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Electrochemical Behavior of Conventional and Rheo-High Pressure Die Cast Low Silicon Aluminum Alloys in NaCl Solutions

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ABSTRACT

The electrochemical behavior of a low silicon aluminum alloy cast by the conventional and rheo-high pressure die cast processes is evaluated using polarization test and electrochemical impedance spectroscopy in 0.01 M, 0.05 M, 0.1 M, and 0.6 M sodium chloride solutions.

Compared to the conventional high pressure die cast process, rheocasting introduces some alterations in the microstructure including the presence of aluminum grains with different sizes, formed at different solidification stages.

According to the results of the anodic polarization test, conventional cast and rheocast samples show similar breakdown potentials. However, the rheocast samples present enhanced oxygen reduction kinetics compared to the conventional cast sample.

Based on scanning electron microscopy examinations, localized micro-galvanic corrosion is the main corrosion mechanism for both alloys and it initiates at the interface of aluminum with iron-rich intermetallic particles which are located inside the eutectic regions. The corrosion further develops into the eutectic area.

Although the rate of the cathodic reaction can be influenced by the semisolid microstructure, according to the results of anodic polarization and electrochemical impedance spectroscopy tests, the corrosion behavior is not meaningfully affected by the casting process.

INTRODUCTION

Despite its reactive nature, pure aluminum is resistant to most environments and chemicals thanks to the formation of a protective (passive) oxide layer. The growth and the properties of the passive oxide film are affected by the alloying elements, impurities, and microstructure. The corrosion of aluminum only occurs once the oxide film has been dissolved or damaged. This film is stable in neutral

conditions, but soluble in acidic and alkaline environments and is sensitive to the presence of halide ions such as chloride ¹.

Aluminum is anodic to many metals. When it is coupled with them in an electrolyte, the resultant potential difference causes a galvanic couple and considerable corrosion can result. Similarly, the potential difference between the aluminum matrix and secondary phases can result in micro-galvanic coupling and severe corrosion ².

Different microstructural components in aluminum-silicon (Al-Si) alloys, including the eutectic silicon and intermetallic (IM) particles, exhibit various electrochemical potentials with respect to the aluminum matrix, rendering the alloy susceptible to localized forms of corrosion such as pitting ²⁻⁵.

For high pressure die cast process, the presence of iron in the composition is necessary to prevent the "soldering" of the molten alloys to the die ^{6, 7}. The resultant precipitation of brittle iron-rich IM particles is harmful to the mechanical properties ⁶.

There is a general agreement that iron-rich IM particles are deleterious to the alloy's corrosion resistance as well ^{2-4, 8-10}. These particles are noble with respect to the aluminum matrix and exhibit enhanced cathodic kinetics. Addition of Mn and Mg results in the formation of AlFeSiMn and AlFeSiMg compounds with reduced cathodic effects ^{2, 4, 7}. For the cathodic particles, circumferential pits appear as trenches around the intact particle and the corrosion attack is mainly in the matrix phase ⁵. It is reported that on the alloy's surface the oxide is not continuous (from the IM particles to the aluminum matrix), leading to a significant defect site and easier breakdown of the passive oxide at these interfaces ⁵.

Apart from the micro-galvanic coupling mechanism, the alkaline dissolution of the matrix at the aluminum/particle interface (so-called cathodic trenching) where the pH of the solution is increased due to the oxygen reduction reaction (ORR) on the particle's surface can be another corrosion mechanism ¹¹. However, the results reported by Schneider et al. ¹² on AA2024-T3 (UNS A92024) introduce several challenges to the simple high pH-induced trenching model. For instance, this model is unable to explain the different trenching behavior of various IM particles such as AlCuMnFe and AlCu, with analogous ORR kinetics. If the pH increase near the particle due to the ORR was the only cause of trenching, then the mentioned particles should behave equally. In this case, the anodic trenching model can be used. According to this model as the propensity to promote trenching of the aluminum matrix is not the same near each IM particle type (for example in the sense of copper concentration), at low chloride concentrations different degrees of trenching susceptibility (due to different pitting potentials) is observed for various IM particles. It should be mentioned that this model depends on chloride concentration.

Silicon is also cathodic with respect to the aluminum matrix but its galvanic effect is minimal due to the low current density, promoted on the silicon surface, as a result of the high polarization resistance of silicon ⁴. The effect of silicon on the corrosion resistance of aluminum is not quite clear yet ^{2, 13}. For instance, Rehim et al. ^{13, 14} showed that the rate of pit nucleation, in a chloride-containing environment, decreases by increasing the silicon content from 0 to 6 and 18 %. According to their kinetic study, this trend does not change by variation in halide ion (chloride) concentration, temperature or applied potential. However, no clear explanation is provided for this behavior.

Pech-Canul et al. ¹⁵ have shown that for Al-12 % Si, the presence of silicon oxide in the passive layer makes it more resistant to the pitting corrosion. Thanks to its electric properties, silicon oxide has shown the ability to retard the adsorption of chloride ions. It can also block the entry sites and restrict the transport of chloride ions through the passive film.

Silicon also increases the corrosion potential of the aluminum solid solution, decreasing its potential difference with the secondary phases ^{16, 17}.

The 3D corrosion study by Mingo et al. ⁹ showed that in the rheocast aluminum alloy A356 (UNS A13560), aluminum/iron-rich IM particles interfaces are the preferential corrosion sites rather than those of aluminum/eutectic silicon phase. A recent study by Qi et al. ^{10, 18} on the effect of rheo-high pressure die cast (Rheo-HPDC) process on the corrosion resistance of Al-8 Si-Fe alloy shows improved corrosion resistance of the alloy as a result of the semisolid process and correlates it to the lower volume fraction of β -Al₅FeSi particles.

