Investigation of corrosion behavior of SSM-HPDC aluminum-silicon alloys

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Abstract

Rheocasting process integrated with High Pressure Die Casting (Rheo-HPDC) as a new casting method has established itself as a promising technology to produce high quality components and to cast thin walls. However, in Semi-Solid Metal (SSM) casting method, surface liquid segregation phenomenon exists and it can effect properties such as wear and corrosion resistance. In the present study, electrochemical behaviour of two low Al-Si alloys, (2.5 and 4.5 wt. %), produced by Liquid-HPDC and Rheo-HPDC methods were investigated and compared. The microstructure of these alloys was investigated using optical and scanning electron microscopies. Effect of the percentage of silicon and casting technology on the microstructure and the corrosion resistance of the samples were examined by means of polarization test and electrochemical impedance spectroscopy (EIS) measurements in diluted Harrison solution both on as-cast and polished surfaces. The microstructural inhomogeneity in Rheo-HPDC samples was observed as different fraction of the primary α-Al to the eutectic phase from the surface to the bulk. The microstructure of Liquid-HPDC materials revealed a dendritic structure. The corrosion resistance of the sample was mainly dependent on the percentage of Si and the distance from the surface.

Key words: Aluminium alloys, semi-solid metal process, high pressure die casting, electrochemical evaluation.

1. Introduction
High pressure die casting (HPDC) is the process that is primarily used for manufacturing the majority of Al and Mg alloys applications, due to its low cost and high efficiency [1]. One of the most important disadvantages of this process is gas entrapment during the high speed mold filling step [2].

Semi-solid metal (SSM) casting is mostly considered as a process which increases the inhomogeneity of the microstructure in the final component, in comparison to conventional HPDC process, but allows to produce more complex geometries. This phenomenon arises from the fact that the formation of primary α-Al phase during the slurry preparation, characterized with low solubility of the alloying elements, increases the amount of these elements in the remnant liquid phase [3]. In addition, during the filling process both separation of solid and liquid phases in the gating system (longitudinal macrosegregation) [4] and the tendency of solid particles to migrate to the core of the component (transverse macrosegregation) [5, 6] increase the inhomogeneity of the final component. The inhomogeneous microstructure leads to variations of properties in different locations of the component either in microscopic or macroscopic scale.

SSM-HPDC technique provides parts with many advantages such as low porosity, heat treatability and high performance [7]. In addition, such a technology introduces a new opportunity to enhance the performance of a component, which is impossible to achieve by traditional manufacturing methods. The way towards such an improvement requires both the capability of this process to produce components with a complex geometry and the possibility to cast alloys with reduced amount of alloying elements, which adversely affect material properties for specific applications such as thermal conductivity for telecommunication applications [8]. Rheocasting is one of the semisolid casting processes. Proper materials for Rheo-HPDC process are limited to those which have good castability with HPDC process and also have low sensitivity of the solid fraction to variations of temperature. In this case hypoeutectic Al-Si alloys in the range of 5-8 wt. % Si content are the suitable choices for this process [3].

Limitation of scientific and technical knowledges makes it essential to evaluate properties and behaviour of materials produced by means of Rheo-HPDC process under different operational circumstances. Corrosion resistance as one of the critical properties of materials, for outdoor applications, is an interesting subject either for researchers or industries.

There are some studies on corrosion behavior of semi-solid casted Al-Si alloys such as those performed by Bastidas et al [9], Yu et al. [10], Park et al.[11], Tahamtan et al.[12, 13], Moller et al [14], Masuku et al. [15] and Arrabal et al [16]. Most of the researches in this field are
focused on alloys A356 [11-13, 16] and A 357 [9, 10]. There are also studies on alloys 7075 and 2024 [15]. These studies mostly have emphasized on the pitting attack in Chloride containing solutions in the eutectic regions, especially at the interface between the silicon particles and the α-Al phase, and demonstrated that primary α-Al grains are mostly protected from corrosion. Bastidas et al [9] emphasized on the cathodic properties of the intermetallic compounds which accelerate the corrosion process in the eutectic region. This is due to the fact that corrosion as an electrochemical process, depends on the relationship between the potential of microstructural phases in a single alloy. Severity and morphology of corrosion is influenced by the compositions of solid solutions and second phases and also their morphology, density and distribution [17].

