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Corrosion behavior of AlSi7Mg0.6 produced by selective laser melting: A comparative approach

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ABSTRACT

Additive manufacturing (AM) has revolutionized metal manufacturing. Indeed, AM of lightweight, mechanically resistant aluminum alloys is becoming increasingly popular in manufacturing. However, corrosion is a threat to aluminum alloy parts. AM produces a different microstructure which could be correlated with its corrosion resistance. In this study, the global and localized corrosion behavior of additive-manufactured AlSi7Mg0.6 is investigated. The corrosion behavior was evaluated by immersion tests in sodium chloride solution (3.5 % NaCl) and monitored by global electrochemical techniques, such as electrochemical impedance spectroscopy (EIS), potentiodynamic anodic polarization, and local electrochemical techniques such as the scanning vibrating electrode technique (SVET). The microstructure was analyzed and characterized by Electron Backscatter Diffraction (EBSD) and X-Ray Diffraction (XRD). The results indicate that the additive manufactured AlSi7Mg0.6 do the reinforcement of the passive alumina layer by a residual Mg/Si layer formed at the grain boundaries during corrosive environment exposition.

1. Introduction

The development of additive manufacturing (AM), popularly called 3D printing, has transformed modern metal manufacturing. In terms of technology and applications, the popularity of this approach for producing metal components from a range of metal alloys has grown exponentially [1–10]. This technique has many benefits, including reduced carbon emissions, net-shape production, effective material utilization, small-scale adaptability (prototyping), and the capacity to investigate alloy compositions that are not achievable using conventional techniques [1–7]. The aerospace industry is especially interested in using additive manufacturing to create lightweight, mechanically robust aluminum alloys that are used extensively in aviation [1–5,8,10, 11]. In this sense, the most researched and widely utilized additively manufactured Al-based alloys are Al-Si alloys. Due their closeness to the eutectic composition, these materials are frequently utilized for applications requiring great strength and low weight [8,10]. in special the

AlSi7Mg0.6 alloy demonstrated attractive properties due to its excellent wear and corrosion resistance, relatively high strength-to-weight ratio, and recycling potential [1–5,12] which are combined with the fact that this alloy is reasonably simple to produce for laser applications, with silicon lowering the melting temperature and increasing melt fluidity [4, 5,12–15]. However the additive manufacturing (AM) process results in a different microstructure to that obtained by conventional processing technologies [1,2] and the metal composition and microstructure have a significant role in the corrosion resistance behavior [1,12,16,17].

For aluminum parts, corrosion is a threat, and corrosion prevention remains an important aspect, although little research has been done on the corrosion behavior of AM alloys, particularly AlSi7Mg0.6 [5,11–14]. Maurer et al. [18] investigated the normalized effects after corrosive immersion tests performed in 5 wt% NaCl for two weeks applied to additive manufactured AlSi10Mg and they highlighted that surface roughness is a key factor for the uniformity of corrosion attack. This study displays while surfaces with a coarse topography first experience

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patchy corrosion before reaching a totally corroded scale, smooth surfaces are more prone to uniform corrosion. As a result, the effects of passivation take more or less time to manifest themselves [18]. In the same sense, Liu et al. [19], after reducing the roughness of AlSi10Mg by electrochemical polishing, observed a reduced corrosion current density in the Tafel test (3.5 % NaCl). They attributed this behavior to AlSi10Mg's surface topography. The unpolished sample presented a higher number of electrochemical reaction sites due the greater surface roughness and defect density, when compared to the electrochemical polished sample [19].

Revilla et al. studied the Si-containing influence on the corrosion resistance of AM Al-Si alloys and found micro-cracks after corrosion exposure in the case of AM AlSi7Mg and AM AlSi10Mg alloys, but not for AM AlSi12Mg, thus showing an association with the Si network and not with the internal stresses for the AM process [9]. Cabrini et al. [5] studied the corrosion behavior of AM AlSi10Mg produced by direct metal laser sintering, with different surface finishes, and used potentiodynamic polarization tests performed in aerated diluted Harrison solution. They showed that the corrosion resistance of the as-produced surface was marginally increased by acid pickling, while on the polished surface, no benefits were observed [5]. Leon et al. [13] studied the corrosion behavior of SLM AM AlSi10Mg using weight-loss measurements and showed that after 45 days of immersion, the SLM AlSi10Mg presented slightly lower weight loss than cast AlSi10Mg [13]. In the same sense, Fathi et al. [14] studied direct metal laser-sintered AlSi10Mg using potentiodynamic polarization measurements. The results of the AM AlSi10Mg showed better corrosion behavior, such as higher corrosion potentials and lower corrosion current densities, than the cast one [14]. On the other hand, Prashanth et al. [20] studied the corrosion resistance of SLM AM AlSi12 with different heat treatments by weight loss in a strong acidic medium (1 M HNO₃). They highlighted that the weight-loss curves of the cast specimens and the as-prepared SLM were extremely close, indicating that the corrosion behaviors of these materials are similar [20].

