PREPARATION OF MG-AL LDH COATING ON AZ31 MAGNESIUM ALLOY UNDER MILD CONDITIONS

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Abstract

Magnesium and its alloys are interesting materials but they have low corrosion resistance. Magnesium-aluminium double layered hydroxide (Mg-Al LDH) coatings were prepared on AZ31 alloy by hydrothermal method at 50 °C, 70 °C and 90 °C at different reaction times (3 h, 6 h and 24 h). The coatings were characterized by scanning electron microscope (SEM) with energy dispersive X-ray spectroscope (EDS), X-ray diffraction (XRD) and potentiodynamic polarization measurements in 0.15 M NaCl. The optimum conditions for the preparation of the coating included a temperature of 90 °C and a reaction time of 24 h, as the coating was composed of Mg-Al LDH and exhibited the highest corrosion resistance.

Keywords: Mg-Al LDH coatings, AZ31 alloy, corrosion, mild conditions

1. INTRODUCTION

Magnesium and its alloys have good mechanical properties and low density, thanks to these properties it can be used in many interesting applications (transport industry, medicine etc.). The disadvantage of magnesium materials is their low corrosion resistance [1]. For this reason, are magnesium alloys surface treated by various methods to increase their corrosion resistance (e. g. superhydrophobic coatings, High Velocity Oxygen Fuel (HVOF) coating, Ni-P coating) [2]. One of the promising and currently popular method is the preparation of a double layered hydroxide (LDH) coating. Special attention is paid to the Mg-Al LDH type coating. This coating has many interesting properties and has the potential to increase the corrosion resistance of magnesium alloy [3-5]. The principle of reducing the corrosion rate of the substrate lies in the mechanical barrier and the ability of these layers to trap corrosive anions (e.g. Cl^-) in their structure. For this reason, the contact between the corrosive environment and the substrate surface is reduced [2].

The structure of LDH is made up of flat layers of octahedral clusters $[Mg(OH)_6]$ that are connected by hydrogen bonds. This structure is formed from the magnesium cations Mg^{2+}, which are octahedrally coordinated by six hydroxyl anions OH^-. The basic structural formula of LDH is $[M^{II}_{1-x}M^{III}_x(OH)_2]^{x+}[A^{n-}_{x/n}\cdot yH_2O]^{x-}$, where M^{II} represents the divalent metal, M^{III} the trivalent metal and A^{n-} the n-potent intercalated anion. In this structure, the positive charge of the magnesium cations is compensated by the negative charge of the hydroxyl anion. [5,6]

The preparation of LDH coatings is usually carried out by the hydrothermal method, which requires higher temperatures. However, this route is not attractive for industrial applications. Recently, several papers have been published on the preparation of LDH coating under mild conditions. Shulha et al. [3] investigated the effect of chelating agents on the preparation of Mg-Al LDH coating on AZ91 alloy. The authors showed that LDH synthesis was achieved under mild reaction conditions (95°C, 6h, pH 10) and facilitated in the presence of chelating agents such as NTA and EDTA. Dou et al. [6] investigated the effect of initial Al^{3+} ion concentration on the preparation of Mg-Al LDH coatings on AZ31 magnesium alloy. Their results suggest that different Al^{3+} concentration has an impact on the corrosion resistance and structure of the prepared LDH coating.

The aim of this work was to prepare Mg-Al LDH coating on AZ31 alloy under mild conditions with emphasis on the effect of temperature and time. The prepared coatings were characterized by potentiodynamic polarization in 0.15 M NaCl.

1. MATERIAL AND METHODS

1.1 Material

Magnesium alloy AZ31 was used in this experiment. 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 in wt.% consist of 3.60 Al, 1.34 Zn, 0.28 Mn, 0.03 Si, 0.002 Fe, 0.01 Sn and Mg. Dimensions of the AZ31 samples were 20 mm × 20 mm × 5 mm. These samples were ground with 800 and 1200 grit SiC paper, rinsed by deionized water and isopropanol, and dried with hot air.

1.2 Coating preparation

The solution for Mg-Al LDH coating was prepared by dissolving 0.1 M EDTA in 50 ml of deionized water. The pH of this solution was adjusted by 2 M NaOH solution at the value of 7 – 7.4. After that 0.25 M $NaNO_3$ and 0.05 M $Al(NO_3)_3$ were added to the solution and the pH value was adjusted by NaOH solution at 10 ± 0.1. The grounded samples were put into beakers with 50 ml of this solution and covered by aluminium foil. The beakers were put into preheated oven. The conditions were used: (i) 50 °C, 3 h, 6 h, 24 h, (ii) 70 °C, 3 h, 6 h, 24 h and (iii) 90 °C, 3 h, 6 h, 24 h. After the reaction the samples were rinsed by deionized water, isopropanol and dried with hot air.

