Electrochemical profiling of multi-clad aluminium sheets used in automotive heat exchangers

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Abstract

A combination of glow discharge optical emission spectroscopy sputtering and local electrochemical measurements was used to determine electrochemical changes upon brazing in a multi-layered Aluminium sheet (AA4343/AA3xxx/AA4343) with an additional low-Cu (AA3xxx) interlayer. Ecorr values from potentiodynamic polarization, galvanic corrosion behaviour by ZRA, microstructure and composition by SEM and TEM were investigated and compared to those obtained for sheet without the interlayer. Inward diffusion of Si from clad, and outward diffusion of Cu from core are found to degrade the corrosion properties of conventional sheet, whereas presence of interlayer reduced outward diffusion of Cu and hence improved corrosion protection.

Keywords	A. Aluminium; A. Intermetallics; B. SEM; B. Polarization; B. TEM;
Taxonomy	Corrosion, Intermetallic, Elemental Analysis, Brazing, Microscopy, Aluminium
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8th November 2017

To
J.M.C. Mol, PhD
Editor-in-Chief
Corrosion Science

Dear Editor,

I have enclosed the revised version of the manuscript titled “***Electrochemical Profiling of Multi-Clad Aluminium Sheets used in Automotive Heat Exchangers***” with reference number CORSCI_2017_1486 after incorporating the suggestions and modifications from the review process. I am also attaching a separate document listing the individual rebuttal and responses to the reviewer and editor comments.

I request you to kindly let me know the outcome of this revised submission or if any other information is required.

Yours Sincerely,

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Rebuttal to the comments from the editors and reviewers:

Editor

- Please find attached an annotated version of the manuscript submitted by reviewer 2, please address accordingly in the revised manuscript.

The authors have incorporated the reviewer suggested modifications in the revised version of the manuscript.

-Reviewer 1

I don't understand the significance of table 3 which appears to be a compilation of own and literature results. Own results are based on EDS compositional analyses. The equilibrium stoichiometries appear to be listed. Have the authors tried to determine the phase structures by electron diffraction as part of their TEM investigations? Nonequilibrium variants of the phases can also be present. Is there a need for table 3 at all in reaching the objectives and conclusions of this work? It can perhaps be published separately as a review paper.

The table lists measured EDS composition of several intermetallic phases observed in the multicladd brazing sheets in as received, and brazed condition.

The measured concentrations are then related to possible phases (or family of phases) from literature for these material systems.

The authors have not determined the crystal structure of these phases using electron diffraction as it is out of the scope for the current paper.

Table 3 is presented in the manuscript to emphasize the fact that the precipitates formed after brazing in the interlayer region do contain some amount of Copper, which implies that the Cu content in the surrounding Aluminium solid solution is now reduced thus making it more anodic and more susceptible to galvanic coupling with intermetallic phases and corrosion.

In the author's opinion, this is essential to the discussion on lateral propagation of corrosion restricted to the interlayer region, and the conclusions presented in the manuscript.

The relevant text in the manuscript has now been modified accordingly to convey this in a better manner to the reader.

Similar comments apply to the claim in the text that the Al_2Cu phase may form during different types of thermomechanical treatment applied to the different types of surfaces investigated.

The manuscript has now been revised to exclude the comments on Al_2Cu phases, as these were not characterized/investigated in this present work.

-Reviewer 2

This is high quality well presented work, the style requires some minor attention

The authors have incorporated the suggested modifications to the style in the revised version of the manuscript.

Highlights

1. Microstructure and Local Electrochemistry of multiclاد Aluminium sheets is studied.
2. Electrochemical potential difference between clad layers is reduced after brazing.
3. Intermetallic phases before and after brazing are characterized using TEM-EDS.
4. Low Cu interlayer reduces the negative effect of brazing and protects the core.
5. ZRA measurements show sacrificial nature of clad layers is reduced after brazing.

↓ **Brazing**

↓ **Brazing**

Electrochemical Profiling of Multi-Clad Aluminium Sheets used in Automotive Heat Exchangers

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Abstract

A combination of glow discharge optical emission spectroscopy sputtering and local electrochemical measurements was used to determine electrochemical changes upon brazing in a multi-layered Aluminium sheet (AA4343/AA3xxx/AA4343) with an additional low-Cu (AA3xxx) interlayer. E_{corr} values from potentiodynamic polarization, galvanic corrosion behaviour by ZRA, microstructure and composition by SEM and TEM were investigated and compared to those obtained for sheet without the interlayer. Inward diffusion of Si from clad, and outward diffusion of Cu from core are found to degrade the corrosion properties of conventional sheet, whereas presence of interlayer reduced outward diffusion of Cu and hence improved corrosion protection.

