

PREPARATION AND STRUCTURAL ANALYSIS OF MGFE LDH COATINGS ON AZ31 MAGNESIUM ALLOY

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Abstract

Deposition of layered double hydroxides (LDH) on metal surfaces, especially Mg alloys, is considered a promising approach for protective conversion surface treatments. For Mg materials, the formation of LDH coatings on the surface is carried out in an autoclave at elevated temperature or in solution. MgFe-based LDH coatings may find application in medicine. However, their issues are poorly described. In this paper, the growth of MgFe LDH conversion coatings on AZ31 magnesium alloy is described. In this study, MgFe LDH coatings were prepared on hydrothermally treated AZ31 Mg alloy. The morphology was characterized by scanning electron microscopy (SEM). The chemical and phase composition was determined by X-ray diffractometry (XRD) and energy dispersive X-ray spectroscopy (EDS). Two-step synthesis at laboratory temperature was performed. First, a FeOOH layer with a thickness of about 2 μm was prepared at room temperature. While at higher temperature (60 $^{\circ}\text{C}$), a Fe₃O₄ layer with a thickness of about 0.7 μm is formed. These FeOOH and Fe₃O₄ layers are transformed to form MgFe LDH in the second step when reacted in 0.1 M magnesium nitrate for 12 h. The thickness of the resulting MgFe LDH layer ranged from 0.5 to 1.5 μm . The results suggest that this synthesis method leads to the synthesis of non-traditional LDH coatings that can improve the corrosion and bioapplication behavior of Mg materials.

Keywords: AZ31, Magnesium alloy, Hydrothermal treatment, MgFe LDH

1. INTRODUCTION

Magnesium and its alloys are increasingly gaining attention from scientists focused on the development of new bioimplants [1]. Magnesium is not only a naturally occurring biogenic element in the human body, but it also offers favorable mechanical properties. One of its greatest advantages is its specific strength, which is comparable to that of human bone. Thanks to this, implants made from magnesium alloys behave more naturally within the body than many traditional materials, such as titanium or steel alloys — a key factor for long-term integration. [2-5].

A crucial benefit is that the corrosion products of magnesium are non-toxic to the body, and therefore do not trigger adverse biological reactions. However, a major obstacle to the broader use of these materials in clinical practice remains their rapid degradation. During corrosion, not only does the material itself break down, but hydrogen gas is also released, which can lead to inflammatory responses in the body.

One of the promising approaches to slowing down magnesium corrosion is the application of protective surface coatings. These coatings can be made from various materials — from biopolymers such as chitosan, to phosphates (CaP) [6], fluorides (MgF₂), and even magnesium oxides (MgO) or hydroxides (Mg(OH)₂). Particular attention has recently been directed toward so-called layered double hydroxides (LDHs), which provide highly effective protection while being biocompatible [7-11].

LDHs are mineral structures similar to the well-known hydrotalcite. The most commonly used variant is MgAl LDH, but alternative formulations are now being explored. One such alternative is magnesium-iron-based LDH

(MgFe LDH), which is structurally similar to the mineral iowaite. The key advantage of MgFe LDH over the more traditional MgAl LDH is the absence of aluminum — a potentially toxic element in the human body — while iron, like magnesium, is a biogenic and essential element for the body [12].

Research has shown that an LDH coating can be applied directly to the alloy surface or as a top layer over a base protective coating such as MgO or Mg(OH)₂. This multilayered approach not only improves the corrosion resistance of the material but also enhances its interaction with cells, thereby increasing the likelihood of successful implant integration.

The study by Zhang et al. [12] investigated the application of an LDH coating on AZ31 alloy pretreated using the micro-arc oxidation (MAO) method. The results demonstrated that such surface treatment significantly improved both stability and biocompatibility.