1.3 Characterization

SEM – EDS Analysis

The surface morphology and elemental composition of the Mg-Al LDH coating was characterized using scanning electron microscope (SEM, ZEISS, EVO LS-10) with an energy dispersive X-ray spectroscope (EDS, Oxford Instruments plc, Abingdon, UK).

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.

XRD Analysis

The phase composition of Mg-Al LDH coating was analysed by X-ray diffraction (XRD; Panalytical, Malvern, UK). The X-ray source was Cu Kα1 radiation (λ =1.540598 Å), which was operated at a voltage of 40 kV and a current of 30 mA within the range of 5° and 90° 2θ at a scanning rate of 0.01313° 2θ time per step of 46 s.

2. RESULTS AND DISCUSSION

Visual observation of the samples showed that the coating changed from dark grey to light grey with increasing temperature and time, **Figure 1**.
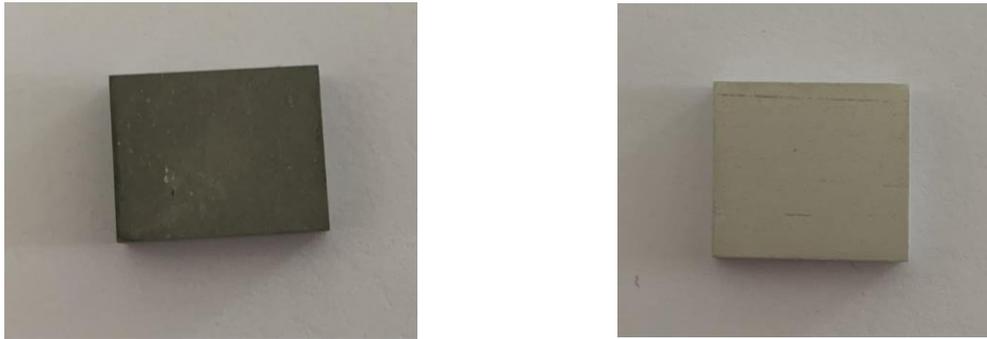
Figure 1 Colour transition of the Mg-Al LDH coating with increasing time and temperature. Mg-Al LDH prepared for 3 h at 50 °C (left), Mg-Al LDH prepared for 24 h at 90 °C (right)
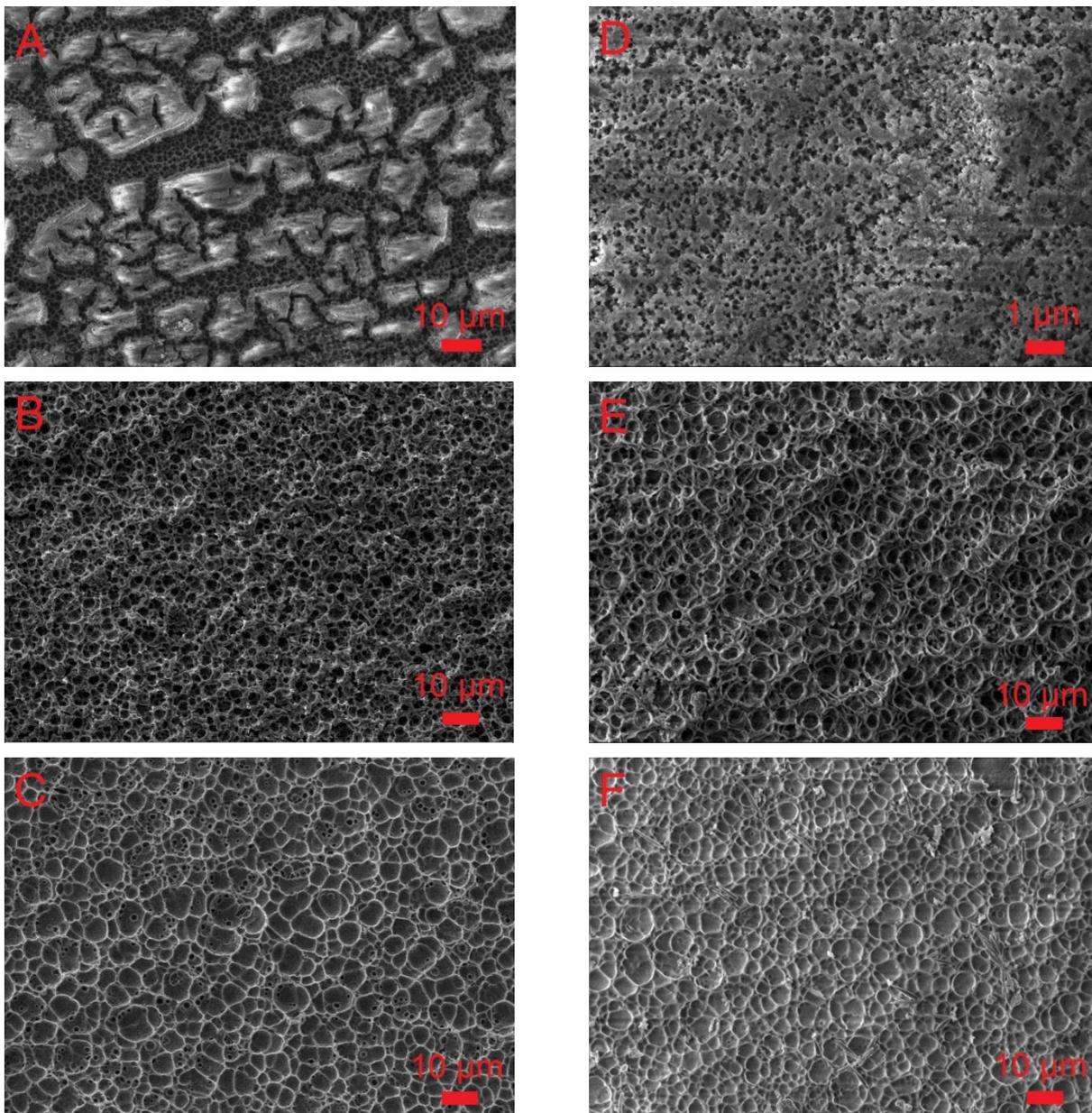

