

The Role of Mg₂Si in the Corrosion Behavior of Al-Si-Mg Alloys for Pressureless Infiltration

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Abstract: The role of Mg₂Si in the electrochemical behavior of Al-Si-Mg aluminum alloys has been studied using four experimental aluminum alloys with variations in the Si/Mg molar ratio (A1-0.12, A2-0.49, A3-0.89, A4-1.05), in neutral aerated 0.1M NaCl solutions. Accordingly, the corrosion potential in open circuit (E_{oc}) and polarization resistance (R_p) were measured. Results show that the augment in Si/Mg molar ratio increases the presence of Mg₂Si intermetallic phase. During immersion tests in neutral aerated chloride solutions the anodic activity of the Mg₂Si intermetallic decreased rapidly, as indicated by a fast ennoblement of open circuit potential. After the immersion period (7 days), higher R_p values for alloys A3 and A4 (21 and 26 K Ω cm², respectively) as compared to those for alloys A1 and A2 (5 and 10 K Ω cm², respectively), suggest a greater corrosion resistance in Cl⁻ containing environments for alloys A3 and A4.

Keywords: Al-Si-Mg alloys, corrosion potential, polarization resistance, NaCl solutions, Mg₂Si.

1. INTRODUCTION

Owing to their light weight, suitable strength and strong resistance to corrosion, aluminum alloys are used in a broad spectrum of engineering applications. The corrosion resistance of aluminum is attributed to an exceptionally stable oxide film that forms on its surface. This film is resistant to attack from water and oxygen in a wide range of temperatures and pH levels, making aluminum alloys useful in a variety of environments [1]. However, the presence of aggressive ions like chloride creates extensive localized attack [2]. In addition, it is well known that the corrosion behavior of aluminum alloys is significantly affected by the presence of particles in the matrix. Particles that contain Al, Cu and Mg tend to be anodic relative to the alloy matrix, while those that contain Al, Cu, Fe and Mn tend to be cathodic relative to the matrix [3]. Previous works [3-7] show that Mg₂Si tends to be anodic with respect to the matrix and can act as initiation sites for corrosion, too. It has been reported that this phase dissolves leaving behind a cavity, which can act as a nucleation site for pitting [7, 8]. Moreover, the role played by Mg₂Si becomes as important when it is present in aluminum-based metal matrix composites as when it is formed in the alloy matrices only, because although it may be dissolved during composite processing (by the liquid state route), it is formed again during the solidification of the alloy as the composite matrix.

The related literature shows that, regarding studies on the corrosion behavior of aluminum alloys, most of the investigations are carried out with conventional or commercial aluminum alloys having low Si/Mg molar ratios [9-12]. However, for Al/SiC composites prepared by the

non-assisted infiltration route – or pressureless infiltration –, it is necessary to use alloys with high Si/Mg molar ratios. As it is generally accepted, Mg and Si play important roles during the infiltration of SiC_p preforms because they impact the wetting behavior of the aluminum alloy, acting Si more specifically on the contact angle (θ), while Mg favors the liquid-vapor surface tension (γ_{lv}). But the case is that, associated to an increase in the Si/Mg molar ratio there is also a variation in the amount of secondary phases formed during the infiltration and solidification processes. Specifically, magnesium silicide (Mg₂Si) is typically found in the microstructure of the composites. Its presence may affect not only the corrosion behavior, but also the mechanical behavior of the composites either in humid or ion chloride environments. Hence, even when a composite may exhibit satisfactory mechanical properties under controlled laboratory tests, it is pertinent to conduct an investigation on its corrosion behavior. However, irrespective of their use in the preparation of Al/SiC composites by pressureless infiltration, it should be recognized that Al-Si-Mg alloys represent by themselves an interesting alloy system, and that any study conducted to understand corrosion phenomena, may be useful to a considerable number of researchers. In this work, the authors present a study on the corrosion behavior of aluminum alloys with high Si/Mg molar ratios. The main attention is focused on the role on the Mg₂Si intermetallic phase, which is anodic with respect to the aluminum matrix and may improve, to a certain extent, the corrosion resistance of the alloys.