Keywords: A. Aluminium; A. Intermetallics; B. SEM; B. Polarization; B. TEM;

1. Introduction

Aluminium and its alloys are widely used in the automotive, construction, and aerospace industries due to their high strength to weight ratio, inherent corrosion resistance, ease of formability, their ability to be surface modified for different functional applications and their ease of recycling [1–6]. Aluminium is used extensively in the automotive industry for heat exchangers in radiators, air conditioner evaporators, exhaust gas recirculation (EGR) and water and air charge air cooling (W & A CAC) systems [7]. This is due to its favourable combination of mechanical, thermal, and electrochemical properties [8,9]. Over the last two decades, mechanical assembly in the production of heat exchangers has been continuously replaced by brazing due to its reduced manufacturing costs and compliance with the increased safety requirements and issues related to recyclability [10–12]. Brazed heat exchangers are manufactured from clad aluminium sheets where the high melting point core alloy provides the mechanical strength (typically an Al-Mn, AA3xxx), and the clad alloy with a low melting point such as Al-Si (AA4xxx) type alloy acts as a filler for the brazing process [13,14].

In EGR and ACAC systems, the use of aluminium alloys is limited due to corrosion by the exhaust gases, which are acidic in nature and contain water [15,16]. Corrosion occurring on the air side of heat exchanger tubes is a critical issue and is currently the main issue for continued down-gauging and weight reduction [11,17,18]. The conventional AA3xxx alloy used as core material in the heat exchanger tubes is prone to intergranular corrosion (IGC) and this results in penetration of the tube walls causing leakage and failure [19,20]. This corrosion is enhanced by diffusion of Si from the AA4xxx clad after brazing [21,22]. Afshar et al. [23–25] studied the microstructure and electrochemical behaviour of brazed clad AA4xxx/AA3xxx sheets and observed that the presence of α -Al(Fe,Mn)Si intermetallic phases up to a depth of 5 μm below the surface sheet support galvanic coupling with the internal layers and enhance dissolution and IGC attack. It was postulated that elimination of these corrosion susceptible

sites would improve corrosion performance. Recently, significant improvement in the air-side corrosion resistance has been achieved by using cladding of multiple layers of different Al alloys where the interlayer between the AA4xxx clad and the AA3xxx core acts as an additional sacrificial layer [1,26]. This approach allows for increased diffusion distances for Si and Cu from the AA4xxx clad and the AA3xxx core respectively, and thus is expected to prevent localised precipitation of Al(Fe,Mn)Si intermetallic phases that contain Cu. In addition, the Cu concentration gradient from the core to the clad is optimized and hence the electrode potential of the metal, and thus better corrosion protection properties of the core.

The objective of the present study was to understand the specific effect of an additional low-Cu AA3xxx interlayer on the microstructural and electrochemical modifications occurring in a clad Al heat exchanger sheet after being subjected to controlled atmosphere brazing treatment (CAB, hereafter referred to as ‘brazing’). In order to characterize the local changes in the electrochemical properties as a function of depth below the surface, a combination of controlled glow discharge optical emission spectroscopy (GDOES) sputtering [27] and localized electrochemical measurements [28–33] with a lateral resolution of 1 mm was employed. Electrochemical depth profiling of the clad Al structure with a low-Cu AA3xxx interlayer was studied before and after brazing. Zero resistance ammetry measurements were also performed by coupling the individual adjacent layers before and after brazing. The microstructural and compositional modifications were analysed by scanning and transmission electron microscopy and energy dispersive X-ray spectroscopy techniques. The results were correlated with the electrochemical depth profiling data and compared to those obtained for a conventional three-layer Al clad product without a low-Cu interlayer.

2. Experimental Details

2.1. Materials

Aluminium coupons of approximately 8 cm x 20 cm were cut from rolled brazing alloy sheet. The ‘core’ of the brazing sheet was a modified AA3xxx aluminium alloy, which had been clad with an AA4343 (~36 µm thick, ‘clad’) on the top of a low-Cu AA3xxx (~38 µm thick, ‘interlayer’) as shown in Figure 1 (a). For comparison, brazing sheet without the low-Cu interlayer was also analysed (Figure 1 (b)). The brazing sheet with the low-Cu interlayer is referred to as ‘**Multiclad**’ and those without the interlayer as ‘*Reference (Ref)*’. The composition of the materials used in the as-rolled condition are shown in **Table 1**.

Figure 1

Table 1

2.2. Brazing

The Al samples were degreased in acetone, dried and placed into a Controlled Atmosphere Brazing (CAB) furnace in a dry, inert nitrogen gas atmosphere for simulating the temperature cycle during the brazing treatment. The materials were heated up to 600 °C (at 30 °C/min), and were held at that temperature for 2 min. and then cooled down at a specified rate of 60 °C/min. The process temperature was selected to be close to the liquidus temperature of the clad material (~612 °C) and much lower than the solidus temperature of the core material (~640 °C) [11,34] .