The focus of this study is the preparation of a MgFe-based LDH coating on AZ31 alloy that already has a layer of magnesium hydroxide (Mg(OH)₂). The choice of MgFe LDH is deliberate — in addition to avoiding aluminum, iron brings added value due to its natural presence in the human body and its important role in numerous biological processes. The goal is to develop a material that is not only mechanically stable and corrosion-resistant but also as biocompatible and body-friendly as possible.

2. EXPERIMENTAL PART

2.1. Material preparation

AZ31 magnesium alloy sheets, with a chemical composition of 3.6 wt.% Al, 1.34 wt.% Zn, 0.28 wt.% Mn, 0.03 wt.% Si, 0.002 wt.% Fe, 0.01 wt.% Sn, and the balance Mg, were used as the substrate material. The sheets were cut into smaller samples with dimensions 20 × 20 × 5 mm. Prior to use, the samples were ground using 2500-grit silicon carbide abrasive paper to ensure a smooth and uniform surface.

2.2. Layer synthesis

Mg(OH)₂ interlayer was formed on the AZ31 samples via hydrothermal synthesis, carried out in a 2 M NaOH solution at 120 °C for 24 hours in a Teflon-lined SS vessel. An intermediate Fe precursor interlayer was subsequently prepared by immersing the Mg(OH)₂-coated samples in a 0.02 M FeCl₂ solution for 3 hours at either room temperature (RT) or 60 °C. The final MgFe-layered double hydroxide (LDH) coating was synthesized using a hydrothermal method in a 0.1 M Mg(NO₃)₂ solution at 120 °C, with reaction times of 12 hours using Memmert UF55 universal heating and drying oven.

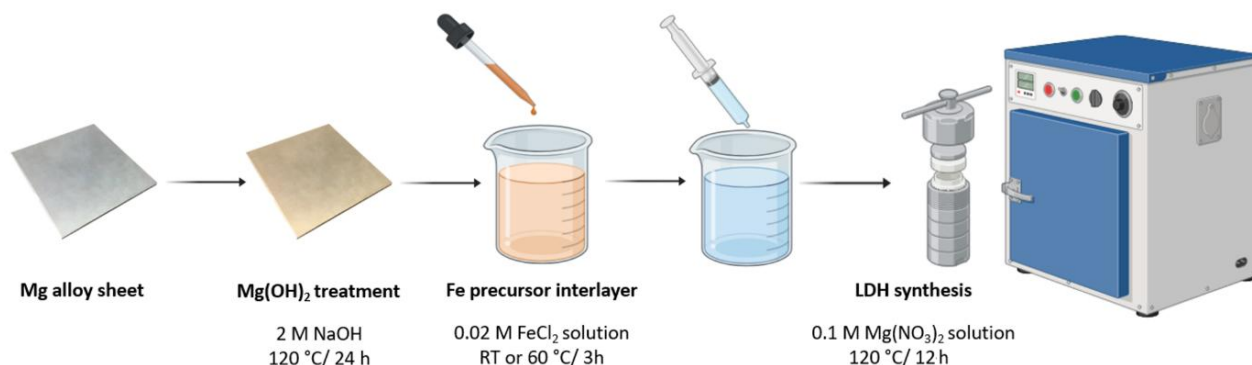


Figure 1 Scheme of deposition process

2.3. Samples characterization

The crystalline structure of the coatings was analyzed using X-ray diffraction (XRD, Empyrean, PANalytical, Malvern, UK) with Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$), operating at a scan rate of $0.013^\circ/\text{s}$. The surface microstructure and elemental composition of the LDH-coated samples were examined using a Zeiss EVO LS-10 scanning electron microscope (SEM) (Carl Zeiss Ltd., Cambridge, UK) equipped with an Oxford Instruments X-Max 80 mm² energy-dispersive X-ray spectrometer (EDS) and Aztec software (Oxford Instruments plc, Abingdon, UK). For high-resolution imaging and detailed surface analysis, a JEOL JSM-7600 field-emission scanning electron microscope (FE-SEM) equipped with an Ultim[®] Max EDS detector (Oxford Instruments plc, Abingdon, UK) was employed.

