

## EFFECT OF PRECURSOR CONCENTRATION IN THE REACTION MIXTURE ON THE MORPHOLOGY AND CORROSION BEHAVIOUR OF MgAl-LDH COATINGS ON AZ31 MAGNESIUM ALLOY

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### Abstract

The aim of the present study was to investigate the effect of the concentration of precursors in the reaction mixture on the microstructure and electrochemical corrosion properties of MgAl-LDH coatings deposited on magnesium alloy AZ31. The concentrations of precursors  $\text{Mg}(\text{NO}_3)_2$  and  $\text{Al}(\text{NO}_3)_3$  were set to 0.10, 0.05, and 0.02 M and 0.10, 0.05, and 0.02 M, respectively. The deposition time ranged from 12 to 48 hours. The microstructure of LDH coatings and their chemical composition were characterized by scanning electron microscopy with an energy dispersive spectrometer (SEM-EDS). Electrochemical corrosion properties were evaluated using potentiodynamic polarization in 0.15 M NaCl solution.

**Keywords:** AZ31, magnesium alloy, LDH, hydrothermal synthesis, potentiodynamic measurement

### 1. INTRODUCTION

Layered double hydroxides (LDH) are materials whose composition can be expressed by the formula  $[\text{M}^{\text{II}}_{1-x}\text{M}^{\text{III}}_x(\text{OH})_2]^{x+}[\text{A}]^{n-x/n}\cdot m\text{H}_2\text{O}$ , where  $\text{M}^{\text{II}}$  and  $\text{M}^{\text{III}}$  denote the divalent and trivalent cation and  $\text{A}^n$  the  $n$ - is valent anion [1-2]. The value of  $x$  corresponds to the molar fraction of  $\text{M}^{\text{III}}$  in the hydroxide layers present (i.e.  $\text{M}^{\text{III}}/(\text{M}^{\text{II}}+\text{M}^{\text{III}})$ ) and ranges from 0.2-0.4. These are readily available and biocompatible materials whose major advantage is their wide applicability in a variety of applications. They are used, for example, in the addition and stabilization of polymer blends and pharmaceuticals, catalyst preparation, decontamination, and sorption processes [1,3-4]. At present, more and more attention is being paid to the efforts to use LDHs, especially in medicine as host structures enabling the intercalation of active substances, or in the corrosion protection of metallic materials by coating [1, 2]. This ability is made possible by the intercalation of anions into the LDH structure. These LDH layers work as active corrosion protection, which is triggered only in the presence of so-called corrosion triggers. Thus, LDH layers can effectively delay the corrosion process by trapping the anions of corrosion triggers (e.g.  $\text{Cl}^-$  ions) [5].

### 2. EXPERIMENTAL

The samples of AZ31 magnesium alloy were cut from origin sheets to samples with dimensions of 20 × 20 mm. The elemental composition of AZ31 magnesium alloy was the same as in our previous studies [6-7]. During the pre-treatment, magnesium alloy samples were ground using #1200 SiC paper. Then, the samples were rinsed in distilled water, ethanol and air-dried.

The reaction mixture for deposition of LDH coatings was composed of solution A containing the precursors 0.02, 0.05, or 0.10 M of  $\text{Mg}(\text{NO}_3)_2$  and same concentrations of  $\text{Al}(\text{NO}_3)_3$  and solution B containing 0.8 M of NaOH and 0.2 M of  $\text{Na}_2\text{CO}_3$ . Solution B was dropwise added into the vigorously stirred solution A and preheated to 65 °C. The reaction mixture was stirred at 65 °C for the next 48 hours. This was followed by the aging of the mixture for 12 h. Subsequently, the aged suspension was homogenized for 5 min on a magnetic stirrer.

The pre-prepared samples were placed in a 250 ml Teflon liner in a stainless-steel pressure vessel and were coated at 120 °C for 12-96 h in 150 ml of the reaction mixture. The coated samples were then removed, rinsed with water, ethanol and air-dried.