2.3. RF-GDOES

Both the as-rolled, and brazed sheet materials were then etched to certain depths by Argon ion sputtering using radio frequency glow discharge optical emission spectroscopy (RF-GDOES, GD-Profilier 2, Horiba Jobin Yvon). The applied sputter power was 40 W and the Ar pressure in the sputtering chamber was 650 Pa. The diameter of the sputter crater was 4 mm. The compositional depth distributions of the main alloying elements (Si, Cu, Fe and Mn) in the sheet materials were used to identify the interfaces between the individual cladding layers and to define the required sputtering depth for further electrochemical depth profiling analysis.

2.4. Electrochemical Behaviour

The electrochemical behaviour of both the as-rolled, and brazed materials was determined at different depths using a Dualscope EC localized electrochemical cell (Semilab Germany GmbH, formerly DME Nanotechnologie GmbH, Germany) having a small opening (1 mm diameter plastic pipette tip) which ensured the contact between the electrolyte and the working electrode (see Figure 2). The system employed an electrochemical head consisting of the reference and counter electrodes, which were open to a reservoir cavity containing the electrolyte. A plastic pipette tip with 1 mm diameter opening was attached to this reservoir cavity to create a hanging droplet of the electrolyte onto the test surface. The hanging droplet was achieved by the precise airtight solution pumping mechanism. The size and shape of the droplet were continuously monitored and controlled using a microscope and a digital video camera attached to the cell [23,35,36]. Prior to each experiment, a small amount of solution was always dispersed from the tip followed by gentle cleaning by scrubbing against a flat surface. The tip was then brought into contact with the surface of the working electrode and then slowly retracted to a height of 100 μm from the surface of the working electrode. The hanging droplet of the electrolyte (of 1 mm diameter) is achieved due to surface tension, and guarantees wetting of the working electrode surface while maintaining the size and shape of the droplet.

For all the electrochemical measurements a saturated Ag/AgCl reference electrode and a Pt wire counter electrode were used. Potentiodynamic polarization scans were performed with a scan rate of 1 mV/s. Prior to each measurement, the open circuit potential (OCP) was allowed to stabilize for 30 min. A solution of 0.1M HCl (pH $\sim$ 1, analytical grade) was used as the electrolyte based on a parametric study by Peguet et al. [37,38] which compared the use of ASTM G69 solution (1M NaCl + H₂O₂ 9 mL/L) [39] with 0.1M HCl. Results showed that the 1M NaCl based electrolyte was very aggressive and penetrating pits of more than 100 μm depth

were formed which was not suitable for thin gauge sheets. Lower Cl concentration with use of 0.1M NaCl resulted in longer time for stabilization of potential. The 0.1M HCl solution allowed faster de-passivation of the surface and stabilising of the surface potential. All experiments were conducted at room temperature and no aeration was applied to the electrolyte.

Figure 2

Zero Resistance Ammetry (ZRA) measurements were performed in a conventional 3-electrode cell using the same potentiostat. The measurements were conducted in a 0.1M NaCl solution of pH 2.8 (adjusted with HCl; 400 mL volume electrolyte) at room temperature for 3 h to determine the evolution of the galvanic current density between the individual layers in the brazing sheet and the galvanic potential. These measurements were conducted before and after the brazing treatment. In each ZRA experiment, two pieces of the similar sheet material which had been sputtered to different depths by GDOES were used. This allows for coupling between the clad (WE1) and the interlayer (WE2); and the interlayer (WE1) and the core (WE2). Only the sputtered craters (of 4 mm diameter, 12.56 mm² area; surface area ratio 1:1) were exposed to the electrolyte in the ZRA setup, and the remaining surface of each sample was covered with a protective lacquer. The samples (electrodes) were placed facing each other and the distance between the anode and the cathode was 5 ± 0.5 cm. The potentiodynamic polarization tests and the ZRA testes were repeated at least three times.

2.5. Microstructural Characterization

The microstructures of the as-rolled, and brazed materials were examined using a scanning electron microscope (SEM, Quanta 200 ESEM FEG, FEI) equipped with an energy dispersive X-ray spectrometer (EDS, 80 mm² X-Max silicon drift detector, Oxford Instruments). Additional characterization of the microstructure before and after brazing was performed using a transmission electron microscope (TEM, Tecnai T20 G2, FEI) coupled to an

energy dispersive X-ray spectrometer (EDS, 80 mm² X-Max silicon drift detector, Oxford Instruments). Samples for TEM analysis were prepared using site specific in-situ lift out of 1 µm thick lamella from the cross section of the Al sheets using a dual beam focused ion beam microscope (FIB-SEM, Helios EBS3, FEI) [40–44]. For the in-situ lift out procedure, a Pt layer (3 µm thick) was deposited onto the region of interest to protect the underlying sample surface from high energy ion milling. A Ga liquid metal ion source was employed for focused ion beam milling of the sample, and a Mo TEM grid was used for mounting the TEM lamella that was lift out from the region of interest using Pt deposition as a means to weld the lamella to the Mo grid. The lamella were further thinned down to ~120 nm thickness for electron transparency using focused ion beam milling, and final milling was performed using low energy ion beam milling (2 keV) to remove any high energy milling induced artefacts. The EDS analysis on the thin lamella was performed in the TEM, and the quantification of the elements was done after deconvolution of C, Ga, Pt and Mo that arise due to the sample preparation using EDS software coupled to the TEM (Aztec EDS TEM, Oxford Instruments).

