

CORROSION BEHAVIOUR OF AZ31 ALLOY IN AN ALKALINE ENVIRONMENT OF 0.1 M NaCl IN THE PRESENCE OF LIGNITIC HUMIC ACID

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Abstract

Magnesium alloys are characterized by high corrosion rates. This undesirable phenomenon can be slowed down by corrosion inhibitors. Particularly environmentally friendly molecules are in the spotlight. A possible candidate for a green inhibitor may be humic acid isolated from lignite. In this work, the corrosion behavior of AZ31 was investigated in 0.1 M NaCl with and without humic acid at pH 9. Surface analysis was performed using a scanning electron microscope (SEM) with an energy dispersive X-ray spectroscope (EDS) and Fourier-transform infrared (FTIR) spectroscopy. Corrosion behavior was investigated using potentiodynamic polarization (PDP) measurements. The results showed that lignitic humic acid accelerates corrosion in 0.1 M NaCl at pH 9 and this effect was concentration dependent.

Keywords: AZ31 alloy, humic acid, corrosion

1. INTRODUCTION

Magnesium and its alloys have a great potential for use in the metals industry (e.g. aerospace and automotive). The property that makes magnesium and its alloys so attractive is their high specific stiffness and low density. Another very important engineering properties are their good castability and formability [1,2].

The downside of magnesium and its alloys is the high reactivity and low corrosion resistance in many environments, even though the surface of these materials is coated with Mg(OH)₂. This is because the magnesium hydroxide layer is porous and readily dissolves to MgCl₂ in a chloride-containing environment [1].

The high reactivity of magnesium materials is reflected by the low electrode potential, which can be used to provide cathodic protection. Magnesium and its alloys can act as sacrificial anodes of undersea and underground metallic structures, submarines, ships, aircraft etc. In addition to inorganic components, there may also be interaction with organic compounds such as humic acids [1,2].

Humic substances are natural organic compounds that are most often formed by biological and chemical decomposition of organic substances (plant and animal remains) or by synthetic activity of microorganisms. Humic substances are divided into three groups based on solubility according to pH. In this work, humic acids, which is a fraction soluble in alkaline aqueous solution and insoluble at pH lower than about 2, were used. Humic acids represent the major fraction of humic substances [3-4,7-9]. Humic acids have good sorption properties for water and plant nutrients. They are now widely used as fertilizers in agriculture, which can lead to increased concentrations in soil and water [4-8].

The study of corrosion of magnesium alloys in the presence of humic acid is minimally investigated. Recently, a paper was published on the role of humic acid in the corrosion of magnesium alloy AZ31. The results showed that humic acid contributes to the depletion of magnesium ions by forming complexes and thus to the increase in corrosion rate. The study also suggested that the presence of humic acid could promote the formation

of magnesium hydroxide nanoparticles on the surface of AZ31 alloy [10]. There are also studies on the effect of humic acids on the corrosion behavior of other metallic materials such as low carbon steel [11].

Authors of the article [12] studied corrosion of steel API 5LX65 in 0.01 M sodium sulfate solution with addition of humic and fulvic acids both isolated from peaty soil. Also, authors of the article [13] studied corrosion of steel in lake water with high humic acids concentration. Both these articles concordantly suggest that humic acids accelerate corrosion behavior of steel by passivation layer disturbance and then initiating pitting corrosion. These articles also found out, that humic acids accelerate corrosion by supporting anodic reaction of steel. Furthermore, authors discovered, that humic acids can adsorb on the surface of corrosion products of steel (hematite and goethite) forming a protective layer on the steel surface. However, the layer had low adhesion [12-13]. The corrosion effect of humic acid on aluminum alloy 3SR in alkaline environment was also investigated [5]. Humic acid acted as a corrosion inhibitor for aluminum under alkaline conditions. The corrosion inhibition efficiency increased with increasing concentration of humic acid. The authors also hypothesized that this inhibition took place by adsorption of humic acid on the surface of aluminum alloy [5].