2. EXPERIMENTAL PROCEDURE

Four aluminum alloys were fabricated, varying the Si/Mg molar ratio in A1-0.12, A2-0.49, A3-0.89, and A4-1.05, starting from aluminum of commercial purity. The alloys were prepared in a Power-Track 75-30 induction furnace, with capacity for 10 Kg. Once melted the aluminum, the alloying elements silicon and magnesium were added,

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respectively, in quantities needed to obtain the desired Si/Mg molar ratios. Previous to casting into metallic molds, the alloys were degassed in ultra high purity (UHP) argon for 15 min. The chemical compositions of aluminum and alloys are shown in Table 1.

Table 1. Si/Mg Molar Ratio and Chemical Composition of Aluminum and Alloys (wt. %)

Identification	Si/Mg Molar Ratio	Fe	Cu	Mn	Si	Mg	Al
Commercial Al	----	1.02	0.10	0.42	0.12	0.23	98.11
A1	0.12	0.63	0.06	0.12	1.78	13.29	84.12
A2	0.49	0.59	0.04	0.29	8.28	14.56	76.24
A3	0.89	0.82	0.03	0.14	12.97	12.54	73.50
A4	1.05	0.66	0.02	0.11	17.51	14.44	67.27

Microstructure characterization was carried out using X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy dispersive X-ray spectroscopy (EDX). For electrochemical measurements, the alloys were embedded into epoxy resin leaving an exposed area of 1 cm². Each specimen was ground with SiC abrasive paper, up to 1200 grit, before polishing with alumina suspensions of 1.0 and 0.3 μm. Immersion tests during 7 days under open circuit conditions in normally aerated 0.1 M NaCl solutions at room temperature were carried out. The electrochemical measurements were performed using a Volta Lab 32 potentiostat. The open circuit potential (OCP) of the composites was monitored throughout the test using a saturated calomel reference electrode (SCE). Linear polarization (LP) tests were performed during a 7-day interval using the same specimens for each alloy type and a three-electrode set-up, in order to obtain polarization resistance (Rp) values. Accordingly, an SCE and a platinum counter electrode were used. Right after the LP test the specimens were removed from the solution, cleaned thoroughly in an ultrasonic bath (to remove corrosion products), dried and examined by SEM.

3. RESULTS AND DISCUSSION

Fig. (1) shows XRD patterns corresponding to the four aluminum alloys having different Si/Mg molar ratio (A1-0.12, A2-0.49, A3-0.89, A4-1.05), before the electrochemical tests. The Mg₂Si phase was formed in situ during solidification according to reaction (1); in addition, and as observed previously, Al and Si were also detected [13].



The SEM photomicrographs in Fig. (2) (A1, A2, A3 and A4), show the typical microstructure of the aluminum alloys before the corrosion tests. It is observed that the alloys contain the Mg₂Si and AlFeSiMn intermetallic phases. The presence of the AlFeSiMn intermetallic with needle-like morphology only was detected during the characterization by SEM and EDX, suggesting that its amount was not detectable by X-ray diffraction. Fe and Mn impurities contained in the aluminum account for the formation of this

