“Corrosion Behaviour of aluminium alloys used in heat-exchangers”
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1. Introduction to Aluminium Science and Technology

Although many metals can alloy with aluminium, only few have enough solid solubility to serve as major alloying elements. Zinc, magnesium, copper and silicon have significant solubility. However, other elements with solubility below 1 at% are important as alloying elements because they confer important improvements in alloy properties. Some examples of these elements are chromium, manganese and zirconium. Electrochemical properties and corrosion resistance are strongly affected by the nature and content of alloying elements.

Manganese is the major alloying element in 3xxx series. These alloys add about 20% more strength compared to pure aluminium. These alloys are widely used for moderate-strength applications requiring good workability [1]. The major alloying element in the 4xxx series is silicon, which can be added in sufficient quantities (up to 12%) to cause substantial lowering of the melting range without producing brittleness. Figure 1 shows the phase diagram of this alloy, showing the eutectic point where the melting point is lower. For this reason, Al-Si alloys are used as brazing alloys.

![Aluminium-silicon phase diagram](image1)

Figure 1 – Aluminium-silicon phase diagram [1]

2.2 Cladding Alloys

The main materials used in manufacturing heat exchangers are aluminium-brazing sheets. It consists of a core alloy, typically belonging to the 3xxx series, which provides the strength and life cycle requirements of the heat exchanger and a clad layer from the 4xxx series, which is an Al-Si alloy with a low melting point. During the brazing process, the Al-Si alloy melts and seals the joints in the heat exchanger between the different sheet components. The typical morphology of a brazing sheet composed of a core alloy and cladding on both side is shown in Figure 2.

![Cross-section morphology of a double-side brazing sheet](image2)

Figure 2 – Cross-section morphology of a double-side brazing sheet [2].
The brazing process modifies the geometry and the microstructure of the core. The partial dissolution of the core takes place in the brazing joint with the formation of a “band of dense precipitates” (BDP) in the core material due to diffusion of Si coming from the liquid film of the clad alloy (Figure 3).

![Figure 3 - Optical microscope images an aluminium brazing sheet before and after the brazing process [3].](image)

Figure 3a shows the nearly uniform cladding, before brazing, in white contrast while the core has a grey colour with dark spots. The enlarged image of the clad in Figure 3c reveals elongated coarse particles with a dark grey contrast, the precipitates of Al-Si phase. In the core, light grey particles are observed, containing high levels of Al, Mn and Fe within Al matrix that should be Al₆(Mn,Fe) precipitates. In Figure 3b, after brazing, re-solidification of the brazing joint shows dendrites of Al solid solution in white contrast and multiphase deposits of Al-Si that appears as elongated thin plate. The precipitates on the BDP are composed of Al, Fe, Mn and Si. The white film covering the flat surfaces of the material (an enlarged image is shown in Figure 3d) results from the re-solidification of the remaining molten cladding [3]. Figure 4 presents a SEM image of this re-solidified molten clad. It consists of well-defined aluminium grains, surrounded by multiphase deposits of Al-Si eutectic with a needle-like appearance and blocky precipitates, like the ones found in the brazing joint.

![Figure 4 - SEM image of the re-solidified clad [3].](image)
2. Experimental Procedure

Techniques

Optical microscopy / Scanning Electron Microscopy (SEM) / Energy Dispersive Spectroscopy (EDS)

The equipment used were Leica DMS300, a Leica DMS2700 M. The equipment used for the acquisition of SEM-FEG images was a JEOI JSM-7001F with an Oxford INCA EDS unit for chemical composition analysis.

Potentiodynamic polarization

The tests were carried out in a three electrode electrochemical cell, in which the samples constitute the working electrode (WE). The reference electrode (RE) was a Saturated Calomel Electrode (SCE) and the counter electrode (CE) was a platinum coil. All electrodes are immersed in the test cell, a single-compartment O-ring cell with a working surface of 1cm². Potentiodynamic Polarization tests were performed in VoltaLab PGZ 100 potentiostat. The cathodic polarization curve was determined with the following parameters [26]: 1) Initial-final potential: -0.01V – 0.5V (cathodic branch), 2) Scan rate: 1 mV/s, 3) Sample period: 0.5 s, 4) Sample area: 1 cm², 5) OCP time: 1800 s

