



Corrosion behavior of Al/Mg/Al multilayered composite elaborated by accumulated roll bonding

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Abstract: The corrosion behavior of an Al1050/AZ31/Al1050 multilayered hybrid composite fabricated by the accumulated roll bonding (ARB) technique up to six cycles in a 3.5 wt.% NaCl solution was studied through potentiodynamic polarization tests (PDP), electrochemical impedance spectroscopy (EIS), scanning electron microscopy (SEM–EDS), Raman spectroscopy and X-ray diffraction (XRD). In order to deeply apprehend the corrosion resistance and corrosion products of the Al1050/AZ31/Al1050 multilayered hybrid composite, almost similar investigation was performed on the Al1050/Al1050/Al1050 multilayered sample elaborated by ARB up to one cycle. Potentiodynamic polarization plots and electrochemical impedance spectroscopy show that the corrosion rate is strongly affected by the ARB strain level. A higher corrosion rate and reduced polarization resistance are evidenced compared to the Al1050/Al1050/Al1050 multilayered sample. The AZ31 layers seem to dominate the corrosion process. Raman and XRD analyses confirm the presence of the main corrosion product of $\text{Mg}(\text{OH})_2$ and the absence of any chloride such as $(\text{Mg}(\text{OH})_2) \cdot \text{MgCl}_2$.

Key words: accumulated roll bonding (ARB); Al1050/AZ31/Al1050; multilayered composites; corrosion; intermetallics

1 Introduction

Recently, several efforts have been made to produce metallic multilayered composites, and this has attracted great interest from engineers and researchers due to their special advantages in electrical, magnetic, and mechanical properties. To manufacture these multilayered composites, various techniques have been proposed like magnetic sputtering [1], jet-vapor deposition [2], physical vapor deposition [3], electroplating [4], and accumulated roll bonding (ARB). Especially, the

ARB process, which has been proposed for thirty years is a kind of severe plastic deformation (SPD) processing such as high-pressure torsion (HPT), equal channel angular extrusion (ECAP), constrained groove pressing (CGP), cyclic extrusion compression (CEC), multiaxial forging (MAF), and repetitive corrugation and straightening (RCS). ARB processing comprises multiple cycles of rolling, cutting, stacking, and solid-state deformation bonding and is characterized by any change in the sheet's geometry despite the significant amount of strain. ARB is an excellent technique for producing similar or hybrid metallic

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multilayered composites with ultrafine-grained (UFG) microstructure [5]. To date, the ARB technique has been effectively applied to copper alloys, steel, aluminum alloy, and multilayered composite systems such as Al/Ti [6], Cu/Zr [7], and Al/Cu [8]. Magnesium alloys are extremely attractive for aerospace technology, automotive, military as well as biomedical industries due to their high specific strength, high abundance of Mg, and biocompatibility. However, one of the main issues of magnesium alloys is their corrosion behavior, which has limited their widespread applications. Contrarily, aluminum alloys constantly exhibit better formability and better corrosion resistance than magnesium alloys [9]. Actually, the poor corrosion resistance of several magnesium alloys was attributed to two essential reasons: (1) the presence of impurities or second phases leads to internal galvanic corrosion [10]; (2) the hydroxide film on magnesium surface is much less stable compared to the passive films that are formed on the surface of metals such as stainless steel or aluminum.

Because of the different crystallographic configurations, it should be predicted that light metallic Mg/Al multilayered composites prepared by the ARB technique could collect the merit of magnesium and aluminum alloys, such as minimizing the weight. In addition, Mg/Al multilayered composites obtained a lot of attention in the domain of lightweight constructions when excellent impacting or damping capacities are needed [11]. The relative corrosion of the materials involved has been already explored. The ARB accentuates the problems by leading to inter-metallics, which are formed during the intermediate annealing at the interfaces.

FATTAH-ALHOSSEINI and collaborators have already carried out several studies through potentiodynamic polarization and EIS analysis which allowed to acquire considerable new knowledge about the electrochemical behavior of AA1050 alloy [12–15] and Al/B₄C/SiC hybrid composites [16,17] after ARB processing and immersion in many aqueous solutions. These alloy systems exhibited appreciable corrosion properties owing to the protective oxide film formed on their surface. Increasing the ARB cycles number assured better conditions for the oxide film morphology and

growth on the AA1050 alloy surface [13]. For the Al/B₄C/SiC hybrid composites, the oxide layer was characterized by inhomogeneities and porosities owing to the existence of SiC and B₄C particles. Such morphological features are favored sites for the initiation of corrosion [17]. However, recently, published data about the correlation between crystallographic texture and electrochemical behavior of nano/ultrafine-grained AA2024 alloy processed by ARB and tested in a phosphate buffer solution [18] revealed quite contradictory electrochemical behavior. Indeed, it has been evidenced that the grain refinement increases the corrosion current density and decreases the passive film resistance of AA2024 alloy. These authors have brought new insights about the correlation between grain size distribution/crystallographic texture and electrochemical properties. Interestingly, they have shown that the electrochemical properties may be improved by uniform grain size distribution and the domination of Cube {001}<100> and Copper {112}<111> components. Comparatively to Al-based alloys, the effect of SPD processing via severe plastic deformation on the corrosion of Mg-based alloy in general and AZ31 in particular, is not clear. In the authors opinion, the corrosion behavior of the Al1050/AZ31/Al1050 multilayered composites processed by ARB has not so far been reported in the literature.

In this work, the corrosion behavior of an Al1050/AZ31/Al1050 multilayered hybrid system fabricated by the ARB technique up to six cycles has been studied through potentiodynamic polarization, electrochemical impedance spectroscopy, scanning electron microscopy (SEM), Raman spectroscopy and X-ray diffraction. The main motivation was to study the effect of increasing strain on the corrosion of the Al1050/AZ31/Al1050 multilayered composites that seems to be quite complicated galvanic system.

2 Experimental

2.1 Materials

The materials used in this study were AZ31 and Al1050 alloys. The AZ31 sheets with 2.2 mm in thickness and average grain size of about 18 μm were kindly supplied by MagIC Magnesium Innovations Center, Germany. The Al 1050 alloy

sheets with 1 mm in thickness and average grain size of around 25 μm were supplied by PIMA (Produits Industriels et Métallurgiques SARL, Algeria) Company, Algeria. The chemical compositions of commercial AZ31 and Al 1050 alloys are listed in Table 1 and Table 2, respectively.

Table 1 Chemical composition of AZ31 alloy (wt.%)

Mg	Al	Zn	Mn	Ca	Si	Cu
Bal	2.5–3.5	0.6–1.4	0.2–1.0	0.04	0.1	0.01

Table 2 Chemical composition of Al1050 alloy (wt.%)

Al	Cu	Fe	Mg	Mn	Si	Ti	V	Zn
99.5	0.05	0.4	0.05	0.05	0.25	0.03	0.05	0.05

2.2 Accumulative roll bonding (ARB) process

The initial sheets with dimensions of 65 mm $\times$ 30 mm were cut from the AZ31 and Al 1050 sheets. After being degreased in acetone and wire brushed to remove the surface oxide film and hence ensure a good bonding, one AZ31 sheet, and two Al 1050 sheets were stacked in the following order Al1050/AZ31/Al1050 (Fig. 1). The stacks were tightly tied with a soft steel wire to avoid any lateral slipping during rolling and subsequently held at 400 $^{\circ}\text{C}$ for 10 min in a preheated furnace. They were then warm roll-bonded by applying a thickness reduction of 50% in a single cycle without any lubricant. The sheets were air-cooled and then cut in halves to start the second cycle. For Al1050/AZ31/Al1050, the operation was successful up to six cycles of ARB. A one-cycle ARB Al1050/Al1050/Al1050 sample was prepared to serve as a reference sample for the purpose of comparison and hereafter labeled as ARB Al. This consideration was based on the fact that the one-cycle ARB led to the less nobler Al1050/Al1050/Al1050 multilayered non-hybrid composite among the processed samples up to six ARB cycles [19].

