

Article

Initial Stages of Al-AM60-Modified Surface of Magnesium Alloy Activity Exposed to Simulated Marine Environment

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Abstract: The surface of AM60 magnesium alloy was modified with Al-nanocoating ~65.62 nm, using DC magnetron sputtering to enhance its resistance to degradation under aggressive marine ambience. The sputtered Al film showed adhesion to the α -Mg matrix, covering the dispersed particles of the β -Mg₁₇Al₁₂ secondary phase. The aluminum nanofilm was composed of (111) and (200) crystal planes of metallic aluminum (Al⁰) and Al₂O₃ (Al³⁺). After 30 days of immersion in a simulated marine environment (SME, pH 7.8), the Al-AM60 maintained a lower alkaline value (pH~8.13) of SME than that of uncoated AM60, attributed to α -Mg electrochemical oxidation to Al₂O₃ and its posterior dissolution, consuming OH[−] ions. Consequently, the concentration of the released Mg²⁺ ions from the Al-AM60 surface was reduced ~2.3 times (~15 mg L^{−1}). The *R_p* (polarization resistance), as inversely proportional to the corrosion current, was extracted from the EIS impedance data fitted to an equivalent electrical circuit. After 30 days in SME solution, the *R_p* value of the Al-AM60 modified surface was ~3.5 times higher than that of AM60 (~15.46 kΩ cm²), confirming that the sputtered aluminum nano-deposit layer can hinder the corrosion process. These reported findings indicated that sputtered Al nano-coatings can mitigate the surface degradation of Mg-Al alloys in saline aggressive marine environments.

Keywords: surface modification; magnesium-aluminum alloy; aluminum coating; magnetron sputtering; corrosion resistance; electrochemical tests; marine environment



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1. Introduction

Magnesium alloys are among the lightest structural materials, offering an excellent balance of mechanical properties, including high specific strength and stiffness, superior damping capacity, high dimensional stability, and good machinability [1–5]. Due to these advantages, magnesium alloys are highly desirable for applications in the automotive, aerospace, communication and computer industries [6–14].

Mg-Al alloys are the most used material in the transport, electronics, and sports industries to produce lightweight elements [15,16], improving mechanical, fabrication and welding characteristics and reducing the production cost as compared to pure metal. Besides the excellent physical and mechanical properties of these alloys, the weight reduction makes them ideal materials for automotive and aerospace applications. A commercial magnesium-aluminum alloy-extruded AM60 was selected as it is used in the manufacture of high-pressure die castings for the automotive industry. In contact with air oxygen, a thin, stable passive layer of aluminum oxide (Al₂O₃) is formed on Mg-Al alloy surface, which provides a decrease in the Mg-matrix corrosion rate, giving it corrosion resistance. However, in the industrial atmosphere (acid rain) or marine environment (rich in chloride

ions), the corrosion layer of insoluble $\text{Mg}(\text{OH})_2$ is transformed to soluble MgCl_2 , and the Mg-matrix suffers degradation, limiting certain Mg alloy applications, particularly in the automotive industry [17–24]. Previous investigations have revealed that in chloride-polluted atmospheric environments, the corrosion rate of AM50 increases up to $250 \mu\text{g cm}^2$ as a function of NaCl concentration [19]. It has been reported that the corrosion layer of AM50 presents two parts: $\text{MgO}/\text{Mg}(\text{OH})_2$ (outer layer) and Al_2O_3 (thin inner layer) [25]. However, the corrosion layers do not have the same composition when the corroded areas possess lower Al-contents (2–3% wt.).

To improve the corrosion performance of Mg alloys, surface modification techniques have been proposed as alternative strategies, such as anodizing treatment [26,27], Al- Al_2O_3 composite [28], coatings by plasma electrolytic oxidation and sol-gel technique [29], microarc oxidation [30], magnetron-sputtered nano-hydroxyapatite coating [31], fluorocarbon polymeric film [32], aluminum electroplating [33], polymer-graphene oxide as self-healing monomolecular films [34], and Mg-Al-layered double hydroxide [35].

The selection of coating material plays a crucial role in ensuring adequate anti-corrosion protection, with most effectively delaying corrosion damage. The surface of the obtained coating must be uniform and strongly adhered to the material substrate [36,37]. The smaller the difference between the electrochemical potentials of the always active Mg matrix (anode) and the applied coating (more noble in potential), the better the anti-corrosive protection for the substrate material [38,39]. Such galvanic cells of two metals closer in potentials will provide smaller input for the progress in the corrosion process. Among the available options, aluminum coatings have been employed for corrosion protection on various metal surfaces, mainly because their air-formed passive Al_2O_3 layer acts as an efficient barrier against aggressive environments [40–43]. However, in the presence of air oxygen, a layer of MgO is formed on the magnesium alloy surface, which reduces the adhesion strength of the coating and thus negatively impacting its protective effectiveness. The introduction of an interlayer metallic element between the substrate and the coating may potentially extend its service life [44].