Other studies on the corrosion behavior of semisolid cast Al-Si alloys such as A356 (UNS A13560) and A357 (UNS A13570) include those performed by Yu et al. ¹⁹, Park et al. ²⁰, Tahamtan et al. ^{21, 22} and Masuku et al. ²³. They have mostly emphasized on the localized corrosion in the eutectic regions, at the interface of the eutectic silicon and iron-rich IM particles with the α -Al phase. Although both of the eutectic silicon phase and iron-rich IM particles contribute in the localized corrosion, as mentioned before, some authors consider the contribution of IM particles to be more important ^{4, 10}.

Arrabal et al. ⁴ showed that rheocasting can increase the concentration of silicon in α -Al particles in A356 (UNS A13560) aluminum alloy, leading to smaller potential differences between this phase and the eutectic silicon phase and β -AlFeSi IM particles. As a result, the semisolid alloy shows a higher resistance to pitting corrosion.

However, the effect of semisolid process on corrosion of aluminum alloys is still controversial. Previous researches ^{24, 25} have shown that the higher amount of eutectic phase on the surface as a result of surface liquid segregation (SLS) in semisolid-HPDC aluminum alloys can increase the pitting susceptibility.

Depending on the silicon percentage, Al-Si alloys are categorized into hypoeutectic alloys with 5 to 10 % silicon, eutectic alloys containing 11–13 % silicon, and hypereutectic alloys with a silicon content commonly between 14 and 20 %. The development of low silicon aluminum alloys (enabled by the semisolid process ²⁶) to increase the thermal conductivity ^{27, 28} has been the subject of some studies. These alloys are promising candidates for applications such as heatsink for electronics cooling. To the best of our knowledge, the electrochemical and corrosion behavior of these cast alloys have been rarely studied.

There are some corrosion studies on hypoeutectic ²⁹⁻³¹, eutectic ³²⁻³⁴, and hypereutectic ³⁵ cast Al-Si alloys. In some of them, the effect of eutectic modifiers (e.g. Na and Sr) on the corrosion resistance has been studied. In one study ²⁹, the deleterious effect of sodium on corrosion resistance has been attributed to the increased aluminum/silicon interface as a result of fibrous morphology of the eutectic silicon in the presence of the modifier. It is noticed that in both modified and unmodified alloys, the eutectic morphology is not lamellar and it is formed by silicon particles disseminated throughout the aluminum-rich phase. Strontium has shown to be less problematic than sodium ³⁴. It is reported that more α -Al dendrites ordered in parallel to the direction of heat flow (the thickness of the casting) in Sr-modified alloy restrict the transverse penetration of corrosion channels compared to those in the Na-modified alloy, resulting in lower weight loss in 4% sulfuric acid solution. Without presenting any electrochemical results, it is also stated that the pitting potentials are lower for Na- and Sr-modified alloys compared to unmodified Al-11.7 % Si alloy.

Variation in silicon and magnesium contents in eutectic and hypoeutectic alloys are the subject of some other studies. It is shown that a higher eutectic fraction in Al- 9 % Si compared to that in Al- 5% Si alloy results in the higher corrosion rate ³⁰. Increasing magnesium content from 0 to 5, 10 and 20 % in Al-12 % Si alloy, increases the fraction and size of Mg₂Si particles, leading to the higher corrosion

current density and weight loss in the solution of 30 gr/l NaCl + 10 ml/l HCl. It is concluded that Mg₂Si particles acted as a cathodes resulting in the dissolution of aluminum ³³. This can be due to the selective dissolution of magnesium from the particles which transforms them from anodic to cathodic (with respect to the aluminum matrix), however, this is not stated in the paper.

To the best of our knowledge, there is no study contrasting the corrosion behavior of hypoeutectic, eutectic and hypereutectic Al-Si alloys. However, there is one study comparing the corrosion behavior of Al-12.3 % Si-0.26 % Mg to that of AA6063 (UNS A96063) ³². It is reported that the Al-Si alloy shows higher weight loss in 4% sulfuric acid solution compared to AA6063 (UNS A96063), possibly due to the presence of more cathodic silicon phase.

Despite the lean lit on the corrosion properties of cast Al-Si alloys, there are studies available on Al-Mg-Si-(Cu) alloys to be reviewed as a guideline.

These alloys are susceptible to intergranular corrosion (IGC). IGC is derived by the micro-galvanic interaction between the grain boundary precipitates and the surrounding aluminum solid solution as a result of a potential difference ³⁶. This susceptibility is caused by the precipitation of silicon or copper-containing phases, the presence of silicon or copper depleted zones and the anodic dissolution of Mg₂Si phase along the grain boundaries ³⁷.

Thermal treatment can alter the microstructure of the grain boundaries in Al-Mg-Si-(Cu) alloys resulting in the change in corrosion attack mode from IGC to pitting and vice versa ^{36, 38}. Under unfavorable heat-treatment, excess in copper content may increase susceptibility to IGC. The presence of a nearly continuous nano-scale copper film along the grain boundary in underaged conditions leads to micro-galvanic coupling with solute-depleted zones and therefore IGC ³⁷.

In a copper-free alloy, excess in silicon content does not result in severe IGC susceptibility under different temper conditions. This is because silicon is an inefficient cathode. In this condition, the iron-rich phases are the only cathodes available. In both alloys with excess in either copper or silicon, the IGC susceptibility depends on the presence of silicon and copper-depleted zones adjacent to the grain boundaries ³⁹. High Mg/Si ratio can decrease the IGC susceptibility of high copper alloys, by forming fine discontinuous Q' phase. While in low Mg/Si ratio AlFeSi (Mn, Cu) dispersoids on the grain boundaries form a continuous corrosion channel by connecting with Q' phase and accelerate corrosion. Their other negative effect is that they can provide the heterogeneous nuclei of Q' and make this phase coarsen ⁴⁰.

The systematic study by Fleming et al. ⁴¹ gives insight into comparing the corrosion behavior of eutectic Al-Si alloy to those with lower hypoeutectic silicon levels. In this study, aluminum alloys 6061 (UNS A96061) and 4047 (UNS A94047) were brazed to construct a tapered model braze joint.

