

DEPOSITION CONDITIONS FOR CARBONATE COATINGS ON AZ31 MAGNESIUM ALLOY IN THE PRESENCE OF AMMONIUM IONS

Martin BUCHTÍK, Eliška KOBZINKOVÁ, Matěj BŘEZINA, Leoš DOSKOČIL

Brno University of Technology, Faculty of Chemistry, Brno, Czech Republic, EU, buchtik@fch.vut.cz

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Abstract

This study investigates the deposition conditions of carbonate-based coatings on AZ31 magnesium alloy pretreated with an $\text{Mg}(\text{OH})_2$ interlayer in the presence of ammonium ions. The effect of temperature and exposure time on phase formation, growth mechanism, and corrosion performance was evaluated. At laboratory temperature, no continuous carbonate coating was even formed after 12 or 24 h of deposition. Instead, substrate corrosion occurred, accompanied by further $\text{Mg}(\text{OH})_2$ and hydrotalcite formation and crack development within the surface layer. Increasing the temperature to 50 °C led after 6 h primarily to chemical destabilization and partial dissolution of the $\text{Mg}(\text{OH})_2$ interlayer rather than controlled carbonation. The first nuclei appeared after 12 h of exposure, and after 24 h the surface was fully covered by the newly formed layer. However, EDS and XRD analyses revealed that the coating predominantly consisted of hydromagnesite rather than anhydrous magnesium carbonate. Increasing the temperature up to 90 °C under hydrothermal conditions, hydromagnesite remained the dominant phase. The resulting hydromagnesite coating was compact, homogeneous, and significantly improved the corrosion resistance of the system. The results demonstrate that increasing temperature in the presence of ammonium ions is insufficient to induce controlled carbonation of the $\text{Mg}(\text{OH})_2$ interlayer. Hydrothermal conditions primarily enhance the crystallinity and protective performance of hydromagnesite-based coatings.

Keywords: AZ31 magnesium alloy, ammonium ions, carbonate coating, hydromagnesite, corrosion

1. INTRODUCTION

Magnesium alloys have attracted attention due to their properties, such as low density and high specific strength, making them promising candidates for lightweight structural and biomedical applications. However, their widespread use is limited by poor corrosion resistance, chemical reactivity, and the instability of its native hydroxide layer [1-4].

Various surface treatments and coatings have been developed, including conversion coatings (PEO), anodizing, organic coatings, and inorganic layers based on oxides, hydroxides, and phosphates [5-7]. In recent years, carbonate-based coatings have emerged as a promising alternative due to their potential to form relatively compact and protective layers under mild conditions [5,8]. In particular, the formation of MgCO_3 can improve surface stability and corrosion resistance. The deposition process of carbonate-based coatings is sensitive to environmental factors, such as pH, CO_2 availability, and the presence of complexing species [8-9]. Among these, ammonium ions play an important role, as they can influence both solution chemistry and the stability of intermediate phases, thereby affecting the growth, composition, and protective properties of the resulting carbonate coatings [10-11]. Current studies indicate that carbonate-based coatings lead to the formation of hydrated magnesium carbonates, particularly hydromagnesite, rather than MgCO_3 [8-9]. Such coatings are typically formed under CO_2 -rich conditions and typically, sodium carbonate or sodium bicarbonate electrolytes are employed [1,8-9]. While carbonate-based electrolytes are commonly employed, the role of ammonium-containing systems remains comparatively less explored. This study focuses on the preparation of

coatings and the influence of processing parameters, such as temperature and deposition time, in aqueous solutions on the AZ31 magnesium alloy in environments containing ammonium ions.

2. EXPERIMENTAL PART

2.1 Substrate pre-treatment

AZ31 magnesium alloy plates with dimensions 20 × 20 × 5 mm and 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 ground using 1200-grit SiC paper to ensure an uniform surface. In the pretreatment step, ground Mg samples were hydrothermally treated in 2 M NaOH for 24 h at 120 °C in a stainless steel (SS) vessel with a Teflon liner. The samples were subsequently rinsed and air-dried.

2.2 Coating synthesis and its characterization

The synthesis of carbonate-based coatings was carried out in a 0.1 M NH₄HCO₃ solution at pH = 8.0±0.1 for 6-24 h at temperatures ranging from 20 to 90 °C under mild conditions, either in a beaker or in an autoclave (at 90 °C), using a Memmert UF55 universal heating and drying oven. Subsequently, the samples were rinsed with demineralized water and air-dried.

