol on the properties of PEO coating. Their results showed that the as-prepared PEO coatings had better corrosion resistance than those without the use of organic substances. The growing interest in the preparation of PEO coatings on magnesium alloys in the presence of organic additives is evidenced by a recently published review article by Kaseem et al. [6].

In this work, the electrolytic bath was modified by the addition of humic acid, which is characterized by its environmental friendliness. Humic acids are a mixture of organic substances with a high molecular weight and a high content of oxygen functional groups (carboxylic and hydroxyl groups) [7]. Humic acids are insoluble in water at a pH below 2. They occur naturally in water, but also in soil, peat and coal, from which they can be isolated.

The aim of this work was to prepare a PEO coating in the presence of humic acid on AZ31 magnesium alloy. The effect of the deposition time and humic acid concentration on the resulting corrosion resistance was investigated. Corrosion tests were carried out by potentiodynamic polarization in 0.15 M NaCl.

2. MATERIAL AND METHODS

2.1 Material

AZ31 magnesium samples were used in this experiment. The alloy elemental composition was determined by Glow-Discharge Optical Emission Spectroscopy (GDOES; Spectrumat GDS 750, Spectruma Analytik GmbH, Hof, Germany) and summarized in **Table 1**. Dimensions of these samples were 50 mm × 20 mm × 5 mm. The sample were surface treated by grinding with 800 and 1200 SiC paper, rinsed with deionized water and isopropanol and dried with hot air. Humic acid was isolated from South Moravian lignite.

Table 1 Elemental composition of magnesium alloy AZ31

Content (wt.%)	Al	Zn	Mn	Si	Fe	Sn	Zn	Mg
AZ31	3.60	1.34	0.28	0.03	0.002	0.01	-	Bal.

2.2 Coating preparation

The PEO coating was prepared by plasma electrolytic oxidation. The electrolytic bath consisted of 12 g Na_3PO_4 12 H_2O, 1 g KOH and various concentrations of humic acid (0 to 50 mg/L). The volume of the prepared electrolytic bath was 1.5 L. The ground AZ31 alloy samples were placed in the bath and formed the anode. Stainless steel was used as the cathode. The PEO coating was deposited under constant stirring of the bath at a voltage of 630 V and a current of 1.303 mA. The value of the applied DC current was determined by calculation based on the area of the sample. The deposition time ranged from 5-15 min.

First, PEO coatings were prepared in an electrolytic bath containing 0, 5, 15, 25 and 50 mg/L humic acid for a deposition time of 10 min. Subsequently, another series of PEO coatings were prepared in a bath containing 0, 5 and 25 mg/L humic acid for 5 and 15 min. After completion of the plasma electrolytic oxidation, the samples were removed from the electrolytic bath and rinsed with deionized water and isopropanol and dried with hot air.

2.3 Characterization

SEM and EDS analysis

A scanning electron microscope (SEM, ZEISS, EVO LS-10) with an energy dispersive X-ray spectroscope (EDS, Oxford Instruments plc, Abingdon, UK) was used to characterize the surface morphology and elemental composition of the PEO coatings.

PDP measurements

Potentiodynamic polarization (PDP) measurements were performed using a Bio-Logic VSP-300 potentiostat (BioLogic, Seyssinet-Pariset, France). The measured samples were used as working electrode. The exposed area of the measured samples was 1 cm^2. The saturated calomel electrode (SCE) was used as the reference electrode and Pt mesh as the counter-electrode. A 0.15 M NaCl solution without pH adjustment was used as a corrosive medium in the corrosion cell with a volume of 200 ml. Open circuit potential (OCP) were stabilized during 60 min of exposure. Afterwards, PDP measurements were performed in the potential range from −150 mV to 500 mV vs. OCP at a scan rate of 1 mV/s.

FTIR spectrometry

Fourier transform infrared (FTIR) spectrometry (Nicolet iS10 spectrometer) was used to characterize humic acid and PEO coatings prepared in the presence and absence of humic acid. Measurements were performed by attenuated total reflection (ATR) in the spectral range 4000-400 cm^{-1} and a resolution of 1 cm^{-1} with an average of 128 scans. A clean and dry diamond crystal was used for the ATR measurements.