In the braze area before and after brazing formation of the following phases is thermodynamically possible:

-Pre-braze (Al balance, 0.1 Mg, 13 Si, 0.3 Cu): Eutectic Al-Si, precipitated Si, Q (Al₄Cu₂Mg₈Si₇), and θ (Al₂Cu) in Al-rich phase

-Post-braze (Al balance, 0.49 Mg, 5.51 Si, 0.3 Cu): Eutectic Al-Si, precipitated Si, Q, β (Mg₂Si), in Al-rich phase

After brazing, in this region the micro-galvanic coupling leads to corrosion of aluminum phase near to silicon-rich phases in the solution tested (0.51 M NaCl + 12 mL 10.0 N HCl). No particular effect of other precipitates beyond the pitting of the Al-rich portion of the eutectic microstructure was observed.

Further from the braze alloy, there were two mixed regions and a region of thermally cycled AA6061-T6 (UNS A96061). The post-braze microstructure of the mixed regions (0.5-0.62 Mg, 4.8-4.68 Si, and 0.2 Cu) contained eutectic Al-Si microstructure at solidification boundaries and precipitated Si, Q, and β in Al-rich phase. The

thermally cycled AA6061-T6 (UNS A96061) region (Al balance, 0.72 Mg, 1.46 Si, 0.2 Cu) contained aluminum matrix with Q, β , and Si precipitates. In these three regions IGC and pitting corrosion were observed. According to this study, the IGC mechanism possibly involves β and Q phase corrosion based on their anodic potential to the matrix, assuming the Q phase behaves similar to the S phase (Al_2CuMg). Furthermore, eutectically formed silicon along grain boundaries can increase IGC by providing additional cathodic sites. Coherent β and Q phase dissolution can be the cause of matrix pitting in AA6061 region ⁴¹.

The current work focuses on the investigation of corrosion behavior of a low silicon aluminum alloy, with a composition which has been rarely studied in the past. The alloy is processed by the conventional and Rheo-HPDC methods and the corrosion behavior is studied in sodium chloride solutions of different concentrations by means of electrochemical tests (electrochemical impedance spectroscopy (EIS) and polarization), scanning electron microscopy (SEM), and energy-dispersive X-ray spectroscopy (EDXS).

EXPERIMENTAL

Sample Preparation

Samples of aluminum-silicon alloy, with the measured composition provided in Table 1, were produced by means of HPDC and Rheo-HPDC processes. The chemical compositions of the alloys were measured by optical emission spectroscopy. Both the conventional and rheocast samples were produced from the same melt, therefore they have the same composition. The details of the casting process can be found in the previous works on the same alloy ^{25,42}.

Briefly, both casting methods utilize the same HPDC machine, however, for Rheo-HPDC components the mold is fed by a slurry generated using RheoMetal™ process ⁴³.

In Rheo-HPDC process, a mold with complex geometry can result in longitudinal and transverse segregations, meaning that the sample may have various fractions of the solid and liquid parts of the initial slurry based on its position in the mold, its thickness, and from the surface to the bulk ²⁵.

To assure the integrity of comparison between the corrosion properties (possibly) affected by the casting technology, samples of the same thickness are used. In addition, rheocast samples of different thicknesses are studied. The details regarding these samples are provided in Table 2. In this table, Rh_s and Rh_l refer to the samples cast by Rheo-HPDC technique, which due to their thicknesses can possibly contain a higher fraction of solid (s) and liquid (l) parts of the initial slurry ²⁵, respectively. L refers to the sample cast by HPDC.

The same surface condition is granted for the samples by removing the SLS layer. Samples were wet ground using 600, 1200 and 4000 grit SiC abrasive papers followed by a polishing using 1 μm diamond paste. Electrical connection to each sample was provided by attaching a copper wire to the sample before embedding it inside the epoxy resin.

Electrochemical Corrosion Studies

The corrosion behavior of different samples was studied and compared using global EIS and anodic polarization tests in stagnant sodium chloride (NaCl) solutions of different concentrations (0.01 M and 0.6 M for polarization and 0.01 M, 0.05 M, 0.1 M, and 0.6 M for EIS). The electrochemical cell was a homemade set up exposing an area of 0.8 cm^2 of the working electrode (the sample) to the electrolyte. The reference and counter electrodes were Ag/AgCl (3 M KCl) and a platinum electrode, respectively.

EIS measurements were collected at the open circuit potential (OCP) at the frequency range of 10 mHz to 100 kHz during 24 h immersion in the NaCl solutions. The amplitude of the applied sinusoidal signal was 10 mV (RMS). Values of OCP for each sample were monitored and recorded every hour during this test.

For the polarization test, each sample was immersed in NaCl solutions for 2 ks and then anodically/cathodically polarized with respect to the OCP. The scanning rate was 0.166 mV/s. Samples' surfaces before and after the immersion tests were examined using an optical microscope (OM), SEM, and EDXS.

RESULTS

Summary on the Microstructural Features

The OM images (Figures 1 [a through c]) show that the microstructure in both rheo- and conventional HPDC samples contains α -Al phase and Al-Si eutectic phase.

As a result of the stirring during the slurry preparation, the usual dendritic structure is absent in the rheocast alloy (Figures 1 [a] and [b]) ⁴⁴⁻⁴⁶. While the microstructure of the conventional HPDC alloy (Figure 1 [c]) may occasionally reveal a dendritic structure. Besides, in the semisolid microstructure, two different sizes of α -Al grains are present. The coarser α -Al grains (α_1 -Al) are solidified during the slurry preparation, at the higher temperature, and they form the solid part of the slurry (solidification from 675 to 610 $^\circ\text{C}$ ⁴²). The finer α -Al grains (α_2 -Al) are formed during the solidification stage, at a higher cooling rate, inside the mold. The primary α_1 -Al phase is characterized by low solubility of alloying elements, therefore, the remnant liquid part of the slurry (α_2 -Al the eutectic phase) has a higher concentration of these elements ⁴⁷.