Zhou et al. [21] compared the corrosion resistance of additive manufactured AlSi10Mg and a Zr modified AA5083 alloy. They noticed pitting corrosion on the additive manufactured AlSi10Mg during immersion and electrochemical tests, in special the EIS measurements which show the phase angle curves with large variability (width and height) as a function of time, suggesting continual pitting [21]. In this regard, Estupiñan-Lopez et al. [22] studied the corrosion behavior of additive manufactured AlSi10Mg through immersion tests in H_2O and 3.5 wt% NaCl solutions at room temperature using the electrochemical noise technique. They noticed the presence of a poor passive layer, produced during the immersion tests, which induced pitting corrosion due its lack of uniformity [22].

This work investigates the global (EIS and anodic polarization curves) and localized (SVET) corrosion behavior of additivemanufactured AlSi7Mg0.6 and correlates it with its microstructure and immersion tests. The experiments were conducted on both the SLM AM AlSi7Mg0.6 surface and the as-cast AlSi7Mg0.6 to evaluate the impact of any variation in the microstructure on the corrosion resistance of these alloys.

2. Experiment

Plates (20 cm x 9 cm) of additive-manufactured (AM) AlSi7Mg0.6 (Al-6.7Si-0.57Mg-0.08Fe-0.1Ti-<0.01Zn-<0.01Mn-<0.05Cu(wt%) samples, provided by the Sirris research institute, were used for the experiments. They were prepared using an SLM280 device from Nikkon SLM, equipped with a 400 W laser in an argon atmosphere with a resulting oxygen content of < 50 ppm. The processing, with a layer thickness of 30 µm, took place with the parameters given in Table 1. As a raw material, TEKMAT AlSi7Mg-63/20 aluminum alloy spherical powder was utilized and this material exhibited a granulometric distribution when measured by laser diffraction, with D10 at 26 µm, D50 at 43 µm,

Table 1 SLM parameters.

	Hatch	Contour
Power	350 W	275 W
Speed	1650 mm/s	520 mm/s
Hatch spacing	0.13 mm	/
Build plate temperature	200°C	
Number of contours	1	

and D90 at 66 μ m. Sieve analysis indicated that 93 % of the particles were smaller than 63 μ m, while only 7 % were larger than 63 μ m.

The AM superficial roughness of the plates was measured by a 2D laser technique and an average roughness (Ra) of 7.03 μ m was found. The results are presented in Table 2.

The relative density of the sample was evaluated using Archimede's method, which is based on the material's buoyancy in water and air, providing values related to the material's porosity and density. The values are provided in Table 3.

For comparison, an as-cast AlSi7Mg0.6 sample (Al-7.0Si-0.575Mg-<0.35Fe-<0.15Ti-<0.07Zn-<0.3Mn-<0.1Cu-< 0.05Ni(wt%) was used as standard. For both samples, heat treatment was not applied.

All the samples were sequentially polished to a 1 μ m surface finishing using SiC papers and diamond pastes before microscopic observations, immersion tests and global electrochemical tests. For the macrographs, to reveal the grain boundaries, the sample was exposed for 15 s to Weck's reagent (1 g NaOH + 4 g KMnO₄ + 100 ml deionized water) for a metallographic etching.

The immersion test was carried out in naturally aerated 3.5 % NaCl solution at room temperature for 45 days. Weight loss measurements were carried out on the specimens before and after exposure to the aerated 3.5 % NaCl solution.

Macro and microstructural characterizations of the alloys were carried out by optical microscopy (OM), using a KH 8700 Hirox Digital Microscope, and scanning electron microscopy (SEM-FEG), using a Model SU8020 microscope equipped with an energy-dispersive X-ray spectroscopy (EDX) detector.

X-Ray Diffraction analyses (XRD) were performed using a Panalytical Empyrean diffractometer operating in Bragg–Brentano geometry with a CuK\alpha1 radiation ($\lambda=0.1540598$ nm). Patterns were recorded from 10° to 100° with a step size of 0.026° and a dwell time of 1 s per step. To assess the phases obtained during the additive manufacturing, CalPhaD modeling was performed. ThermoCalc software, with the TCFE11 database, was used to model the ternary Al-Si-Mg phase diagram at low temperature.