Figure 2 SEM images of AZ31 after surface treatment at 50 °C for 3 h (A) and 24 h (D), at 70 °C for 3 h (B) and 24 h (E), at 90 °C for 3 h (C) and 24 h (F)

SEM analysis showed that the morphology of the coatings changed with increasing temperature and time, **Figure 2**. The surface of the sample prepared at 50 °C for 3 h consisted of a network structure of $Mg(OH)_2$ and islands of $Mg(OH)_2$, **Figure 2A**. EDS analysis also revealed the presence of alumina around 8 at.%, but the presence of LDH was not detected by XRD. These islands grew with longer time and subsequently covered the surface of AZ31, **Figure 2D**. However, the surface was not compact and contained pores through which the corrosive environment could penetrate to the magnesium alloy of AZ31. Samples prepared at 70 °C again exhibited a network structure that appeared to be a honeycomb structure at longer times, **Figure 2B** and **2E**. The honeycomb structure obtained at 70 °C for 24 h had a larger cell diameter and the cells were discontinuously filled with spherical formations, consistent with a chemical composition dominated by $Mg(OH)_2$. The honeycomb-like structure was also observed at 90 °C at various temperatures, but at shorter reaction times the surface of some cells was observed to be partially perforated, **Figure 2C** and **2F**. This observation suggests that the higher temperature facilitated the growth of $Mg(OH)_2$ inside the cells, leading to their almost complete closure. The coating prepared at 90 °C for 24 h showed a closed surface and was covered with very fine Mg-Al LDH crystals, **Figure 2F**.

This means that the sample surface was degraded without forming a protective LDH coating, as can also be observed from the SEM analysis, **Figure 2A**. The longer preparation time of the coating resulted in i_{cor} values similar to those of untreated AZ31. These results suggest that the surface was covered with a layer of $Mg(OH)_2$, as shown by SEM analysis (**Figure 2E**), which provided partial protection for AZ31. The value of i_{cor} of the samples prepared at temperature of 70 °C for 3 h and 6 h were three times higher than untreated AZ31. A twofold decrease in the i_{cor} value was observed with increasing preparation time of the coating (24 h). This improvement is attributed to the incipient formation of the LDH coating, although it was not detected by XRD analysis. This could be due to the low content of LDH crystals and/or their nanoscale size. At a preparation temperature of 90 °C and a preparation time of 3 h, the corrosion resistance of the sample decreased relative to the AZ31 alloy. Longer preparation times of 6 h and 24 h improved the i_{cor} values by a factor of 2 and 6 compared to untreated AZ31. With respect to SEM and XRD analysis, the presence of LDH coating was confirmed for the samples prepared at 90 °C and 24 h. Thus, the increased corrosion resistance of the sample can be attributed to the presence of Mg-Al LDH coating on the AZ31 alloy. These results are consistent with the experiments performed by Shulha et al. [5] on the AZ91 alloy.