Scanning Vibrating Electrode Spectroscopy

This technique detects local current density changes originated by potential differences in the surface as consequence of ionic fluxes generated between anodic and cathodic sites. The commercial equipment used in this study was manufactured by Applicable Electronics™ and controlled using ASET software (Science Wares™). The equipment contains the following parts: a main amplifier-potentiostat and a preamplifier. To position the microprobe the preamplifier is mounted on a 3D stepper-motor system. An insulated Pt-Ir probe (Microprobe Inc.) with a spherical layer of Pt black deposited on the tip probe was used as vibrating electrode. Each sample was tested during 24 hours of non-stop immersion in 0.05M NaCl solution. Scans were performed in 31 per 31 grid generating 961 points.

Localized Electrochemical Impedance Spectroscopy

Tests were carried out using a Solatron 1250 frequency response analyzer coupled with a Uniscan Electrochemical Station. LEIS equipment uses a five-electrode configuration consisting of a conventional three-electrode cell: (i) saturated calomel electrode (SCE) as reference, (ii) platinum coil as counter electrode and (iii) sample as working electrode; and the LEIS probe (Pt bi-electrode) to measure the local potential gradient in solution (0.005M NaCl) above the sample surface. The dimension of the scanned area is 6 mm².

Preparation of samples

All samples were obtained from JDEUS Company. Aluminium sheet that compose the tube and fin were provided unbrazed and with different thicknesses. Chemical compositions of the different samples are detailed in Table 1.

Table 1 – Chemical composition of the alloys used in this study.

<table>
<thead>
<tr>
<th></th>
<th>Si</th>
<th>Fe</th>
<th>Zr</th>
<th>Cu</th>
<th>Mn</th>
<th>Mg</th>
<th>Zn</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>FIN</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FIN Al-Si-Fe</td>
<td>0.8-1.0</td>
<td>1.4-1.7</td>
<td>-</td>
<td>≤0.05</td>
<td>0.6-0.9</td>
<td>≤0.05</td>
<td>0.45-0.65</td>
<td>Bal.</td>
</tr>
<tr>
<td>FIN Al-Mn-Zn</td>
<td>0.5-1.0</td>
<td>≤0.07</td>
<td>0.05-0.2</td>
<td>≤0.1</td>
<td>1.4-1.8</td>
<td>-</td>
<td>1.2-1.8</td>
<td>Bal.</td>
</tr>
<tr>
<td>CORE Al-Mn</td>
<td>0.6-0.8</td>
<td>≤0.3</td>
<td>-</td>
<td>0.5-0.7</td>
<td>1.2-1.7</td>
<td>≤0.05</td>
<td>≤0.05</td>
<td>Bal.</td>
</tr>
<tr>
<td>CLAD1 Al-Si</td>
<td>9.0-10.0</td>
<td>≤0.8</td>
<td>-</td>
<td>≤0.3</td>
<td>≤0.05</td>
<td>≤0.05</td>
<td>≤0.10</td>
<td>Bal.</td>
</tr>
<tr>
<td>CLAD2 Al-Si-Zn</td>
<td>6.0-7.0</td>
<td>≤0.8</td>
<td>-</td>
<td>≤0.3</td>
<td>≤0.05</td>
<td>≤0.05</td>
<td>2.5-2.9</td>
<td>Bal.</td>
</tr>
</tbody>
</table>
Specimen with different material combinations consist of two brazed sheet of the tube’s material and a sample of the fin’s material between them. The materials used in each specimen are presented in Table 2.

Two solutions were used: for the corrosion studies - 3.5% NaCl solution, pH 4.7 and for the polarization curves - 1M NaCl, pH 5.8.

### 3. Results and Discussion

**LEIS**

LEIS was performed on the three samples after immersion in 3.5% NaCl for 24 hours. Figure 5 represents the admittance distribution in sample 1, for different immersion times (the higher the admittance the lower the impedance). These maps show that the fin is more anodic than the tube. The corrosion activity presents no significant variation throughout the immersion time.