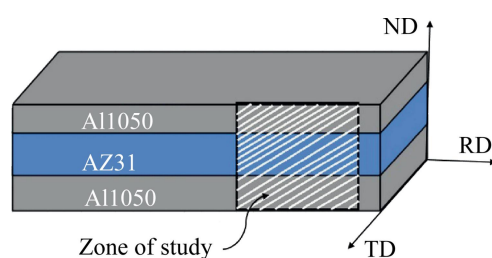


Fig. 1 Schematic illustration of cutting of Al/Mg/Al laminated composite samples

2.3 Electrochemical measurements

Electrochemical measurements were performed on the RD–ND cross-section plane (Fig. 1) using Potentiostat–Galvanostat–ZRA Gamry reference 3000 with a Gamry Instruments Framework operational software (version 7.05). A Gamry paracell with a standard three-electrode configuration was used. The multilayered composite sample was the working electrode, a standard Ag/AgCl electrode (the potential of the Ag/AgCl electrode was the same as the saturated calomel electrode SCE and equal to 0.24 V (vs SHE)) was the reference electrode and graphite was used as the counter electrode. Rectangular 0.24 cm $\times$ 1.7 cm specimens were cut on the ND–RD cross-section, and then the samples were embedded in an epoxy resin to isolate 0.4 cm² area from the non-analyzed surfaces on one hand, and on the other hand to insulate the cell and prevent electrolyte leakage (the dimensions of the embedding mold were 3.2 cm $\times$ 3.2 cm). All samples were polished with SiC paper up to 4000 grit and cleaned with distilled water and ethanol. All tests were carried out at room temperature (~ 24 $^{\circ}\text{C}$) in 3.5 wt.% NaCl solution. The initial pH of the NaCl solution was measured and amounted to 5.5. The OCP (open circuit potential) was recorded for at least 1 h for all samples to reach a steady state. Potentiodynamic polarization measurements were made at a scan rate of 2 mV/s from the cathodic potential of -2.7 V to the anodic one of $+1.2$ V in order to assess the corrosion potential (ϕ_{corr}). The Tafel coefficients (β_a and β_c) were calculated from the slope after ± 80 mV (ϕ_{corr}) due to the presence of a degree of nonlinearity in the Tafel slopes. The impedance measurements were performed after the open circuit potential ones with a sinusoidal potential signal having an amplitude of 10 mV in the frequency range from 10^{-2} to 10^5 Hz. The choice of the EIS parameters was based on published studies on similar systems [19]. A Kramers–Kronig fit was applied to all EIS spectra for the validation of the measurements. An equivalent circuit analysis was carried out using the Gamry Echem Analyst software (Version 7.05, Gamry Instruments). To ensure reproducibility of the experimental results, each test was repeated 3 times.

2.4 Scanning electron microscopy (SEM) analysis

The surface corrosion morphology of Al1050/

AZ31/Al1050 laminated composite in the corrosive media was examined by a scanning electron microscope (SEM, JEOL 6360) operating at 15 kV and equipped with an energy-dispersive X-ray microanalysis system (EDXMA, Inca Energy 200). The accelerating voltage used for SEM and EDS analysis was 15 kV.

2.5 Raman spectroscopy

Raman spectroscopy is commonly used for the identification of corrosion products, despite its limitations, the most important of which is the fact that some compounds are inactive during the analysis. In our present investigation, the Raman spectra of corroded samples were acquired using Horiba LabRAM HR evolution spectrometer. He–Ne laser of 633 nm with 17 mW power was used as an excitation source. The spectra were recorded over the range of $150\text{--}4000\text{ cm}^{-1}$ and $150\text{--}2000\text{ cm}^{-1}$ for Al1050/AZ31/Al1050 and one-cycle ARB Al, respectively. The spectra were collected at different points at the surface to check the reproducibility of results and to identify various corrosion products.

2.6 X-ray diffraction (XRD)

X-ray diffraction has been used in studies of magnesium corrosion since 1933 and specifically when WHITBY attempted to investigate the nature of corrosion products generated on Mg after an outdoor exposure [20]. Since then, X-ray diffraction has been widely used in corrosion studies. In our work, to examine the phase composition and determine the corrosion products, X-ray diffraction analysis was carried out on a PANalytical, X'Pert3 powder facility operating at 40 kV and 40 mA using Cu K_{α} radiation ($1.542\text{ \AA}$). 2θ Bragg angle ranged $20^{\circ}\text{--}80^{\circ}$ with a step size of 0.026° and step time of 1 s.

3 Results and discussion

3.1 Open circuit potential

The open-circuit potential plots (OCP) of Al1050/AZ31/Al1050 multilayered composites up to six cycles and of ARB Al for one cycle immersed in 3.5% NaCl solution are shown in Fig. 2. As it is defined, the OCP is the potential of the electrode at which the cathodic and anodic reaction rates are in equilibrium in the absence of an applied potential in

a given corrosive environment.

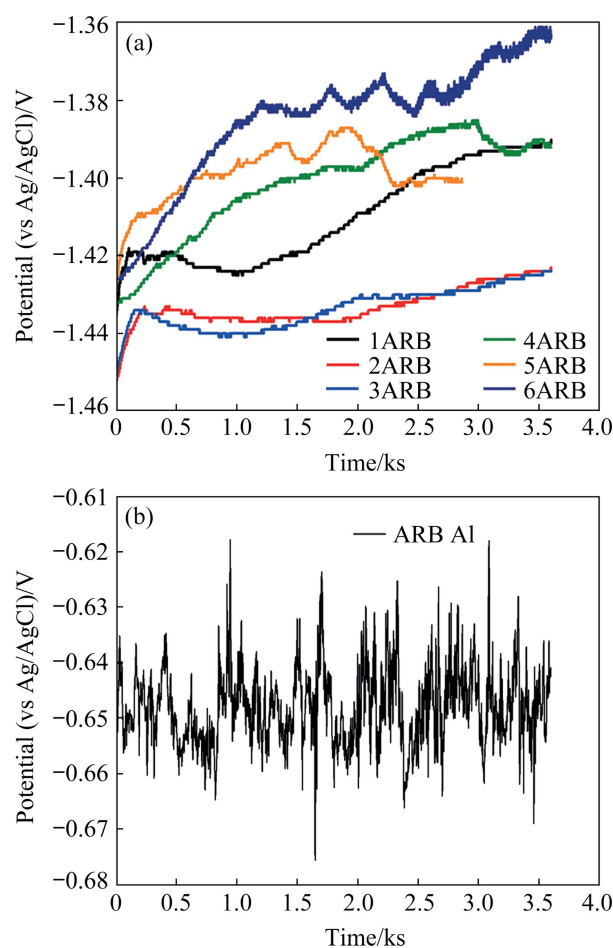


Fig. 2 Open circuit potential curves in 3.5% NaCl solution: (a) Al1050/AZ31/Al1050 up to six-cycle ARB; (b) ARB Al after one cycle

Metallic materials with nobler OCP are thermodynamically more stable than materials with less noble OCP. As clearly seen in Fig. 2(a), the corrosion potential of Al1050/AZ31/Al1050 multilayered composite is between -1.390 V (for $N=6$, and N is the cycle number) and -1.440 V (for $N=2$). However, it is -0.648 V for the ARB Al sample, as shown in Fig. 2(b). The obtained data for Al1050/AZ31/Al1050 multilayered composite are quite close to those of as-received AZ31 alloy immersed in 0.9% NaCl [21] but somewhat higher (-1.59 V (vs SCE)) than those of AZ91 alloy immersed in 3.5% NaCl solution after ECAP processing [22]. The corrosion potential of the ARB Al sample for one cycle is also close to the tabulated data in the literature. FATTAH-ALHOSSEINI and GASHTI [19] have found -0.5 V (vs Ag/AgCl) for ultra-fine grained 1050 aluminum alloy fabricated by ARB process in a

buffer borate solution. ABDULSTAAR et al [23] have evidenced -0.708 V (vs SCE) for Al1050 alloy severely deformed by rotary swaging immersed in 3.5% NaCl solution.