In Mexico there are around 11,000 km of marine-coastal areas, the aggressive atmosphere of which leads to accelerated corrosion of transport vehicle metal structures, shorting their service life. To improve the corrosion resistance of AM60 alloy, exposed to simulated marine ambience, the surface has been modified in different ways: by reinforcement with aluminum nitride (AM60-AlN nanocomposite) [45], polystyrene- ZrO_2 coating [46], vanadium and V_2O_5 sputtered deposit [47], and by electroless ZnO coating [48]. The initial stages of AM60-modified alloy have been monitored by applying different techniques.

The comparison of the AM60-Vanadium (~450 nm) and AM60- V_2O_3 (~350 nm) surface corrosion activities showed that the AM60-V presented a lower concentration of Mg^{2+} ion release (lower degradation rate), which was attributed to the possible intercalation of these cations into the conductive tunnels of V_2O_3 , as the main component of the vanadium sputtered deposit. V_2O_3 oxide has been reported as a material for high-capacitive energy storage and in this way, the V-deposit provided longer partial protection for the AM60 surface (Mg matrix) from localized pitting attacks.

The present study aims to explore a new approach to improve the corrosion resistance of the AM60 surface through an Al-metallic deposit achieved by non-reactive DC magnetron sputtering. The electrochemical activity of AM60 and Al-AM60 were compared, after immersion over 30 days in a simulated marine ambience (SME). The variation in SME solution pH and the concentration of released Mg^{2+} ions were monitored, to correlate with the change in free corrosion potential value (OCP). The surface microstructural characteristics were analyzed using scanning electron microscopy coupled with energy-dispersive spectroscopy (SEM-EDS), X-ray photoelectron spectroscopy (XPS), and X-ray diffraction

(XRD). The electrochemical impedance spectroscopy (EIS) was carried out to provide the characteristic parameters of the alloy-electrolyte (SME) interface.

2. Materials and Methods

2.1. Sample Preparation and Model Solution

Samples of AM60 (6.0% Al, 0.2%–0.4% Mn) magnesium alloy were extruded in rod shape with a 10 mm diameter and cut into ~ 1 mm thickness. The AM60 alloy was provided by the Magnesium Innovation Center in Bottrop, Germany. The preparation of samples involved grinding with silicon carbide (SiC) sandpaper of up to 1000 grit, followed by ultrasonic cleaning in ethanol for 5 min and drying at room temperature. The SME marine-coastal model solution was composed of analytical-grade Aldrich reagents, specifically 5.84 g L^{-1} NaCl, 4.09 g L^{-1} Na_2SO_4 , and 0.20 g L^{-1} NaHCO_3 , dissolved in ultrapure deionized water ($18.2 \text{ M}\Omega \text{ cm}$). The pH solution of the as-formed solution was 7.80 (PH60 Premium Line pH tester, Apera Instruments, LLC., Columbus, OH, USA).

2.2. Coating Deposition

Al-deposition on the AM60 Mg-Al alloy surface was performed through DC magnetron sputtering (Figure 1). The vacuum chamber achieved a base pressure of 1×10^{-5} Torr. Argon (Ar) was used to generate an Ar plasma at a constant working pressure of 4 mTorr. The Al-film was obtained by sputtering the Al target (99.5%) for 5 min at 100 W power and a temperature of about 45°C . The working distance was maintained at 60 mm, and the deposition rate was $\sim 13 \text{ nm min}^{-1}$.

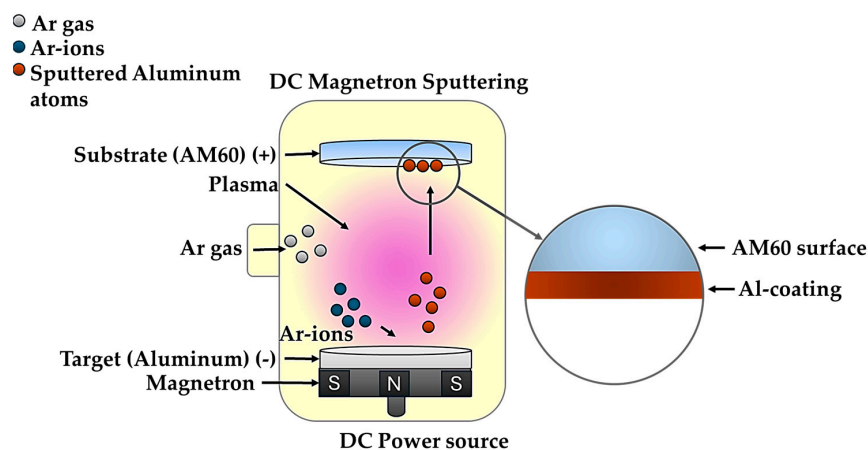


Figure 1. A schematic illustration of the DC magnetron sputtering deposition process.