The surface morphology of deposited coatings and their elemental composition were analyzed 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). The phase composition of the selected coatings was evaluated using X-ray diffraction (XRD, Empyrean, PANalytical, Malvern, UK) with Cu-Kα radiation (λ = 1.5406 Å), operating at a scan rate of 0.013°/s.

3. RESULTS AND DISCUSSION

During deposition at 20 °C, both after 12 and 24 hours, the surface Mg(OH)₂ coating cracked (**Figure 1**) and no carbonate-based coatings were observed (**Table 1**). The Mg:O ratio is close to 1:2, which indicates a significant proportion of Mg(OH)₂. This likely indicates that the Mg(OH)₂ precursor interlayer was disrupted, leading to corrosion of Mg alloy. This behavior is evidently related to the instability of Mg(OH)₂ at the presence of HCO₃⁻ ions, as indicates equation (1) [12].



Carbonate can affect the compact Mg(OH)₂ layer [12-13]. Instead of serving as a stable substrate for MgCO₃ nucleation, the Mg(OH)₂ interlayer may partially dissolved and degraded. Once the Mg(OH)₂ layer is locally disrupted, the underlying metallic Mg becomes exposed, dissolves. This leads to a local increase in pH, formation of porous Mg(OH)₂, and the development of mechanical stress, which may result in cracking of the Mg(OH)₂ compact coating. At laboratory temperature, an additional issue is the relatively slow nucleation kinetics of carbonates [14]. In the Mg-HCO₃⁻-H₂O system, basic carbonates, such as hydromagnesite tend to form rather than pure MgCO₃. If the surface is unstable and corrosion occurs, the system becomes governed by dissolution kinetics rather than controlled precipitation. Instead of a controlled deposition process, corrosion of the Mg substrate likely predominated [12].

At a deposition temperature of 50 °C, the initial stage (6 h) is still dominated by chemical destabilization of Mg(OH)₂ rather than controlled carbonatation (**Figure 2a**). After 12 h, the system reaches a supersaturated state with respect to MgCO₃. The concentration of Mg²⁺ near the surface, resulting from dissolution, attains the necessary level, leading to the formation of stable nucleation sites (**Figure 2b**) and after 24 hours almost complete coverage of the surface was observed (**Figure 2c**). It is unlikely that pure MgCO₃ (magnesite) is

formed, as its crystallization is very slow at 50 °C [12,15-17]. As shown in **Table 1**, the carbon content in the coatings gradually increases in time of deposition, while the Mg content decreases proportionally.

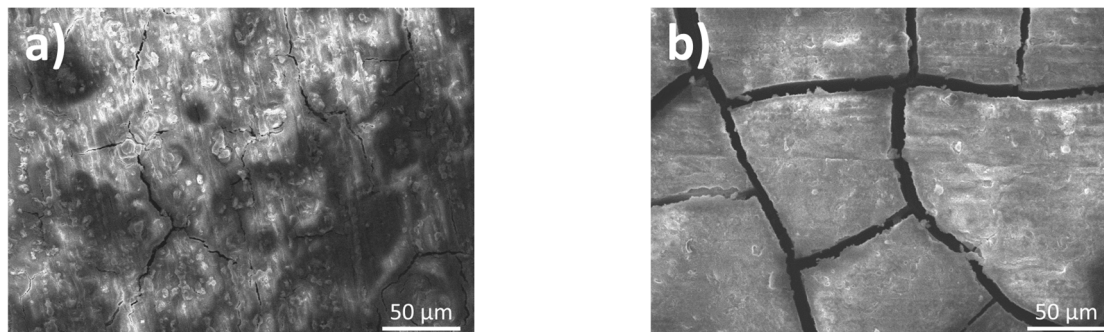


Figure 1 Surface morphology of coated samples at 20 °C; deposition times a) 12 hours, b) 24 hours

Instead, hydromagnesite or a poorly ordered basic magnesium carbonate is more likely to form, which would explain the irregular morphology of the coating. Thus, the process initially involves dissolution of $Mg(OH)_2$, followed by nucleation and precipitation of carbonates once local supersaturation of Mg^{2+} ions is achieved [12,15,18].