3. Results and Discussion

3.1. Elemental depth profiling by GDOES

Figure 3

Figure 3 shows the compositional elemental depth profiles of Si, Fe, Mn, and Cu for the as-rolled (AR) and brazed (BZ) sheets. For the as-rolled sheets, the drastic decrease in the concentration of Si, and increase in the concentration of Mn after approx. 8 min of sputtering in Figure 3 (a) corresponds to the interface between the clad AA4343 layer and the AA3xxx core. Similar behaviour is observed in Figure 3 (b) indicating the interface between the AA4343 clad and AA3xxx interlayer. The increase in the concentration of Cu after ~20 min of sputtering

indicates the transition across the interface between the AA3xxx interlayer and the AA3xxx core material.

Table 2

The surface regions of the as-rolled sheets are slightly enriched with Si, while in the deeper layers of AA4343 the concentration of Si is almost constant (~5.5 wt.%). After brazing, the concentration of Si next to the surface is dramatically increased (up to 42 wt.%) and the interfaces between the individual layers are not well defined. The change in concentration of Mn in the individual layers after brazing is weak when compared to that of Si and Cu. This is due to the limited diffusion of Mn in this system under brazing conditions. Overall, the brazing treatment has caused inward diffusion of the Si from the top layer into the AA3xxx interlayer and outward diffusion of Mn to a lower extent into the AA4343 layer. Similar trends are observed for Cu, which diffuses from the AA3xxx core to the surface layers, and Fe from the AA3xxx interlayer. It is interesting to note that most of the Fe from the interlayer is found to be localized at a certain depth in the brazed multicladd sheets.

In order to expose different layers of the material for electrochemical investigation, the as-rolled and brazed sheets were sputtered for different time intervals. These time intervals are marked by arrows in Figure 3. The representative compositions corresponding to these sputtered depths before and after brazing are summarized in Table 2.

3.2. Microstructural Analysis

The microstructure of the multicladd sheets before and after brazing is shown in Figure 4. The multicladd sheet in as rolled condition shows distinct layers of different materials with different size, shape, and morphology of constituent/intermetallic particles (Figure 4 (a), (b)). The AA4343 clad shows primary Si particles in the Al matrix. Both the AA3xxx interlayer and the AA3xxx core shows bright intermetallic particles of a few micron in size in addition to sub-micron sized particles. The EDS analysis performed (not shown here) on the individual bigger

intermetallics reveals the presence of Al, Si, Mn and Fe, while the smaller particles showed presence of Al, Si, Mn, Fe and Cu. The multiclاد sheets that are subjected to brazing do not show any distinct interfaces between the clad layers (Figure 4 (c), (d)). In addition, the primary Si particles have re-distributed and appear as dendrites after the melting of the AA4343 clad and re-solidification. The primary Si now is mostly present at the top surface of the resolidified clad [45] and also at the grain boundaries, which is associated with other bright intermetallic particles that are precipitated along the grain boundaries in the form of a '*band of dense precipitates*' (Figure 4 (d) and (f)). The interface between the clad and the interlayer appears to have moved inwards (Figure 4 (d)). The band of dense precipitates in the reference sheet after brazing has been observed by others [1,46] and is generally associated as the reason for enhanced galvanic coupling and corrosion of the brazed clad sheets. The higher number of the cathodic intermetallic phases combined with lower dissolved Cu, and Mn in the surrounding Al matrix promote dissolution of the Al matrix and result in corrosion propagation through the inner layers of the brazed material [47].

Figure 4

In order to analyse the microstructure and the constituent phases in detail, transmission electron microscopy was performed on the as rolled and brazed multiclاد sheet materials. Samples were prepared as explained in the experimental section using focused ion beam milling and lift out. The sample areas were chosen from the interface of the clad and the interlayer (Figure 5 (a)); and interlayer and the core for the as rolled material (Figure 5 (b)). For the brazed multiclاد sheets, samples were prepared from similar locations corresponding to equal depth from the surface as that for the as rolled samples (see Figure 5 (c) and (d)).