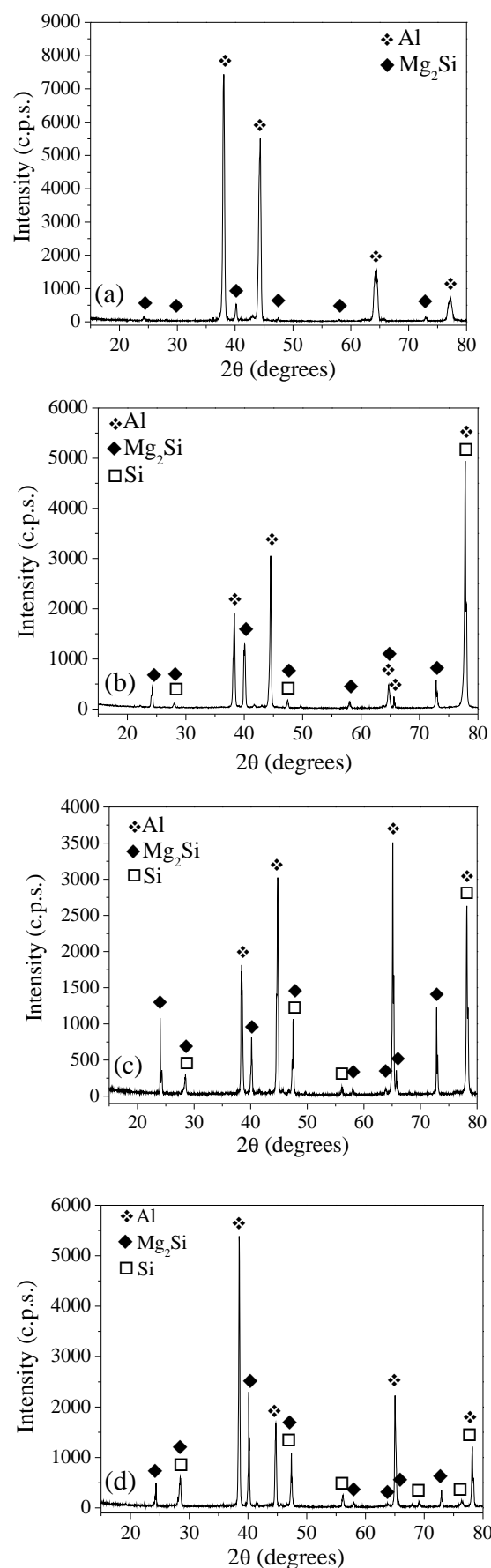


Fig. (1). XRD patterns of aluminum alloys A1, A2, A3 and A4 before the electrochemical measurements.