The surface morphology and chemical composition of the prepared LDH coatings were analyzed using Zeiss EVO LS-10 scanning electron microscope (SEM) (Carl Zeiss Ltd., Cambridge, UK) with energy dispersive spectrometer (EDS) Oxford Instruments Xmax 80 mm<sup>2</sup> (Oxford Instruments plc, Abingdon, UK). The obtained EDS data were analyzed using AZtec software (version 2.4, Oxford Instruments, High Wycombe, UK).

Potentiodynamic measurements were performed using the Bio-Logic VSP-300 potentiostat/galvanostat (BioLogic, Seyssinet-Pariset, France) in 0.15 M NaCl solution at laboratory temperature. The open circuit potential (OCP) was recorded during 30 min of exposure. The potential was measured from -200 mV to +500 mV vs. OCP. The scan rate was 1 mV/s. The range was chosen regarding to the previous study [7]. The measurements were performed in a standard three-electrode cell with a saturated calomel electrode-SCE (reference electrode), a platinum mesh (counter electrode), and a working electrode (measured sample with an exposed area of 1 cm<sup>2</sup>). Results were evaluated using Biologic EC-Lab® software.

### 3. RESULTS AND DISCUSSION

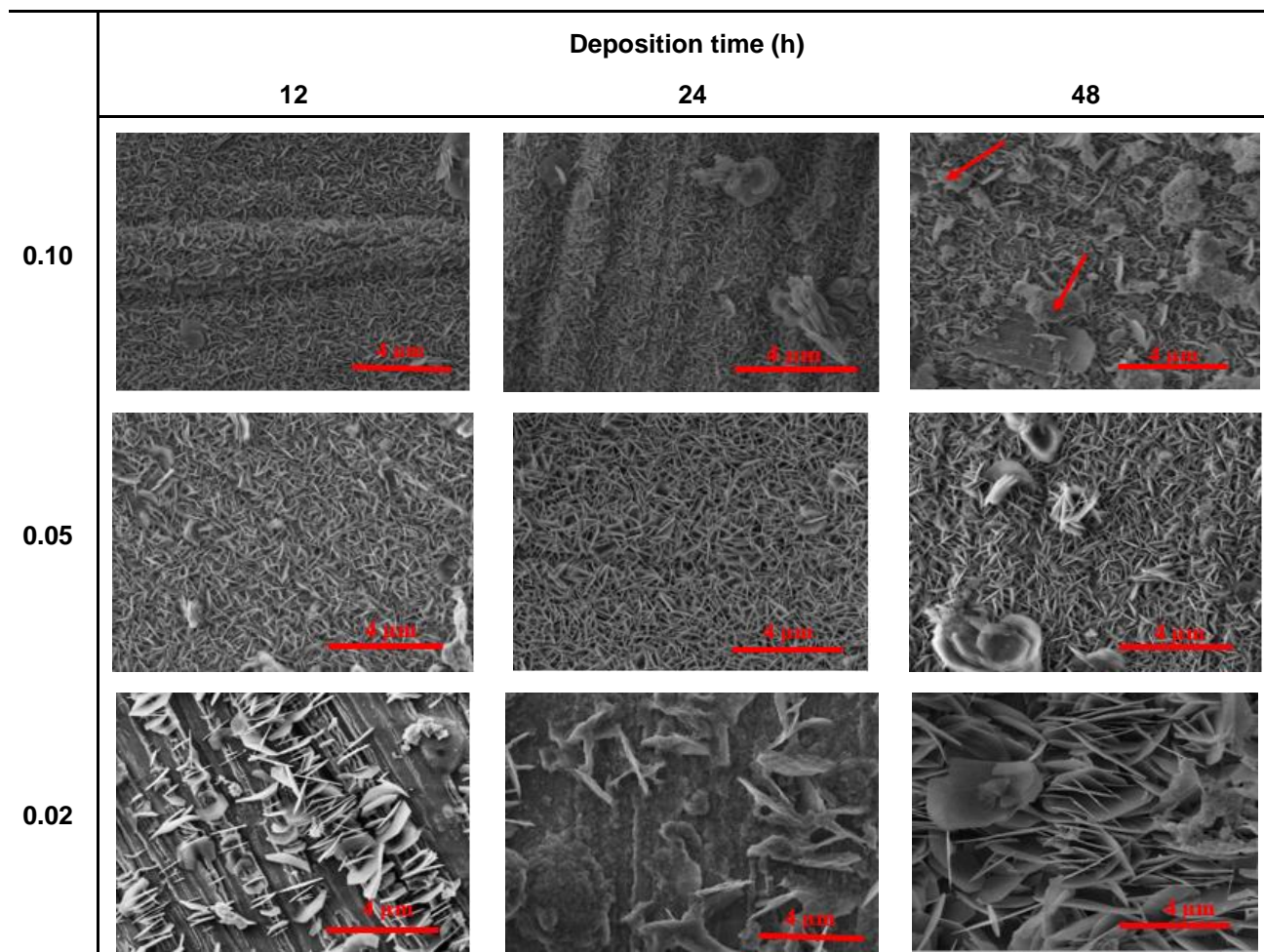
As shown in **Figure 1**, after 12 h of deposition, the densest surface coverage was achieved at a precursor concentration in the reaction mixture of 0.10 M. At a precursor concentration of 0.02 M, complete coverage of the surface by the LDH layer did not occur after 12 h, and a largely exposed Mg substrate surface was observed.