2.3. Surface Characterization and Immersion Test

The morphology and composition of the uncoated AM60 and Al-AM60 surfaces were characterized before and after the immersion test in SME, using scanning electron microscopy coupled with energy dispersive X-ray spectrometry (SEM-EDS, XL-30 ESEM-JEOL JSM-7600F, JEOL Ltd., Tokyo, Japan). X-ray diffraction (XRD) patterns (Siemens D-5000 diffractometer, Munich, Germany, 2θ at 34 kV and 25 mA/CuK), configured in grazing incidence (penetration depth of about $2 \mu\text{m}$), were used for defect metallic and oxide crystal structures. Additionally, X-ray photoelectron spectroscopy (XPS, K-Alpha Surface Analyzer, Thermo Scientific, Waltham, MA, USA) was carried out at various erosion stages of the sample surface, achieved by a scanning Ar-ion gun. The binding energies of the XPS spectra were normalized to the C1s emission peak at 284.8 eV to ensure consistency in the measurements. Cross-sectional SEM imaging was performed on a fractured surface to verify the uniformity of the Al-deposit and estimate its thickness.

Immersion tests were conducted in 20 mL of SME for different periods of 1, 7, 10, 15, and 30 days (in triplicate), following the procedure of ASTM G31-12a standard [49]. Throughout the immersion process, the SME temperature was maintained at room temperature ($\sim 22^\circ\text{C}$), and the pH of the solution was monitored. The residual solutions were collected in separate containers for further analysis by photometry (HI83200, Hanna Instruments, Woonsocket, RI, USA) to quantify the concentration of Mg-released ions. The withdrawn metal samples were carefully rinsed with deionized water and air-dried at room temperature for their further surface characterization.

2.4. Electrochemical Characterization

The tests involved monitoring the variation of open circuit potential (OCP, free corrosion potential) over time during the immersion of uncoated AM60 and Al-AM60 surfaces. The samples (working electrodes), with a working area of 0.78 cm^2 , were immersed in 20 mL of SME solution, and measurements were conducted using a three-electrode cell configuration. A saturated calomel electrode (SCE, CH Instruments Inc., Austin, TX, USA) was used as the reference electrode, while a Pt-mesh (Alfa Aesar, Ward Hill, MA, USA) served as the counter electrode. The electrodes were connected to an Interface-1000E potentiostat/galvanostat/ZRA system (Gamry Instruments, Philadelphia, PA, USA) to record the Electrochemical Impedance Spectroscopy (EIS) Nyquist diagrams, obtained with a perturbation amplitude of $\pm 10\text{ mV}$ (vs. stabilized OCP after 2 h) over a frequency range of 100 kHz to 10 mHz. The EIS data were analyzed (V.7.1 Gamry Echem Analyst software, Gamry Instruments, Inc.) and fitted to electrical equivalent circuit to determine the characteristics parameters of the metal-electrolyte interface.

3. Results

3.1. X-Ray Diffraction Analysis

The X-ray diffraction (XRD) patterns for the AM60 alloy and Al-AM60 systems are shown in Figure 2. On the uncoated AM60 surface (Figure 2a) the XRD spectra suggested the presence of the α -Mg (majority phase of the matrix, JCPDS 01-077-6797) as well as the secondary phase of β - $\text{Mg}_{17}\text{Al}_{12}$ (JCPDS 01-076-2702) in a very low intensity, previously reported for Mg-Al alloys [50–52]. On the Al-AM60 surface (Figure 2b) the XRD signals were dependent on the thickness of the sputtered thin Al-film and the diffracted signals originated mainly from the underlying Mg-based alloy, reducing the relative intensity of aluminum peaks. The slight diffraction peaks observed at $2\theta \approx 38.44^\circ$ and 44.61° correspond to (111) and (200) crystal planes of α -metallic aluminum (JCPDS 00-004-0787), previously reported in the literature [53,54], confirming the presence of Al-deposit. The diffraction pattern of β - $\text{Mg}_{17}\text{Al}_{12}$ secondary phase was still detectable.

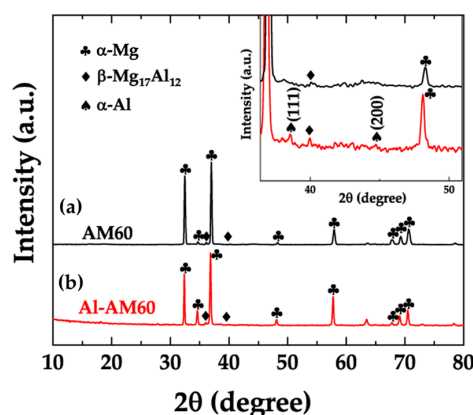


Figure 2. XRD patterns of (a) bare AM60 and (b) Al-AM60 surface.