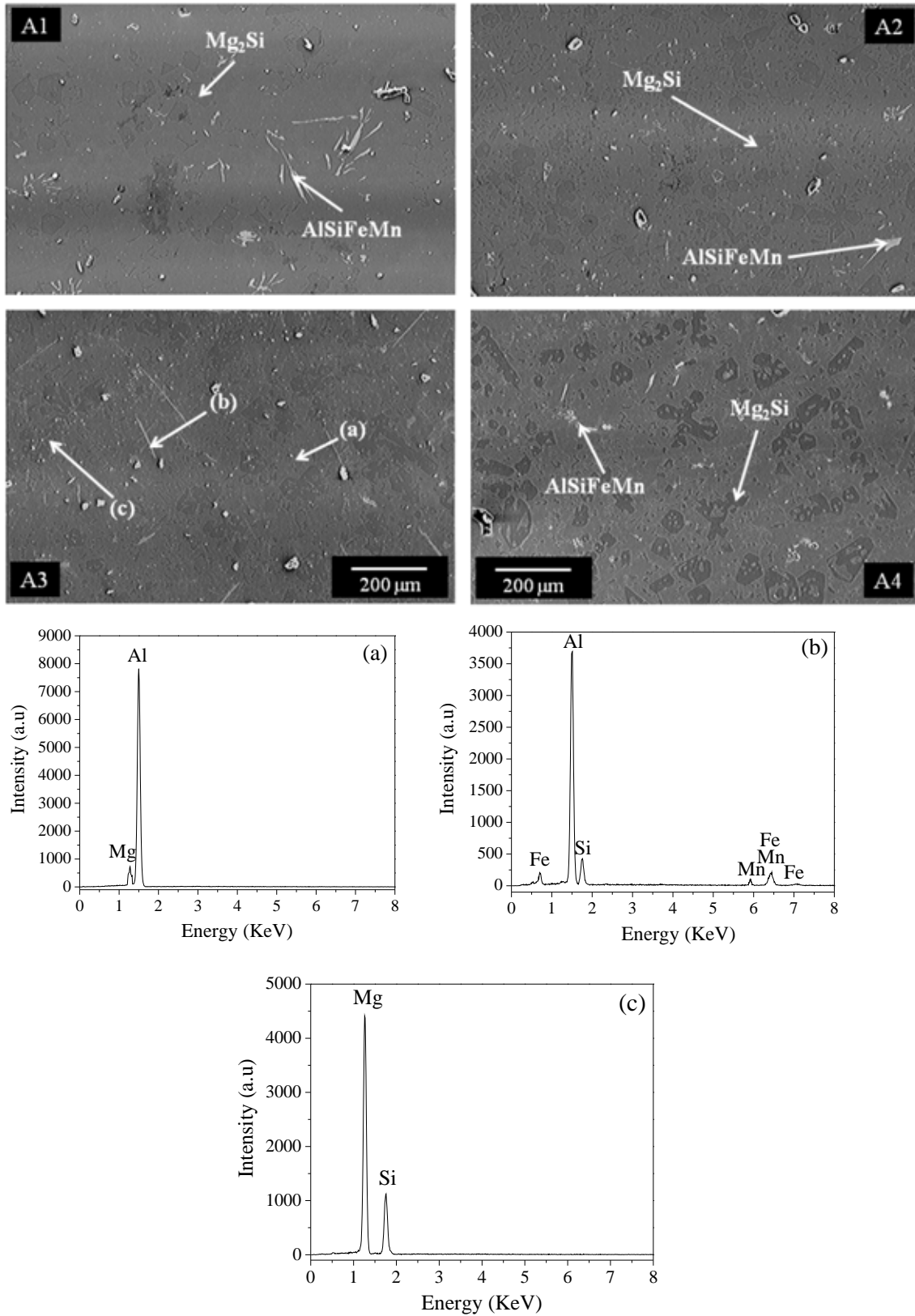


Fig. (2). SEM photomicrographs and EDX spectra showing the microstructure of aluminum alloys A1, A2, A3 and A4 before the electrochemical measurements.

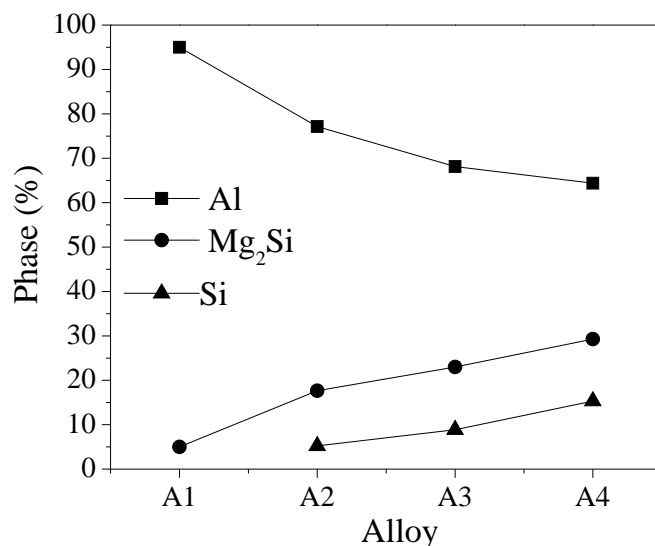
intermetallic phase. On the other hand, the amount and size of Mg_2Si intermetallic phase increase with increasing Si/Mg molar ratio. The EDX spectra [(a), (b) and (c)] in Fig. (2)

show the elements present in each of the phases in the aluminum alloys, and Table 2 shows the values of semi-quantitative analysis of each of the elements.