The aim of this work was to investigate the effect of lignitic humic acid on the corrosion of magnesium alloy AZ31 in an alkaline environment of 0.1 M NaCl. Potentiodynamic polarization measurements were performed at low and higher humic acid concentrations.

2. EXPERIMENTAL

Humic acid was extracted from South Moravian lignite, which was obtained from Mikulčice. Humic acid was extracted using a procedure recommended by the International Humic Substances Society. First, dried lignite was demineralized by 0.1 M HCl, then suspension has been washed by demineralized water until neutral pH was obtained. Then suspension was shaken overnight in the presence of 0.1 M NaOH and 0.1 Na₄P₂O₇. After centrifugation supernatant was acidified to pH < 2 by 6 M HCl and once again precipitate was separated by centrifugation. Then precipitate of humic acid was purified by dialysis using a Spectra/Por cellulose membrane (1 kDa) until no chloride ions were detected. Finally, lignitic humic acid was freeze-dried.

A 200 mg·l⁻¹ humic acid solution was prepared by dissolving humic acid in 0.1 M NaOH containing 0.1 M NaCl. The initial pH value, which was around 12.5, was then adjusted to 9 using HCl. The solution was stirred for 24 h and after this time it was filtered using a 0.45 μm porous filter. The finished stock solution was then stored in a refrigerator and used for corrosion testing.

For corrosion tests magnesium alloy AZ31 samples were used with dimensions: 20 × 20 × 6 mm. The elemental composition of AZ31 alloy was determined by Glow-Discharge Optical Emission Spectroscopy (GDOES; Spectrumat GDS 750, Spectruma Analytik GmbH, Hof, Germany). The elemental composition of AZ31 alloy was Al 3.6 %, Zn 1.3 %, Mn 0.3 % and Mg 94.8 %. Before testing samples were grinded using 320 and 1200 SiC grit abrasive papers. Then samples were washed in distilled water and isopropyl alcohol and then dried by hot air.

Total organic carbon (TOC) analysis was determined by accredited testing laboratory LABTECH using a Shimadzu TOC 500A analyzer according to Czech technical standard norm ČSN EN 1484.

For the structural characterization of organic substances, FTIR spectrometer with the Attenuated Total Reflectance technique (Nicolet iS50, ThermoFisher Scientific, Waltham, MA, USA) was used.

The short-term potentiodynamic measurements were performed in 0.1 M NaCl solution with 0, 24 and 96 mg·l⁻¹ humic acid. Test were measured using Bio-Logic VSP-300 potentiostat (BioLogic, Seyssinet, Pariset, France). Sample with exposed area 1 cm² of served as the working electrode. As reference electrode saturated calomel electrode (SCE) was used and Pt wire as counter-electrode. Open circuit potential (OCP) was set to 1 hour. Potentiodynamic polarization curves were obtained by performing potentiodynamic polarization over the potential range from -200 mV to 250 mV from OCP at the potential scan rate of 1 mV·s⁻¹.

The surface of the corroded samples was analyzed using scanning electron microscopy (SEM, EVO, ZEISS LS10, Carl Zeiss Ltd., Cambridge, UK). Energy-dispersive X-ray spectroscopy (EDS, Xmax 80 mm², Oxford Instruments plc, Abingdon, UK) was used to characterize the corrosion products.

3. RESULTS AND DISCUSSION

TOC analysis showed that the prepared humic acid solution contained 96 mg·l⁻¹ of organic carbon. For corrosion tests, three solutions containing 0, 24 and 96 mg·l⁻¹ humic acid in 0.1 M NaCl were prepared and the pH was set to 9.

FTIR spectra of humic acid and its fractions were analyzed (not shown). Both spectra were identical. They contained aliphatic groups around 2880 cm⁻¹, including methyl and methylene groups. These groups were confirmed by a deformation band at 1457 cm⁻¹. There were also indication of aromatic substances and methyl groups bonded to aromatics at 1560 and 1374 cm⁻¹. Then there was a distinct band at approximately 1700 cm⁻¹ which indicate carboxylic groups. Furthermore, small bands of aryl ether compounds (1263 cm⁻¹), phenols and ethers (1200 and 1149 cm⁻¹) and alcohols (1091 and 1038 cm⁻¹) were present in the spectra. There were found out-of-plane C-H deformation bands in the wavenumber range 900-700 cm⁻¹. The presence of oxygen functional groups allows the formation of complexes of humic acids with metal cations such as Mg²⁺.