In the case of the LDH coating, when the precursor concentration was 0.10 M, there was a uniform coverage of the surface by the fine LDH lamellae. With increasing deposition time, the thickness of the coating increased, and cracks appeared (**Figure 1**, 48 h deposition, 0.10 M). Moreover, the inhomogeneous formations and local delamination of the LDH coating occurred (arrows).

A similar was the case for the LDH coating prepared in the reaction mixture with a precursor concentration of 0.05 M. However, at lower precursor concentrations (0.05 M), larger spaces between the lamellae were observed and the individual LDH lamellae were coarser than in the previous case. At deposition times of 12 and 24 hours, the coating is uniformly covered without structural defects. After 48 hours, larger LDH-based precipitates were observed embedded on the surface. These precipitates were probably precipitated in the reaction mixture and subsequently were incorporated into the LDH coating (**Figure 1**, 48 h deposition, 0.05 M). At 0.02 M precursor concentration, the coating was not uniform and was covered with coarse lamellae. However, it was evident that with increasing deposition time, there was further coarsening of the LDH coating lamellae (**Figure 1**).

**Table 1** shows the elemental EDS analysis of uncoated AZ31 alloy and AZ31 alloy with deposited LDH coatings. EDS analysis was performed from the surface of the samples. In the case of LDH coatings, EDS was performed for samples deposited for 12 hours, and the individual measurements were compared.

In the case of the AZ31 alloy, the elements such as Al and Zn were detected in addition to Mg. The small amount of oxygen on the surface is related to the formation of a thin Mg(OH)<sub>2</sub> layer [8,9]. The deposition of LDH coatings resulted in an increase in the oxygen, aluminum, and sodium content on the surface. However, it is evident that with the decreasing concentration of precursors in the reaction mixture, a decreasing trend of Al and Na contents was observed in the LDH-coated samples. This may be related to the decreasing thickness of the LDH coatings [10]. In the case of the sample prepared in the reaction mixture at a precursor concentration of 0.02 M, the presence of small amounts of Al was detected and even Zn appeared in the spectrum. This may be related to the fact that the surface was not completely covered, the LDH layer was thin, and Zn was from the AZ31 magnesium substrate.