3. RESULTS AND DISCUSSION

The surface of the sample after immersion in a FeCl₂ solution for 3 hours at room temperature (RT) is shown in **Figure 2a**, and after immersion in FeCl₂ at 60 °C in **Figure 2c**. In terms of morphology, the coatings do not exhibit significant differences. Both coatings appear homogeneous and free from structural defects. They are composed of very fine submicron crystals. The composition of these coatings, measured by EDS, is presented in **Table 1**. Elemental analysis revealed differences in elemental composition. In the case of pre-treatment at RT, a higher oxygen content was detected, with a Fe:O ratio of approximately 1:2. In the case of immersion at 60 °C, the Fe:O ratio is 2:3, or close to 3:4.

XRD phase analysis (**Figure 3**) confirmed the presence of Mg and Mg(OH)₂ phases, as well as the presence of FeOOH phase (Goethite and Lepidocrocite) on the surface. These findings are also supported by the results of elemental EDS analysis. The phase analysis further showed that immersion of the sample in FeCl₂ solution at 60 °C preferentially leads to the formation of the Fe₃O₄ (Magnetite) phase, while FeOOH phases are no longer formed [10].

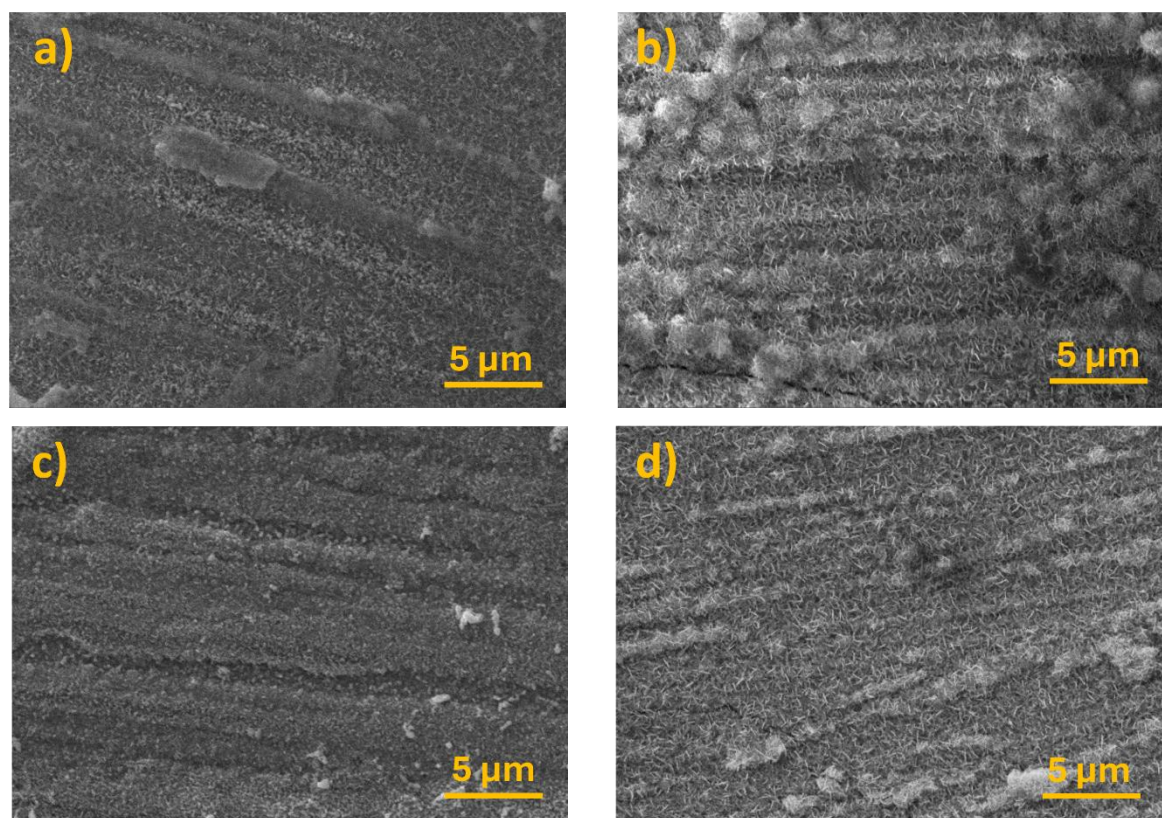


Figure 2 Morphology of coated samples, a) RT; b) RT+HT; c) 60°C; d) 60°C+HT