For the ARB processed samples with cycle $N=1-3$, the OCP slightly increased during the first 100 s of immersion and then drops to more negative values. The slight increase in potential is associated with the formation of a corrosion layer (oxide or hydroxide) on the metallic surfaces, whereas the drop in potential is related to its dissolution [22]. Pseudo-stability of OCP after longer immersion time achieved with prolonged immersion suggests a steady-state condition between the anodic dissolution and the repassivation of the oxide layers as already stated by LI et al [24]. In contrast, the OCP for $N=4-6$ ARB cycles continuously increases for about 3000 s, after which it seems to level off. This suggests the formation and growth of a more stable and protective corrosion layer than the $N=1-3$ ARB cycle samples. Furthermore, it is evident that the OCPs of the ARB-processed alloys are more positive when the ARB cycle number increases. This behavior suggests that the fine-grained samples exhibit nobler behavior compared with the coarse-grained ones. This ennoblement seems rather unexpected since the NaCl solution has an initial pH of 6.5. It is worth noting that in general magnesium alloys are stable in basic solutions whereas in neutral and acidic media they dissolve at high rates. This is somewhat different to aluminium alloys which are normally stable in neutral media but are unstable in both basic and acidic solutions. The OCP curves show some fluctuations with enhanced amplitude at high strain level ($N=5, 6$) during the immersion of magnesium alloy in NaCl solution, which is explained by the fact that the equilibrium at the electrode/solution interface was not reached or by the weakness of the corrosion layer.

3.2 Potentiodynamic polarization test results

Potentiodynamic polarization (PDP) curves were acquired using 3.5 wt.% NaCl solution as electrolyte (Fig. 3). The corrosion potential (ϕ_{corr}) and the corrosion current density (J_{corr}) of the samples were determined by extrapolating the linear Tafel segments of the anode and cathode polarization curves (Table 3). Based on Fig. 3, for the six Al1050/AZ31/Al1050 multilayered composites

samples, manifestly there is no important change in the overall shapes of the polarization curves with the number of cycles. The anodic and cathodic branches are not symmetrical and their trends are very similar. Indeed, the change is only in the corrosion rate and the mechanism of corrosion is preserved. On the other hand, the difference between the curve shapes of Al1050/AZ31/Al1050 and ARB Al indicates a net difference in the corrosion rate and the mechanisms of corrosion reactions.

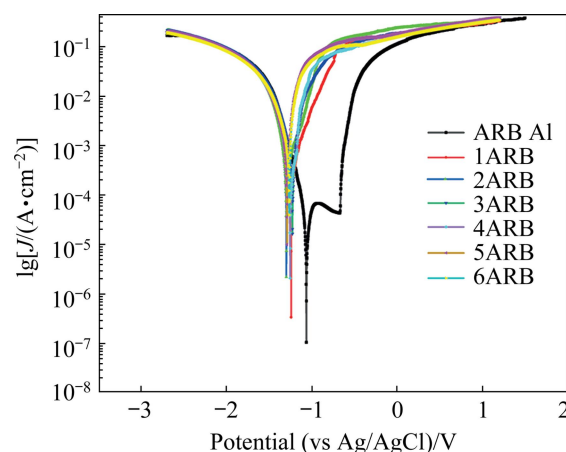


Fig. 3 Potentiodynamic polarization curves of Al1050/AZ31/Al1050 samples up to six cycles ARB and ARB Al after one cycle in 3.5% NaCl solution

Table 3 Fitting parameters of potentiodynamic polarization curves of ARBed samples of Al1050/AZ31/Al1050 up to six-cycle ARB and ARB Al in 3.5% NaCl solution

Sample	ϕ_{corr} (vs Ag/AgCl)/V	J_{corr} ($\mu\text{A}\cdot\text{cm}^{-2}$)	Corrosion rate/($\text{mm}\cdot\text{a}^{-1}$)
1ARB	-1.260	84.5	2.601
2ARB	-1.240	133.0	3.553
3ARB	-1.300	179.0	4.888
4ARB	-1.230	178.0	5.204
5ARB	-1.290	241.0	8.031
6ARB	-1.260	319.0	9.829
ARB Al	-1.070	13.9	0.371

As is seen in Table 3, the corrosion potentials obtained according to the OCP plots (Fig. 2) are not similar to those from potentiodynamic polarization (PDP) curves (Fig. 3). These differences may result from the structure of the corrosion films and their chemical composition. Passivation phenomenon is manifested in polarization curve of ARB Al sample

but is not in Al1050/AZ31/Al1050 ones. The pitting potential which is very close to the corrosion potential for aluminium alloys in NaCl solutions (-0.62 V (vs SCE)) is higher than the tabulated value (-0.72 V (vs SCE)) for Al1050 alloy in aerated 0.5 mol/L NaCl solution [25] and even higher (-1.43 V (vs SCE)) than that of Al/20%Zn composites processed by cross accumulative roll bonding up to one cycle and immersed in 3.5% NaCl [26]. In this study, from the potential dynamic polarization (PDP) results, ϕ_{corr} and J_{corr} of Al1050/AZ31/Al1050 multilayered composites are significantly lower than those of ARB Al, which indicates that they have worse corrosion resistance. The corrosion rate of Al1050/AZ31/Al1050 multilayered composites increases proportionally to the ARB cycle number. Such a systematic increase was not observed by PERON et al [27] during their study of the effect of ECAP processing on the corrosion resistance of AZ31 alloy. The authors did not establish any clear relationship between corrosion rate and the number of ECAP passes. According to their study [27], one pass of ECAP improved the corrosion resistance, and the corrosion resistance of the second and fourth passes of ECAP was poorer than that of the as-received material.

BIRBILIS et al [28] have also proven that the rate of corrosion decreases as the logarithm of the grain size decreases in pure Mg processed by ECAP. These authors recognized that normally the mechanical properties enhancement after SPD processing should be accompanied by an increase in the corrosion rate (strength and corrosion resistance may obey inverse proportionality).

In the Al1050/AZ31/Al1050 multilayered composites, the grain refinement of AZ31 and Al1050 layers was somewhat different. HABILA et al [29] evidenced that the microstructure of AZ31 layers was characterized by fine equiaxed grains. The average grain size was about $0.8 \mu\text{m}$ after 5 ARB cycles. Meanwhile, the microstructure of Al1050 layers contained elongated grains parallel to the rolling direction. The value of the mean spacing of HAGB along ND was $1\text{--}4 \mu\text{m}$ after 5 ARB cycles. Indubitably, the effect of grain refinement via severe plastic deformation on the corrosion of Al- or Mg-based alloy is not clear. PU et al [30] have proven that grain refinement caused by cryogenic burnishing which is a new SPD technique improves

the corrosion resistance of Mg-based alloy. In contrast, SONG et al [31] found that corrosion resistance decreased because of grain refinement of pure Mg and AZ91D Mg alloy after ECAP processing and immersion in 3.5 wt.% NaCl aqueous solution.

In Fig. 4, the evolution of the corrosion resistance (R_p) is plotted in function of the reciprocal of the square of the grain size of the AZ31 layers. R_p has been estimated from Stern–Geary equation given by

$$R_p = \frac{\beta_a \beta_c}{2.30(\beta_a + \beta_c) J_{\text{corr}}} \quad (1)$$

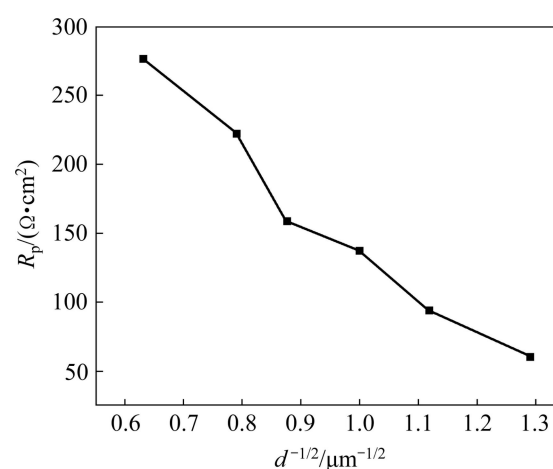


Fig. 4 Evolution of polarization resistance (R_p) in function of reciprocal of square of grain size (d) of AZ31 layers

The observed evolution in Fig. 4 can very reasonably be described by the following equation that reminds Hall–Petch equation:

$$R_p = A + B d^{-1/2} \quad (2)$$

where the constant A is dependent on the corrosive media and B is a material-dependent factor (chemical composition, deformation conditions, etc). Similar observations have been reported in pure Mg and Mg alloys, and the results were compiled in Ref. [32]. But it is worth noting that [32c] compilation revealed controversial trends in the grain size/corrosion resistance. These controversies may be associated with the effects of other microstructural features which may be concomitant to grain refinement and which are often underestimated.