Table 2. Semiquantitative Analysis by EDS in the Regions Corresponding to AlMg, Mg₂Si and Al-Si-FeMn Phases

Point/Phase	Element	at. %	wt. %
(a)/AlMg	Al	91.52	92.32
	Mg	8.48	7.68
(b)/AlSiFeMn	Al	70.38	54.41
	Si	1.49	1.03
	Fe	25.79	41.27
	Mn	2.34	3.29
(c)/Mg ₂ Si	Mg	65.23	61.30
	Si	34.91	38.70

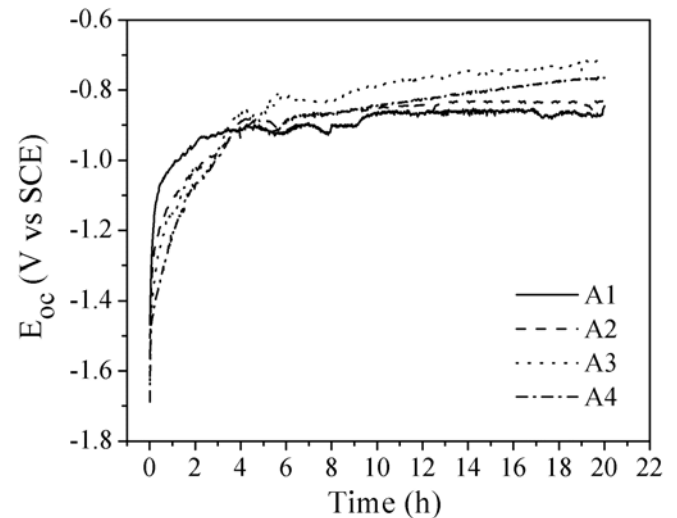
A plot of quantitative analysis from the XRD peaks for the four respective alloys shows (See Fig. 3) how Mg₂Si increases with augment in the Si/Mg molar ratio. Moreover, the increase in the size of Mg₂Si was measured from photomicrographs taken for the 4 aluminum alloys. Table 3 summarizes the average particle size determined in representative specimens.

**Fig. (3).** Graph showing the variation of phase amount as a function of the Si/Mg molar ratio (alloys A1, A2, A3 and A4).**Table 3. Average Particle Size of Mg₂Si in the Alloys as a Function of the Si/Mg Molar Ratio**

Alloy	Si/Mg Molar Ratio	Average Particle Size (μm)
A1	0.12	42 ± 22
A2	0.49	59 ± 23
A3	0.89	71 ± 20
A4	1.05	93 ± 38

Fig. (4) shows the evolution of the open-circuit corrosion potential of the aluminum alloys during an immersion period

of 20 hours in a 0.1M NaCl solution. In this graph it can be observed that the onset of the corrosion potential is shifted in the direction of more electropositive values, and according to the literature, the rise in potential in the electropositive direction is commonly observed in samples that exhibit passivity [14].

**Fig. (4).** Evolution of E_{corr} for aluminum alloys immersed in 0.1M NaCl solution during 20 hours, in the presence of oxygen.

On the other hand, it is evident that the greater the Si/Mg molar ratio, the more negative the corrosion potential is, at least during the first 3 hours of immersion, after which this behavior changes. This behavior can be attributed to the electrochemical activity of magnesium silicide, an intermetallic with corrosion potential of -1.5 V at pH 6 in 0.1M NaCl solutions [15].

However, after eight hours it appears that alloys A1 and A2 with Si/Mg molar ratios of 0.12 and 0.49 respectively, tend to stabilize the corrosion potential to more negative values than alloys A3 and A4 which have Si/Mg molar ratios of 0.89 and 1.05 respectively, and tend toward more positive potentials. The ennobling in E_{corr} values in the first hours of immersion is attributed to the adsorption of chloride ions on the surface of the sample, as reported by Ambat [16].