The Electron Backscattered Diffraction technique (EBSD, HKL Channel 5, Oxford instrument) was used to characterize the microstructure of the samples. Electron microscopy was carried out using TESCAN GAIA 3 equipment with an Oxford instrument NordlysMax3 EBSD detector.

For the EBSD analysis, the specimens were embedded, mechanically polished up to 1 µm with diamond paste, and finished with OPS solution (colloidal silica suspension). Given the difficulty of polishing aluminum alloys mechanically, some scratches remained present on the studied maps. Samples were mounted on the stub with silver paste to avoid image shift during the acquisition. EBSD data were collected on the 70° tilted sample at 20 KV using Oxford instrument AZTEC software. EBSD data were collected using a 5 μ m step size with a magnification of 82, and 0.7 µm step size with a magnification of 670, respectively, for the reference sample (cross-section & surface) and for the additive sample (cross-section & surface), and an additional EBSD map was produced at lower magnification (x300, with a step size of 1.5 μ m) to have an overview of the cross-section for the additive sample. Different crystal phases were included for the EBSD mapping, especially for the AM samples. Special attention must be paid to indexation when the different crystal phases are close to each other. Raw data were post-processed in

Table 2

AM AlSi7Mg0.6 2D surface roughness.

	Rp (µm)	Rv (µm)	Rz (µm)	Rc (µm)	Rt (µm)	Ra (µm)	Rq (µm)
Ν	88	88	88	88	88	88	88
Mean	26.1	17.2	43.3	22.7	83.6	7.03	9.08
Std. error mean	0.831	0.483	1.22	0.676	3.77	0.206	0.267
95 % CI mean lower bound	24.5	16.2	40.9	21.4	76.2	6.63	8.55
95 % CI mean upper bound	27.8	18.1	45.7	24	91	7.43	9.6
Standard deviation	7.79	4.53	11.4	6.34	35.4	1.93	2.51

Table 3

AM AlSi7Mg0.6 relative density.

	Volumetric mass density (g/ cm ³)	D relative (%)	
Ν	26	26	
Mean	2.63	98.1	
Std. error mean	0.0106	0.394	
95 % CI mean lower bound	2.61	97.3	
95 % CI mean upper bound	2.65	98.8	
Standard deviation	0.0538	2.01	

Oxford Instruments Channel 5 software by removing spikes and reducing zero solutions with cyclic iterations (up to 6 neighbors).

Electrochemical Impedance Spectroscopy (EIS) tests were conducted in 0.1 M NaCl solution using a Bio-Logic potentiostat SP-300. A threeelectrode system was used, comprising the sample as a working electrode, a Pt counter electrode, and an Ag/AgCl (saturated KCl) reference electrode. EIS measurements were obtained from 50 kHz to 10 mHz at 10 points per decade with a perturbation of 10 mV rms. Potentiodynamic anodic polarization curves were obtained in the 0.5 M Na₂SO₄ electrolyte (for this technique, a less aggressive electrolyte was chosen for testing, as it was not possible to observe significant differences between the materials when using a 0.1 M NaCl electrolyte) in the potential range of -0.030 V in relation to the open circuit potential (OCP), up to + 1 V in relation to the reference electrode, with a scan rate of 1 mV s⁻¹.

The area of the samples exposed to the aggressive solution was 1.0 cm^2 . For each group of samples, at least three measurements were carried out at any immersion time to investigate their reproducibility.

Employing Applicable Electronics (AE) equipment, the localized corrosion properties of various alloys were examined through the Scanning Vibrating Electrode Technique (SVET) in a 15 mM NaCl (604Ω cm) electrolyte. The samples were embedded in epoxy resin (EpoFix) followed by mechanical polishing. The exposed area was limited to 1.5 mm^2 , utilizing 3 MTM ScotchrapTM 50 tape. The vibration amplitude, frequency, and vibrating electrode distance from the sample were 45

 μ m, 65 Hz, and 200 μ m, respectively, which were the operating parameters. At least two SVET measurements, using 31 \times 31 grid points, were carried out to ensure the accuracy of the findings.

3. Results

3.1. Microstructural characterization

The initial characterization of AM AlSi7Mg0.6 was made using optical microscopy. Fig. 1 shows the cross-section view (surface perpendicular to the building platform, XZ). It can be observed that the characteristic melt pools (melt pools are the localized molten region created by a heat source (laser) to fuse the material layers), resulting in the additive manufacturing process, present a half-cylinder-like feature. In Fig. 2, a higher magnification was used to show the melt-pool borders (the boundary between the fully melted zone and the surrounding material). Fig. 3 displays the top surface (surface parallel to the building platform, XY) which presents a scale-like feature due to the elongated laser tracks. These observations are in accordance with the literature [1, 4,9,12,14].