Figure 5

The interface between the AA4343 clad and the AA3xxx interlayer can be clearly seen in Figure 5 (a). The AA3xxx interlayer is characterised by a homogenous distribution of very fine precipitates with a spheroidal shape. The average size of these precipitates is in the order of 150-200 nm. In addition, there are intermetallic (constituent) particles in the micrometre size range. The structure of the AA3xxx core can be seen in Figure 5 (b) and is characterized by the presence of sub-micron size precipitates with cuboidal morphology, and are elongated in one direction. The precipitates found in the interlayer are finer than those found in the AA3xxx core.

As can be seen from the images in Figure 5 (c) and (d), the interface cannot be clearly delineated after brazing of the multiclاد sheets. However, the AA3xxx interlayer retains the fine spheroidal precipitates as seen in Figure 5 (c). The interface of the clad and the interlayer here displays the nature of the dense band of precipitates observed in Figure 4 (d). A dark appearing intermetallic particle of the size of a micron is observed, the boundary of which with the surrounding Al matrix is decorated with very dense distribution of fine precipitates. Though not clearly visible, the intermetallic particle has formed at the boundary between the Al matrix and a primary Si particle (marked at top left corner of the image in Figure 5 (a)) which is formed after the melting and re-solidification of the AA4343 clad. In addition there is a 'precipitate free zone' in the areas around the bigger intermetallic phases. This is due to the dissolution of the fine Al-Mn dispersoids from the Al matrix and diffusion and preferential formation of Al-Fe-Mn-Si phases at the band of dense precipitates [48]. The interface between the interlayer and the core after brazing shows very little number of fine precipitates. This corresponds to the region in the brazed multiclاد sheet that is just below the previously existing interface between the interlayer and core (see Figure 4 (d)). The SEM images also show a narrow zone below the interface, which has a very low density of precipitates.

Combining the images in Figure 4 and Figure 5, it is clear that the number density of the fine intermetallic particles is lower, and the bigger intermetallics is higher in the as-rolled AA3xxx interlayer when compared to that in AA3xxx core (Figure 4 (b)). In addition, the brazing treatment has caused the number density of fine sub-micron sized precipitates to increase and that of the bigger intermetallic particles to reduce in the AA3xxx interlayer. A closer look at the structure of AA3xxx core before and after brazing also reveals a reduction in the number density of the fine sub-micron sized precipitates (Figure 4 (b), (d)) just below the interface with the AA3xxx interlayer. The EDS (TEM) analysis performed on individual features observed in the different layers of the multilayered sheet in as rolled and brazed condition and the summary of the analysis is shown in Table 3 [49–52]. The general observation from comparing the compositions of different precipitates at different depths from the surface before and after brazing is that the intermetallic (constituent) phases and the fine dispersoids in brazed structure show presence of Cu unlike the AA3xxx interlayer before brazing. Formation of these numerous precipitates that contain Cu upon brazing causes loss of dissolved Cu (diffusing outwards from the core to the interlayer) from the Al matrix, which in turn makes the Al matrix in the interlayer region more anodic compared to the intermetallic phases that are formed and thus more susceptible to corrosion compared to the core Al matrix.

Table 3

3.3. Electrochemical measurements

The potentiodynamic anodic polarization scans obtained in 0.1M HCl solution for the reference and multilayered sheet materials in as-rolled, and brazed conditions are shown in Figure 6. The scans for different depths are recorded from the surfaces obtained by controlled sputtering using GDOES to different depths as mentioned in Figure 3. The anodic current densities (see Figure 6) for the clad sheet remains unchanged for the multilayered sheet when

compared to the reference sheet after brazing. For the interlayer, the anodic current density at a given potential is lower after brazing than in as-rolled condition. The scans do not display any significant passive regions during anodic polarization due to the highly acidic nature of the electrolyte. The key factor for assessing the corrosion protection ability of the clad and the interlayer can be deduced from the E_{corr} values of the individual layers before and after brazing.

Figure 6

Figure 7

Figure 7 shows the E_{corr} values obtained from potentiodynamic polarization measurements for the individual layers before and after brazing. The E_{corr} values for the AA4343 clad and the AA3xxx interlayer in as-rolled condition are lower than that measured for the AA3xxx core. The interlayer is the most anodic of the three different layers in the multiclاد sheet in as rolled condition. The brazing treatment of the multiclاد sheet raises the potential of the clad (approx. 25 mV) and the interlayer (approx. 50 mV), but does not greatly affect the AA3xxx core. The AA3xxx interlayer now shows a higher potential than the AA4343 clad, but is still anodic when compared to the brazed AA3xxx core. The reference sheets without the interlayer also show an increase in the potential for the AA4343 clad after the brazing treatment. The increase in potential is higher for the clad in the reference material (approx. 60 mV) when compared to that in the multiclاد sheet (approx. 25 mV) due to higher Cu diffusion towards the surface in the absence of an interlayer. In addition, the potential for the AA3xxx core in the diffusion zone has increased significantly when compared to the bulk of the core (approx. 25 mV). In terms of depth below the interface with the core, the reference sheet shows considerably higher potential values (approx. -650 mV vs. saturated Ag/AgCl) when compared to that of the multiclاد sheet (approx. -700 mV vs. saturated Ag/AgCl) upon brazing.