Due to the segregation of the liquid and solid part of the initial slurry, the thinner rheocast sample (Rh_l (Figure 1 [a])), is likely to contain a higher fraction of α_2 -Al grains compared to the thicker one (Rh_s (Figure 1 [b])). In addition, as a result of the lower cooling rate in thicker parts, α_2 -Al grains are coarser in the sample Rh_s . This phenomenon can occur for the conventional cast sample as well ⁴⁸. The effect of thickness and the geometry of the mold (component) on the segregation of liquid and solid parts of the slurry (microstructure) is addressed in an earlier publication ²⁵.

The backscattered (BSE) SEM image (Figure 1 [d]) depicts the morphology of the eutectic silicon and the presence of needle shape IM particles inside the eutectic area, for the sample Rh_l . These phases are located at the aluminum grain boundaries. The mapping analysis of this image is provided to show the distribution of Al, Si, Fe, and Mg. Based on the morphology and distribution of Fe (Figure 1 [g]), the intermetallic particles are likely to be iron-rich β -AlFeSi ^{4,7}. According to Figure 1 (h), the grain boundaries also contain Mg. Unlike the results reported by Arrabal et al. ⁴ on A356 (UNS A13560), the morphology and distribution of secondary phases (the eutectic silicon and IM particles) are not different in these conventional and the semisolid cast alloys ^{42,49}.

Electrochemical Behavior

The representative results of anodic and cathodic polarization tests in 0.01 M and 0.6 M NaCl solutions are presented in Figure 2.

Regarding Figure 2 (a), in 0.01 M NaCl, the anodic responses are characterized by a passive region and then passivity breakdown. The breakdown potential ($-0.56 \text{ V}_{\text{Ag/AgCl}}$, as shown in the graph), is similar and quite repeatable for the three samples.

According to Figure 2 (b), at a higher chloride concentration, passivity breakdown occurs at a lower potential ($-0.68 \text{ V}_{\text{Ag/AgCl}}$, as shown in the graph). It seems that the thinner rheocast sample (Rh_l), with a higher

fraction of liquid part of the slurry, presents a small passive range, while for the other two samples corrosion commences at the OCP. The passivity breakdown potential is similar for all samples.

Table. 3 summarizes the values of breakdown potential (E_{BD}) for different samples in the two NaCl solutions. According to these results and the low variation of the data (presented as standard deviation values), no significant difference in the anodic behavior of samples exists.

The cathodic polarization curves of the three samples in 0.01 M NaCl solution (depicted in Figure 2 [c]) present relatively higher current densities for the rheocast samples (Rh_I and Rh_S) during the ORR compared to the conventional cast sample (L). This test was repeated at least five times for each sample to assure the reliability of the data. The results of OCP monitoring for 24 h (during the EIS test) in NaCl solutions (0.01 M, 0.05 M, 0.1 M, and 0.6 M) are presented in Figure 3. The presented data is the average values of three measurements for each sample.

According to this figure, at the beginning of the immersion in all solutions, the thicker rheocast sample (Rh_S), potentially with a higher percentage of primary α_1 -Al grains (the solid part of the slurry), shows the least noble OCP value. Samples Rh_I and L are next in the ranking towards nobler OCP values. For all samples, the OCP values increase during the first hour of immersion, which can suggest spontaneous passivity⁵⁰. In addition, the OCP values show some fluctuations until ~ 4 to 5 h.

Considering relatively high values of standard deviations (shown as the error bars in Figure 3), no systematic difference is observed in the OCP values of these samples.

Bode presentations of EIS spectra (performed at OCP) after 24 h immersion in NaCl solutions are presented in Figure 4. Each measurement has been repeated three times and the representative data are presented.

These EIS results seem similar for the different samples. Some scattering is observed at the low frequency range which can be associated with the constant change of the active surface area during the localized corrosion⁴. The effect of chloride concentration on the resistance of the solution is obvious at the high frequency range⁵¹. The presence of more than one time-constant is clear from the phase angle spectra (the inserted graphs in Figure 4). Considering the heterogeneous nature of Al-Si surface, the equivalent model circuit corresponding to the EIS data consists of parallel pathways for charge transfer reactions at the active anodic sites (e.g. trenching, pitting), through the aluminum oxide, and cathodic reactions (e.g. ORR) occurring on the iron-rich IM particles and the eutectic silicon phase⁵².

It is noted that the performed EIS (and also the polarization test) is, in fact, a global measurement. It presents the average behavior resulting from all the electron transfer reactions occurring on the alloy's surface and identification of these reactions locally is not possible in this way.

Considering that the real and imaginary components of Warburg elements are inversely proportional to the square root of the applied frequency, their contributions to the impedance at intermediate frequencies are minor. Therefore, at these frequencies, the circuit (Figure 5) reduces to the solution resistance (R_s) in series with a simple parallel resistive-capacitive circuit (total resistance and capacitance [R_{tot} and C_{tot}])⁵³.

As in a parallel circuit, R_{tot} and C_{tot} are given as follows:

$$1/R_{tot} = (1 - s - i - a)/R_{ox} + s/R_{Si} + i/R_{IM} + a/R_a \quad (1)$$

$$C_{tot} = (1 - s - i - a)C_{ox} + sC_{Si} + iC_{IM} + aC_a \quad (2)$$

The small letters (s, i, and a) are related to the area fraction of each component on the surface.

Terms related to the presence of corrosion products probably should be added to the equations (1) and (2) after long immersion times (≥ 12 h, as it will be shown later).

R_a (polarization resistance related to the anodic reactions) and R_{IM} are considerably lower compared to R_{ox} ($10^5 \Omega \cdot \text{cm}^2$ for pure aluminum in the passive region⁵²) and R_{Si} (the resistivity of silicon is $10^5 \mu\Omega \cdot \text{cm}$ (significantly higher than that of iron [$9.6 \mu\Omega \cdot \text{cm}$]) at 20°C ⁵⁴). Therefore, R_{tot} is dominated by anodic and cathodic reactions mostly related to the micro-galvanic corrosion.

On the other hand, C_{ox} is significantly lower compared to C_a , therefore an increase in the localized corrosion activity results in a noticeable increase in C_{tot} ⁵².