3.2. SEM-EDS Characterization

The SEM micrographs (Figure 3) illustrate the morphological differences between the uncoated AM60 surface (Figure 3a) and that of the Al-AM60 (Figure 3b), modified through Al-sputtering. The SEM image of the uncoated AM60 substrate showed the multiple dispersed clusters of white color on the Mg-matrix, where EDS analysis (Table 1) is suggested as Al-Mn phase (average size about 5 μm), with a portion of the non-passive manganese added to the Mg-Al matrix. The elongated grains (in gray) of several microns of the $\beta\text{-Mg}_{17}\text{Al}_{12}$ secondary phase were also observable. Studies have reported that Mn, as an alloying element, can promote an increase in corrosion resistance of Mg-Al alloys, reducing the metastable pit initiation in aluminum and decreasing the alloy anodic dissolution [55–58].

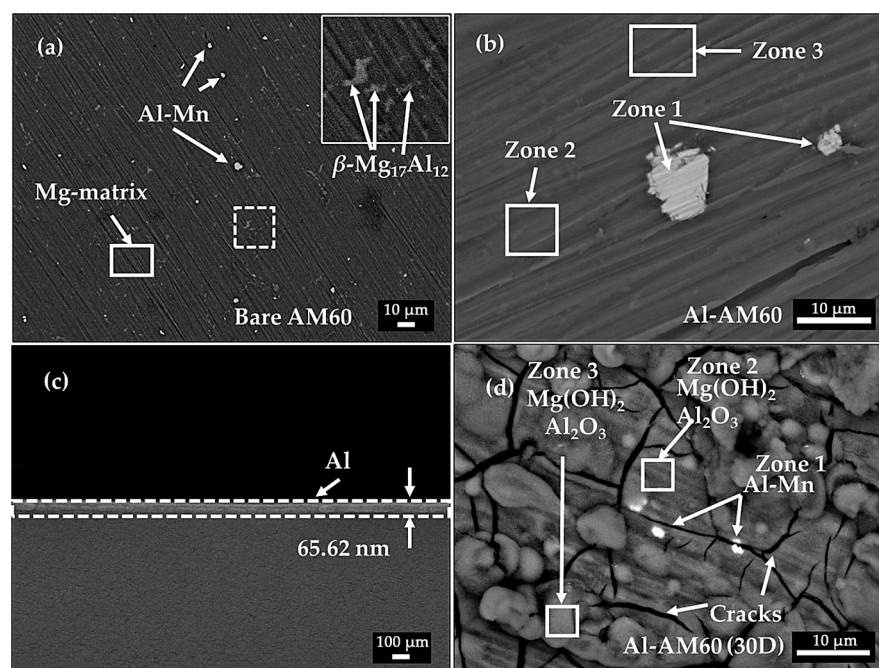


Figure 3. SEM micrographs of (a) bare AM60 ($\times 500$) and (b) Al-AM60 ($\times 2000$), (c) cross-section of Al-sputtered deposit ($\times 20,000$), and (d) Al-AM60 surface after 30 days of SME exposure ($\times 2000$).

Table 1. EDS elemental analysis (wt. %) of randomly selected surface areas (Figure 3) of the AM60 and Al-AM60 surfaces.

	Element	O	Mg	Al	Mn
AM60	Al-Mn	2.52	26.26	34.17	37.05
	Mg matrix	2.21	95.20	2.59	-
	$\beta\text{-Mg}_{17}\text{Al}_{12}$	1.43	79.65	18.92	-
Al-AM60	Zone 1	5.67	3.56	38.88	51.89
	Zone 2	7.38	78.99	13.63	-
	Zone 3	5.49	81.86	12.65	-
Al-AM60 (30 days exposure)	Zone 1	45.06	21.43	18.55	14.96
	Zone 2	58.63	31.66	9.23	-
	Zone 3	64.68	28.21	6.70	-

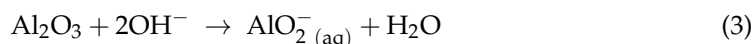
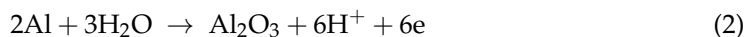
In saline ambience, Mn at the surface may suffer selective dissolution, favoring the formation of a compacted protective layer of thinner surface aluminum oxide, enhancing the corrosion resistance of the alloy. After the modification of the AM60 surface by sputtered aluminum (Figure 3b, Table 1), it seems that the deposition of aluminum did not occur on the cluster surface of Al-Mn particles (Zone 1), but instead formed a thin film of ~ 65.62 nm

(Figure 3c) on the AM60 matrix, covering the microparticles of the β -Mg₁₇Al₁₂ secondary phase (Zones 2–3), presenting a stable deposition (~13.14 wt.%) in this area.