Figure 8 shows the evolution of galvanic current density and galvanic potential vs. time obtained from the ZRA measurements performed by coupling the AA4343 clad with the AA3xxx interlayer; and the AA3xxx interlayer with the AA3xxx core for the multiclاد sheets in as-rolled (Figure 8 (a)) and brazed conditions (Figure 8 (b)). Results show that in the as-rolled condition, the clad is anodic to the interlayer which is in turn anodic to the core material. This is expected to provide sacrificial protection to the core by the top layers. The brazing treatment has modified this and it can be observed that there is no longer a clear observable trend in the current flow between the adjacent layers in the multiclاد material. The results observed here are generally in accordance with the E_{corr} values obtained from localized electrochemical measurements in Figure 7 with exception for the relative E_{corr} values between the clad and the interlayer in as rolled condition.

Figure 8

In general, the electrochemical profiling and microstructural analysis performed here indicates that presence of a low-Cu interlayer in between the clad and the core modifies the changes occurring during the brazing process in terms of the evolution of microstructure due to diffusion based phenomenon and also the local electrochemical nature of the different layers. During brazing, Si from the AA4343 clad diffused inwards to the low-Cu AA3xxx interlayer (Figure 3) which caused the Mn from the solution along with the Fe in the interlayer to precipitate out as Al(Fe,Mn)Si based precipitates [48,53,54] (Figure 4 (d)). The interfacial region between the resolidified clad and the interlayer displayed the highest density of such precipitates. Similarly, precipitation also took place at the interface between the AA3xxx core and the resolidified AA4343 clad for the reference sheets which do not have an interlayer. However, in this case outward diffusion of Cu along with Mn from the core towards the clad promoted precipitation of Al(Fe,Mn,Cu)Si based precipitates (see **Table 3**) [55–58]. This resulted in depletion of Cu and Mn as solute in the Al matrix in the core material for the

reference sheets. In the case of the presence of a low-Cu interlayer, the Cu diffused outwards from the core to the low-Cu interlayer, which restricted the formation of the Cu containing precipitates to the interlayer region. As the Si diffusion from the clad up to the core is not significant, Cu in core material is retained in the Al solution to a higher extent. This is observed in the RF-GDOES profiles for the reference and multiclاد sheets before and after brazing in Figure 3 as well as in **Table 3**.

The local electrochemical analysis showing the E_{corr} values for the various layers before and after brazing process (Figure 7) along with the ZRA measurements (Figure 8) reveal that the AA3xxx core in as-rolled condition is cathodic when compared to the AA4343 clad as well as to the low-Cu AA3xxx interlayer. This is due to higher Mn and Cu in the core and lower Cu in the interlayer [59]. The AA4343 clad is designed to act as a sacrificial layer for allowing corrosion to propagate through the clad and protect the core material. However, upon brazing due to the outward diffusion of Cu from the core material, the E_{corr} value of the resolidified clad increases thus lowering the gap between the E_{corr} values of the core and the clad. The formation of Al(Fe,Mn,Cu)Si precipitates which are cathodic in nature when compared to the Al matrix enhances the potential difference between these materials and allows for galvanic coupling and corrosion propagation between the matrix and the precipitates [60–67] even though the overall E_{corr} value is higher.

In the case of presence of a low-Cu interlayer, the Cu diffusing out from the core to the interlayer formed Cu based precipitates in the interlayer region. However, the Cu in the core material remained in the Al matrix to a higher extent due to lower available diffused Si from clad restricting precipitation [11]. An increasing concentration of dissolved Cu with depth due to outward diffusion from core material also results in an increasing (shift towards positive direction) potential of the Al matrix towards the core. This protects the core material as the corrosion propagation faces Al material that is more cathodic with depth from the surface thus

promoting lateral corrosion within the interlayer region and preventing through failure. In addition, the formation of the precipitates upon brazing at the grain boundaries as shown in Figure 5 (c) also restricts the corrosion to propagate laterally. The effect of higher Cu in solution of the core material due to the added low-Cu interlayer improves the corrosion protection of the core layer thus enhancing the life of the brazed multi-clad sheets when compared to those without a low-Cu interlayer.