C_{tot} is determined from the slope of the imaginary component of admittance ($Y(\omega)''$) versus frequency (ω) using linear regression analysis⁵³:

$$C_{tot} = -jY(\omega)''/\omega \quad (3)$$

$Y(\omega)''$ is calculated as follows:

$$Y(\omega)'' = \frac{-Z(\omega)''}{Z(\omega)'^2 + Z(\omega)''^2} \quad (4)$$

Where $Z(\omega)'$ and $Z(\omega)''$ are real and imaginary components of impedance, respectively. It should be noted that R_s (the real component of the impedance at the high-frequency phase angle minimum) is subtracted from $Z(\omega)'$ prior to the calculation of $Y(\omega)''$. While calculating C_{tot} , regression coefficients were usually 0.98-0.99. R_{tot} is calculated by integration of $Z(\omega)''$ from infinite frequency to the frequency associated with the maximum value of $Z(\omega)''$, according to the Kramers-Kronig expression⁵⁵:

$$R_{tot} = \frac{4}{\pi} \left| \int_{\infty}^{\ln \omega_{max}} Z(\omega)'' d \ln \omega \right| \quad (5)$$

Figures 6 and 7 respectively present the variation in R_{tot} and C_{tot} with the immersion time in different NaCl concentrations. These results are the average values of three measurements for each sample in each solution.

In 0.01 M NaCl a small difference in the values of R_{tot} of various samples is observed (Figure 6 [a]). Rh_S presents the highest resistance values at this concentration. However, considering the values of standard deviations (shown as the error bars in the graph), the difference among the samples can be neglected.

At higher NaCl concentrations (0.05 M, 0.1 M, and 0.6 M, Figures 6 [b] through [d]), all samples behave almost the same.

In all conditions, R_{tot} decreases as a function of immersion time indicating to a higher charge transfer over the surface.

Concerning the values of C_{tot} , in 0.01 M and 0.05 M NaCl solutions (Figures 7 [a] and [b]) a slight increase with the exposure time is observed (except for the sample Rh_S in 0.01 M) but all samples behave almost similarly.

At higher concentrations (0.1 M and 0.6 M, Figures 7 [c] and [d]), C_{tot} increases more remarkably with the immersion time. It seems that the rheocast samples (Rh_I and Rh_S) present higher C_{tot} in comparison to the conventional cast sample (L). As mentioned earlier this can be an indicator of progressive localized corrosion.

Figure 8 presents SEM images (paired secondary electron (SE) and BSE) of the sample Rh_I immersed in 0.6 M NaCl solution (at OCP) for 1 h. Figures 8 (a) through (d) present the initial stage of the localized corrosion, which evidently starts at the interface of aluminum/iron-rich IM particle located inside a eutectic region. Many initial breakdown sites were checked and always a trace of iron-rich IM particles was found.

In A356 (UNS A13560), a potential difference of ~ 310 -360 mV between the aluminum matrix and β -AlFeSi and ~ 260 -280 mV

between the aluminum matrix and silicon has been reported ⁴. Therefore it is expected that the anodic breakdown caused by the galvanic coupling between the aluminum matrix and the cathodically active particle initiates the corrosion ³. The corrosion continues in the eutectic region, dissolving aluminum in this region. The presence of a defective oxide layer at the interface of aluminum with the secondary phases facilitates the breakdown.

Figures 8 (e) and (f) show an area with more developed corrosion attack in a eutectic region with several intermetallic particles. The morphology of the eutectic silicon and IM particles are well observed in the SE image (Figure 8 [e]). According to this image the corrosion progresses far from the starting interface. Due to the lower electric resistance of Iron-rich IM particles compared to the eutectic silicon, more cathodic reactions is expected on them.

Cathodic trenching due to a higher pH (as a result of ORR) can be also occurring at the localized attack sites ¹¹.

The representative backscattered SEM images of the sample Rh₁ after 1 h, 6 h and 12 h immersion in 0.6 M NaCl solution are presented in Figure 9. For 1 h immersion time, the presented SEM image in Figure 9 is at lower magnification compared to those in Figure 8 to show the overall surface and not just the corrosion initiation sites.

According to these images, the number and the extent of the localized attacks increase by the immersion time. No precipitation of corrosion product is observed after 12 h immersion.

Figure 10 presents backscattered SEM images of the samples Rh₁, Rh_s, and L after 24 h immersion in 0.01 M and 0.05 M NaCl solutions. After one day, precipitation of corrosion products is observed. Additionally, as it can be seen in Figure 10 (d), for the rheocast alloy, the localized corrosion may occur preferentially at α_2 -Al grain boundaries (solidified from the liquid part of the slurry). This can be easily observed by comparing the localized corrosion on the conventional cast sample (Figure 10 [i]) with no preferential sites. However, for the rheocast sample, some of the primary α_1 -Al particles are corroded at their borders as well.

Accumulation of corrosion products forms rings around the active sites. The corrosion products show two types of morphology: a fine powdery and a gel (dry mud)-like morphology. At the center of a corrosion ring, part of the gel-like layer is removed and Figure 10 (b) provides SEM image at a higher magnification to show the anodic dissolution of aluminum.

For all samples, sites of accumulation of corrosion products and the uncovered localized micro-galvanic corrosion exist at both NaCl concentrations. For the sample Rh₁ immersed in 0.05 M NaCl solution, these are featured in Figures 10 (c) and (d), for the sample L in Figures 10 (h) and (i), and for the sample Rh_s in an overall view (at a lower magnification) in Figure 10 (f).

The morphological view of an initial micro-galvanic corrosion site on the surface of the sample Rh_s is presented in the SEM (SE) image inserted in Figure 10 (e). Similar initiation site to those previously shown in Figure 8 is observed here.

The morphology of corrosion products can be seen more clearly on the surfaces exposed to the more concentrated solution. Figure 11 depicts the surface of the samples Rh₁, Rh_s, and L after 24 h immersion in 0.6 M NaCl solution.