Arrabal et al [16] showed that the deleterious effect of intermetallic compounds on the corrosion properties of rheocast A356 alloy is reduced. They demonstrated that this effect is mainly due to the reduced potential differences between Si/iron-intermetallics and the eutectic aluminium phase which is richer in Si due to the nature of rheocast process. Therefore they reported an improvement in corrosion properties in comparison to the traditional cast A356 alloy. The improvement in the corrosion resistance of A 356 alloy cast by semisolid process was also reported by Park et al [11] and Tahamtan et al [12]. They attributed this improvement to the reduced area ratio of noble silicon particles to less-noble eutectic aluminum phase around silicon particles. It can be concluded that the volume fraction, size, shape and area ratio of eutectic silicon particles to the aluminum phase define the corrosion behavior of aluminum alloys processed by semi solid-casting [9-16]. It is also shown that the interface between iron-containing intermetallics and the eutectic α-Al phase is a preferred location for corrosion as well [8].

In the present study, effect of two casting technologies, Rheo-HPDC and Liquid-HPDC on the microstructure characteristics and the corrosion behavior of two Al-Si alloys is investigated. More importantly, the effect of transverse macrosegregation on the electrochemical responses of these alloys is examined by running electrochemical measurements on their as-cast surfaces and the bulk material.

2. Experimental

2.1. Materials and casting

Cast samples were produced with a 400 tons HPDC machine equipped with an automated RheoMetalTM slurry generator. An experimental cavity filter (Fig. 1), demonstrator for
telecom applications, was cast. Both Rheo- and Liquid-HPDC samples were casted with 2 alloy compositions, alloy 2.5 and alloy 4.5, which differ in the Si content. Measured compositions of these alloys are presented in Table 1. The alloys melts were prepared in a resistance furnace at a temperature of 675 °C. Ladling was done using a standard cast iron ladle and the shot weight was approximately 5 kg. The Enthalpy Exchange Material (EEM) as a cooling agent was immersed into the melt in an amount of 5-6 % of the shot weight, while stirring at 900 rpm, to generate a slurry.

In order to eliminate the effect of longitudinal macrosegregation [4] samples for characterization are taken only from the region near the feeding gate. Samples are taken from the thin walls, representing the as-cast surface and from the thick plate, underneath the component, representing the bulk material. It is worth mentioning that, in the case of samples which are taken from thicker plate the surfaces were grounded to the middle of each sample to reach the bulk microstructure. The detailed designation symbols for different samples are presented in Table. 2.

![Fig. 1. The cavity filter.]

**Table. 1. Measured composition (wt. %) of 2 alloys**

<table>
<thead>
<tr>
<th>Name</th>
<th>Si</th>
<th>Fe</th>
<th>Cu</th>
<th>Mn</th>
<th>Mg</th>
<th>Zn</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alloy 2.5</td>
<td>2.41</td>
<td>0.462</td>
<td>0.131</td>
<td>0.019</td>
<td>0.58</td>
<td>0.038</td>
<td>96.338</td>
</tr>
<tr>
<td>Alloy 4.5</td>
<td>4.5</td>
<td>0.481</td>
<td>0.137</td>
<td>0.019</td>
<td>0.58</td>
<td>0.035</td>
<td>94.223</td>
</tr>
</tbody>
</table>