The corrosion potentials of alloys A1 and A2, shown in Fig. (5), attain stabilization at an approximate potential of -0.98 V and -0.87 V, respectively. For alloys A3 and A4, corrosion potentials stabilize at more positive potentials, -0.71 V and -0.68 V, respectively. The stabilization of E_{corr} upon long periods of time can be attributed to the formation of corrosion products on the sample's surface, which avoid the interaction of the metal with the solution. Moreover, since pH increases, the solubility of Al³⁺ decreases, by inducing the precipitation of Al(OH)₃ [16, 17]. Fig. (6) shows an XRD pattern of gelatinous-white-powder corrosion products, indicating the presence of aluminum hydroxide.

The evolution of corrosion potentials is a manifestation that phase type and amount play a decisive role in the alloys corrosion behavior, indicating that they do not corrode in a similar way. Based on the XRD patterns of the alloys, shown in Fig. (1), a variation in the amount of Si and Mg₂Si phases is observed. The amounts of both, Si and Mg₂Si increase

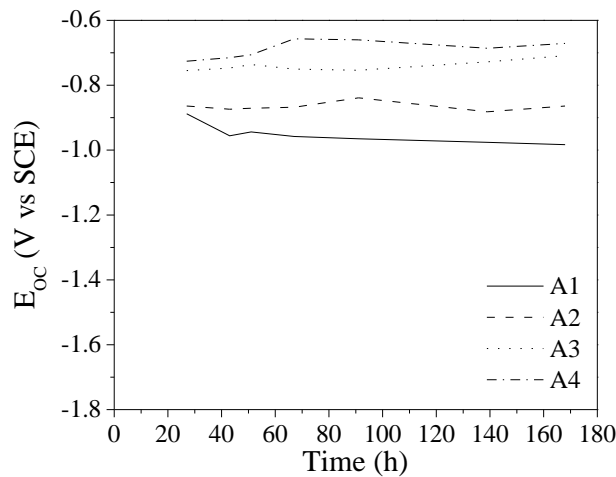


Fig. (5). Evolution of E_{corr} for aluminum alloys A1, A2, A3 and A4 immersed in 0.1M NaCl solution during 168 hours, in the presence of oxygen.

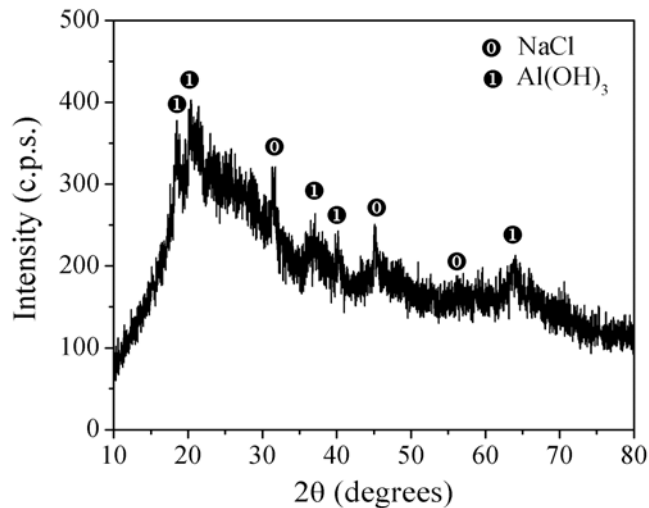


Fig. (6). XRD pattern of gelatinous-white-powder corrosion products, indicating the presence of aluminum hydroxide.

with Si/Mg molar ratio in the alloys; this difference in the amount of the phases can fairly affect the corrosion behavior of the composites. Mg_2Si acts as an anode and is dissolved preferentially. On the other hand, in the presence of water, Mg_2Si tends to form oxides like SiO_2 and MgO which, as it is widespread, protect the Mg_2Si particles and reduce the galvanic coupling with the matrix [1].