3.3 EIS test results

Figure 5 depicts the Nyquist plots of Al1050/

AZ31/A11050 up to 6 cycles ARB and ARB Al for one cycle immersed in 3.5% NaCl solution for 1 h. Figure 5(a) indicates that the shape of the plots of the six samples is the same and consists of a large high-frequency capacitance loop and one low-frequency inductance loop. This similarity corroborates the fact that all six A11050/AZ31/A11050 samples do bear the same corrosion mechanisms. As stated in many published works, the capacitive loop at the high-frequency region is often ascribed to a charge transfer reaction between the metal interface and the solution and also to the formation of a corrosion film. Interestingly, there is no low-frequency inductance loop on the Nyquist plot of the ARB Al reference sample which contains only one capacitance loop associated with the formation of a passive film, as shown in Fig. 5(b). The Nyquist plots of Al alloys fabricated by the ARB process often involve imperfect semicircles. As stated earlier, these semicircles depict a capacitance loop having only one time constant. The difference in Nyquist plot shapes between the A11050/AZ31/A11050 multilayered composites up to 6 cycles and the ARB Al reference sample indicates that the corrosion mechanism and the corrosion rate are different. At high frequencies of the Nyquist plots of the A11050/AZ31/A11050 multilayered composites, the capacitive loops describe the characteristics of the electric double layer and the inductive behavior could be associated with the formation of the $\text{Mg}(\text{OH})_2$ and/or MgO and the coverage due to adsorption of $\text{Mg}(\text{OH})_{\text{ad}}^+$ [33]. Even though, any published data on Mg-based alloys present EIS data with inductive response but the inductive response is often disregarded [23]. The inductive loop could disappear as is the case for the ARB Al sample when the corrosion protective layer is formed and totally engulfs the surface. Moreover, the Nyquist plots diameter represents the corrosion resistance of the sample, and its evolution is in the following order : 1ARB > 2ARB > 3ARB > 4ARB > 5ARB > 6ARB. These trends are in agreement with the polarization curves. It is well known that the high frequency in the Nyquist plot represents the properties of the coatings which in fact are the thick oxide or hydroxide films whereas the low part is associated with Faradaic processes occurring in the metal [34]. The presence of poor capacitive behavior at high frequencies suggests a more corrosive behavior. It

is worth noting that the absence of capacitive loops in the low-frequency region is often a mark of the continuation of the Faradaic process mainly in the diffusion process at the metal/solution interface.

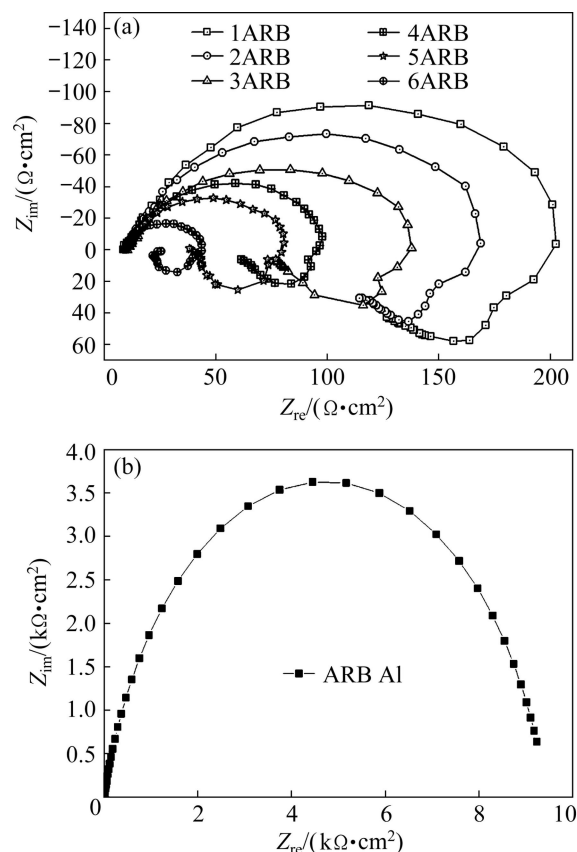


Fig. 5 Nyquist plots of A11050/AZ31/A11050 samples up to six-cycle ARB (a) and ARB Al after one cycle (b) in 3.5% NaCl solution

The impedance values of A11050/AZ31/A11050 multilayered composites decrease with increasing ARB cycles. In order to analyze the EIS, the data were fitted using equivalent circuit elements. The appropriate fitting equivalent circuits for the A11050/AZ31/A11050 multilayered composite and ARB Al are given in Fig. 6. The circuit elements parameter values are listed in Tables 4 and 5, respectively, where R_s is the solution resistance and R_{ct} denotes the charge transfer resistance or film resistance [35]. Constant phase elements CPE was used in place of a capacitor to compensate for the non-homogeneity of the sample surfaces. A CPE represents the film capacity. Usually, a CPE is defined by two parameters, Y and n . When $n=1$, CPE is identical to an ideal capacitor, while for $n=0$, CPE is represented by a resistance. The low-frequency

inductance loop is described by the inductance

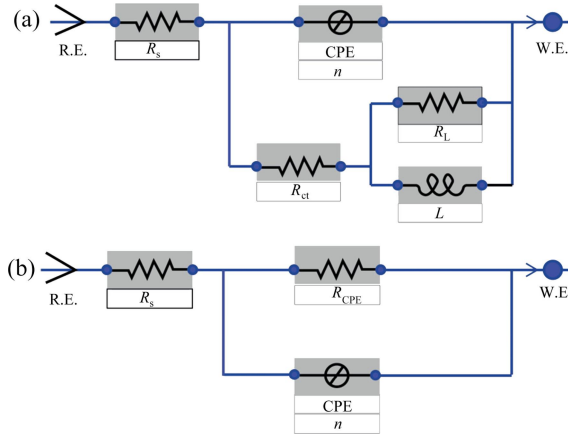


Fig. 6 Equivalent electrical circuits used for modeling experimental EIS data: (a) Al1050/AZ31/Al1050 samples up to six-cycle ARB; (b) ARB Al after one cycle (R.E.–Reference electrode; W.E.–Working electrode)

Table 4 Fitting results of EIS of Al1050/AZ31/Al1050 laminated composite

Sample	$R_s/$ ($\Omega \cdot \text{cm}^2$)	CPE		$R_{ct}/$ ($\Omega \cdot \text{cm}^2$)	$R_l/$ ($\Omega \cdot \text{cm}^2$)
		$Y/(\text{F} \cdot \text{cm}^{-2})$	n		
1ARB	10.54	0.932×10^{-6}	0.960	106.5	93.8
2ARB	10.05	3.023×10^{-6}	0.871	98.6	83.7
3ARB	12.34	0.709×10^{-6}	0.999	61.8	58.0
4ARB	10.06	1.62×10^{-6}	0.792	53.1	47.9
5ARB	9.859	4.109×10^{-6}	0.859	28.8	47.4
6ARB	10.26	1.011×10^{-6}	0.976	11.8	22.9

Table 5 Fitting results of EIS of ARB Al

$R_s/$ ($\Omega \cdot \text{cm}^2$)	$R_{CPE}/$ ($\Omega \cdot \text{cm}^2$)	CPE/ ($\Omega^{-1} \cdot \text{cm}^{-2} \cdot \text{s}^{-n}$)	n
2.95	9443.4	77.64×10^{-6}	0.835

element L whilst the inductance resistances are denoted R_L . In Fig. 6(b), R_{CPE} is the polarization resistance of the passive film of the Al1050 layer. Table 4 gives that for the six Al1050/AZ31/Al1050 multilayered composites, the value of R_s evolves very little ($R_s = (10.51 \pm 0.92) \Omega \cdot \text{cm}^2$), confirming that they behave similarly in the contact with the 3.5% NaCl solution. The charge transfer resistance, R_{ct} , reduces from 106.5 to 12.8 $\Omega \cdot \text{cm}^2$, corroborating the decline of the corrosion resistance upon increasing strain as stated above. Globally, the values of R_{ct} and CPE are well in accordance with the corrosion rate estimated by the Tafel

extrapolations. The value of n shows some scatter around a mean value of 0.940 and indicates a character of non-ideal capacitor.