**Table. 2. Designation of samples**

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Section</th>
<th>Rheo-HPDC</th>
<th>Liquid-HPDC</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5</td>
<td>Thin wall surfaces</td>
<td>2.5 R</td>
<td>2.5 L</td>
</tr>
<tr>
<td></td>
<td>Thick plate (bulk)</td>
<td>2.5 RB</td>
<td>2.5 LB</td>
</tr>
<tr>
<td>4.5</td>
<td>Thin wall surface</td>
<td>4.5 R</td>
<td>4.5 L</td>
</tr>
<tr>
<td></td>
<td>Thick plate (bulk)</td>
<td>4.5 RB</td>
<td>4.5 LB</td>
</tr>
</tbody>
</table>
2.2. Microstructural studies

For metallographic analysis, samples were wet ground through successive grinding using silicon carbide abrasive papers from P500 to P4000, followed by alumina polishing to mirror finish. The 10% NaOH etchant was used to reveal the constituents of the microstructure. The microstructure of the surfaces and the bulk of the components were studied using light optical (LOM) and scanning electron microscopies (SEM) (JSM-IT300). Energy-dispersive X-ray spectroscopy (EDXS) was used to measure the composition of the different phases.

2.3. Electrochemical measurements

A computer-controlled potentiostat (Parstat 2273) connected to a three-electrode cell was used for the electrochemical measurements. The working electrode was the test material with an immersed area of 1 cm² and platinum and silver/silver chloride (Ag/AgCl 3M KCl) electrodes were used as the counter and reference electrodes, respectively. Potentiodynamic polarization test was performed using diluted Harrison solution (0.5 g/L NaCl and 3.5 g/l (NH₄)₂SO₄), with and without chloride ions. The sweep rate was 0.1666 mV/s and the delay time before the test was 600 s. Electrochemical impedance spectroscopy (EIS) measurements were also conducted during 24 hours of immersion in diluted Harrison solution with chloride ions at the room temperature. The frequency ranged from 100 kHz to 10 mHz with 36 points/decade and the amplitude of the sinusoidal potential was 10 mV with respect to the OCP. EIS and potentiodynamic polarization measurements were conducted on as-cast surfaces and the bulk to investigate the effect of transverse macrosegregation. Repeatability of the results was tested by conducting each experiment on at least three specimens. ZsimpWin™ software was used to analyse the impedance spectra and to fit the data. After the corrosion tests, corroded surfaces were examined using SEM/EDS analysis in order to study the morphology and composition of the corrosion products.

3. Results and discussion

3.1. Microstructural Features

Generally the microstructure of rheocast Al-Si alloys exhibits the presence of non-dendritic α-Al phase together with Al-Si eutectic phase and some intermetallic particles. Two different range sizes of α-Al phases are usually observed. A coarse α-Al phase (referred to α₁-Al) and a finer α-Al phase (referred to α₂-Al). The formation of α₁-Al and α₂-Al particles is related to the
multi-stage solidification in the semi-solid metal process. The formation of $\alpha_1$-Al particles is related to the nucleation during slurry preparation, while $\alpha_2$-Al particles are mostly formed during the secondary solidification stage inside the cavity, in a higher cooling rate and in the absence of shear force [18].

LOM micrographs of the surface of the thin walls of two aluminium alloys casted by Rheo- and Liquid-HPDC methods are presented in Fig.2. As it is expected the surface of R samples show some big $\alpha_1$-Al particles but the main microstructure is formed by fine $\alpha_2$-Al particles and the eutectic phase. This is due partially to transversal segregation as well as surface liquid segregation. Considering the two rheocast alloys, alloy 4.5 has coarser $\alpha_2$-Al particles. The microstructure in liquid cast alloys has a dendritic structure dispersed randomly on the surface. In the case of Liquid-HPDC again alloy 4.5 shows coarser microstructure. LOM images of the surface microstructure of the thicker plate (bulk) of samples 2.5 R and 2.5 L are presented in Fig.3. In the case of Rheo-HPDC alloy 2.5, more primary $\alpha_1$-Al particles and coarser $\alpha_2$-Al particles can be seen compared to the same sample taken from the thin walls. Presence of more primary $\alpha_1$-Al particles can be due to the mobility of the liquid fraction of the slurry which moves to the thinner parts of the cavity (walls) and leaves the solid fraction at the bottom. Coarser microstructure of $\alpha_2$-Al particles can be due to the lower cooling rate in the thick plate. This phenomena can also be seen in sample 2.5 LB, which shows coarser grains compared to the sample 2.5 L.