Fig. 4 shows the EBSD band contrast maps of as-cast AlSi7Mg0.6 (Fig. 4(a)) and AM AAlSi7Mg0.6 (Fig. 4(b) and (c)). The as-cast AlSi7Mg0.6, presented in Fig. 4(a), shows the typical cast microstructure due to low solidification velocity, which produces large grains (diameters higher than 100 μ m) and a dendritic structure in this eutectic alloy [12]. The literature describes this microstructure as composed of aluminum matrix (α -Al), Si eutectic, and coarse intermetallic compounds (β -phase) rich in Fe, Mg, and Si [12,23–25]. For the AM AlSi7Mg0.6, a higher magnification was needed due to the smaller grain size. Fig. 4(b) shows the top surface of AM AlSi7Mg0.6, which displayed a grain size of about 13 μ m. The cross-section view, Fig. 4(c), shows the elongation of the grains and it is possible to notice the influence of the melting edges on the microstructure, identified with a white arrow.

The XRD plot, Fig. 5(a), displays the diffraction patterns where the black line is AlSi7Mg0.6 and the red one is AM AlSi7Mg0.6. For both samples, the pattern is quite similar. The main phases are composed of Al and Si and a very small peak for eutectic Mg₂Si is detected due to the



Fig. 1. Cross-section view of microstructure of AM AlSi7Mg0.6 Alloy.



Fig. 2. Melt pool (cross-section view) of microstructure of AM AlSi7Mg0.6 Alloy.





Fig. 3. Top surface view of AM AlSi7Mg0.6 Alloy.

low quantity of Mg in these alloys and the limitation to detect crystallites lower than 10 nm [12,26]. The presence of the small amount of eutectic Mg₂Si in as-cast AlSi7Mg0.6 could be attributed to the amount of eutectic Si which developed steadily throughout, under stable conditions, due to the slow solidification rate of the casting process [12]. For the AM AlSi7Mg0.6, the detection could be attributed to the temperature on the building platform which was 150° C during the process. Therefore, a certain amount of Si atoms precipitated out of the α -Al matrix for as-built SLM samples. The separated Si then reacts with Mg to form the β -phase (Mg₂Si) resulting in a kind of artificial aging after a period of SLM [12,27,28]. In this sense, the ternary Al-Si-Mg phase diagram, generated using ThermoCalc software (Fig. 5(b)) corroborates with the results obtained from the XRD analysis. Indeed, at a temperature of 150°C, which corresponds to the building platform conditions, the formation of Mg₂Si precipitates is thermodynamically predicted. It is also possible to notice an enlargement in the Si peaks in the AM AlSi7Mg0.6 (red), although the as-cast AlSi7Mg0.6 presented more intense Si peaks. This Si peak enlargement suggests a supersaturation of Si in the Al matrix [12,15].

The EBSD phase map is presented in Fig. 6. For the as-cast AlSi7Mg0.6, Fig. 6(a) shows the distribution of Mg₂Si and Si phases in the surface alloy. The Mg₂Si phase, indicated in yellow, is concentrated in the grain boundaries. Some Mg₂Si agglomeration is noticed, indicated by the white arrow. It is worth mentioning that the Si phases are spread overall surface area. The Si phase is broadly distributed but concentrated around Mg₂Si agglomerations. For the AM AlSi7Mg0.6, higher magnifications were needed due to the smaller grain size. For the Mg₂Si phase, the same behavior was observed, with the phase being found at the grain boundaries (Fig. 6(b) and (c)). For the Si-phase, its distribution is observed as being spread over the whole surface with some agglomeration over Mg₂Si rich areas. Although both samples showed similar behavior, it is worth noting that the phase distribution is more homogenous in the case of AM AlSi7Mg0.6, due to the smaller grain size which provides more grain boundaries. Consequently, the Mg₂Si is better distributed, avoiding large agglomerations compared to its as-cast counterpart. The distribution of Mg₂Si particles at the grain boundaries has been reported. These continuous distribution provides a labyrinth structure which provides a path for corrosive processes [25]. Ji et al. [29] suggest that the Mg concentration at the grain boundaries, according to the results of density functional theory, are related to the potential sites. Adsorption is provided by the local electron buildup at the interface between the oxide and the subsurface Al atoms. In comparison to the grains, grain boundaries are more prone to oxidation [29]. On Mg-segregated grain borders, Mg-enriched oxides are formed due to



Fig. 4. EBSD Band maps, with (a) as-cast AlSi7Mg0.6 surface, (b) AM AlSi7Mg0.6 top surface, and (c) AM AlSi7Mg0.6 Cross-section.