3.4 Determination of effective capacitance and corrosion layer thickness

Four approaches used in the literature for extracting the effective capacitance (C_{eff}) from CPE parameters are summarized in Table 6: simply distribution (equating C_{eff} to Y_0), BRUG et al, HSU–MANSFELD and HIRSCHORN et al (Power-law). All these models are well described in the literature (MOHAMMADI et al [36]). The models were used for the CPE parameters of Al1050/AZ31Al/1050 composites immersed in 3.5% NaCl solution by considering only the effect of the AZ31 layers since the major contribution to the corrosion arose from them. The calculated values of C_{eff} in the present work are almost below $10 \mu\text{F} \cdot \text{cm}^2$ and therefore CPE is the hydroxide film capacitance and R_{ct} is its resistance [35]. C_{eff} , surprisingly, does not show any systematic correlation with strain level.

Table 6 Used models for determination of effective capacitance from EIS results [36]

Model	Equation
Simple substitution	$C_{\text{eff}} = Y_0$
HSU–MANSFELD	$C_{\text{eff}} = (Y_0^{1/n} R_{nct}^{1-1/n})^{1/n}$
BRUG et al	$C_{\text{eff}} = Y_0^{1/n} (R_s^{-1} + R_{ct}^{-1})^{n-1/n}$
HIRSCHORN et al (Power-law)	$C_{\text{eff}} = g Y_0 (\rho_0 \varepsilon \varepsilon_0)^{n-1/n}$

In the model of HIRSCHORN et al, ρ_0 stands for the boundary value of resistivity at the interface and was taken approximately equal to $10^{11} \Omega$ and g is a function of the CPE exponent n given by [36]

$$g = 1 + 2.88(1-n)^{2.375} \quad (3)$$

Moreover, the corrosion layer thickness (l_{eff}) was evaluated using the following equation [37]:

$$l_{\text{eff}} = \frac{\varepsilon \varepsilon_0}{C_{\text{eff}}} \quad (4)$$

where ε is the dielectric constant and $\varepsilon_0 (= 8.85 \times 10^{-14} \text{ F/cm})$ is the permittivity of the vacuum. Calculated results of the optical properties for $\text{Mg}(\text{OH})_2$ by the first-principles method have shown that this compound exhibits low dielectric property with $\varepsilon = 2.86$. Figure 7 shows that the estimated

hydroxide thickness via the Brug model is the highest and does not depend systematically on the ARB cycle number. Our results are not in line with the results of MOHAMMADI et al [36] for which BRUG's model and HSU-MANSFELD's formula underestimate the oxide passive film thickness on 304L, 316L, and duplex 2205 stainless steel alloys while the PL model gives more precise values.

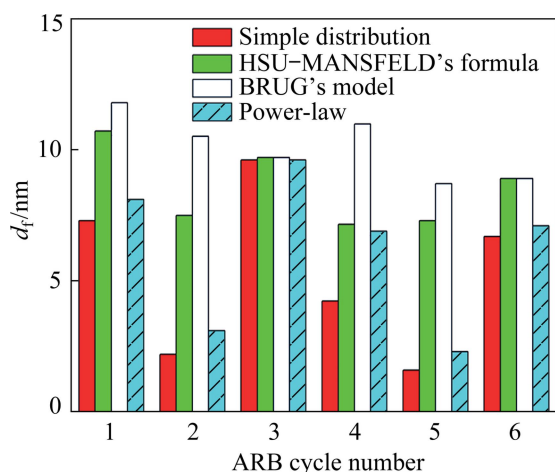


Fig. 7 Calculated thickness of hydroxide films formed on Al1050/AZ31/Al1050 samples up to six cycles ARB in 3.5% NaCl solution using Simple distribution, HSU-MANSFELD's formula, BRUG's model and Power-law

3.5 SEM-EDS analysis

The corrosion morphology of the Al1050/AZ31/Al1050 multilayered composite was observed by SEM, as shown in Fig. 8. A complicated corrosion microstructure is usually observed in Mg and Al alloys [20]. As expected, the corrosion attacks occur more likely in AZ31 alloy layers and there is no dramatic corrosion (evidenced by the white color) of the Al1050, which confirms its passivation in the presence of AZ31 alloy in NaCl solution. Figure 8(a) shows that layers of AZ31 are totally covered by corrosion product while the Al1050 layer seems relatively free and the small amounts of black phase are plausibly the residue of contamination. A massive un-localized (often termed as uniform or general) corrosion is observed over the whole surface of the AZ31 layers. The surfaces present a crackled appearance due to the dehydration of the layer after drying in warm air and under the vacuum of the SEM chamber as already observed [38]. Unfortunately, localized corrosion is rather difficult to evidence in the present study even through a close inspection of

many areas. Following a general nomenclature, localized corrosion comprises galvanic corrosion, pitting corrosion, filiform corrosion, intergranular corrosion (IGC), exfoliation corrosion (EFC), crevice corrosion, stress corrosion cracking (SCC), corrosion fatigue (CF), and erosion-corrosion. Among these corrosion types, EFC and crevice corrosion, however, have been rarely reported. Pitting corrosion should very probably occur since it is one of the most common corrosion types of Mg alloy. At a micro-scale level, micro-galvanic corrosion may also certainly occur between the α -Mg matrix with a lower open circuit potential (OCP) and the second phases or intermetallic compounds with a higher OCP in Mg alloys. The Mg matrix is anodic and is preferentially corroded. However, it is worth noting that pitting could not occur since it is known to be affected by grain size. Refined grains as those achieved in AZ31 layers (down to 0.8 μm) should make the corrosion morphology from pitting to uniform corrosion. Filiform corrosion has already been evidenced in AZ31 alloy after cold rolling in 0.9% NaCl solution [21] and in twin roll cast (TRC) AZ31 [39] alloy after immersion in 3.5% NaCl solution. The achieved grain size after cold rolling was nearly 8 μm and the distribution of coarse, as well as fine (60–600 μm) dendritic α -Mg grains possessing irregular shapes characterized the TRC AZ31 alloy. Very plausibly, the difference in grain size might play in favor of its occurrence contrarily to the present study.

Besides the often evidenced $\text{Mg}(\text{OH})_2$ hydroxide and Al_2O_3 oxide indexed through EDS analysis in Figs. 8(a, b) and 8(c, d), respectively, another unusual corrosion product is identified by punctual (shown by the (+) symbol) EDS analysis in Figs. 8(e, f) which should be thought as being magnesium oxalate ($\text{Mg}_2\text{C}_2\text{O}_4$). But a close interrogation of the literature has shown that this compound has never been evidenced in corroded Mg-based alloys. Rather, it should be indexed as MgCO_3 because it is quite common that MgCO_3 is detected within the surface film of Mg-based alloys [40]. Such discrepancy may result from the bad data acquisition due to signal convolution from analyzed points. GODARD et al [41] have shown the presence of nesquehonite ($\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$) and lansfordite ($\text{MgCO}_3 \cdot 5\text{H}_2\text{O}$) that seem not present in the present study. Corrosion products of Mg-based

alloys mainly contain magnesium carbonate and the dominant one is hydromagnesite [42]. Moreover,