Similar corrosion features including trenching around the eutectic silicon and iron-rich IM particles and corrosion rings are observed. No particular difference among the corroded surfaces of different samples is detected.

Figure 11 (d) presents the circumferential trench around a eutectic area containing IM particle on the surface of the sample Rh_s. The EDXS analysis of the indicated area in this figure confirms the high concentration of alloying elements (Fe, Mg, and Cu).

The results of EDXS analysis on different representative areas on the corrosion products (shown in Figure 11) are provided in Table 4.

DISCUSSION

The present and previous ²⁵ microstructural studies on these Al-Si alloys show that the rheocasting process does not necessarily alter the distribution or morphology of the secondary phases (the eutectic silicon and IM particles). However, it produces two α -Al grains with different sizes which their fractions (and sizes), as shown in Figure 1, can be influenced by the thickness of the sample.

In addition, during the rheocasting process, the two-step solidification can cause a silicon concentration profile in the primary α_1 -Al globular grains. It is shown that due to a back diffusion from adjacent regions richer in silicon, the silicon concentration close to the surface of α_1 -Al increases to a higher value than that at the center of the particle ⁵⁶. This high silicon concentration at the grain boundaries can decrease the potential difference between the α_1 -Al grains and the secondary phases. However, at the center of α_1 -Al grains pitting may occur more easily.

According to the results of the polarization test in two sodium chloride concentrations (Figures 2 (a), (b) and Table 3), the rheocast and conventional cast alloys show similar anodic responses and similar breakdown potentials. This can imply that the composition of the passive layer is similar for these two alloys. The same can be stated for the rheocast samples of different thicknesses. Similar OCP values are also observed for the different samples in NaCl solutions of various concentrations during 24 h (Figure 3).

A difference in behavior is noticed in the cathodic responses (Figure 2 [c]), where the rheocast samples (Rh₁ and Rh_s) show enhanced ORR kinetics. This might be related to a higher content of alloying elements segregated in the liquid part of the slurry in the rheocast samples.

Both rheocast samples contain a combination of α_1 -Al and α_2 -Al grains (maybe with different fractions). While the conventional cast sample contains α -Al grains. Due to the different conditions of solidification at various temperatures from a melt (L) or a slurry (R), the three kinds of α -Al grains, based on the concentration of alloying elements, can be ordered as follows: α_1 -Al < α -Al < α_2 -Al. Macroscopically α_1 -Al + α_2 -Al lead to the same overall composition of α -Al. The eutectic phase in the rheocast samples will be richer in alloying elements such as iron as it is solidified from the liquid part of the slurry, with a higher concentration of these elements segregated in it. While the conventional cast sample solidifies directly from the initial melt (with the measured composition) ⁵⁶. This difference in the microstructure can influence the kinetics of the cathodic reaction.

As observed in Figures 8 and 9, from the first hour of exposure to the NaCl solution (at OCP) corrosion attacks at the interface of aluminum with the iron-rich IM particles start. As the iron-rich particles are located inside the eutectic region (as shown in Figure 1 [d] and Figure 8), this localized corrosion further grows into this region. Some pits inside big α_1 -Al particles are also seen (Figure 9 [a]).

It should be noted that progressive corrosion is supported by the continues silicon network in the eutectic cell (as additional cathodes ⁴¹) as it grows as a branched structure (as partially shown in Figures 8 [e] and [f]). The overall connection of the silicon phase depends on the amount of eutectic fraction. The iron-rich IM particles, from which the localized corrosion initiates, are not connected but they may precipitate near each other (Figures 8 [e] and [f]).

Evidently, the micro-galvanic corrosion extends by the immersion time. The enhanced ORR kinetics on the cathodic sites ⁵⁷ and specifically on iron-rich IM particles in this alloy ⁴² can feasibly increase the local pH and exacerbate aluminum dissolution ¹². Furthermore, as the corrosion rate increases by the chloride concentration, which has no effect on ORR kinetics, it can be concluded that cathodic dissolution of aluminum is not the sole cause of trenching. Inversely, in this case anodic trenching at the micro-galvanic sites can be suggested as the main corrosion mechanism.

Accordingly, the decrease in the values of R_{tot} extracted from the EIS results (Figure 6), indicates progressive localized corrosion which increases by the chloride concentration and the immersion time. The decrease in R_{tot} can also imply that the oxide becomes thinner or its dielectric constant increases⁵³.

The initial R_{tot} values are usually higher for the samples Rh_s and L, however, they decrease by the exposure time leading to similar values to those of the sample Rh_l at the end of the test. As stated earlier, due to the scattering of the data, no meaningful difference between the total resistance values of the different samples is claimed here.

The decrease in R_{tot} is accompanied by an increase in the total capacitance as localized corrosion attacks are formed and increased. Comparing the values of C_{tot} when the samples are immersed in the more concentrated NaCl solutions (0.1 M and 0.6 M), a more significant increase with the immersion time and a more pronounced difference between the rheocast samples (Rh_l and Rh_s) and the conventional cast sample (L) are observed (Figures 7 [c] and [d]). This can be due to the fact that the breakdown of the passive oxide layer is sensitive to the chloride concentration and increases when the solution is more concentrated. In this condition, more localized corrosion is expected. For the rheocast samples, the total capacitance values increase faster and are higher compared to those of the conventional cast sample proving the formation of more sites of passivity breakdown due to the presence of the liquid part of slurry with faster ORR kinetics. This difference, however, is not a decisive factor in establishing a significant distinction in the corrosion behavior of the rheocast and the conventional cast samples.

After 24 h immersion (in solutions of different concentrations), corrosion product precipitated in the form of rings are observed (Figures 10 and 11). In the case of other aluminum alloys such as AA2024 (UNS A92024), this type of corrosion is called “co-operative corrosion” and is attributed to the clustering of IM particles^{57, 58}. Typical co-operative corrosion sites create corrosion rings.