Fig. 5. XRD patterns and ternary diagram.

a high concentration of Mg, which also improves adsorption and electron localization on the grain boundaries.

The inverse pole figure (IPF) maps are presented in Fig. 7. For the ascast AlSi7Mg0.6 sample (Fig. 7(a) and (c)), the grain orientations are randomly distributed. This random distribution is not observed on the top surface of the AM AlSi7Mg0.6 sample. Fig. 7(b) shows that the c-axis of the aluminum crystal is aligned with the z-axis < 001 > of the map by a predominance of red on the IPF Z map, which indicates a preferential orientation in the direction of growth. The presence of elongated grains in the cross-section of AM AlSi7Mg0.6 is observed in Fig. 7(d). Moreover, Fig. 7 indicates the IPF Z (d) and IPF Y (e) of the cross-section of AM ALSi7Mg0.6 at lower magnification, which reveals that the c-axis of the aluminum crystal is preferentially oriented along the Y-axis of the map (Fig. 7(e)). These observations confirm the orientation of the aluminum grains along the AM growth direction.

Fig. 8 shows the EIS measurements for the AM AlSi7Mg0.6 and as-



Fig. 6. EBSD phase maps, with (a) As-cast AlSi7Mg0.6 surface, (b) AM AlSi7Mg0.6 top surface, and (c) AlSi7Mg0.6 Cross-section.



Fig. 7. Inverse pole figure maps (IPF_Z), with (a) as-cast AlSi7Mg0.6 surface, (b) AM AlSi7Mg0.6 top surface, (c) AM AlSi7Mg0.6 Cross-section, (d) IPF Z AM AlSi7Mg0.6 Cross-section in high magnification, and (e) IPF Y AM AlSi7Mg0.6 Cross-section in high magnification.

cast AlSi7Mg0.6 samples which were carried in a 0.1 M NaCl solution after 2 h, 4 h and 6 h of immersion. No surface is an optimal interface due to heterogeneity and roughness. Consequently, instead of using an ideal capacitor, the constant phase element (CPE) was implemented as shown by formula (1):

$$Z_{CPE} = \begin{bmatrix} 1 \\ \overline{Y_0 \quad (i\omega)^n} \end{bmatrix}$$
(1)

where n is the frequency dispersion coefficient with a domain of 0-1. The ideal state of the system is either pure capacitance (n = 1) or pure

resistance (n = 0). The CPE's admittance is denoted by Y_0 .

The AM AlSi7Mg0.6 presents a higher modulus at low frequency than the as-cast counterpart meaning a slightly better corrosion resistance (values given in Table 4). In the Nyquist plot (Fig. 8(a)), a slight increase of the modulus at low frequency can be observed for both samples with immersion times. AM AlSi7Mg0.6 is characterized by a higher charge transfer resistance, indicated by larger semicircles, showing a more effective corrosion resistance. In the same sense, in the Bode plot (Fig. 8(b)), AM AlSi7Mg0.6 presents higher |Z| values in the low frequencies, which suggests a higher resistance to charge transfer than the as-cast AlSi7Mg0.6. In the phase angle plot (Fig. 8(c)), a larger



Fig. 8. Electrochemical Impedance Spectroscopy plots obtained in 0.1 mol L^{-1} NaCl solution after 2, 6 and, 8 hours: Nyquist (a), Bode (b) plots, -phase angle (c), EEC (d) and fitting plots after 6 hours, (e) AM AlSi7Mg0.6 and, (f) as-cast AlSi7Mg0.6.

Table 4

$ \mathbf{Z} $	Values	at	low	frequency
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-		
Sample	Time (h)	$ Z /\Omega.cm^{-2}$ at 0.014 Hz
As-cast AlSi7Mg0.6	2	64,375
As-cast AlSi7Mg0.6	4	54,873
As-cast AlSi7Mg0.6	6	73,504
AM AlSi7Mg0.6	2	111,131
AM AlSi7Mg0.6	4	84,178
AM AlSi7Mg0.6	6	114,781

phase angle (around -80 degrees) is highlighted for the AM AlSi7Mg0.6, indicating a more capacitive behavior.