SEM micrographs and EDS analysis of thin walls surfaces of rheocast and liquid cast of alloy 4.5 are reported in Fig. 4. In these images the morphologies of the eutectic phase and the intermetallic particles are visible. It can also be seen that these phases are located in the intergranular regions in both rheocast and liquid cast alloys. The eutectic silicon phase has a fibrous morphology which is similar to the observations made by Arrabal et al [16] on A356 rheo and gravity cast alloys. EDS analysis on the spot number 2 confirms the presence of a relatively high amount of iron rich intermetallics corresponding to the bright needle shape particles. These intermetallic particles, as it is expected in hypoeutectic Al-Si alloys and also due to their needle like morphology, are $\beta$-AlFeSi [19].

LOM micrograph of cross-section of the thicker plate of rheocast Alloy 2.5 is depicted in Fig. 5. According to this figure, a finer microstructure on the surfaces, consists of a higher fraction of the eutectic phase and $\alpha_2$-Al particles, and a courser one at the centers of the samples, consists of higher amount of $\alpha_1$-Al particles, are formed in the rheocast alloys. It has been shown that due to the nature of the semi-solid slurry, in component casted using this method,
solid particle migrate to the center of component and surface layer consists of mainly liquid or eutectic phase [6, 20]

Fig. 2. LOM images of sample (a) 2.5 R, (b) 2.5 L, (c) 4.5 R, (d) 4.5 L.

Fig. 3. LOM images of sample (a) 2.5 RB, (b) 2.5 LB.
Fig. 4. SEM (SE) image and EDS analysis of surface microstructure of the sample (a) 4.5 R, (b) 4.5 L.

Fig. 5. LOM images of cross-sectional view of sample 2.5 RB.

3.2. Potentiodynamic polarization curves

Potentiodynamic polarization curves of as-cast surfaces of the thin walls of 2.5 R, 4.5 R, 2.5 L and 4.5 L in diluted Harrison solution with and without chloride ions are depicted in Fig. 6. These experiments have been repeated at least three times to make sure that the results are reliable.

According to these curves in diluted Harrison solution without chloride, the current densities are in the range of passive behaviour of the surfaces. The corrosion potential is nobler for the liquid samples but the corrosion current are higher. From the anodic branch of the curve it seems that the Rheo-HPDC alloys form a more stable passive layer on the surface stable up to -5 mV and even higher for alloy 4.5. Since the measurements were carried out on the as-cast
surface, the different behaviour is due both to the surface microstructure but also to the surface quality.

The corrosion potential in the Harrison solution in the presence of chloride ions is nobler for the samples with higher silicon content and also passivation current is lower for these samples. Moreover liquid samples are nobler compared to rheocast but the corrosion current density is slightly higher. All the samples show the pitting breakdown at the same pitting potential.

Fig. 6. Potentiodynamic polarization curves in diluted Harrison solution (a) without and (b) with Chloride ions.

Considering the rheocast bulk microstructure, the results of potentiodynamic polarization test in diluted Harrison solution with and without chloride ions of samples 2.5 RB and 4.5 RB are presented in Fig. 7.