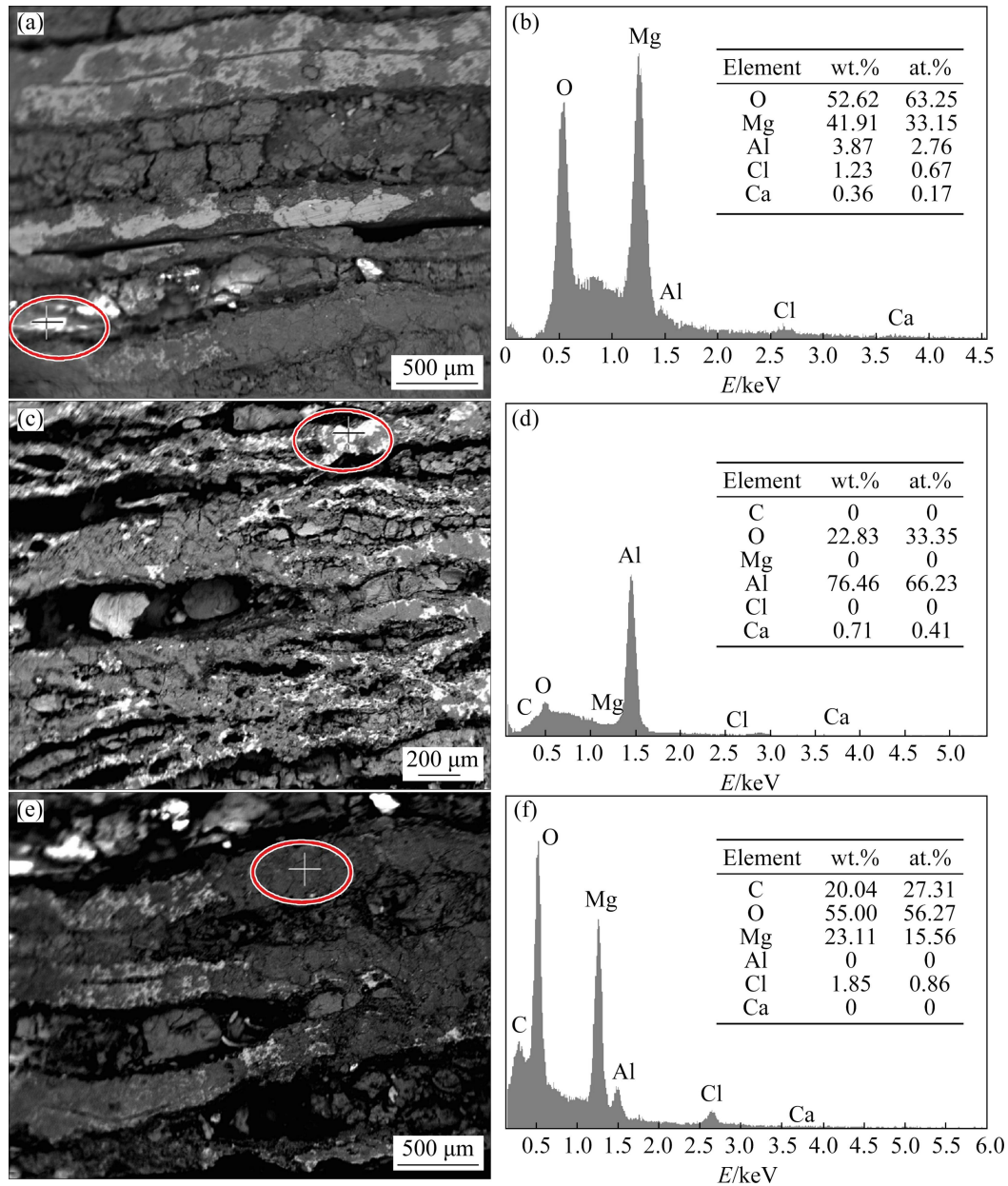


Fig. 8 SEM micrographs and punctual EDS analysis results of Al1050/AZ3/Al1050 samples after different cycles of ARB in 3.5% NaCl solution: (a, b) 2 cycles; (c, d) 4 cycles; (e, f) 6 cycles

mixed oxides such as $Mg_xAl_y(OH)_z \cdot nH_2O$ may also exist in AZ91 alloy in NaCl solution as claimed by AMBAT et al [43].

3.6 Raman spectroscopy and XRD analysis

To get deeper information about corrosion products, Raman spectra have been collected. In this work, Raman spectra were collected for Al1050/AZ31/Al1050 multilayered composites fabricated by ARB up to 6 cycles and ARB Al reference sample for 1 cycle ARB, as shown in Fig. 9. The Raman spectra of $N=3$ and 5 ARBed and

immersed multilayered composites in 3.5% NaCl solution are presented since the spectra of the remnant samples look very similar.

According to the RRUFF project database and other reports [44], the Raman peaks around 448 and 282 ($lattice$ vibrations, $A1g$, and Eg , respectively) and 3652 cm^{-1} could belong to the $Mg(OH)_2$ compound. Indeed, the presence of microcrystalline brucite has been evidenced by a strong peak at 3652 cm^{-1} corresponding to $A1g$ O—H stretching mode in $Mg(OH)_2$ crystals. The peak near 3400 cm^{-1} should correspond to the characteristic

peak of H_2O [45]. Considering the fact that the samples were exposed to the ambient environment

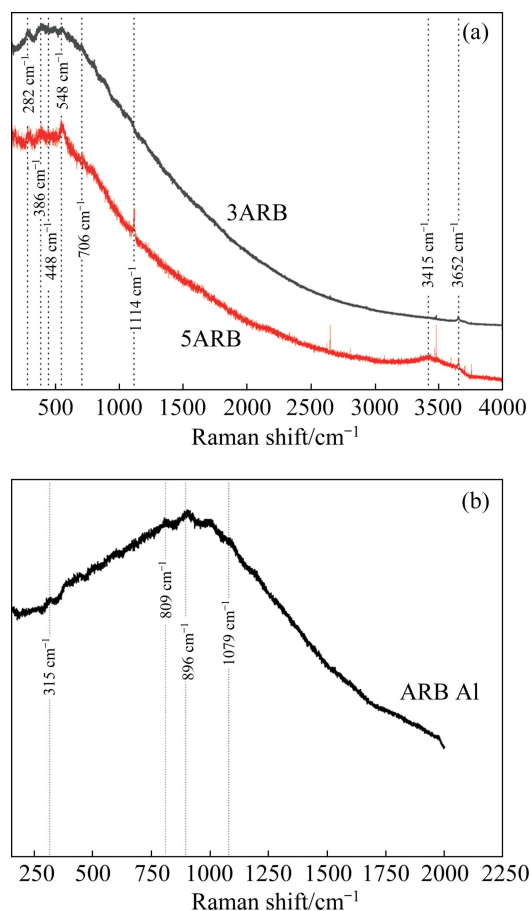


Fig. 9 Raman spectra of Al1050/AZ31/Al1050 samples after 3 and 5 ARB cycles (a), and ARB Al after one ARB cycle (b)

during Raman spectra analysis, the 3400 cm^{-1} peak could appear owing to the strong hygroscopicity of magnesium chlorides [46]. In magnesium and its alloys immersed in NaCl solution, different compounds containing chlorides such as $(\text{Mg}(\text{OH})_2) \cdot \text{MgCl}_2$, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, and $\text{Mg}_3(\text{OH})_5\text{Cl} \cdot 4\text{H}_2\text{O}$ were identified by Auger electron spectroscopy and/or infrared spectroscopy, and X-ray diffraction [47]. The presence of Cl extending to the inner MgO-base film region was frequently reported [44]. Some authors have postulated the presence of carbonates on the surface layer either after humid air exposure or after aqueous corrosion [48]. It is worth noting that none of the above cited corrosion products is evidenced in the Raman spectroscopy apart from $\text{Mg}(\text{OH})_2$ and H_2O . Furthermore, in the present study, manifestly, any peak could be attributed to any chloride containing compounds. In addition, in

ARBed samples with $N=3$ and 5, some characteristic and pertinent peaks near 382 and 1114 cm^{-1} are not clearly indexed.