Fig. 8(d) displays how the physical model is fitted for the samples after 6 hours of immersion, using one-time constant. For the EEC proposed, R_{sol} represents the electrolyte resistance; the CPE_{dl} (Constant phase element) and the resistor R_{ct} are related to the corrosion processes (double layer capacitance and charge transfer resistance). In this sense, CPE values indicate and model the deviation from an ideal capacitor, these deviations being attributed to factors such as material heterogeneities and surface roughness, among others. The results are presented in Table 5 and the fitting plots displayed in Fig. 8(e) and (f).

As observed in Table 5, The AM AlSi7Mg0.6 presented a lower CPE_{dl}

Table 5

Fitting results after 6 hours.

Sample	R _{sol} (Ω. cm ⁻²)	CPE_{dl} $(\mu F. cm^{-2}.$ $S^{(n-1)})$	n _b	R _{ct} (Ω. cm ⁻²)	C _{eff} (μF/ cm²)
As-cast AlSi7Mg0 6	166.7	14.21	0.80	76594	14.8
AM AlSi7Mg0.6	166	12.37	0.85	110000	13.0

value (12.37 μ F.cm⁻².S⁽ⁿ⁻¹⁾) compared to the as-cast AlSi7Mg0.6 (14.21 μ F.cm⁻².s⁽ⁿ⁻¹⁾), suggesting a smaller active corrosion area. The n_b for the AM AlSi7Mg0.6 is 0.85, closer to 1 compared to the as-cast AlSi7Mg0.6 (0.80), indicating a more homogeneous layer at the interface for the AM material. The charge transfer resistance R_{ct} for the AM AlSi7Mg0.6 (110000 Ω ·cm²) is significantly higher than for the as-cast AlSi7Mg0.6 (76594 Ω ·cm²), indicating a higher resistance to charge transfer on the surface. The effective capacitance (C_{eff}) is a quantity that represents the real capacitive response of an electrochemical system. [30,31] The relationship between CPE and C_{eff} is given by the Brug equation [30,31] (formula 2):

$$C_{eff} = Q^{1/n}$$
. $R_{eq}^{(1-n)/n}$ (2)

Where *Q* is the CPE parameter, *n* is the CPE exponent and R_{eq} is the resistance associated to CPE.

Using this relationship, the C_{eff} value for as-cast AlSi7Mg0.6 is 14.8 μ F/cm² and exhibits a higher effective capacitance compared to AM AlSi7Mg0.6 (13 μ F/cm²). A lower measured capacitance on AM AlSi7Mg0.6 alloy indicates a less defective and more protective surface, which can enhance the corrosion resistance of the alloy and higher capacitance measured on surface of as-cast AlSi7Mg0.6 surface implies a larger electrochemically active surface area with/or improved interfacial conductivity by defects on the surface layer. This may indicate that the as-cast AlSi7Mg0.6 surface is more reactive and more defective (more conductive).

Fig. 9 displays the anodic polarization curves of both samples. Compared to the as-cast sample, a less aggressive electrolyte (Na₂SO₄ 0.05 M) was selected for this test to confirm the differences between the samples. Compared to the as-cast sample, the polarization curve of the AM AlSi7Mg0.6 sample shows a passive layer which is more resistant to localized corrosion. The AM AlSi7Mg0.6 sample demonstrates a passivity range from approximately- 0.5 V to + 0.13 V with a low current density (less than 0.03 mA/cm²), indicating the formation of a stable passive oxide layer. Its corrosion potential (E_{cor}) is approximately



-0.47 V, quite near to the as-cast sample (approximately 0.51 V). However, the most important finding is that the AM AlSi7Mg0.6 sample is affected by localized corrosion only at a significantly higher pitting potential (around +0.12 V), compared to the as-cast sample, which undergoes localized attack at a much lower potential (around -0.34 V). On the other hand, the as-cast AlSi7Mg0.6 sample shows less passivity, with a more limited passivity range (from -0.5 V to - 0.3 V) and higher current densities (around 0.02 mA/cm²) within this range. This result is in accordance with the EIS results presented earlier.

Fig. 10 shows the comparison bar plot of weight-loss measurements after 45 days of exposure to 3.5 % NaCl solution. The weight loss corresponding to the AM AlSi7Mg0.6 was 8.21 g/m² and was 26.1 g/m² for the as-cast AlSi7Mg0.6. This result indicates that the generalized corrosion resistance of the samples is also improved for the samples obtained by AM. The mass loss of as-cast AlSi7Mg0.6 parts was ~3.2x more affected than the AM counterpart in the highly corrosive environment.