4. Conclusions

In the present work, a combination of micro-scale electrochemical measurements and glow discharge optical emission spectroscopy was used to investigate the electrochemical properties of multi-clad Al structures as a function of local alloy composition and microstructure before and after brazing. In general, the obtained results reveal that:

1. Brazing of the clad Al sheet material leads to inwards diffusion of Si from the clad and outwards diffusion of Cu from the core forming a band of dense precipitates.
2. The difference between the electrode potentials and hence the corrosion protection provided to the core by the outer layers is reduced after brazing.
3. The addition of a low-Cu interlayer reduces the formation of Al(Fe,Mn,Cu)Si based phases in the band of dense precipitates and helps retain the cathodic nature of the core compared to the outer layers after brazing.
4. ZRA measurements show that the clad and the interlayer are anodic when compared to the core in as rolled condition but no clear distinction can be made after brazing treatment.

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(a) Multiclad

AA4343 – 36 μm (Clad)
AA3xxx Low Cu – 38 μm (Interlayer)
Modified AA3xxx (Core)

(b) Reference

AA4343 – 36 μm (Clad)
Modified AA3xxx (Core)

Figure 1: Schematic cross-section of (a) Multiclad and (b) Reference Aluminium brazing sheets used in this study. The relative thicknesses are not to scale.

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Table 3: Representative elemental composition analysis (in at.%) measured by EDS (TEM) of the individual features of the multiclاد sheets in as rolled and brazed condition.

Table 1: Composition of the materials (in wt.%) used in the Aluminium brazing sheets.

	Si	Fe	Cu	Mn	Mg	Cr	Ni	Zn	Ti	Al
AA4343	7.2	0.3	0.1	0.1	0.0035	0.05	0.03	0.05	0.05	Bal.
AA3xxx Interlayer	0.22	0.57	0.08	1.15	0.02	0.05	0.03	0.1	0.05	Bal.
AA3xxx Core	0.2	0.2	0.65	1.35	0.02	0.05	0.05	0.1	0.08	Bal.

Table 2: Representative elemental composition analysis (in wt.%) measured by RF-GDOES at different sputter depths of the multiclاد and reference sheets in as rolled and brazed condition.

Condition		Material	Al	Si	Fe	Cu	Mn	Others (Cr, Zn, Ti, Mg, Ni & O)
As Rolled		AA4343 Clad	92.4±0.7	5.3±0.1	0.3±0.1	0.03	0.06	1.7
		AA3xxx Interlayer	96.3±0.6	0.2±0.1	0.7±0.1	0.1	1.1±0.1	1.5
		AA3xxx Core	96.2±0.4	0.2±0.1	0.3±0.1	0.4±0.1	1.4±0.3	1.5
After CAB	With Interlayer	AA4343 Clad	96.7±0.5	2.1±0.2	0.2	0.1	0.1	0.7
		AA3xxx Interlayer	96.5±0.4	0.9±0.1	0.3±0.1	0.2	1.2±0.1	0.8
		AA3xxx Core	96.9±0.4	0.3±0.1	0.2	0.4±0.1	1.3±0.1	0.8
	Without Interlayer	AA4343 Clad	96.5±0.4	2.3±0.1	0.2	0.2	0.1	0.6
		AA3xxx Core - 1	96.6±0.3	0.9±0.1	0.2	0.3	1.3±0.1	0.7
		AA3xxx Core -2	95.2±0.8	0.3±0.1	0.2	0.4±0.1	1.3±0.1	2.5

Table 3: Representative elemental composition analysis (in at.%) measured by EDS (TEM) of the individual features of the multiclad sheets in as rolled, and brazed condition.