**Figure 1** Surface morphology of prepared LDH coatings

**Table 1** EDS data (wt%) of LDH-coated samples, 12 h of deposition

Element	Concentration of precursors (M)			
	0 (uncoated AZ31)	0.1	0.05	0.02
O	2.00	56.39	59.16	46.75
Mg	93.80	26.55	28.01	43.30
C	-	3.98	2.58	1.09
Al	2.80	9.84	9.13	7.02
Na	-	3.24	1.15	1.07
Zn	1.40	-	-	0.77

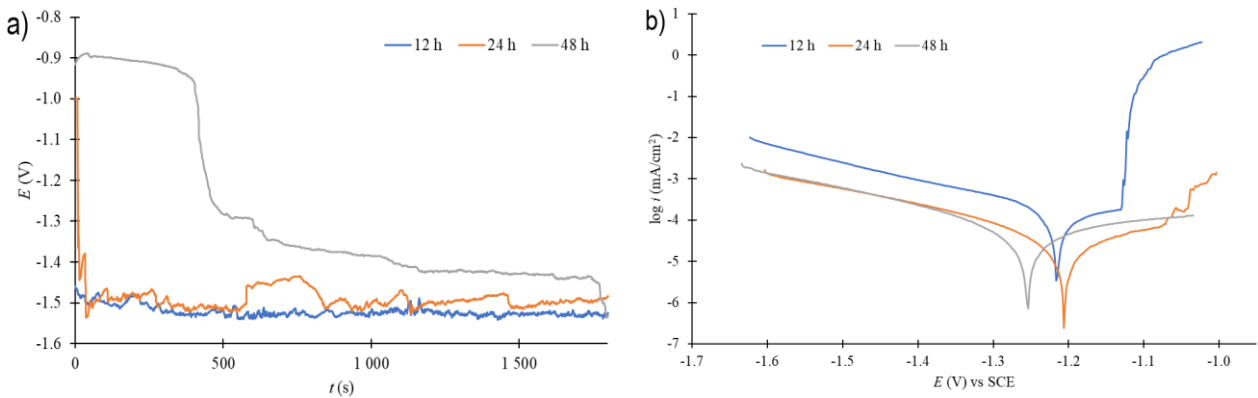
Potentiodynamic polarization tests were performed to understand the corrosion behavior of LDH-coated samples. In **Figures 2-4** there can be seen OCP curves and potentiodynamic curves for LDH-coated samples. The results of the potentiodynamic measurements, such as  $E_{OCP}$  and the  $E_{corr}$  and  $i_{corr}$  values, obtained from the Tafel extrapolation analysis, are summarized in **Table 2**.

The worst corrosion properties were achieved in the case of uncoated AZ31 magnesium alloy, where the  $E_{corr}$  value was determined to  $-1.45$  V and the  $i_{corr}$  value was  $29.71 \mu A/cm^2$ .

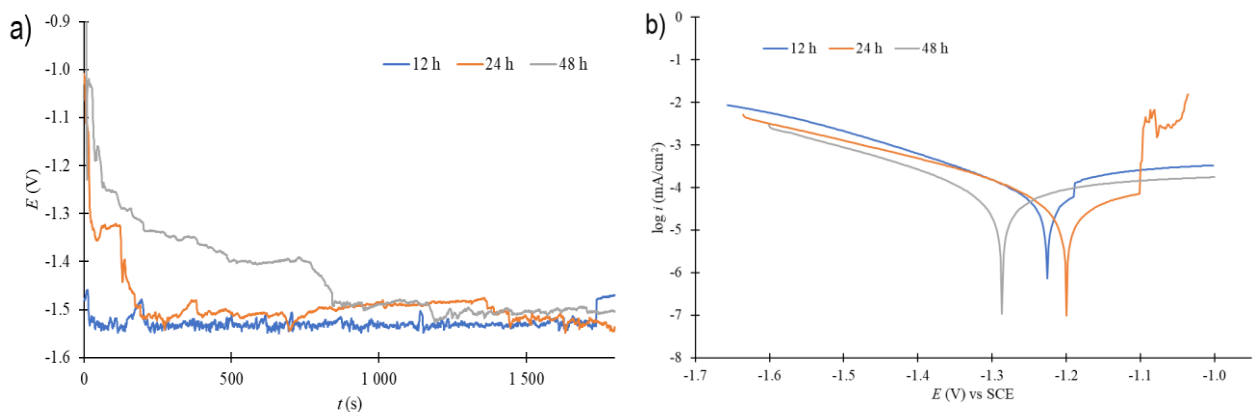
In the case of LDH-coated samples, the  $E_{corr}$  shifted to more positive values and there was a decrease in  $i_{corr}$  by 3 orders of magnitude compared to the uncoated AZ31 magnesium alloy. The corrosion potential  $E_{corr}$