Fig. 11 presents to the SVET maps of the as-cast AlSi7Mg0.6 and AM AlSi7Mg0.6 (from both sides) obtained in 15 mM NaCl electrolyte after 12 h immersion. The optical image at the end of the exposure was taken to visually compare the samples to each other. For the as-cast AlSi7Mg0.6, in both immersion slots (3 h and 12 h), a relatively homogenous anodic region at the exposed area shows somewhat uniform corrosion, intensifying from the 3 h to the 12 h test. However, on both sides of the AM AlSi7Mg0.6, the corrosion activity was initiated by localized corrosion (after 3 h of immersion), as the anodic activity illustrates. Interestingly, the localized corrosion activity diminished after 12 h, revealing the occurrence of a somewhat self-healing action in the alloy. The SVET maps after 12 h indicate that the anodic spot is no longer visible, and a cathodic region surrounds the former localized anodic activity. The emergence of a bubble at the exact location of the cathodic activity in the optical images (on both sides of AM AlSi7Mg0.6) reveals this activity at the localized site. All in all, the SVET findings are in keeping with the global electrochemical analyses, illustrating the presence of a kind of passive layer in the AM AlSi7Mg0.6 alloy, which is why the localized corrosion activity is found at the beginning exposure.

Fig. 12 presents EDS maps of the corrosion on the surface of the ascast AlSi7Mg0.6 and AM AlSi7Mg0.6 obtained in 15 mM NaCl electrolyte after 12 h immersion. The maps reveal a significant disparity in the elemental distribution across the surface of the samples. In the as-cast AlSi7Mg0.6 sample, there is evident heterogeneity in the distribution of Si on the surface, along with a noticeable accumulation of Mg in the region affected by the corrosive attack. In contrast, the AM AlSi7Mg0.6 samples exhibit a more homogeneous distribution of Si and Mg across



Fig. 10. Weight-loss after immersion test in 3.5 % NaCl; RT after 45 days.



Fig. 11. SVET maps after 3 h and 12 h immersion in 15 mM NaCl electrolyte. The black circle on the maps shows the exposure area.

the surface. Notably, in the region associated with the highest electrochemical activity (as observed in the cross-section of the AM AlSi7Mg0.6 during the SVET test (Fig. 11) - a depletion of Si is evident, as indicated by the arrows). Fig. 13 presents the maps that highlight the differences in the elemental distribution between the surfaces of the as-cast AlSi7Mg0.6 and AM AlSi7Mg0.6 samples. The maps reveal a homogeneous distribution of Si and Mg in the sample produced via additive manufacturing, whereas, in the as-cast sample, Si is primarily distributed along the grain boundaries. Mg also accumulates in these regions, as shown in the phase maps (Fig. 6). The homogeneous distribution of Si and Mg on the surface of the AM sample suggests the formation of a continuous passive film. This observation aligns with the results of the EIS measurements and polarization curves (Fig. 9). To assess Si depletion in localized corrosion, Fig. 14 shows SEM images and EDS maps of pitting corrosion on the surface of AM AlSi7Mg0.6 after 12 hours of exposure to a 0.1 M NaCl electrolyte solution, complemented by EIS measurements. The SEM image in Fig. 14(a) shows a localized cavity, indicating a breakdown of the passive layer. The EDS maps in Fig. 14(c), (d), and (f) reveal the surface composition, highlighting a depletion of silicon in the pitting. The depletion of silicon in the pitting areas, as shown in the EDS maps, can be a nucleating localized corrosion. This depletion creates small anodic sites surrounded by a larger cathodic area, which accelerates the corrosion process. The imbalance between the anodic and cathodic regions likely contributes to the breakdown of the passive layer and the progression of pitting corrosion in these specific areas, suggesting that localized corrosion is initiated in regions with lower Si content.

4. Discussion

The results presented in this work highlight the impact of microstructure variation on the corrosion resistance of these alloys. The study identified a passive layer on the surface of AM AlSi7Mg0.6, as evidenced by the anodic polarization test, which indicated an increase in localized and uniform corrosion as shown by the electrochemical results (Figs. 9 and 11). The AM process produces a distinct microstructure compared to casting methods, as demonstrated in the optical microscopy and EBSD analyses (Figs. 1, 2 and 3). The surface morphology, directly influenced by the microstructure, significantly affects the surface behavior, particularly the corrosion resistance.

Based on the results obtained, a mechanism is proposed in Fig. 15. As shown in the EBSD Band contrast maps (Fig. 4), AM AlSi7Mg0.6 exhibits finer grains due to the high cooling rate associated with the additive manufacturing process (Fig. 15(a)). This results in a different surface



Fig. 12. Elemental EDS map of an exposed area of the samples after immersion in naturally aerated 15 mM NaCl electrolyte solution after 12 hours of exposure.