Table 1 Elemental analysis of coated samples (at. %)

Sample	Mg	Fe	O	Others
RT	1.72	33.43	64.86	
60°C	1.00	40.11	59.89	
RT + HT	26.58	7.78	63.91	1.73
60°C + HT	16.02	17.64	66.34	

Subsequent hydrothermal treatment (HT) in 0.1 M $\text{Mg}(\text{NO}_3)_2$ at a temperature of 120 °C resulted in a morphological change, with coarser lamellar structures forming on the surface (**Figure 2b,d**). XRD phase analysis (**Figure 3**) showed a decrease in the intensity of both FeOOH and Fe_3O_4 phases in both cases and the appearance of a new peak at $2\theta = 11.5^\circ$. This peak corresponds to the FeMg-LDH (Iowaite) phase.

Elemental analysis (**Table 1**) revealed a significantly higher Mg content compared to the FeCl_2 pre-treatment. In the RT+HT sample, the Mg:Fe ratio was 3:1, while in the 60 °C+HT sample, the ratio was 1:1. This may suggest a thinner LDH layer formed on the Fe_3O_4 interlayer. Metallographic cross-sections showed that the final thickness of the LDH layer on FeOOH was greater than on Fe_3O_4 . The LDH layer thickness on FeOOH was around 1,5 μm , whereas on Fe_3O_4 it was about 0.5 μm .

It can therefore be assumed that FeOOH is more reactive under the given conditions than the more stable Fe_3O_4 , which may facilitate easier formation of the LDH phase.