![LEIS maps](image)

**Figure 5**– LEIS maps performed on sample 1. Each scan was obtained every 5 hours.

In the case of sample 2, in Figure 6, the maximum activity is visible across the brazing joint, while the fin and the region of the tube away from the brazing joint is more cathodic. During immersion time there is a slight decrease in anodic activity, evidenced by a fainter red region in the brazing joint after 10 hours of immersion.
Figure 6– LEIS maps performed on sample 2. Each scan was obtained every 5 hours.

Figure 7 represents the LEIS test performed on sample 3 and show that corrosion occurs mainly in the brazing joint, while the tube and the fin remain cathodic. This behaviour is similar to sample 2. There is no evident variation of activity during immersion e.

Figure 7– LEIS maps performed on sample 3. Each scan was obtained every 5 hours.

SVET

After immersion in 3.5% NaCl solution for 24 hours, the current density maps provided by SVET are presented in Figure 13 and show anodic activity on the fin, while the tube’s surface and brazing joint show cathodic activity, suggesting that the fin corrodes preferably compared to the tube. These results are in good agreement with LEIS. In Sample 1, the fin is an Al-Mn alloy with a Zn content around 1.5% while the tube was cladded with an Al-Si alloy and a higher Zn than the fin. The presence of zinc increases its potential and is used in protective cladding [6]. The preferential corrosion of the fin appears to protect the tube’s integrity.
Figure 13 – SVET scan performed on sample 1. Current density units are in µA /cm².

The current density maps of sample 2 (Figure 14) show the brazing joint with strong anodic activity, while the tube is more cathodic. It is also visible in the image an absence of localized corrosion both on the tube and fin, suggesting that the brazing joint is corrodes preferentially, protecting the tube and the fin.

The tube is the same as in sample 1, but the fin is an Al-Si alloy with lower Zn content. Mn is also present in lower amounts. The iron content is about 1.6%, as detailed in Table 6. Iron is more noble than aluminium and zinc and is, therefore, beneficial to improve the fin’s integrity.

Figure 14 – SVET scan performed on sample 2. Current density units are in µA /cm².

SVET tests on sample 3 are presented in Figure 15. The brazing joint presents anodic activity, very active on the right side. The tube and the left side of the brazing joint present cathodic activity. Visual observation shows that a region of the tube and brazing joint on the left side present a different aspect than the right side, whose surface appears to be more degraded and irregular. This could be caused by a part of the fin being entrapped this area affecting the corrosion behaviour of this region. In this sample, the tube’s surface in contact with the fin was cladded with an Al-Si alloy (around 9%) but less zinc content (0.1%) than the external clad. The fin presents an iron content of 1.5%. Once again, iron is beneficial to improve fin’s corrosion resistance.
Surface Characterization

The three samples were immersed for 24 hours in NaCl 3.5% solution and monitored by optical microscopy to evaluate the progression of the corrosion process in the tube, fin and brazing joint.

Figures 16 presents the progression of the corrosion process for sample 1. Corrosion of the brazing joint progresses toward the centre of the brazing joint compromising the union between the fin and tube. The coloration turns darker with a needle-like appearance. After 24 hours, the tube and fin are almost completely separated from each other. Pitting corrosion is present on the surface of the tube. Crevice corrosion is visible on the bottom side of the tube and presents the same appearance of the corrosion in the brazing joint.

This brazing joint was analysed in SEM. The darker regions in the brazing joint present a needle-like and structure which is consistent with the previous discussions for this type of structures, in Section 1. EDS analysis, shows that the areas surrounding this darker area are very rich in Al (around 80%) while the darker zones are poorer in Al and much richer in Si, suggesting that there is a selective dissolution of the aluminium grains that compose the typical Al-Si microstructure. Manganese and iron also appear in these regions which is consistent with the known structures of the brazed alloys, with precipitates composed of Al, Si, Mn and Fe. Zinc is also present in small amounts.
Progression of the corrosion process of sample 2 are presented in Figures 17. Corrosion is more evident on the right side of the brazing joint, where it appears with a dark colour and a needle-like appearance. Degradation of the brazing joint does not appear as aggressive as in sample 1, although localised corrosion is visible in the tube on the right side, under the brazing joint, but its overall structure appears relatively intact. Crevice corrosion is also visible on the bottom side of the tube, although not as evident as sample 1.