Fig. 13. Elemental EDS comparative maps of as-cast AlSi7Mg0.6 and AM AlSi7Mg0.6 alloys.

microstructure from cast material, characterized by smaller grain size and a distinct structure comprising α -Al with Si precipitates, as identified in the XRD analysis (Fig. 5). The presence of Mg clusters in the form of Mg₂Si was observed in the EBSD phase map (Fig. 6) and EDS maps (Fig. 15(b)). These clusters form due to the platform temperature, which acts as an aging treatment[12]. As observed in Fig. 6, Mg agglomerations are preferentially located in the grain boundaries (Figs. 6, 12 and 13) and are accompanied by the presence of Si. As the material produced by the additive manufacturing process has smaller grains than the cast material, a more homogeneous distribution of the Mg and Si agglomerates can be reached, as there are more grain contours. In contact with a corrosive environment, Mg-rich particles have an anodic behavior with respect to α -Al matrix. This means that these particles are capable of sustaining anodic currents resulting in high Mg dissolution rates [1,17, 32,33]. As corrosion progresses, the selective dissolution of Mg from the Mg₂Si phase leads to the formation of Mg(OH)₂ and SiO₂-nH₂O hydroxides at grain boundaries and defects (Fig. 15(c)) [34–37]. This process results in a local enrichment of Si. (Fig. 15(c)). In a corrosive environment, Al(OH)₃ and SiO₂ can serve as corrosion-protective barriers, which cover localized corrosion areas (corrosion pits) [24], and disrupting the labyrinth-like structures formed by the distribution of Mg₂Si at grain boundaries suppressing the corrosion expansion and increasing the corrosion resistance [25,37], and Mg(OH)₂ acts as an extra diffusion barrier to stop Al from eluting into the electrolytes and reduces the



After exposition on NaCl 0.1M; RT; 12 H

Fig. 14. Elemefntal EDX map of localized corrosion of the AM AlSi7Mg0.6 sample after immersion in naturally aerated 0.1 M NaCl solution after 12 hours of exposure.



Fig. 15. Proposed mechanism for localized corrosion of the AM AlSi7Mg0.6 Alloy.

corrosion activity of Mg-containing IMPs [17,24,25,35-37]. The formation of Mg(OH)₂ and SiO₂·nH₂O hydroxides at grain boundaries and defects. In this sense, this combination acts as a barrier to corrosion. This residual layer enhances the overall corrosion resistance in these regions. The presence of this layer strengthens the protection provided by the native passive alumina layer on the surface. The combined effect of the oxy/hydroxide Si and Mg residual layer and alumina layers contributes to a more robust protective barrier, even though it has a more porous surface, mitigating the ingress of corrosive agents. These effects could be observed in the increase in the localized potential of AM AlSi7Mg0.6 (Fig. 9), and with the more capacitive behavior of the surface (around -80 degrees) on the EIS Bode phase angle plots (Fig. 8). The effect on corrosion resistance of this combined effect is confirmed by the weight-loss tests (Fig. 10).

On the other hand, the reinforcement in the passive layer makes the material susceptible to localized corrosion as indicated in the SVET tests.

When defects occur in this layer, a small anodic area is formed and supported by a large cathodic area, which intensifies the localized attack in the form of localized pitting corrosion (Fig. 15(d)).

5. Conclusion

The results of this study prove that the corrosion resistance of AlSi7Mg0.6 alloys is strongly influenced by the microstructural variations brought about by the additive manufacturing technique. In addition to the natural alumina layer, a reinforced passive silicon dioxide layer forms, offering improved resistance to general corrosion. Nevertheless, the research also emphasizes how any flaws in these layers could enhance the vulnerability to localized corrosion. In practical applications, these insights are essential for optimizing processing parameters and material treatments to balance localized corrosion susceptibility with general corrosion resistance.

CRediT authorship contribution statement

Rafael Emil Klumpp: Writing – review & editing, Writing – original draft, Visualization, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. Alexandre Mégret: Formal analysis. Delaunois Fabbien: Writing – review & editing. Marie-Georges Olivier: Writing – review & editing, Writing – original draft, Supervision, Project administration, Methodology, Funding acquisition, Data curation, Conceptualization. Sajjad Akbarzadeh: Writing – original draft, Formal analysis. Thomas Kairet: Resources, Methodology. Védi Ölmez: Methodology, Formal analysis. Gonon Maurice François: Formal analysis.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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