values of all LDH-coated samples were comparable ( $E_{\text{corr}}$  ranged from -1.3 to -1.2 V). In terms of corrosion current density, the samples prepared for 24 h in the reaction mixture, where the precursor concentrations were set to 0.10 M and 0.05 M, gave the best results. The  $i_{\text{corr}}$  value for these samples was determined to be  $0.02 \mu\text{A}/\text{cm}^2$ .

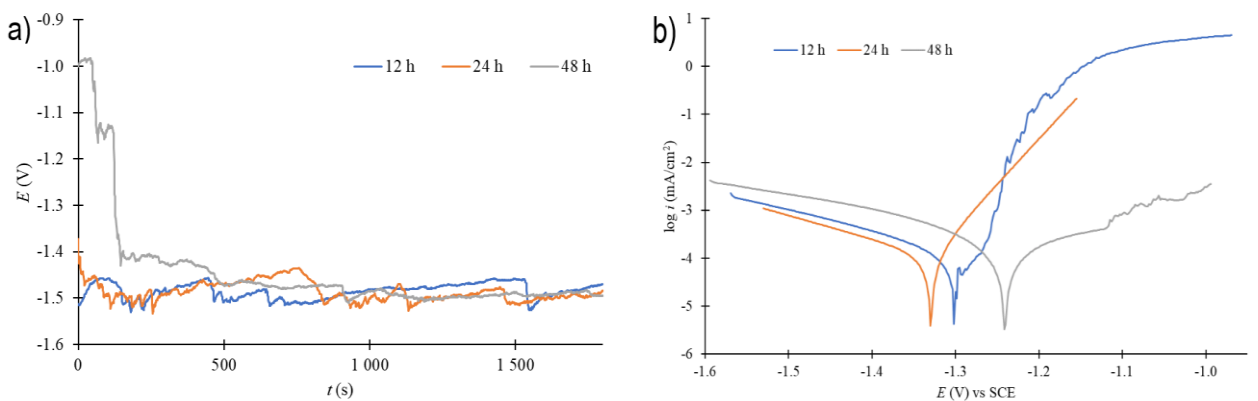
However, the evaluation of the polarization curves by Tafel extrapolation analysis was performed only from the cathodic branch, since some curves (see **Figures 2-4**) show a rapid increase in current density, which may indicate corrosion attack of the Mg substrate or pitting.



**Figure 2** Results of potentiodynamic measurements of LDH coatings - 0.1 M, a) Open circuit potential curves, b) polarization curves



**Figure 3** Results of potentiodynamic measurements of LDH coatings - 0.05 M, a) Open circuit potential curves, b) polarization curves



**Figure 4** Results of potentiodynamic measurements of LDH coatings - 0.02 M, a) Open circuit potential curves, b) polarization curves

**Table 2** Obtained results of potentiodynamic measurements of LDH coatings

Dep. time (h)	0.10 M			0.05 M			0.02 M		
	E <sub>OCP</sub> (V)	E <sub>corr</sub> (V)	i <sub>corr</sub> (μA/cm <sup>2</sup> )	E <sub>OCP</sub> (V)	E <sub>corr</sub> (V)	i <sub>corr</sub> (μA/cm <sup>2</sup> )	E <sub>OCP</sub> (V)	E <sub>corr</sub> (V)	i <sub>corr</sub> (μA/cm <sup>2</sup> )
12	-1.52	-1.22	0.11	-1.47	-1.24	0.03	-1.47	-1.30	0.09
24	-1.49	-1.21	0.02	-1.54	-1.20	0.02	-1.48	-1.33	0.09
48	-1.53	-1.25	0.04	-1.50	-1.29	0.06	-1.49	-1.24	0.15