As mentioned before, the morphology of corrosion products in the active rings shows two types:

- (i) A domed cracked gel (dry mud)- like layer, which seems to be the first layer of the corrosion product
- (ii) A fine powdery layer which apparently is placed on top and around the domed layer

The corrosion products initially dissolve in the solution (Figure 9), however, some of them deposit in longer immersion times. The dissolution may be due to the alkaline pH over the cathodic sites (the iron-rich IM particles and the eutectic silicon phase) that can reach as high as 9.5¹² and it can dissolve any hydrated aluminum oxide product⁸. According to Hughes et al.⁵⁸ domes of corrosion products indicate the sites of H_2 evolution. The cracked morphology of these corrosion products can be also the result of dehydration⁵⁸ or even simply the air evacuation during SEM examination.

The difference between the morphology of domes (gel-like layer) and fine corrosion products can be due to the fact that they have been formed under different solution conditions such as compositional or pH differences.

The EDXS results (Table 4) indicate that both types of corrosion products contain chloride. While a low amount of silicon (and in one case magnesium) was detected in the composition of corrosion products, iron was always absent, apparently not dissolving from IM particles. Silicon oxide is soluble in the alkaline environment⁵⁹.

The alkaline pH due to the intense cathodic activity inside the corrosion rings results in the formation of the gel (dry mud)-like layer of corrosion products within them. This gel layer can be a diffusion barrier for the corrosion reactants.

The high pH value over the corrosion rings inhibits the precipitation of the other type of corrosion products. While the pH drops around the periphery of these active corrosion sites leading to the deposition of powdery corrosion products. With further growth, this fine powdery corrosion layer can cover the gel layer. As observed in Figures 10 and 11, the size of corrosion rings is more than 50 μm and Hughes et al.⁵⁸ mentioned that the maximum distance from a cathodic IM particle for the pH to drop (below 9) is $\sim 25 \mu\text{m}$. Therefore, in a similar case, they have considered the possible effect of convection currents caused by H_2 evolution on the dispersion of anolyte solution into the bulk solution above the corrosion ring.

Although in the case of Al-Si alloy, the cathodic sites are the iron-rich IM particles and the eutectic silicon phase. Therefore, the mentioned distance (and subsequently the size of corrosion ring) can be more.

Figures 10 (a) and (g) display the fact that a big corrosion ring might be the result of the combination of several active sites, which can be joined when the sample is immersed in a more concentrated solution. The presence of some fine powdery corrosion products deposited far from the ring (or active sites) on the alloy matrix is visible in Figures 10 (g) and (h). As it was mentioned earlier, these products have probably been dragged away from the active corrosion site due to either a lower pH on the matrix or the conversion currents caused by H_2 evolution.

On the surface of all samples (both the conventional and rheocast (of different thicknesses)), some casting defects were present. Their appearance and size are quite different and detectable from any pit. While immersing in the NaCl solutions, these defects usually acted as the center of corrosion rings (indicated in Figure 11 [a]). It can be observed that fine powdery corrosion products are mostly deposited out of these flaws.

Here it should be re-emphasized that the OCP measurements, the polarization and the EIS tests have been repeated at least three times for each sample to avoid the effect of inhomogeneity on the final judgment about the corrosion behavior.

No meaningful difference in the morphology and composition of the corrosion products of the samples cast by the conventional and Rheo-HPDC techniques was detected.

The proposed precipitation pattern of the corrosion products on the surface of Al-Si alloy is schematically depicted in Figure 12.

As shown in this figure, chloride ions have a significant effect on the breakdown of the passive oxide layer activating and accelerating micro-galvanic corrosion in the eutectic areas containing iron-rich IM particles at the grain boundaries. As schematically shown in Figure 12, the center of an active corrosion ring with an environment of alkaline pH is covered by the gel (dry mud)-like layer of corrosion product, while the surrounding areas with lower pH values are covered by fine powdery corrosion products. As mentioned earlier, at the final precipitation stage the fine corrosion products may shield the gel (dry mud)-like layer (Figure 11 [e]). At this step some corrosion sites can be probably less active due to the accumulation of the corrosion deposits.

The corrosion of the studied (Rheo)-HPDC Al-Si alloys can involve three steps:

- (i) Micro-galvanic corrosion starts at the aluminum/iron-rich IM particle interface.
- (ii) Extensive corrosion progresses inside the eutectic regions.
- (iii) At the last step (at high NaCl concentrations and after long immersion times), the active corrosion sites can be mostly covered by the corrosion products.

The presented results suggest that micro-galvanic corrosion is the dominant corrosion process for the studied Al-Si alloys. An improved ORR kinetics is observed on the surface of rheocast samples compared to the conventional cast sample. However, the overall

corrosion behavior (based on both anodic polarization and EIS tests) seems comparable for all samples. As shown, the distribution and morphology of the iron-rich IM particles and the eutectic silicon phase are not significantly changed by the casting process. This can suggest that all samples have enough and comparable active micro-galvanic corrosion sites and therefore they electrochemically corrode the same.

Even though the results reported by Arrabal et al. ⁴ show that a lower potential difference between the aluminum matrix and secondary phases in rheocast A356 (UNS A13560) alloy (as a result of Si-enrichment of the α -Al phase during the rheocasting process) leads to less penetration of the corrosion attack, the present results do not confirm such an effect on the corrosion resistance. It should be also noted that the alloy studied in the present research contains a lower percentage of silicon (4.5 %) compared to the rheocast A356 (UNS A13560) with 6.8 % silicon which may influence the results. Furthermore, in their case ⁴, the distribution and morphology of β -AlFeSi intermetallic particles are slightly modified in the rheocast alloy due to a higher Sr content, which can affect the micro-galvanic corrosion behavior. The alloy studied in this research does not contain any modifier.

The results of this paper show that the effect of the rheocasting process on the corrosion properties probably depends on the composition of the alloy and can be negligible for alloys with a low concentration of alloying elements.