After 30 days of exposure to the saline model solution (SME), the Al-AM60 system exhibited significant changes in morphology and composition (Figure 3d, Table 1). The corrosion layer that developed on the surface presented visible cracks, and white particles related to the Al-Mn intermetallic were observable (Zone 1), which confirms their function as local cathodic sites in micro-galvanic pairs with the α -Mg phase (anodic active). Due to the immersion in SME solution, the AM60 alloy surface was subjected to degradation and formation of a corrosion layer of insoluble Mg(OH)₂. The evolution of bubbles of H₂ gas exerted pressure on the formed layer and caused micro-cracks:



EDS analysis suggested that the main corrosion product of the formed layer was Mg(OH)₂, enriched in Al and O (Al-oxide) (Zones 2 and 3) [59,60]. Because of the increase in pH (Equation (1)), it is considered that the surface of the metallic α -Al (reported by the XRD patterns, Figure 2) can suffer electrochemical oxidation to Al₂O₃ (Equation (2)) and its posterior dissolution (Equation (3)) consuming OH[−] ions [59,60]:



A corrosion study of AM50 specimens immersed for 96 h in aerated 1.6 wt%. NaCl (at room temperature) has reported that there are two parts in the formed corrosion layer: outer layer of amorphous MgO/Mg(OH)₂ and a thin inner layer of Al₂O₃ between metal and corrosion products [25,61]. EDS analysis has suggested that at the interface, an Al-rich layer exists, with a location-specific content, depend on the Al content during the solidification of the Mg-Al alloy and an accumulation of Al³⁺ [62]. This is because of the percolation of amorphous Al₂O₃ in MgO/Mg(OH)₂ corrosion layer [63], which improved the corrosion resistance of the alloy.

3.3. XPS Analysis of Al-AM60 Modified Alloy Surface

XPS analysis was performed in addition to XRD and SEM-EDS to verify the principal elements present on the Al-AM60 surface, as a part of the possible compounds. The high-resolution XPS spectra are shown in Figure 4.

The spectrum of Al2p (Figure 4a,d) was composed of two peaks with binding energy at ~72.58 eV attributed to the asymmetric metallic Al 2p_{3/2} peak (Al⁰) and that at ~75.38 eV considered as characteristic of Al³⁺ (Al₂O₃) [64]. The energy separation between these Al2p peaks was estimated to be ~2.8 eV. After immersion for 30 days in the saline model solution (SME) the relative intensity of the Al-metallic peak was reduced by ~3 orders (Figure 4d) because of the reported electrochemical oxidation of the α -Al metallic phase (detected by XRD spectra) to Al₂O₃ (Equation (2)) [59,60]. However, the peak of the formed Al₂O₃ (at ~74.18 eV) still appeared on the Al-AM60 surface (Figure 4d) at lower intensity due to the suggested dissolution of this oxide (Equation (3)) to AlO₂[−] (aq). This way, the presence of the Al₂O₃ content on the AM60 alloy favored the ~2.3 times reduced release of Mg²⁺ ions (degradation of the Mg-matrix), and it is expected to provide protective layer [65]. On the other hand, the spectrum of O 1s (Figure 4b,e) displayed two peaks, at ~531.80 eV and at ~532.10 eV, commonly associated with the OH[−] ion [66]. The XPS analysis indicated that after immersion in the saline solution for 30 days, the peak intensity of the OH[−] ions increased trice, while that peak at ~531.80 eV was nearly constant. By relating the spectrum

of O 1s with that of Mg2p (Figure 4c,f) at ~50.58 eV of MgO and that of ~ 51.68 eV of Mg(OH)₂, it is observable that after immersion in the saline solution (SME), the intensity of the MgO diminished sharply, because it suffered corrosion and was gradually transformed to Mg(OH)₂ (Equation (1)).