As a rule, polarization resistance must be evaluated after the stabilization of corrosion potential (E_{corr}). In this particular case, measurements were conducted on specimens beyond their equilibrium potential, at ± 20 mV; higher variations in E_{corr} would result in unreliable values of R_p . Accordingly, R_p measurements started 20 hours after the immersion. Fig. (7) shows the polarization resistance as a function of time for all aluminum alloys, with the R_p values beginning in a range of 15-25 $K\Omega cm^2$. However, as time passes, the difference in the values was evident, the R_p values for alloy A1 decreased, reaching 5 $K\Omega cm^2$ up to the end of the test. For aluminum alloys A2, A3 and A4 the R_p values show some oscillations; these fluctuations are ascribed to the formation and rupture of passive films on the

surface of the alloy. The R_p values were 10, 21 and 26 $K\Omega cm^2$ for A2, A3 and A4 alloys, respectively. The increase in R_p values suggests that the specimens have a higher resistance to the flow of current, which means that a higher protection against corrosive attack exists; it can also be interpreted as a lower susceptibility to the attack by chloride ions. In good agreement with the work by Rehim [17], silicon confers an increase in the resistance of the passive layers and provides higher resistance to pitting corrosion.

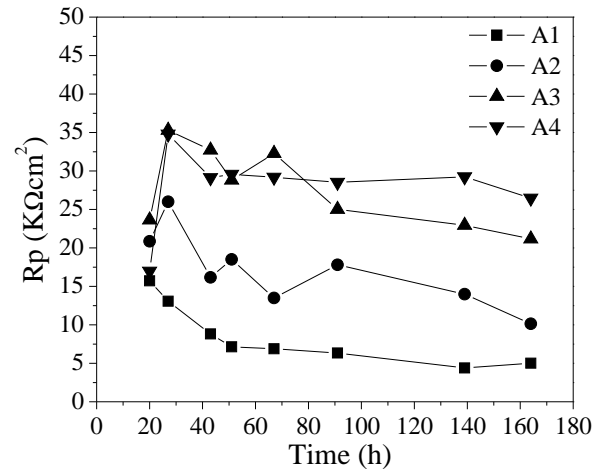


Fig. (7). Polarization resistance as a function of time for alloys A1, A2, A3 and A4, during 168 hours of immersion in NaCl 0.1M.

Fig. (8) shows the same region showed in the photomicrographs presented in Fig. (2), but 7 days after the alloys were immersed in 1M NaCl 0.1 solution. It is apparent that the attack to the magnesium silicide is more aggressive for alloy A1 than for alloys A2, A3 and A4. EDX spectra show an oxygen reflection, corroborating in this way, the presence of oxides or hydroxide on the surface of Mg_2Si . On other hand, the matrix and the $AlFeSiMn$ intermetallic do not show a difference in the chemical composition. Since Mg_2Si content increases in consecutive order from A1 to A4, and in the presence of water this intermetallic tends to form oxides like SiO_2 and MgO which, as it is generally accepted, these oxides protect the Mg_2Si particles and reduce the galvanic coupling with the matrix [1]. Accordingly, although Mg_2Si is dissolved, eventually it plays a beneficial role because oxide/hydroxide formation helps protecting the alloys from further attack by the saline (NaCl) environment.

4. SUMMARY AND CONCLUSIONS

Results from this investigation show that alloys with a high Si/Mg molar ratio A3 (Al-12.97Si-12.54Mg) and A4 (Al-17.51Si-14.44Mg) exhibit a greater corrosion resistance in 0.1 M NaCl solutions, compared with those which have low Si/Mg molar ratio A1 (Al-1.78Si-13.29Mg) and A2 (Al-8.28Si-14.56Mg). This behavior is attributed to the resulting microstructures, with differences essentially in the amount and size of the intermetallic magnesium silicide. Mg_2Si tends to form oxides like SiO_2 and MgO which, as it is widespread, protect the Mg_2Si particles and reduce the galvanic coupling with the matrix. On the other hand, no effect was observed, at least with the characterization carried out in the current study, by the $AlFeSiMn$ intermetallic phase.