Material		Feature	Al	Si	Mn	Fe	Cu	Ti	V	Cr	Proposed Phase
As Rolled	Clad	Primary Si	1.1±0.17	98.9±0.17							Si
	Interlayer	Dispersoid	88.66±0.29	3.51±0.11	7.18±0.15	0.66±0.06					Al ₁₅ (Fe,Mn) ₃ Si ₁₋₂ ; Fe+Mn:Si = 2.23
		Dispersoid	89.8±0.23		5.3±0.11	4.9±0.33					Al ₆ (Mn,Fe)
		Dispersoid	85.8±1.49	5.24±0.58	8.96±0.91						α-AlMnSi; (τ ₉) (Al ₉ Mn ₂ Si)
		Constituent Particle	78.05±0.3	7.52±0.08	5.84±0.86	8.59±1.06					Al ₁₅ (Fe,Mn) ₃ Si ₁₋₂ ; Fe+Mn:Si = 1.92
		Constituent Particle	80.24±2.88	6.2±0.56	6.04±0.56	7.52±1.76					Al ₁₅ (Fe,Mn) ₃ Si ₁₋₂ ; Fe+Mn:Si = 2.19
		Constituent Particle	85.32±0.02		6.74±0.13	7.95±0.13					Al ₆ (Mn,Fe)
	Core	Constituent Particle	77.58±0.23	4.09±0.03	12.27±0.13	6.06±0.34					α-Al(Fe,Mn)Si
		Constituent Particle	77.56±0.05	6.11±0.04	13.28±0.06	3.05±0.07					Al ₁₅ (Fe,Mn) ₃ Si ₁₋₂ ; Fe+Mn:Si = 2.67
		Dispersoid	89.17±1.33		10.83±1.33						Al ₆ (Mn)
		Dispersoid	90.95±1.09	2.59±0.28	3.27±0.39	2.95±0.42	0.24±0.01				Al ₁₂ (Fe,Mn,Cu) ₃ Si _{1.2-2} ; Fe+Mn+Cu:Si = 2.49
		Dispersoid	88.71±0.68		8.76±0.57		0.94	1.4±0.09	0.19±0.02		Al ₆ (Mn,Cu)
		Dispersoid	85.2±1.54	4.31±0.42	10.43±1.14			0.06±0.01			α-AlMnSi; (τ ₉) (Al ₉ Mn ₂ Si)
After CAB	Clad	Primary Si	2.04±0.19	97.96±0.19							Si
	Interface	Constituent Particle	73.67±0.58	10.95±0.29	8.31±0.73	6.54±0.39	0.36±0.02		0.13±0.01	0.05±0.01	Al ₃₂ (Fe,Mn) ₈ (Al,Si) ₄ Si ₂
		Constituent Particle	72.7±0.5	10.2±0.26	7.8±0.14	8.75±0.2	0.34±0.02		0.14±0.08	0.07±0.03	Al ₁₂ (Fe,Mn,Cu) ₃ Si _{1.2-2} ; Fe+Mn+Cu:Si = 1.66
		Dispersoids-Dense Precipitates	75.1±2.6	9.2±0.2	6.4±0.1	7.9±0.2	1.4±0.1				Al ₁₂ (Fe,Mn,Cu) ₃ Si _{1.2-2} ; Fe+Mn+Cu :Si = 1.71;
		Dispersoids-Dense Precipitates	84.9±3.7	6.4±1.1	6.8±0.8	1.1±0.1	0.8±0.1				Al ₃₂ (Fe,Mn) ₈ (Al,Si) ₄ Si ₂
	Interlayer	Constituent Particle	73.13±0.12	10.32±0.1	7.78±0.1	8.42±0.24			0.22±0.02	0.12±0.01	Al ₁₂ (Fe,Mn) ₃ Si _{1.2-2} , Fe+Mn:Si = 1.57
		Constituent Particle	71.95±0.03	11.47±0.07	8.94±0.29	7.17±0.27	0.26±0.01		0.12±0.04	0.07±0.03	Al ₁₂ (Fe,Mn,Cu) ₃ Si _{1.2-2} , Fe+Mn+Cu:Si = 1.43
		Constituent Particle	72.69±0.07	9.25±0.07	5.31±0.13	12.05±0.13	0.7±0.01				Al ₁₂ (Fe,Mn,Cu) ₃ Si _{1.2-2} , Fe+Mn+Cu:Si = 1.95
		Constituent Particle	73.47±0.06	9.66±0.1	11.74±0.83	5.13±0.76					Al ₁₂ (Fe,Mn) ₃ Si _{1.2-2} , Fe+Mn:Si = 1.75
		Constituent Particle	73.10±0.2	10.34±0.04	14.77±0.27	1.78±0.13					Al ₁₂ (Fe,Mn) ₃ Si _{1.2-2} , Fe+Mn:Si = 1.6
		Dispersoid	90.39±2.34	4.86±1.07	4.14±1.12	0.5±0.13	0.11±0.02				α-AlMnSi; (τ ₉) (Al ₉ Mn ₂ Si)
		Dispersoid	84.35±0.1	7.24±0.05	8.41±0.05						α-AlMnSi; (τ ₉) (Al ₉ Mn ₂ Si)
		Dispersoid	95.55±0.27		4.45±0.27						Al ₆ Mn
	Core	Constituent Particle	74.09±0.24	9.57±0.27	12.3±0.44	4.03±0.47					Al ₁₂ (Fe,Mn) ₃ Si _{1.2-2} , Fe+Mn:Si = 1.71
		Constituent Particle	85.07±0.05	1.17±0.01	12.54±0.06	1.22±0.1					Al ₆ (Fe,Mn)Si
		Dispersoid	89.53±2.66	4.48±1.14	5.76±1.43	0.24±0.09					Al ₃₂ (Fe,Mn) ₈ (Al,Si) ₄ Si ₂
		Dispersoid	90.67±0.71	3.87±0.29	4.88±0.4	0.23±0.01	0.18±0.01	0.17±0.01			Al ₁₂ (Fe,Mn,Cu) ₃ Si _{1.2-2} , Fe+Mn+Cu:Si = 1.37
		Dispersoid	86±0.65	4.44±0.59	7.73±0.11		0.48±0.03	1.16±0.03	0.18±0.01		α-AlMnCuSi; (τ ₉) (Al ₉ (Mn,Cu) ₂ Si)