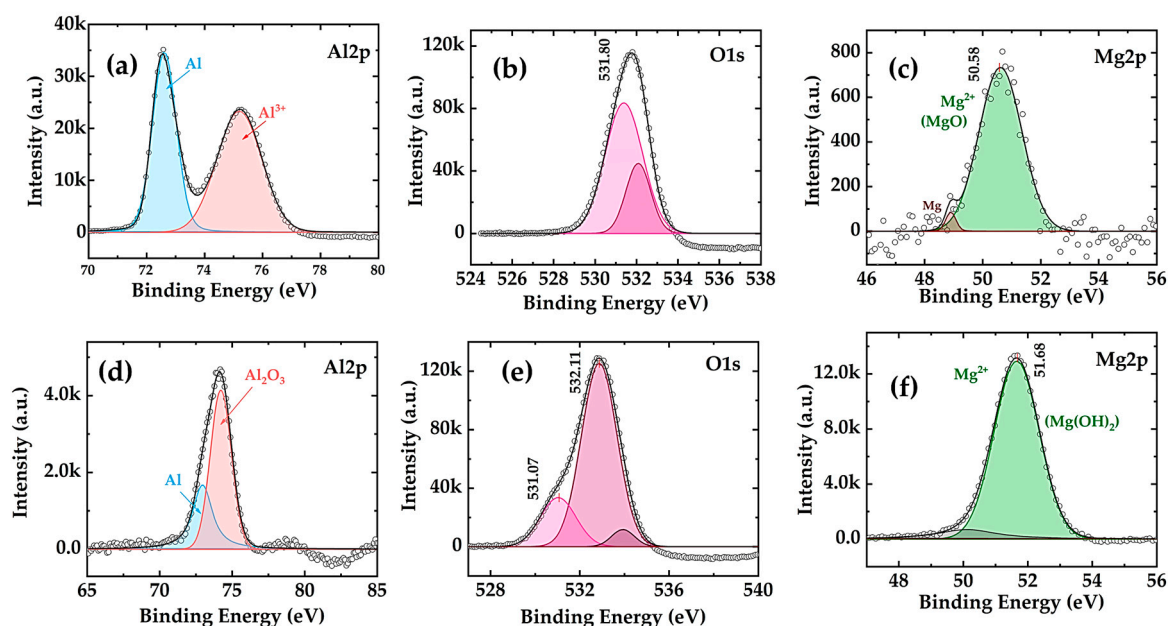


Figure 4. XPS high-resolution spectra peaks of Al 2p (a), O 1s (b), and Mg 2p (c) of Al-AM60 modified alloy surface, and spectra peaks of Al 2p (d), O 1s (e) spectrum of the deposited Al on AM60 magnesium alloy, (a) Al 2p peak, (b) O 1s peak, (c) Mg 2p peak and after 30 days of exposure to SME, (d) spectrum of Al 2p peak, (e) O 1s peak, and (f) Mg 2p peak.

3.4. Immersion Test in Model Saline Solution (SME)

Figure 5 compares the progress in time of pH of the saline model solution (SME) and Mg²⁺ ion release concentration (at 15 and 30 days) during the immersion of the studied uncoated AM60 and the modified surface of Al-AM60 alloys in SME; both parameters are indicators of the Mg-alloy degradation (electrochemical activity).

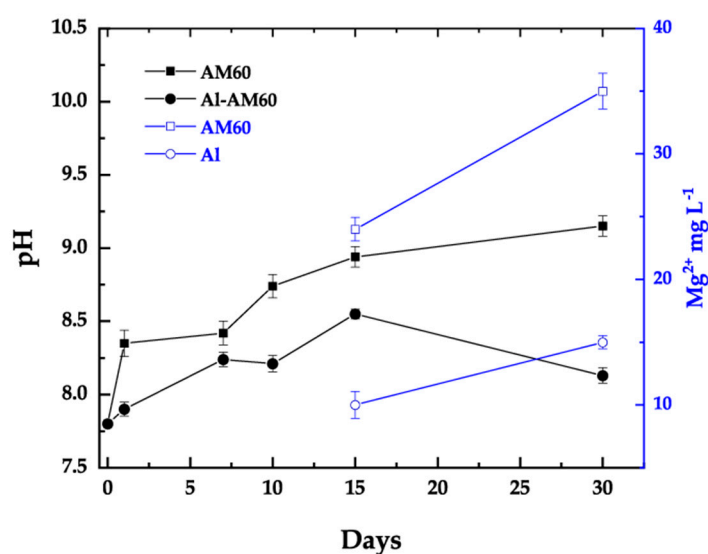
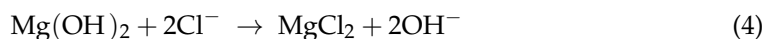


Figure 5. Change in time of SME marine solution pH (black line) and concentration of Mg²⁺ ion release (blue line) during immersion of uncoated AM60 and Al-AM60 alloys for 30 days in SME.

The microcracked first corrosion layer of insoluble $\text{Mg}(\text{OH})_2$ (Figure 3d) was more susceptible to chloride ion (Cl^-) penetration because of the H_2 evolution (Equation (1)) and posteriorly was transformed to the soluble corrosion product of MgCl_2 :