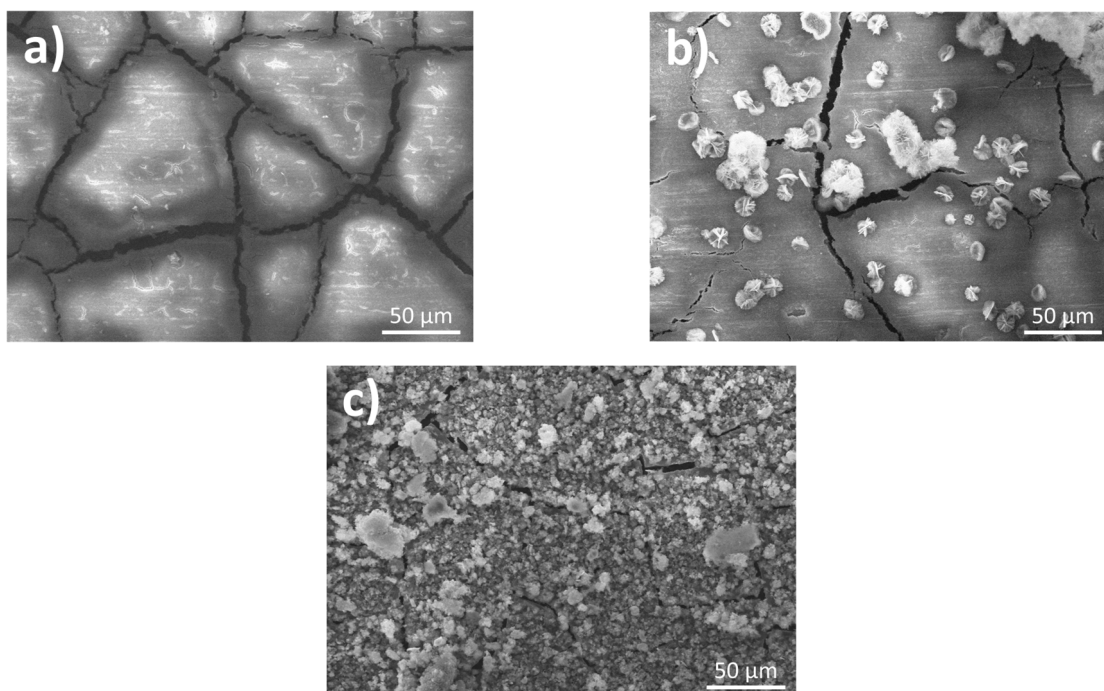


Figure 2 Surface morphology of coated samples at 50 °C, deposition times a) 6 hours, b) 12 hours, c) 24 hours

Moreover, due to the presence of ammonium ions in the solution, the coatings remain cracked (**Figure 2c**). The ammonium ion is a weak acid which means that the system has a lower pH, which contributes to the dissolution of $Mg(OH)_2$, with NH_4^+ directly promoting the dissolution of $Mg(OH)_2$ (equations (2-3)) [6,10-11].



In the case of Mg, this is very sensitive, because $\text{Mg}(\text{OH})_2$ is stable only at $\text{pH} \gtrsim 10$. As soon as the pH decreases locally, the equilibrium shifts toward dissolution.

In the beaker at 90 °C, a negligible coating of small thickness was formed (**Figure 3a**). It is because CO_2 is very easily released from the solution into the atmosphere [19]. Moreover, as the temperature increases, its solubility decreases. As a result, there are not enough carbonate ($\text{CO}_3^{2-}/\text{HCO}_3^-$) ions to form a carbonate coating [16,18]. At the same time, the environment is rather basic, so mainly $\text{Mg}(\text{OH})_2$ is stabilized. Deposition in a vessel at 90 °C resulted in a compact, defect-free coating structure composed of coarse lamellae (**Figure 3b**). Under these conditions, better chemical stabilization of the interface occurs. In a closed vessel, CO_2 has no way to escape and the system is close to equilibrium [19]. The growth kinetics exceed the rate of dissolution, resulting in less local dissolution of $\text{Mg}(\text{OH})_2$ and less exposure of the metallic Mg, which in turn leads to reduced hydrogen evolution. In a vessel at 90 °C, the pressure is higher, diffusion proceeds more rapidly, and the solubility and partial pressure of CO_2 increases. This promotes recrystallization and supports homogeneous growth. Instead of the $\text{Mg}(\text{OH})_2$ interlayer dissolving and re-precipitating, conversion is more likely to occur. As a result, a more compact structure forms, with lower porosity and a lower density of cracks.