The existence of a passive layer on the surface of the aluminum alloy in the form of oxides is characteristic of this type of alloy, as shown in Fig. 9(b). The weak peak near 1079 cm^{-1} represents the Al—O Raman bending mode [49]. The peak at 896 cm^{-1} belongs to the $\text{Al}(\text{OH})_3$ [50] while that near 809 cm^{-1} denotes the vibrating $\gamma\text{-Al}(\text{OH})_3$ group or condensed AlO_4 [50]. It was suggested that surface film on aluminum was made of a duplex layer, the inner layer was a compact amorphous layer and the outer one was a permeable hydrated oxide layer [20]. The vibration of $\alpha\text{-AlOOH}$ groups has a characteristic signal near 315 cm^{-1} [51]. In this study, any peak could be attributed to Al_2O_3 .

Figures 10 and 11 show the XRD patterns of Al1050/AZ31/Al1050 multilayered composites on the RD–ND plane before and after the electrochemical tests, respectively. Before the electrochemical tests, starting from the second ARB cycle (Fig. 9(b)), new peaks appear beside the Mg and Al matrix phases, where these peaks are indexed as belonging to Mg_3Al_2 and $\text{Mg}_{17}\text{Al}_{12}$ intermetallic compounds due to the interdiffusion of Al and Mg species between Al1050 and AZ31 layers [29]. The mechanism of formation of these intermetallic compounds has been discussed [29]. Figure 10 shows the XRD patterns of Al1050/AZ31/Al1050 after the electrochemical test where

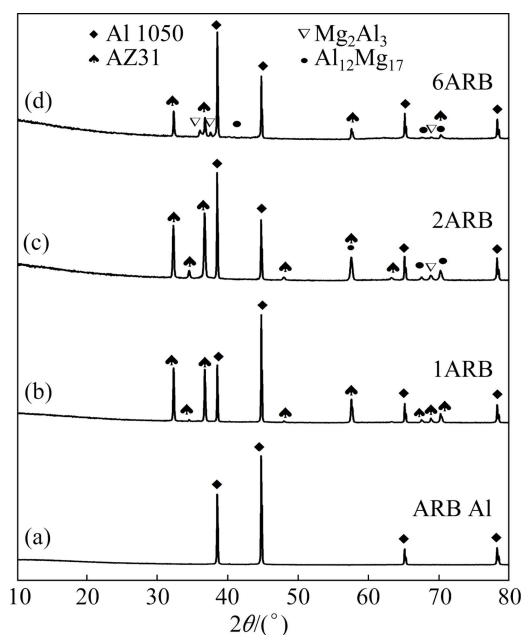


Fig. 10 XRD patterns of different samples on RD–ND plane before electrochemical tests: (a) ARB Al;

(b) 1ARB; (c) 2ARB; (d) 6ARB

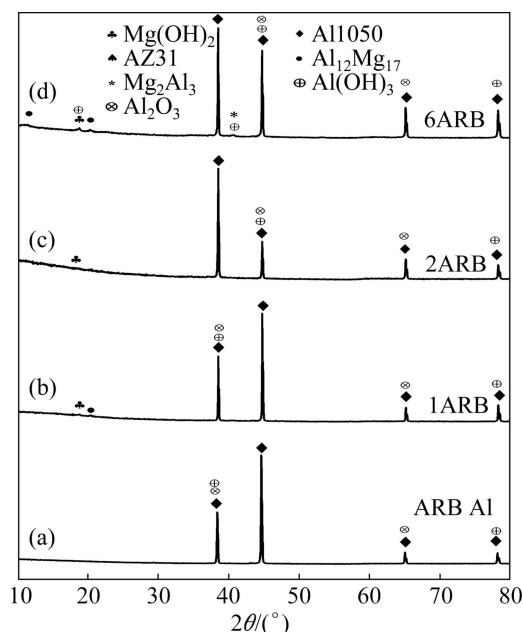
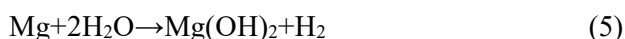


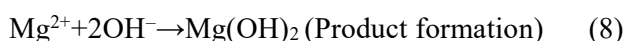
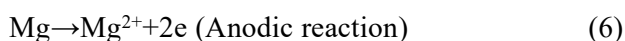
Fig. 11 XRD patterns of different samples on RD-ND plane after electrochemical tests: (a) ARB Al; (b) 1ARB; (c) 2ARB; (d) 6ARB

a new peak with low intensity is depicted around $2\theta=18.77^\circ$, and this peak belongs to the main corrosion product that is magnesium hydroxide $\text{Mg}(\text{OH})_2$ compound for all ARB cycles. FRÜHWIRTH et al [52] have assumed that the hydroxide was more stable than the MgO magnesium oxide. Magnesium oxide can form hydroxide when it reacts slowly with water, and for this reason, oxide films become eventually hydrated [47].

The overall corrosion reaction which leads to the formation of hydroxide is given as follows [47]:



This overall reaction may be stated as the total of the partial reactions listed below:



According to SONG and ATRENS [53], only a small amount of aluminum dissolved along with no evidence of zinc dissolution, whereas Mg was the main component that dissolved into solution during the anodic dissolution on Mg–Al–Zn alloys. The findings indicate that the four reactions mentioned previously are still responsible for the corrosion

processes involved for the Al1050/AZ31/Al1050 during electrochemical tests.

In addition, the effect of $\text{Mg}_{17}\text{Al}_{12}$ on corrosion resistance has been discussed in the literature [53]. In fact, the corrosion resistance of magnesium alloys is affected only after the formation of second phase particles. LEIN et al [54] have found that in chloride solution $\text{Mg}_{17}\text{Al}_{12}$ compound was inert in comparison with the surrounding magnesium matrix, while PEBERE et al [55] have proven that the corrosion resistance of the Mg–Al alloys was determined by the distribution of the $\text{Mg}_{17}\text{Al}_{12}$ phase. The $\text{Mg}_{17}\text{Al}_{12}$ and Mg_2Al_3 intermetallic compounds were clearly evidenced through XRD in the Al1050/AZ31/Al1050 multilayered composites. The present results consigned in the different figures, let us speculate that the corrosion behavior of the Al1050/AZ31/Al1050 multilayered composite should be plausibly governed by the AZ31 layers. Indeed, the Tafel plots and Nyquist diagrams do look very similar to those obtained for other Mg-based alloys in NaCl solution [21,22,38]. Any other effect of Al1050 or $\text{Mg}_{17}\text{Al}_{12}$ and Mg_2Al_3 intermetallic phases is manifestly absent. Recently, BAHMANI et al [56] have pertinently proposed a quantitative analysis of the corrosion rates and combined microstructural parameters correlation. They have clearly identified the main parameters that may influence the corrosion behavior which are alloy composition, grain size and second phase particles. In the present study, the latter two parameters may be active since the grain size decreases while the volume fraction of the second intermetallic phase increases. Indeed, a recently published work [29] has shown that the average grain size of the AZ31 layer was refined down to $0.8 \mu\text{m}$ while it was $18 \mu\text{m}$ in the as-received material. This refinement may be considered as not drastic so that it will not induce a huge change in the corrosion behavior. Intermetallic compounds ($\text{Mg}_{17}\text{Al}_{12}$ and Al_3Mg_2 second phases particles) have also been evidenced in the work of HABILA et al [29] after the second ARB cycle. The intermetallic compound particles nucleated at the interface owing to the fast diffusion of Al and Mg, large rolling strain, and high temperature processing. Their maximum thickness is about $10\text{--}15 \mu\text{m}$. Close inspection of SEM micrographs show that Al_3Mg_2 is at the side of the Al1050 layer while $\text{Mg}_{17}\text{Al}_{12}$ is next to the AZ31 one. $\text{Mg}_{17}\text{Al}_{12}$

intermetallic is almost thinner than Al_3Mg_2 one owing to fast diffusion of Mg than Al (Fig. 12). Up to 2 cycles, the intermetallics seem to lie continuously at the interface of AZ31/Al1050 (not shown here); while beginning from $N=3$, they seem to break down, fracture and rotate with a certain angle (approximately $25^\circ\text{--}30^\circ$) relatively to the rolling direction (Fig. 12). Obviously, their volume fraction increases with increasing ARB cycle number. Indeed, the number of layers is 96 after six ARB cycles while it is only six after the second cycle. The salient parameter for any corrosion study is the available surface area (relative or specific surface coverage of the various phases). Indeed, the surface coverage of the intermetallic has been roughly estimated by the ratio of their total area over the total surface depicted by SEM images. The surface coverage is almost lower than 5% even at 6 ARB cycles. LIU et al [57] reported that depending on the intermetallic composition and the arrangement in the microstructure, they may play a significant role in accelerating the corrosion of the Mg-rich matrix by galvanic coupling or may be a barrier and decrease the overall corrosion. The barrier effect of $\text{Mg}_{17}\text{Al}_{12}$ intermetallic during the corrosion of Mg–Al alloys can be due to the large difference in corrosion kinetics between Mg and $\text{Mg}_{17}\text{Al}_{12}$ ($550\text{ }\mu\text{A}/\text{cm}^2$ versus $5.3\text{ }\mu\text{A}/\text{cm}^2$, respectively) [58].