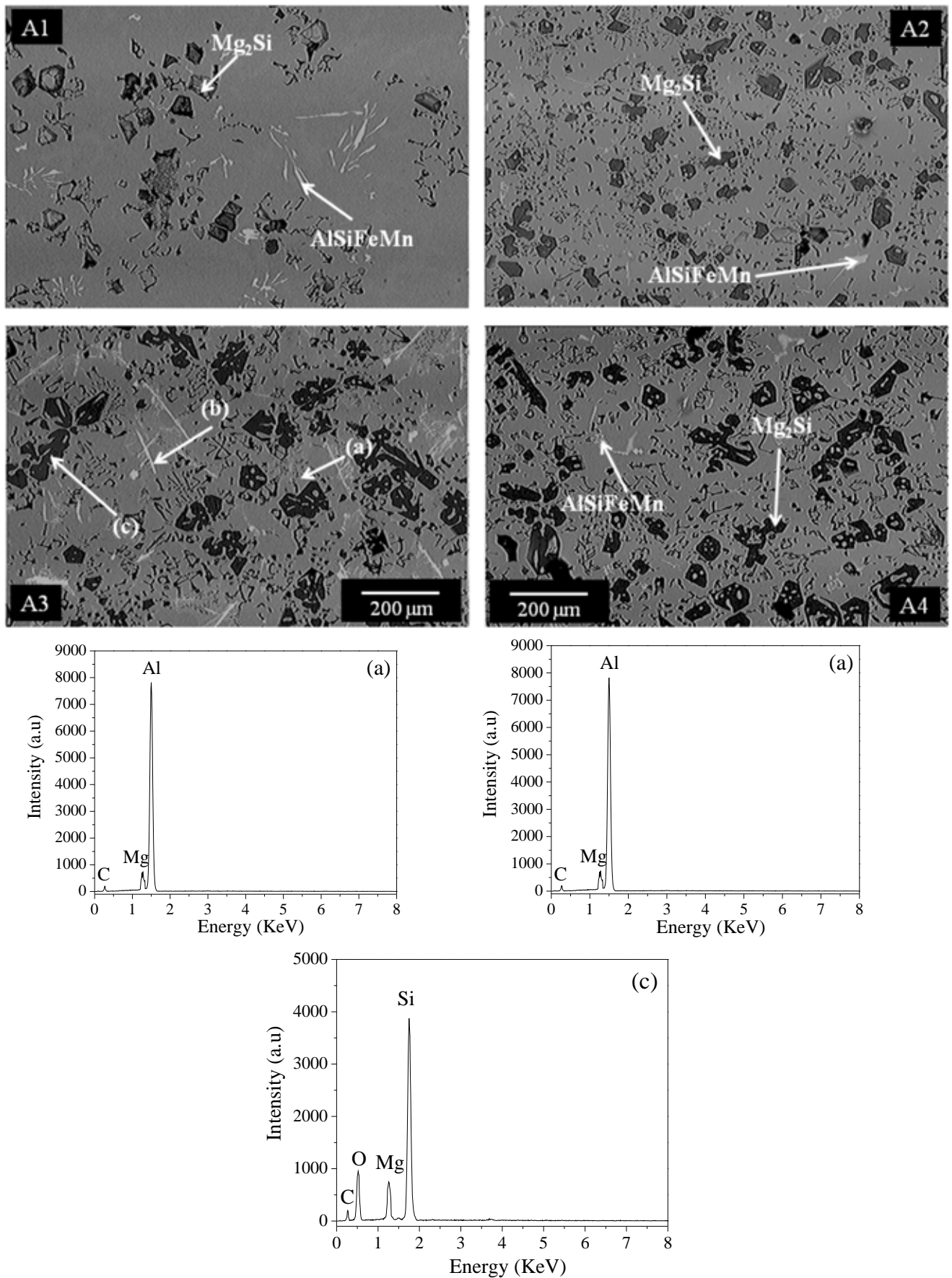


Fig. (8). SEM photomicrographs of alloys after 168 h (7 days) immersion in the aerated chloride solution, and EDX spectra in specific regions.

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