3.   RESULTS AND DISCUSSION

SEM analysis showed that the PEO coatings prepared in the bath with and without humic acid at different deposition times had very similar morphologies. There were open pores and micropores on their surface, and no microcracks were observed. A larger number of pores was observed when a higher concentration of humic acid was used. **Figure 1** shows the typical surface appearance of a coating prepared in the electrolyte bath in the absence of humic acid and in the presence of 5 mg/L humic acid. Arrows in the **Figure 1** show the area of occurrence of pores/micropores. These coatings had the best corrosion resistance (see below) and were prepared at a deposition time of 10 min. The similarity of the morphology of both samples was probably related to the fact that humic acids were not incorporated into the structure of the PEO coating, as shown by the results of FTIR analysis. On the other hand, EDS analysis revealed a higher carbon content (7.5 at. %) for the PEO coating prepared in the presence of humic acid in compared to the PEO coating prepared in a bath without humic acid, which had 5.9 at. % carbon. This suggests that a minor amount of humic acid may have adsorbed on the coating surface from the bath. It is likely that the low molecular fractions of humic acid were preferentially adsorbed.
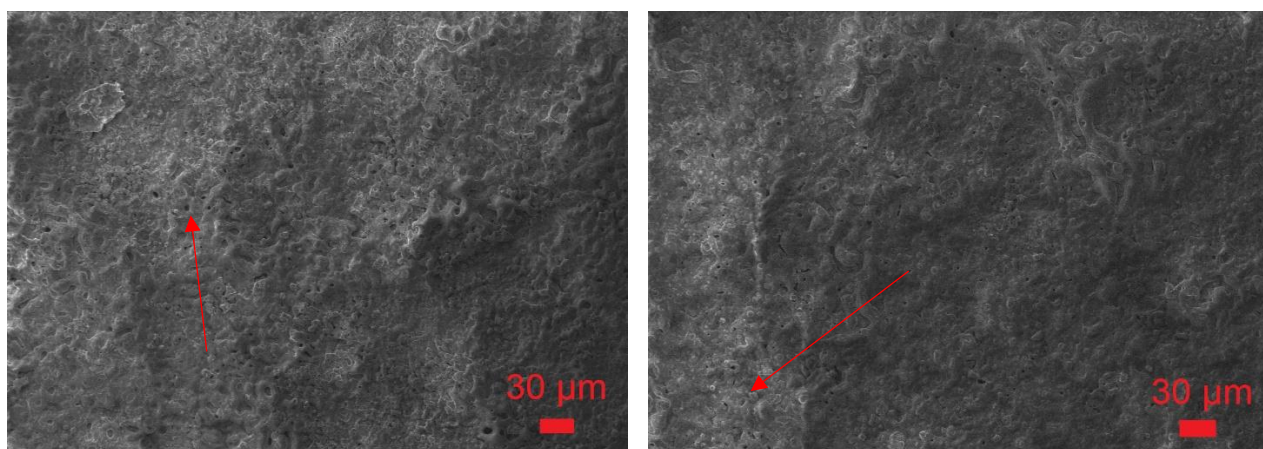

Figure 1 SEM analysis for PEO coatings prepared in a bath without humic acid (left) and with 5 mg/L humic acid (right). The deposition time was 10 min

Potentiodynamic polarization curves were measured in 0.15 M NaCl solution for untreated AZ31 alloy, PEO coating and for PEO coatings modified with humic acid in the amount of 5 – 50 mg/L and at different deposition times of 5 min, 10 min and 15 min. The corrosion parameters such as corrosion current density (i_{cor}) and corrosion potential (E_{cor}) were evaluated and are summarized in **Table 2**.

From the resulting values of corrosion parameters, it is evident that the AZ31 alloy treated with PEO shows better corrosion resistance than the untreated AZ31 alloy. The PEO coating without humic acid was prepared at different deposition times (5, 10 and 15 min) to optimize the preparation conditions. The values of corrosion parameters show that the optimal deposition time was 10 min. Samples of PEO coating prepared in the bath with 5, 15, 25 and 50 mg/L humic acid were prepared at 10 min of deposition time. The best values of corrosion parameters had samples with humic acid addition of 5 mg/L and 25 mg/L. For this reason, these samples were

also prepared with deposition times of 5 min and 15 min. From the values obtained, it can be seen that the optimal deposition time in terms of corrosion resistance was 10 min, if 5 mg/L of humic acid was added to the bath. The improvement in corrosion resistance can be mainly indicated by a positive shift in the corrosion potential compared to the PEO coating prepared without humic acid.