Potentiodynamic polarization measurements were performed in 0.1 M NaCl solution and in 0.1 M NaCl with lignitic humic acid at various concentrations (24 and 96 mg·l⁻¹). The potentiodynamic curves are shown in **Figure 1** and values of corrosion potential E_{corr} and corrosion current density i_{corr} are given in **Table 1**. The results show that the corrosion potential slightly decreased to more negative values with increasing humic acid concentration, indicating that AZ31 alloy in the given environment is susceptible to corrosion. Also, the corrosion current density values show that the corrosion resistance decreased with increasing humic acid concentration. A concentration of 96 mg·l⁻¹ humic acid caused a two and a half times increase in corrosion current density compared to a pure 0.1 M NaCl solution. The negative effect of humic acid may also be indicated by the loss of the passivation region in the anodic branch of the polarization curve. It can be assumed that the humic acid formed complexes with Mg²⁺ ions and this resulted in the inability to form a sufficiently semi-protective Mg(OH)₂ layer. These findings are consistent with the literature [10].

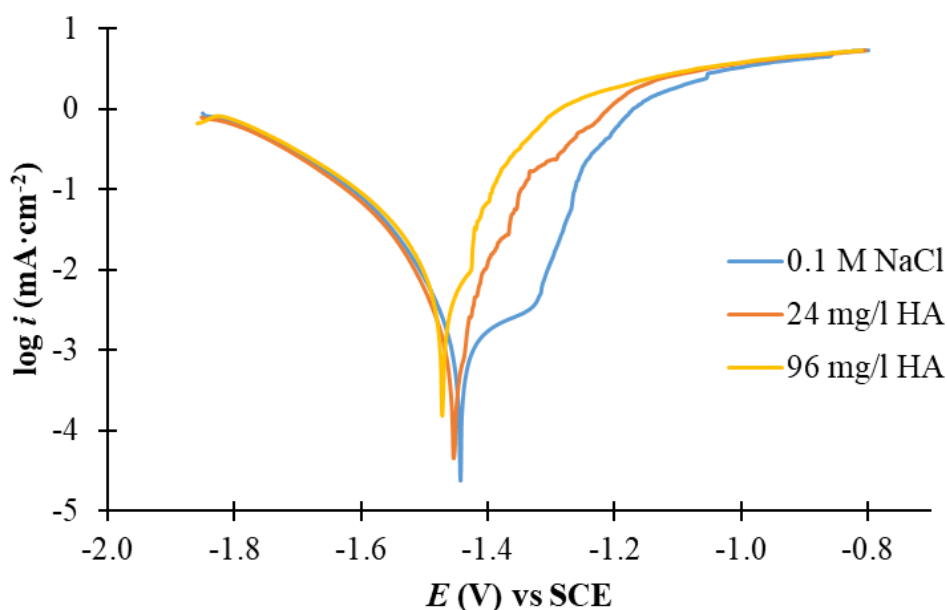


Figure 1 Potentiodynamic polarization curves of AZ31 alloy in the presence of 0.1 M NaCl solution with and without humic acid (HA)

Table 1 Values of corrosion current density (i_{corr}) and corrosion potential (E_{corr}) for 0.1 M NaCl solution with and without humic acid (HA)

Corrosion solution	i_{corr} ($\mu\text{A}\cdot\text{cm}^{-2}$)	E_{corr} (V)
0.1 M NaCl	1.2	-1.44
24 mg·l ⁻¹ HA	2.2	-1.45
96 mg·l ⁻¹ HA	2.9	-1.47