Figure 17 - Microscope images of sample 2 taken every two hours for eight hours and after 24 hours in 3.5% NaCl solution. Surface chemical composition on two distinct points.

<table>
<thead>
<tr>
<th></th>
<th>Al</th>
<th>Si</th>
<th>O</th>
<th>Mn</th>
<th>Fe</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>91.25</td>
<td></td>
<td>7.57</td>
<td>0.46</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>40.77</td>
<td>39.29</td>
<td>18.00</td>
<td></td>
<td></td>
<td>0.78</td>
</tr>
</tbody>
</table>

The SEM micrograph shows the needle-like and plate-like appearance that characterizes this type of structure. EDS analysis shows that the amount of Al and Si in these dark regions are nearly equal. On the other hand, the chemical composition of the regions away from these areas is around 90% Al.

Corrosion propagation in sample 3 is exhibited in Figure 18. The material degradation is propagating towards the centre of the brazing joint, in a dendritic manner, compromising the union between the tube and fin. In general, sample 3 appears to present more corrosion products over its surface and the boundary between tube and fin appears darker. Circular, light grey areas near the brazing joint were detected after 6 hours of immersion in solution, suggesting that gas was produced. Sample 3 is composed of an Al-Si cladded tube, with the remaining elements being less than 1% and the fin has around 1.5% iron, so we may assume that the set external clad/fin with 1.5% is more prone to corrosion.

Figure 18 – Microscope images of sample 3A taken every two hours for eight hours and after 24 hours in 3.5% NaCl solution. Surface chemical composition on two distinct points.

<table>
<thead>
<tr>
<th></th>
<th>Al</th>
<th>Si</th>
<th>O</th>
<th>Mn</th>
<th>Fe</th>
<th>Cu</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>79.50</td>
<td>1.13</td>
<td>17.14</td>
<td></td>
<td></td>
<td>0.56</td>
<td>1.67</td>
</tr>
<tr>
<td>2</td>
<td>8.14</td>
<td>69.31</td>
<td>19.35</td>
<td></td>
<td></td>
<td>1.57</td>
<td>0.49</td>
</tr>
</tbody>
</table>
SEM images of sample 3 show that the dark areas in the brazing joint are a needle-like structure with dendritic ramifications. EDS reveals that these regions are poorer in Al (8.14%), suggesting a selective dissolution of aluminium, exposing the eutectic matrix composed of Al-Si.

Potentiodynamic polarization

Figures 19, 20 and 21 present the polarization curves of the three specimen for the test solution 1M NaCl. All the samples are characterized by negative corrosion potentials ($E_{corr}$). All alloys evolve in a similar manner. All tests performed were repeated and the results are considered to be reproducible.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E_{corr}$ (V SCE)</th>
<th>$i_{corr}$ (A cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TUBE</td>
<td>-0.770</td>
<td>-7.72</td>
</tr>
<tr>
<td>EXT CLAD</td>
<td></td>
<td></td>
</tr>
<tr>
<td>FIN 1 0.07</td>
<td>-0.855</td>
<td>-6.66</td>
</tr>
</tbody>
</table>

**Figure 19 —** Polarization behaviour of the tube with external clad and fin 1 with 0.07mm width. Solution used was 1M NaCl with pH is 5.8 and polarization parameters for the two alloys. These values were obtained by direct graphical analysis.

Polarization curves of sample 1, in Figure 19, shows that the material from the tube presents a less negative $E_{corr}$ than the fin, meaning that the fin corrodes preferably which is consistent with the LEIS/SVET studies previously presented. Also, the corrosion rate of the fin is slightly higher than the corrosion rate of the tube, meaning that it corrodes faster than the latter.