CONCLUSIONS

Corrosion behavior of Al-4.5 %Si alloy cast by the conventional and semisolid HPDC (Rheo-HPDC) techniques was studied and compared in NaCl solutions of different concentrations. The following conclusions can be drawn:

- According to the results of the potentiodynamic polarization test, all samples show similar breakdown potential. By increasing the chloride concentration from 0.01 to 0.6 M, this potential is reduced by 0.12 V.
- An accelerated ORR kinetics is recorded for the rheocast samples compared to the conventional cast sample. This can be due to the presence of the liquid part of the slurry, with segregated alloying elements, in the rheocast samples.
- Micro-galvanic corrosion starts from the aluminum/iron-rich IM particle interface and grows into the eutectic region.
- The EIS results do not reveal any significant difference between the corrosion resistance of the rheocast and conventional cast samples. However, the values of total capacitance show more active anodic sites for the rheocast samples.

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FIGURE CAPTIONS

FIGURE. 1. OM image of the sample (a) Rh_i, (b) Rh_s, and (c) L. (d) SEM (BSE) image of the sample Rh_i. elemental mapping of (e) Al, (f) Si, (g) Fe, and (h) Mg of the SEM image in (d).

FIGURE. 2. (a) and (b) the anodic polarization curves of the Al-Si samples in 0.01 M and 0.6 M, respectively. (c) the cathodic polarization curves of the Al-Si samples in 0.01 M NaCl solution.

FIGURE.3. Average OCP values of the Al-Si samples versus time immersed in (a) 0.01 M, (b) 0.05 M, (c) 0.1 M, and (d) 0.6 M NaCl solution (due to overlapping of the standard deviation bars, to make it clearer for the reader, these bars are shown only in the one direction).

FIGURE.4. EIS spectra of the samples Rh_i, Rh_s, and L after 24 h immersion in (a) 0.01 M, (b) 0.05 M, (c) 0.1 M, and (d) 0.6 M NaCl solution.

FIGURE. 5. Impedance model circuit for the (Rheo)-HPDC Al-Si alloys.

FIGURE. 6. Variation of R_{tot} with the exposure time for the Al-Si samples immersed in (a) 0.01 M, (b) 0.05 M, (c) 0.1 M, and (d) 0.6 M NaCl for 24 h (due to overlapping of the standard deviation bars, to make it clearer for the reader, these bars are shown only in the one direction, in some cases, the standard deviation bar is smaller than the symbol).

FIGURE. 7. Variation of C_{tot} with the exposure time for the Al-Si samples immersed in (a) 0.01 M, (b) 0.05 M, (c) 0.1 M, and (d) 0.6 M NaCl for 24 h (due to overlapping of the standard deviation bars, to make it clearer for the reader, these bars are shown only in the one direction, in some cases, the standard deviation is zero).

FIGURE. 8. (a), (c), and (e) SEM (SE) and (b), (d), and (f) SEM (BSE) images of the sample Rh_i after 1 h immersion in 0.6 M NaCl solution.

FIGURE. 9. SEM (BSE) image of the sample Rh_i after (a) 1 h, (b) 6 h, and (c) 12 h immersion in 0.6 M NaCl solution.

FIGURE. 10. SEM (BSE) image of the sample Rh_i in (a) and (b) 0.01 M, (c) and (d) 0.05 M NaCl. SEM (BSE) image of the sample Rh_s in (e) 0.01 M and (f) 0.05 M. SEM (BSE) image of the sample L in (g) 0.01 M, (h) and (i) 0.05 M NaCl, all after 24 h immersion (the magnified image in (e) is SEM (SE)).

FIGURE. 11. SEM (BSE) image of the sample (a) and (b) Rh_i, (c) and (d) Rh_s and (e) and (f) L after 24 h immersion in 0.6 M NaCl solution (the magnified image in (c) is SEM (SE)).

FIGURE. 12. The possible precipitation pattern of the corrosion products on (Rheo)-HPDC Al-Si alloys.

TABLE CAPTIONS

TABLE. 1. Composition of the Aluminum-Silicon Alloy

TABLE. 2. Designation of Samples

TABLE. 3. Average Breakdown Potential of the Different Samples in 0.01 and 0.6 M NaCl Solutions

TABLE. 4. Results of EDXS Analysis of the Selected Areas in Figure. 11

TABLE. 1

Alloying element	Si	Fe	Cu	Mn	Mg	Zn	Al
Weight percentage	4.50	0.481	0.137	0.019	0.580	0.035	Bal

TABLE. 2

Name of the sample ^(A)	Casting technology	Thickness
Rh _s	Rheo-HPDC	4 mm
Rh _l	Rheo-HPDC	1.5 mm
L	HPDC	1.5 mm

^(A) L: HPDC, Rh: Rheo-HPDC, s and l: solid and liquid parts of the slurry, respectively

TABLE. 3

Sample	E _{BD} ^(A) in 0.01 M NaCl (V _{Ag/AgCl})	E _{BD} ^(A) in 0.6 M NaCl (V _{Ag/AgCl})
Rh _s	-0.556±0.012	-0.687±0.003
Rh _l	-0.563±0.006	-0.685±0.005
L	-0.571±0.012	-0.686±0.008

^(A) Average value of total five measurements

TABLE. 4

Area of analysis	Al (wt%)	Si (wt%)	Fe (wt%)	Mg (wt%)	Cu (wt%)	O (wt%)	Cl (wt%)	Na (wt%)
(b)-1	30.9	0.5	-	-	-	45.6	23.0	-
(b)-2	28.1	0.5	-	-	-	39.3	26.0	6.2
(c)-1	69.0	1.2	-	0.5	-	25.8	3.3	0.1
(c)-2	35.2	0.4	-	-	-	54.7	9.3	0.5
(d)	27.6	16.8	7.1	1.2	4.0	21.1	6.3	15.9
(f)-1	36.7	0.2	-	-	-	48.7	14.4	-
(f)-2	38.7	1.7	-	-	-	43.3	15.8	0.6

FIGURE 1

FIGURE 2

FIGURE 3

FIGURE 4

FIGURE 5

FIGURE 6

FIGURE 7

FIGURE. 8

FIGURE. 11

FIGURE. 9

FIGURE. 12

FIGURE. 10