The AZ31 alloy samples after corrosion in NaCl were characterized using SEM-EDS analysis, see **Figure 2**. The surface of AZ31 alloy after corrosion in 0.1 M NaCl (**Figure 2a**) was largely covered by a layer of Mg(OH)₂, which was indicated by elemental analysis, see **Table 2**. The area with exposed surface of AZ31 alloy was characterized by low oxygen content. The surface of AZ31 alloy showed very low to minimal Mg(OH)₂ coverage after corrosion in 0.1 M NaCl with 96 mg·l⁻¹ HA (**Figure 2b**). This can be explained by the binding of Mg²⁺ ions by humic acid to form complexes. The depletion of Mg²⁺ ions prevents the formation of Mg(OH)₂ coating, which can serve as a barrier against the access of corrosive environment to the surface of AZ31. This can be related to the low corrosion resistance, which is consistent with potentiodynamic polarization measurements. This observation is consistent with previous work [8]. Adsorption of lignitic humic acid was indicated by the higher carbon content compared to EDS analysis for 0.1 M NaCl.

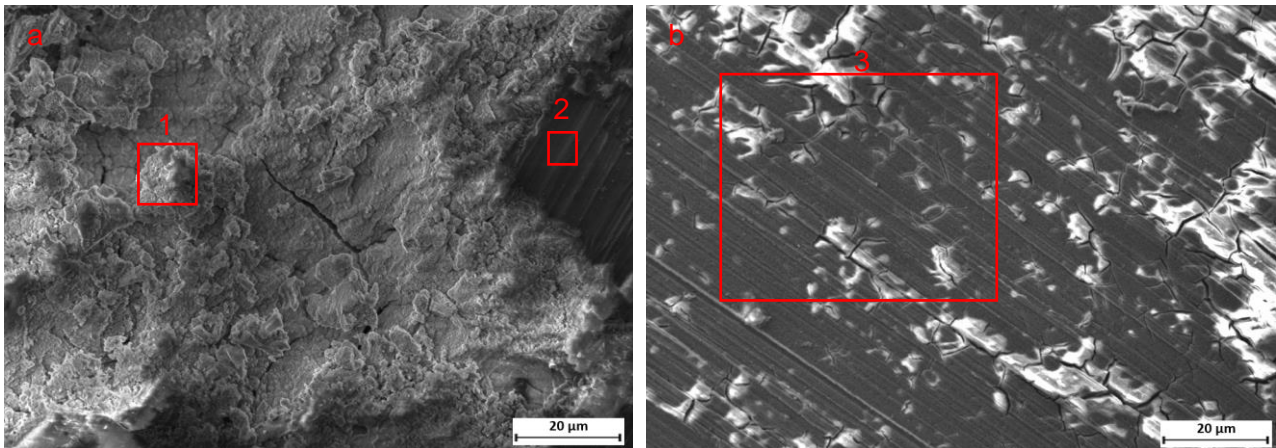


Figure 2 SEM images of AZ31 alloy after corrosion in 0.1 M NaCl (a) and in 0.1 M NaCl with 96 mg·l⁻¹ humic acid (b)

Table 2 EDS analysis of samples corroded in 0.1 M NaCl and in 0.1 M NaCl with 96 mg·l⁻¹ humic acid

Element	Area 1		Area 2		Area 3	
	wt%	at. %	wt%	at. %	wt%	at. %
C	1.2	1.9	0.6	1.3	7.0	11.3
O	48.1	58.0	5.0	7.5	40.2	48.2
Mg	50.0	39.6	89.4	88.0	44.9	36.2
Cl	0.7	0.5	-	-	1.4	0.8
Al	-	-	2.8	2.4	4.0	2.8
Zn	-	-	2.2	0.8	2.5	0.7

4. CONCLUSION

Potentiodynamic polarization tests confirmed that the addition of humic acid increased the corrosion current density value and the corrosion potential value was also more negative. This indicates that humic acid had a negative effect on the corrosion of AZ31 alloy. It was found that the higher the concentration of humic acid, the lower the corrosion resistance. The corrosion products consisted of Mg(OH)₂ and EDS analysis showed that humic acid could partially adsorb on the surface of Mg(OH)₂. The deterioration of corrosion properties was explained by the ability of humic acid to bind Mg²⁺ ions to form complexes, which led to a lower surface coverage of AZ31 alloy with magnesium hydroxide.

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