This localized process is more accelerated around the micro-galvanic pairs of Al-Mn (cathodic active) in contact with the Mg-matrix (local anodes), leading to changes in the pH of the SME to more alkaline values. The change in pH values (Figure 5) indicated that this fact was less pronounced for the Al-AM60 ($\text{pH} \approx 8.13$), in which the surface was modified with Al-sputtered nano-deposit, while the pH of the uncoated AM60 alloy reached a more alkaline value (~ 9.15), as an indication of a higher rate of electrochemical activity of the surface. The lower pH of the SME solution during the immersion of Al-AM60 can be attributed to the suggested electrochemical oxidation of aluminum to Al_2O_3 [25,59], which occurs with H^+ formation and consumption of OH^- ions (Equations (2) and (3)). Notably, at the end of the immersion test, the Mg-ion release was significantly higher ($\sim$ two times) for uncoated AM60 (35 mgL^{-1}), compared to that of Al-AM60 (15 mgL^{-1}). The lower ion release rate for Al-AM60 suggested that the presence of the nano-deposit of sputtered aluminum on the AM60 surface promoted a reduction of its electrochemical activity in the early stages. An explanation for this fact can be attributed to the studies [62,67] that have found an accumulation of $\text{Al}^{3+}/\text{AlO}_2^-$ species (Equation (3)) on the corroded surface because of the percolation of amorphous Al_2O_3 (Equation (2)) within the $\text{Mg}/\text{Mg}(\text{OH})_2$ corrosion layer, improving the corrosion resistance of the alloy.

3.5. Electrochemical Tests

Figure 6 compares the change in time of the free corrosion potential (OCP) of the uncoated AM60 surface with that of Al-AM60, during their immersion in the model saline solution (SME). At 15 days the OCP of the Al-AM60 (modified with sputtered nano-deposit of aluminum) tended to a constant value of $\sim -1.45 \text{ V}$, while the OCP of the uncoated AM60 maintained an increase over time, reaching $\sim -1.52 \text{ V}$ (more negative in $\sim 70 \text{ mV}$), as an indicator of more active corrosion processes.

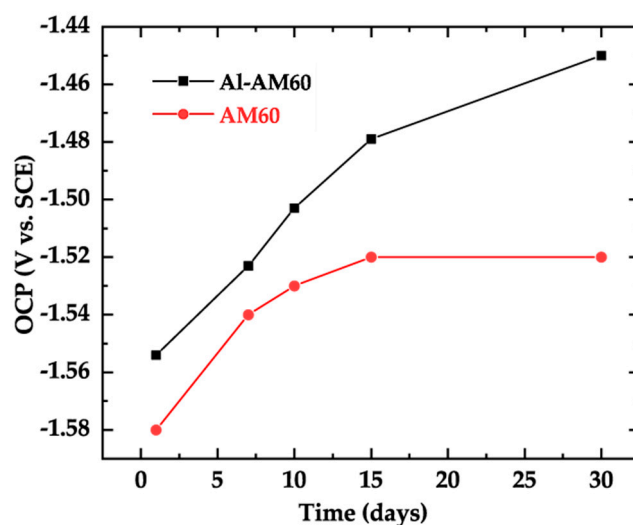


Figure 6. Change over time of the free corrosion potential (OCP) value of uncoated AM60 and Al-AM60 alloys during immersion in simulated marine solution (SME).

Figure 7 compares the Nyquist diagrams (Figure 7a) of uncoated AM60 and modified Al-AM60 surfaces, immersed for 7, 15, and 30 days to saline model solution (SME). The

Nyquist diagrams showed capacitive loops over the time of immersion; the characteristics were influenced by the changes that occurred at the interface alloy/SEM and influenced by the thickness and composition of the formed corrosion layer and mass/charge transport, as well as the existence of the Al-nano-deposit and the change in mass transport.

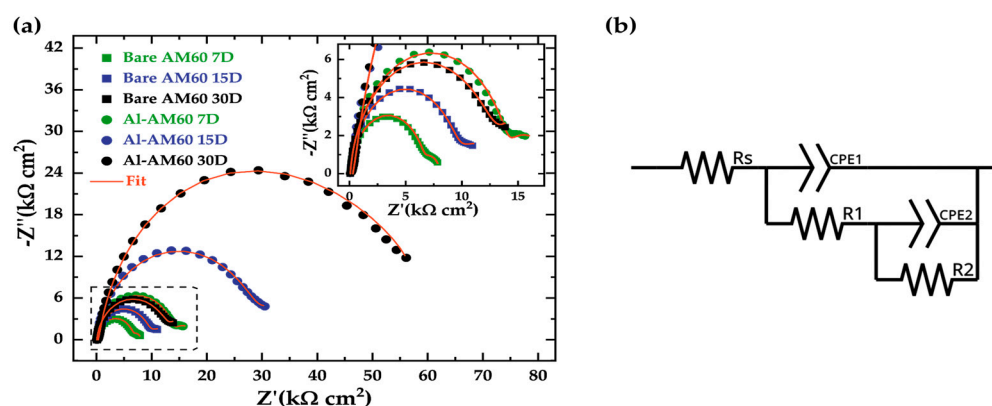


Figure 7. (a) Nyquist plots of EIS for 7, 15, and 30 days of exposure of bare (uncoated) AM60 and Al-AM60 after 30 days of immersion in SME solution, (b) equivalent circuit for fitting experimental EIS data.