In sample 2, once again, the $E_{corr}$ from the tube is less negative than the fin but the two values are very close, as is shown in Figure 20. These results are in good agreement with the LEIS and SVET studies. An iron rich content of the alloy used in this fin might explain this behaviour since iron is more a more noble metal than aluminium or zinc.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E_{corr}$ (V SCE)</th>
<th>$i_{corr}$ (A cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TUBE</td>
<td>-0.770</td>
<td>-7.72</td>
</tr>
<tr>
<td>EXT CLAD</td>
<td></td>
<td></td>
</tr>
<tr>
<td>FIN 2 0.07</td>
<td>-0.789</td>
<td>-6.54</td>
</tr>
</tbody>
</table>

**Figure 20 —** Polarization behaviour of the tube with external clad and fin 2 with 0.07mm width. Solution used was 1M NaCl with pH is 5.8 and polarization parameters for the two alloys. These values were obtained by direct graphical analysis.
In sample 3 the tube revealed a more negative value of $E_{\text{corr}}$ corrodin preferably in relation to the fin, which is coherent with previous results: 1) SVET results in Figure 21 show that the anodic activity in the brazing joint extends partially to the tube, unlike sample 2, where the anodic region is restricted to the corroded brazing joint; 2) progression of corrosion presented in Figures 19 and 20 show that the degradation of the material moves into the tube and not only towards the centre of the brazing joint. This fact is also reinforced by another noticeable feature which is the result in a stronger galvanic couple.

![Sample 3 polarization behaviour](image)

Figure 21 – Polarization behaviour of the tube with internal clad and fin 2 with 0.1mm width. Solution used was 1M NaCl with pH is 5.8 and polarization parameters for the two alloys. These values were obtained by direct graphical analysis.

$E_{\text{corr}}$ of the tube of sample 3 is more negative than $E_{\text{corr}}$ of the tube of previous samples. Reminding that the internal clad is an Al alloy with 9 – 10% Si and less than 0.10% Zn while the external clad possesses 6 – 7% Si and 2.5 – 2.8% zinc, these values of $E_{\text{corr}}$ are not in agreement with what has been studied about the effect of silicon and zinc in the corrosion resistance of aluminium alloys. In fact, an alloy with higher silicon content and less zinc content should present a less negative $E_{\text{corr}}$ value [4, 5]. Instead, the $E_{\text{corr}}$ value of the tube with internal clad is always more negative than the tube with external clad in the several testes performed under the same experimental conditions.

Comparing $E_{\text{corr}}$ on the three fins used in these samples, Fin 1 presents the lowest value which means that it is most likely to corrode compared to Fin 2, regardless of the width. This is consistent with what is known about the alloying elements of these components since Fin 2 has a higher Fe content, which is beneficial to the corrosion resistance of this alloys. In this particular test, $E_{\text{corr}}$ from Fin 2 with a width of 0.07mm has a more negative $E_{\text{corr}}$ than Fin 2 with a width of 0.1mm. Even so, other tests performed under the same experimental condition do not support this fact. LEIS/SVET tests performed with this fins were attached to different cladded tubes and no conclusion can be drawn from those results. So, this specific subject requires further studies.

4. Conclusions

Sample 1 corrodes preferably in the fin while the tube remains more cathodic. Samples 2 and 3 present anodic activity in the brazing joint. It is believed that corrosion in the brazing joint of sample 2 protects the integrity of the tube while in sample 3, that shows a slight dislocation of this anodic area toward the tube the latter, is more susceptible to corrosion attack from the corroded brazing joint. This is sustained by the microscopic analysis performed that show that corrosion always progresses toward the centre of the brazing joint, compromising the union between tube and fin, and in sample 3 this degradation also reaches the tube in a dendritic manner. In general, corrosion is more pronounced in this sample when considering the entire boundary between tube and fin. Measurements on corrosion potential on these alloys show that sample 3 has the highest difference of potential which also supports the fact that the combination of materials is more prone to corrode.

SEM and EDS analysis sustain the conclusions drawn from the previous tests and are in agreement with what is known for the corrosion process of this type of brazing alloys. Selective dissolution of aluminium grains exposes
the Al-Si eutectic phase, characterized by plate-like and needle-like structures, and the precipitates composed of silicon, iron and manganese that are typical of these type of compounds.

Fin 1 corrodes preferably to Fin 2, which is supported by the localized studies and the electrochemical tests, and is according to what is known for these type of alloys. A comparison between different widths was not conclusive. All electrochemical tests performed show that the tube with internal clad corrodes preferably in relation to the tube with external clad. This result is not consistent with previous studies [4, 5] performed on the general effect of silicon and zinc as alloying elements in aluminium alloys, regarding corrosion resistance and cannot be explained under the scope of this work and so further work is required.

1. References