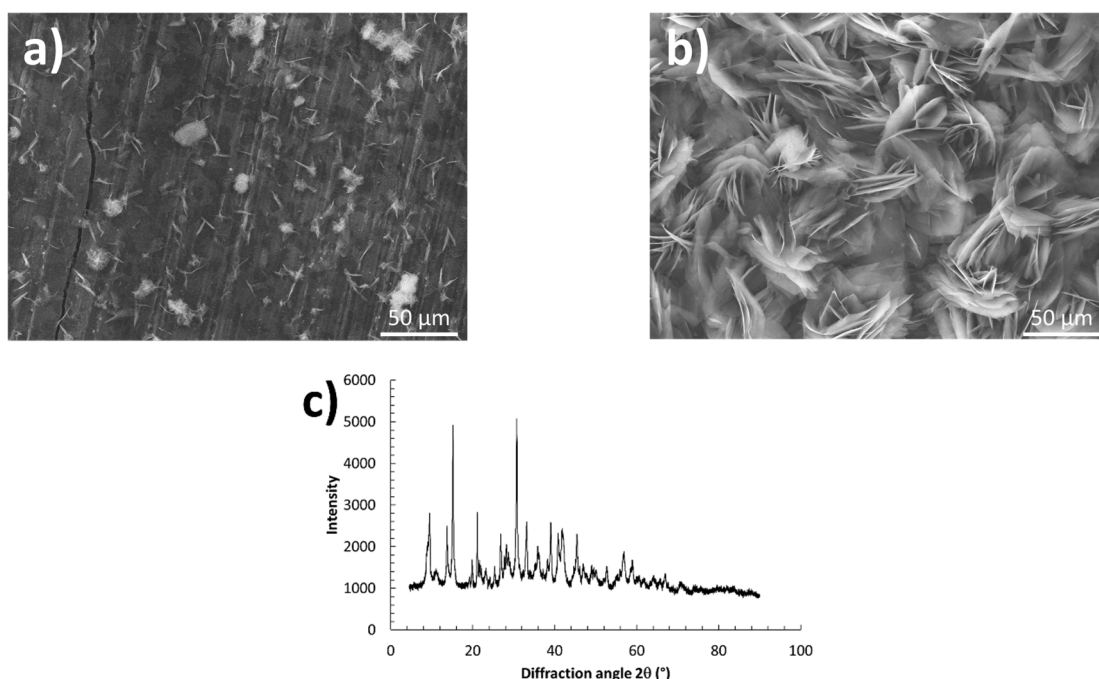


Figure 3 Analysis of coatings: surface morphology of coating deposited a) beaker at 90 °C, b) in SS vessel at 90 °C, c) XRD pattern of deposited coating in in SS vessel

Table 1 Elemental composition of deposited coatings

Conditions		Content of element (at%)			
Temperature (°C)	Synthesis time (h)	C	O	Mg	Al
20	12	4.69	63.79	30.46	1.06
20	24	7.81	68.18	21.59	1.06
50	6	6.00	69.60	22.11	2.29
50	12	8.43	66.86	22.02	2.59
50	24	16.22	63.19	18.04	2.55
90	24	6.97	69.21	21.46	2.36
90	24 in autoclave	16.23	63.95	19.46	0.36

However, according to EDS analysis (**Table 1**), the composition of the coating deposited in vessel (**Figure 3b**) is more consistent with hydromagnesite ($\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$) than magnesite MgCO_3 . The low Mg content and high O content indicated a hydrated phase. These results were confirmed by XRD analysis (**Figure 3c**), where only one phase, hydromagnesite, was detected in the coating deposited at 90 °C in a SS vessel.

Formation of magnesium carbonate coating under the given conditions is difficult, as low-temperature aqueous systems favor the formation of hydrated magnesium carbonates rather than anhydrous magnesite. In the presence of NH_4^+ ions and a $\text{Mg}(\text{OH})_2$ precursor layer, the system promotes the formation of hydromagnesite due to pH effect close to the Mg surface and the availability of OH^- ions. Therefore, hydromagnesite is the thermodynamically favored product under these deposition conditions [20-22].

4. CONCLUSION

The results show that MgCO_3 coating formation on AZ31 alloy is strongly dependent on deposition conditions. At low temperatures, $\text{Mg}(\text{OH})_2$ instability and slow kinetics lead to corrosion rather than MgCO_3 coating formation, while at 50 °C non-uniform hydrated carbonates are formed at longer deposition time. A compact coating is achieved only under autoclave conditions at 90 °C, where hydromagnesite is the dominant phase, confirming that hydrated magnesium carbonates are favored over MgCO_3 under these conditions.

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