#### 4. CONCLUSION

Based on the above presented findings, the following conclusions can be drawn:

- In all cases, LDH coatings were deposited on the surface of AZ31 magnesium alloy.
- Based on the observation of the surface morphology, it was found that with decreasing concentration of precursors in the reaction mixture, deposition of LDH coatings consisting of coarser lamellae occurs and the degree of surface coverage decreases. At a precursor concentration of 0.1 M, there was a uniform surface coverage of very fine LDH lamellae. At lower precursor concentrations (0.05 M), larger gaps between lamellae were observed and the lamellae were slightly coarser.
- At a precursor concentration of 0.02 M, the coating was not uniform, exposed areas of the Mg substrate surface were observed, and LDH coating was formed with coarse lamellae. Moreover, with increasing deposition time, there was further coarsening of the LDH coating lamellae.
- Based on the potentiodynamic measurements, it was found that the worst corrosion properties were obtained in the case of uncoated AZ31 magnesium alloy. The obtained E<sub>corr</sub> value was -1.45 V and i<sub>corr</sub> was 29.71 μA/cm<sup>2</sup>.
- The deposition of LDH coatings resulted in an increase in E<sub>corr</sub> and a significant decrease in i<sub>corr</sub> (up to 3 orders of magnitude).
- The best electrochemical corrosion properties were achieved in the case of LDH-coated samples under the following conditions - deposition time was 24 h, precursor concentration was 0.1 M and 0.05 M. Under these conditions, i<sub>corr</sub> values were determined to be 0.02 μA/cm<sup>2</sup> in both cases.

#### ACKNOWLEDGEMENTS

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#### REFERENCES

- [1] DUAN, X., EVANS, D.G. Layered Double Hydroxides. Springer-Verlag, Berlin Heidelberg, 2006.
- [2] ZHANG, F. et al. Corrosion resistance of Mg–Al-LDH coating on magnesium alloy AZ31. *Surface and Coatings Technology*. 2014, vol. 258, pp. 1152-1158.
- [3] TAN, J. et al. Advances in LDH coatings on Mg alloys for biomedical applications: A corrosion perspective. *Applied Clay Science*. 2021, vol. 202. Available from: <https://doi.org/10.1016/j.clay.2020.105948>
- [4] HIBINO, T., OHYA H. Synthesis of crystalline layered double hydroxides: Precipitation by using urea hydrolysis and subsequent hydrothermal reactions in aqueous solutions. *Applied Clay Science*. 2009, vol. 45, pp. 123-132. Available from: <https://doi.org/10.1016/j.clay.2009.04.013>
- [5] SHULHA, T. N. et al. Chelating agent-assisted in situ LDH growth on the surface of magnesium alloy. *Scientific Reports*. 2018, vol. 8.

- [6] DOSKOČIL, L. et al. Characterization of Prepared Superhydrophobic Surfaces on AZ31 and AZ91 Alloys Etched with ZnCl<sub>2</sub> and SnCl<sub>2</sub>. *Coatings*. 2022, vol. 12.
- [7] DZIKOVÁ, J. et al. Characterization and Corrosion Properties of Fluoride Conversion Coating Prepared on AZ31 Magnesium Alloy. *Coatings*. 2021, vol. 11.
- [8] ZHU, Y. et al. Growth and characterization of Mg(OH)<sub>2</sub> film on magnesium alloy AZ31. *Applied Surface Science*. 2011, vol. 257, pp. 6129-6137.
- [9] TANG, H. Fabrication and Characterization of Mg(OH)<sub>2</sub> Films on AZ31 Magnesium Alloy by Alkali Treatment. *International Journal of Electrochemical Science*. 2017, pp. 1377-1388.
- [10] VALENTE, J. et al. Method for Large-Scale Production of Multimetallic Layered Double Hydroxides: Formation Mechanism Discernment. *Chemistry of Materials*. 2009, vol. 21, pp. 5809-5818.