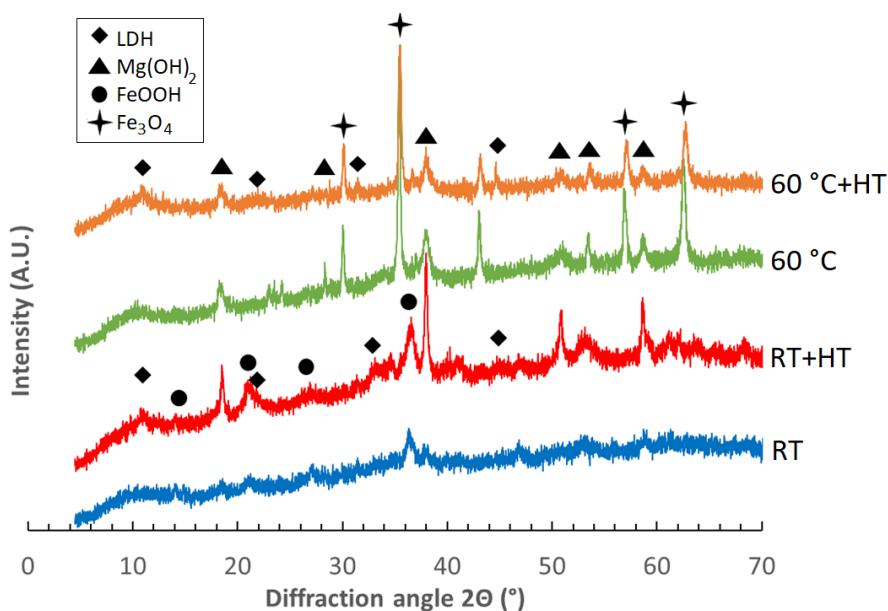


Figure 3 XRD patterns of deposited layers

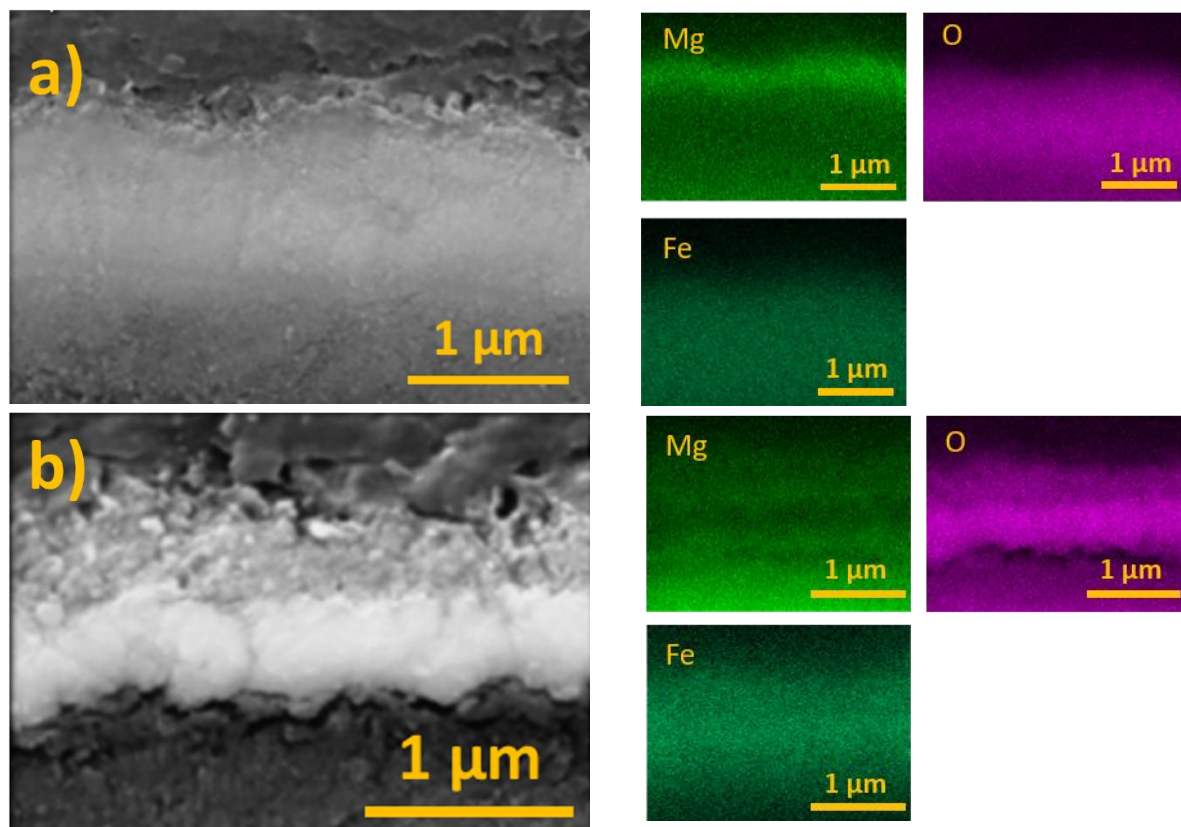


Figure 4 Perpendicular cuts of samples a) RT+HT, b) 60 °C+HT

4. CONCLUSION

Based on the measured data, the following findings were observed:

- Pre-treatment in FeCl_2 solution for 3 hours leads to the formation of the FeOOH phase, whereas at 60 °C the Fe_3O_4 phase is preferentially formed.
- Immersion of these pre-treated samples in a 0.1 M magnesium nitrate solution results in the formation and transformation into a MgFe-LDH layer.
- The FeOOH phase transforms more readily into LDH than Fe_3O_4 , as the LDH layer formed on FeOOH is approximately 1.5 μm thick, whereas on Fe_3O_4 it is around 0.5 μm .

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