As immersion time passed, the diameter of uncoated AM60 semi-circles was approximately thrice lower than those of the modified surface with Al-sputtered thin nano-deposit, indicating that the corrosion resistance of AM60 was improved significantly when exposed to simulated marine environment. The EIS data were fit to the equivalent circuit (Figure 7b) in our previous work for AM60 [46] and also reported in studies with EIS on Mg-alloys [68–71]. The main components are the following: R_s (electrolyte resistance); R_1 resistance and constant phase element (CPE_1) as “capacitance”, used in parallel to model the behavior of a non-ideal capacitor, presenting the double layer at the metal/electrolyte interface, where species of different charge (Mg^{2+} , Cl^- ions) at the electrolyte interface are transported through the formed layer of corrosion products and Al-deposit, acting as a physical barrier; R_2 (R_{ct}) and CPE_2 “capacitance”, introduced to characterize the charge transfer process of Mg^{2+} and H^+ ions at the local anodic and cathodic sites of the alloy surface occurring through the $MgO/Mg(OH)_2$ layer. The obtained values of the alloy/electrolyte interface characteristic parameters are summarized in Table 2 (The circuit has a fitting of about 10^{-4}).

Table 2. Fitting parameters from EIS data of bare (uncoated) AM60 and Al-AM60 modified with sputtered Al-deposit film after immersion of 30 days in SME.

R_s (Ω cm ²)	CPE_1 (μS s ⁿ cm ⁻²)	n1	R_1 (k Ω cm ²)	CPE_2 (μS s ⁿ cm ⁻²)	n ²	R_2 (k Ω cm ²)	R_p (k Ω cm ²)
AM60							
86.1 ± 0.44	60.65 ± 0.36	0.93 ± 0.03	12.85 ± 0.32	296.7 ± 0.40	0.71 ± 0.02	2.53 ± 0.21	15.46 ± 0.26
Al-AM60							
89.6 ± 0.29	25.86 ± 1.34	0.87 ± 0.01	43.07 ± 1.20	11.29 ± 0.26	0.90 ± 0.01	12.87 ± 0.89	55.94 ± 1.04

The overall polarization resistance expressed as $R_p = R_1 + R_2$, was calculated to compare the electrochemical activity of the uncoated AM60 surface with that of modified Al-AM60 surface. The value of R_p (polarization resistance) was thrice higher for the corrosion process progress at the Al-AM60 modified surface (~ 55.94 k Ω cm²), compared to that of uncoated AM60 (~ 15.46 k Ω cm²). These facts coincided with the lower concentration of released Mg^{2+} ions from the Al-AM60 as a consequence of the hindered corrosion process

avored by the sputtered aluminum nano-deposit, providing a protective layer on the AM60 alloy surface exposed to a simulated marine environment (SME).

4. Conclusions

To achieve better corrosion resistance of AM60 (Mg-Al) alloy as engineering construction material, the surface was modified with DC magnetron sputtered aluminum nano-deposit (average thickness of ~ 65 nm). The sputtered Al film adhered to the α -Mg matrix where the particles of β -Mg₁₇Al₁₂ secondary phase were dispersed, while the Al-Mn intermetallic remained isolated. According to XPS analysis and XRD analysis, the aluminum nanofilm was composed of (111) and (200) crystal planes of the metallic aluminum (Al⁰) and Al₂O₃ (Al³⁺). The initial stages of activity of uncoated AM60 and Al-AM60 surfaces were tested by immersion for 30 days in simulated saline solution (SME, pH 7.8). SEM-EDS analysis showed that due to the immersion in SME solution, the Mg-matrix surface of AM60 was subjected to degradation and micro-cracking (by H₂ bubble evolution), and the main corrosion product of the formed layer was Mg(OH)₂ enriched in Al and O (Al-oxide). The Al-AM60 maintained a lower alkaline value (pH $\sim$ 8.13) of SME, than that of the uncoated AM60 (pH $\sim$ 8.13), which was attributed to α -Mg electrochemical oxidation to Al₂O₃ and its posterior dissolution, consuming OH[−] ions. Consequently, the concentration of the released Mg²⁺ ions from the Al-AM60 surface was reduced ~ 2.3 times (~ 15 mg L^{−1}) as an indication of the lower degradation rate. The *R_p* (polarization resistance), as inversely proportional to the corrosion current, was extracted from the EIS impedance data fitted to an equivalent electrical circuit. After 30 days in SME solution, the *R_p* value of the Al-AM60 modified surface was ~ 3.5 times higher than that of uncoated AM60 (15.46 kΩ cm²), confirming that the sputtered aluminum nano-deposit can hinder the corrosion process. The reported results might serve as a platform for further improvement in AM60 alloy corrosion resistance.

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