Table 2 Corrosion parameters obtained from PDP measurements. The abbreviation HA means humic acid

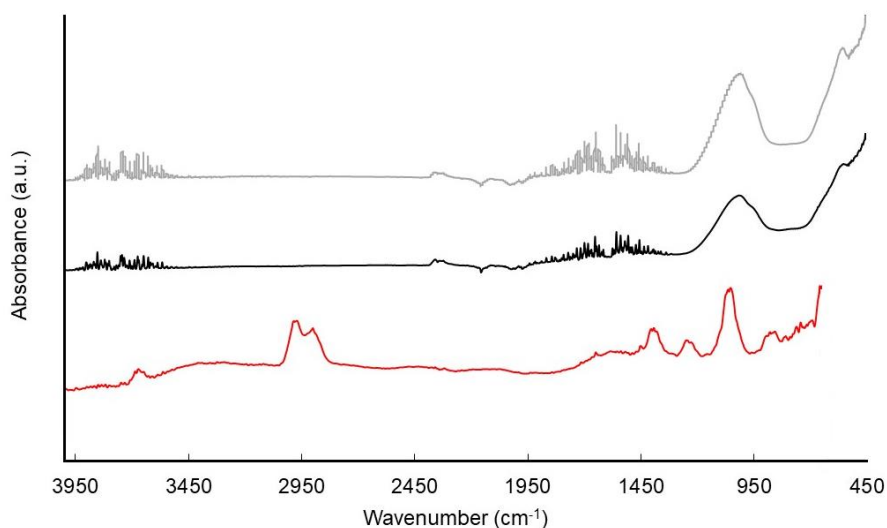| Sample		i_{cor} ($\mu A/cm^2$)	E_{cor} (V)
Concentration of HA (mg/L)	Time of deposition (min)		
Untreated AZ31		6.7 ± 0.6	-1.48 ± 0.02
0	5	0.66 ± 0.11	-1.66 ± 0.01
	10	0.03 ± 0.01	-1.60 ± 0.02
	15	0.04 ± 0.01	-1.56 ± 0.01
50	10	0.45 ± 0.09	-1.50 ± 0.02
25	5	0.32 ± 0.10	-1.70 ± 0.02
	10	0.08 ± 0.02	-1.56 ± 0.04
	15	0.04 ± 0.01	-1.55 ± 0.02
15	10	0.11 ± 0.01	-1.47 ± 0.03
5	5	0.16 ± 0.05	-1.69 ± 0.02
	10	0.02 ± 0.01	-1.50 ± 0.01
	15	0.04 ± 0.01	-1.53 ± 0.01

Figure 2 FTIR spectrum of humic acid (red), PEO coating (black) and PEO coating prepared in the presence of 5 mg/L humic acid (grey)

The FTIR spectrum of humic acid is shown in **Figure 2** and its interpretation was based on the literature [3]. The hydroxyl groups were located in the region 3390-3270 cm^{-1}. The methyl and methylene groups were located in the 2901 and 2982 cm^{-1} bands. These aliphatic groups were also indicated by the 1450 cm^{-1} band. The band in the 1580 cm^{-1} region was attributed to aromatics and the band in the 1380 cm^{-1} region was attributed to methyl aromatics. The band around 1650 cm^{-1} was related to carboxyl groups. Phenols and ethers around 1230 cm^{-1} and alcohols around 1060 cm^{-1} were also present in the spectra. A C-H distortion in the

band 900-700 cm^{-1} corresponding to aromatics was also found in the spectra. The spectra of PEO coatings prepared in the bath with and without humic acid were the same. This implies that humic acid was not present in the PEO coating. Broad bands centered around 1000 cm^{-1} and 550 cm^{-1} can be attributed to phosphate groups [4,5]. This is in agreement with the observation of Hadzima et al. [7] who presented that the PEO coating prepared from a bath of Na$_3$PO$_4$ and KOH was composed of magnesium phosphate. However, EDS analysis indicated a higher carbon content on the PEO coating that was prepared in a bath containing humic acid. This opens the way for experiments related to the modification of the PEO coating by humic acid adsorption, which could prevent the access of ions to the surface of the AZ31 alloy due to its physicochemical properties.

4.   CONCLUSION

The PEO coating prepared in a bath enriched with 5 mg/L humic acid at a deposition time of 10 min resulted in a very similar value of corrosion current density as in the case of the PEO coating prepared without humic acid at the same deposition time. However, the corrosion potential shifted to a more positive value. Thus, the PEO coating prepared in the presence of humic acid appears to be more corrosion resistant. Its preparation requires further experiments. One of the possible directions concerns the use of specific properties of humic acids to significantly increase the corrosion resistance of the coating on the AZ31 alloy.

ACKNOWLEDGEMENTS

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