Table 1 Electrochemical parameters obtained from potentiodynamic curves for the corrosive environment of a 0.15 M NaCl solution

Preparation temperature (°C)	Preparation time (h)	i_{cor} (μA/cm^2)	E_{cor} (mV)
Untreated AZ31		6.4 ± 0.6	-1.47 ± 0.02
50	3	18.6 ± 3.2	-1.44 ± 0.01
	6	3.1 ± 2.1	-1.27 ± 0.03
	24	7.7 ± 1.9	-1.41 ± 0.03
70	3	17.0 ± 2.8	-1.45 ± 0.02
	6	21.6 ± 5.3	-1.46 ± 0.03
	24	3.8 ± 0.9	-1.30 ± 0.02
90	3	19.4 ± 4.1	-1.47 ± 0.02
	6	2.8 ± 2.2	-1.40 ± 0.01
	24	1.1 ± 0.7	-1.34 ± 0.01

Potentiodynamic polarization curves were measured in 0.15 M NaCl solution for untreated AZ31 alloy and for samples coated at 50 °C, 70 °C and 90 °C with reaction times of 3 h, 6 h and 24 h. The potenciodynamic

curves were evaluated and corrosion parameters, including corrosion current density (i_{cor}) and corrosion potential (E_{cor}), were obtained as shown in **Table 1**. These results showed that the value of E_{cor} shifts to more positive values with increasing preparation time and temperature compared to uncoated AZ31. This indicates an improvement in corrosion properties from a thermodynamic point of view.

XRD analysis of the Mg-Al LDH coating prepared at 90 °C for 24 hours is shown in **Figure 3**. The results showed that it was possible to prepare Mg-Al LDH coating on AZ31 magnesium alloy under mild conditions. This fact is confirmed by the peaks at 11.7° 2θ° and 23.3° 2θ°, which are characteristic of LDH. The XRD spectra of the other samples did not contain this pair of peaks, which may indicate that suitable conditions for LDH coating formation were not achieved. However, it cannot be excluded that in some cases LDH crystals may have been present, but only in small amounts and very fine.
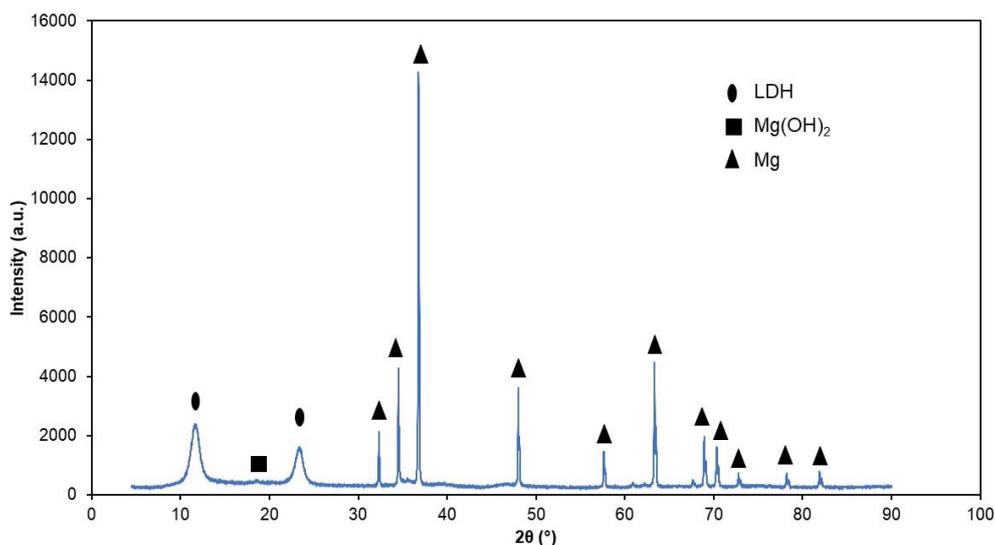

Figure 3 XRD spectrum of AZ31 treated with Mg-Al LDH coating at 90 °C for 24 h

3.   CONCLUSION

The preparation of the Mg-Al LDH coating was carried out at 50, 70 and 90 °C and at different times of 3, 6 and 24 h. Surface analysis showed that the morphology varied depending on the reaction conditions. Fine Mg-Al LDH crystals were demonstrated on the AZ31 magnesium alloy with an observable honeycomb structure when the reaction conditions were at 90 °C and at 24 h. This condition proved to be optimal also from a corrosion point of view, as the coating had the highest corrosion resistance than the other samples including the bare AZ31 alloy.

ACKNOWLEDGEMENTS

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