In the solution without chloride ions, the behaviour of both samples is almost the same (Fig. 7 (a)). The passivation stability is higher for the bulk samples compared to the surface. This is mainly due to the surface condition, since the bulk samples are polished while the thin wall samples are tested in as-cast condition. About the polarization curve in the solution with chloride ions, Fig. 7 (b), there is no significant difference in the corrosion potential of the two samples. This can be attributed to the bulk microstructure which is rich in big primary $\alpha_1$-aluminium particles in both compositions. Also the pitting resistance is higher than the surface, (Fig. 6(b)), due to the better surface quality and higher $\alpha_1$-Al fraction.
Fig. 7. Potentiodynamic polarization curves in diluted Harrison solution (a) without and (b) with Chloride ions.

3.3. Electrochemical impedance spectroscopy

EIS spectra were primarily obtained for the samples taken from the thin walls, during exposure to the diluted Harrison solution for 24 hours. The Bode presentation of some representative EIS spectra for as-cast surfaces of rheocast and liquid cast of thin walls are reported in Fig. 8, which also compares different percentage of silicon. From Fig. 8 it can be seen that, the total impedance values decrease with the immersion time, which indicates the progressive corrosion process on the surface. In addition, the phase angle peak depresses through the immersion time, suggesting that the pitting corrosion activity is increasing [21]. All spectra after 6 to 7 hours show two overlapped capacitive arcs. The capacitive arc at intermediate frequencies is attributed to the presence of an oxide layer on the surface, and the low frequency arc is attributed to localised corrosion phenomena [22].

The equivalent circuits to describe the electrochemical responses of the samples of thin walls of rheocast and liquid cast alloys containing 2.5 and 4.5 weight percentage of silicon are shown in Fig. 9. For all the samples the circuit depicted in Fig. 9 (a) was used to fit the EIS spectra until 6 to 7 hours of exposure. While after that circuit shown in Fig. 9 (b) was exploited.

In the circuits depicted in Fig. 9, $R_{EL}$ stands for resistance of the electrolyte. $R_{EL}$ depends on the distance between the working electrode (sample) and the reference electrode and also on the solution concentration [23] and both remained constant during all immersion.
C\textsubscript{DL} and R\textsubscript{CT} respectively stand for the capacitive behaviour of the electrical double layer at the interface between the aluminium alloy and the solution and for the resistance against the charge transfer at this interface (or polarization resistance). C\textsubscript{CP} and R\textsubscript{CP} stand for the capacitance and the resistance of the corrosion products or the oxide layer respectively. The contribution of the pitting process is considered in this loop. In the first circuit (Fig. 9(a)), CPE is used to describe the non-ideal capacitive behaviour of the electrical double layer.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{fig8}
\caption{Bode plots of Electrochemical Impedance Spectroscopy spectra of samples 2.5 R, 4.5 R, 2.5 L and 4.5 L at (a) 1 hour, (b) 6 hours, (c) 12 hours and (d) 24 hours.}
\end{figure}

The impedance of a CPE is described as:

\[ Z_{\text{CPE}} = \frac{1}{Q(i\omega)^n} \]  

(1)
Q is the CPE constant and it nominally equals to admittance of the system at 1 rad/s; \( i = \sqrt{-1} \cdot \omega \) is the angular frequency (rad/s). The value of \( n \) changes between 0 and 1. When \( n = 1 \), Eq. (1) is the impedance of a pure capacitor; when \( n = 0 \), CPE is a pure resistor.

Fig. 9. Equivalent circuit proposed for the studied rheocast and liquid cast alloys after (a) 6 to 7 and (b) 24 hours.

The fitting results for the thin walls of the rheocast and liquid cast alloys of 2.5 and 4.5 wt.% Si are presented in Fig. 10. Values of \( R_{CT} \) (Fig. 10 (a)) for all the samples decrease with the immersion time, which indicates increase of the active area and/or a higher corrosion rate in the already existing pitting areas [23]. The values of \( R_{CT} \) for rheocast samples with different amount of silicon are close to each other and generally higher compared to liquid samples. While the same values for the liquid cast samples are higher for the sample 4.5 L in comparison to the sample 2.5 L until 12 hours which can be considered as an indication of a better corrosion performance. After 12 hours the values of \( R_{CT} \) are almost the same for these two samples. In addition the analysis of \( R_{CT} \) values shows that the corrosion performance of the both rheocast alloys are higher in comparison to the liquid cast alloys. The evolution of \( R_{CP} \) values (Fig. 10 (b)) is a slight decrease over the immersion time.