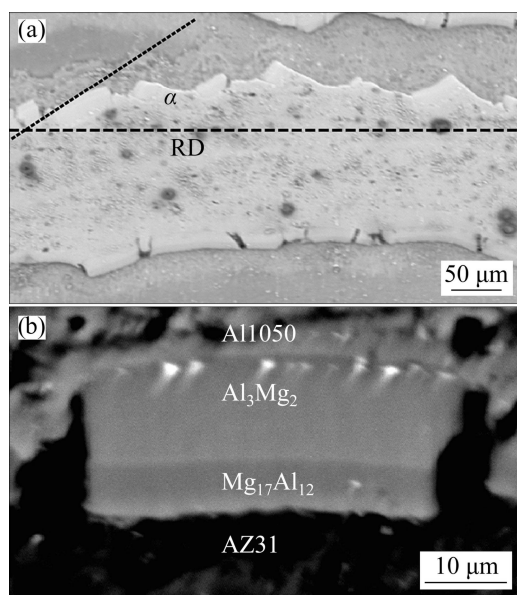


Fig. 12 Microstructures of Al_xMg_y intermetallics at interface of Al1050/AZ31/Al1050 samples on RD–ND plane after electrochemical tests after 4 ARB cycles (a) and magnification around lonely intermetallic (b)

PEBERE et al [55] suggested that the corrosion resistance of Mg–Al alloys is determined by the distribution of the $\text{Mg}_{17}\text{Al}_{12}$ phase. It is noted that in Mg–Al alloys prone to intermetallic precipitation like AZ91, the precipitation of $\text{Mg}_{17}\text{Al}_{12}$ phase is fundamentally stochastic within grain interiors or at grain boundaries while in the multilayered composites it should be considered as non-stochastic, i.e. organized as layered sub-structure contained duplex altered $\text{Mg}_{17}\text{Al}_{12}$ and Al_3Mg_2 phases with high connectivity. Such a form of diffusion controlled germination and growth of intermetallic phases should be assimilated to discontinuous precipitation often observed in AZ91 alloys together with the continuous type which appears in the grain interiors. Maybe these morphological differences may play a role in corrosion behavior of the intermetallics. Interestingly, KIM and BYEON [59] have proven that discontinuous precipitation of $\text{Mg}_{17}\text{Al}_{12}$ phase with high connectivity along the grain boundaries functioned as corrosion barrier. These authors also have also analyzed the correlation between the discontinuous precipitation of the $\text{Mg}_{17}\text{Al}_{12}$ phase and the corrosion rate of AZ91 alloy immersed in 3.5% NaCl solution. Manifestly, they deduced that an area fraction below 5% should result in a barrier mechanism rather than a galvanic one.

The corrosion potential (ϕ_{corr}) and the pitting corrosion potential (ϕ_{pit}) of the Al_3Mg_2 phase in 0.01, 0.1, and 0.6 mol/L NaCl of pH 6 have been analyzed [60,61]. The result clearly has shown that Al_3Mg_2 has a window of passivity in NaCl solution and ϕ_{pit} decreases with the increased chloride activity [62].

It plausibly can be claimed that both $\text{Mg}_{17}\text{Al}_{12}$ and Al_3Mg_2 should be inactive in 3.5% NaCl solution and therefore the only corrosive agent should be the AZ31 layer.

It should also be noted that the relationship between texture and corrosion rate for magnesium-based alloys is not well intelligible. Many researchers [63,64] have proven that the corrosion resistance of basal texture is the most prominent. This might be explained by the fact that the basal planes are the least thermodynamically reactive plane in Mg having the highest binding energy and the lowest surface energy [65]. The effect of texture on the corrosion rate has been classified by BAHMANI et al [56] as a sub-effect of the alloy

composition one. In HCP-structured materials, basal planes followed by prismatic II and then prismatic I planes have the highest corrosion resistance compared to other intermediate planes. Additionally, it has been reported that any misorientation from the packed planes including basal and prismatic planes increases the corrosion rate. HABILA et al [29] have shown that during the ARB processing, a typical strong basal (0002) texture was observed in AZ31 layers that remained very stable upon straining. A huge influence of the texture on the corrosion should credibly be discarded. It is worth noting that conventional potentiodynamic tests or EIS tests cannot provide precise information about the specific corrosion behavior of Al_3Mg_2 and $\text{Mg}_{17}\text{Al}_{12}$ compounds. In order to get a deeper insight into the role of Al_3Mg_2 and $\text{Mg}_{17}\text{Al}_{12}$ intermetallic particles in corrosion of A1050/AZ31/A1050 multilayered composites, a panel of fine and suitable techniques should be used such as scanning vibrating electrode technique (SVET), XPS, ToF-SIMS, confocal laser scanning microscopy, 3-D tomography, Auger spectroscopy, scanning Kelvin probe force microscopy and atomic force microscopy.

4 Conclusions

(1) Potentiodynamic polarization plots and electrochemical impedance spectroscopy show that the corrosion rate is strongly affected by the ARB strain level.

(2) A higher corrosion rate and reduced polarization resistance are evidenced compared to the A11050/A11050/A11050 multilayered sample.

(3) The AZ31 layers seem to dominate the corrosion process.

(4) Raman and XRD analyses confirm the presence of the main corrosion product that is $\text{Mg}(\text{OH})_2$ and the absence of any chloride such as $(\text{Mg}(\text{OH})_2) \cdot \text{MgCl}_2$.

CRedit authorship contribution statement

Ismail BENCHERIFA: Investigation, Methodology, Validation, Visualization, Writing – Original draft, Writing – Review & editing; **Khadidja ABIB:** Conceptualization, Writing – Original draft; **Khereddine ABDEL YAZID:** Investigation, Methodology; **Baya ALILI:** Writing – Review & editing; **Djamal BRADAI:** Conceptualization, Writing – Original draft, Writing –

Review & editing.

Declaration of competing interest

The authors declare that they have no conflict of interest.

Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time, as the data also form part of an ongoing study.

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累积叠轧焊 Al/Mg/Al 多层复合材料的腐蚀行为

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摘 要: 研究累积叠轧焊(ARB)Al1050/AZ31/Al1050 多层复合材料的腐蚀行为, 腐蚀介质为 3.5%NaCl(质量分数)溶液, 分析测试手段包括动电位极化测试(PDP)、电化学阻抗谱(EIS)、扫描电子显微镜(SEM-EDS)、拉曼光谱和 X 射线衍射(XRD)等。为了深入研究 Al1050/AZ31/Al1050 多层复合材料的耐腐蚀性和腐蚀产物, 对 ARB 制备的 Al1050/Al1050/Al1050 多层复合材料进行了相似的测试作为对比。动电位极化曲线和电化学阻抗谱显示, ARB 应变水平会显著影响腐蚀速率。与 Al1050/Al1050/Al1050 样品相比, Al1050/AZ31/Al1050 多层复合材料具有更高的腐蚀速率和更低的极化电阻。AZ31 层对腐蚀过程起主导作用。拉曼和 XRD 分析结果表明主要腐蚀产物为 $\text{Mg}(\text{OH})_2$, 且不含任何氯化物(如 $(\text{Mg}(\text{OH})_2) \cdot \text{MgCl}_2$)。

关键词: 累积叠轧焊; Al1050/AZ31/Al1050; 多层复合材料; 腐蚀; 金属间化合物

(Edited by Bing YANG)