General analysis of EIS spectra and the fitting parameters show that alloys with higher amount of silicon possess higher corrosion resistance. Previous studies on the pitting and uniform corrosion behavior of Al-Si (6 to 18 % Si) alloys in various solutions and on the effect of silicon alloying, suggest that the presence of silicon, as an alloying element, increases the corrosion resistance of aluminium [24-26].
This higher corrosion resistance was attributed to the incorporation of silicon atoms in the passive film, which repairs the film defects and renders it more stable [24, 25]. The protectively of the passive film on the Al-Si alloy has also been explained partly due to its ability to retard the adsorption of chloride ions, and also because silicon oxide helps to block entry sites and restricts the transport of chloride ions through the passive film [26]. Higher corrosion resistance of alloys with higher silicon content can also be attributed to the presence of more areas of silicon phase which is nobler compared to α-aluminum phase. This increases the general corrosion resistance of the alloy however makes it also more vulnerable to the pitting attack due to presence of more favorable areas for pitting. Regarding higher corrosion resistance of rheocast samples in comparison to the liquid cast samples, presence of higher amount of silicon on the surface, due to segregation can be considered as an effective parameter.

SEM micrographs and Map analysis of some selected corroded surfaces are shown in Figs. 11 and 12 respectively. As it is obvious from these figures, corrosion is mainly localized in all the samples, especially in the eutectic region, at the interface of silicon and aluminium and also at the interface of aluminium grains and Fe-rich intermetallic particles. These results are in accordance with results of other researchers [16]. In general, intermetallic particles lead to rather severe micro-galvanic corrosion in a solution with Chloride ions, since their electrochemical behaviour is significantly different from the surrounding Aluminium matrix [27].

Fig. 10. EIS parameters of the rheocast and liquid cast Aluminium alloys (a) $R_{CT}$ and (b) $R_{CP}$. 
Fig. 11. SEM micrographs of corroded surfaces of sample (a) 2.5 R and (b) 2.5 L.

Fig. 12. Map analysis of corroded surface shown in Fig. 11 (a).

EIS spectra of the bulk microstructure of rheocast alloys with 2.5 and 4.5 wt.% Si, which are polished, during 24 hours immersion in diluted Harrison solution are presented in Fig. 13.
As it can be seen from this figure, the total impedance values for both samples increase with the immersion time which can be attributed to the presence of a protective oxide layer on the surface. Growth of this oxide layer is influenced by degree of impurities, alloying elements, temperature and humidity [17]. Since these tests have been performed on the polished surfaces at the center of samples, where there are more of the large α₂-Al particles and less of eutectic phase, this improvement compared to the as-cast surfaces of the thin walls is expectable.

4. Conclusions

Microstructure and the corrosion behaviour of two aluminium-silicon alloys with 2.5 and 4.5 wt.% Si cast by rheo and liquid high pressure die cast methods were investigated and compared.
The results show that the microstructure of both rheocast and liquid cast alloys show the presence of $\alpha$-Al particles, the eutectic phase and iron-rich intermetallics. The rheocast microstructure exhibits two different sizes of $\alpha$-Al phase due to the multistage solidification. It was also shown that the rheocast samples suffer from transverse macrosegregation of solid particles and the eutectic phase. Both the polarization and EIS tests show superior corrosion performance of alloys with higher silicon content, the polished surfaces of the bulk samples compared to the as-cast surface and also for rheocast samples in comparison to the liquid cast samples. It was shown that corrosion is mainly localized in these alloys, especially at the interface between the eutectic silicon and/or iron-rich intermetallics and aluminium rich particles.

References


