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

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

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Summary

The objective of the present study is to understand the mechanisms of corrosion propagation across the multi-clad structure of Al alloys sheets as a function of local alloy composition and microstructure, with and without brazing treatment. Electrochemical behaviour at different depths was profiled using a combination of glow discharge optical emission spectroscopy (GDOES) sputtering, localized potentiodynamic polarization and zero resistance ammetry (ZRA) measurements. Multi-clad structure used was a four layer sandwich consisting of a copper-containing AA3xxx long-life core alloy, AA4343 brazing clad on both sides and a copper-free AA3xxx interlayer on the air-side of the sandwich sheet. The polarization behaviour of both as-rolled and brazed materials (i.e. corrosion potential, pitting potential, cathodic and anodic reactivities) was determined as a function of depth using a localized electrochemical cell and GDOES sputtering. Galvanic corrosion behaviour of individual cladding layers was studied by ZRA in a conventional electrochemical cell. The changes in the microstructure of the material caused by the brazing process were investigated by scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX). The observed evolution of the electrochemical parameters throughout the material depth was analysed and correlated to the respective microstructural features. The obtained results were compared to those obtained for a conventional, three-layer long-life alloy product.

1 Introduction

Aluminium alloys are widely used in all types of heat exchanger applications in automotive, e.g. in radiators, air conditioner evaporators, exhaust gas recirculation (EGR) and water charge air cooling (WCAC) systems. This is due to the favourable combination of properties, such as low density, high thermal conductivity and good corrosion resistance. During the last two decades, mechanical assembly in the production of heat exchangers has been continuously replaced by brazing of aluminium alloys. This change was caused by cost and safety requirements as well as recycling issues [1-3]. Brazed heat exchangers are generally manufactured from clad aluminium sheet materials where a high melting point core alloy, typically Al-Mn (AA3xxx), is clad on one or both sides with a low melting point alloy Al-Si (AA4xxx) family.

In EGR and WCAC systems, the use of aluminium alloys is limited by the corrosion due to the chemistry of exhaust gases, including its acidic nature and water content. Corrosion occurring on the outer side of heat exchanger tubes caused by the species from the exhaust gases in this case is a very important issue and is currently a blocking point for continued down-gauging and weight reduction of several types of heat exchangers. Recently significant increase in this air-side corrosion resistance has been achieved by using clad sandwich materials with multiple layers of different alloys.
In the present work, we employ a combination of micro-scale electrochemical measurements and GDOES sputtering to investigate the corrosion propagation in a four-layer Al structure containing a copper-free AA3xxx interlayer on the air-side. The obtained results are compared to those obtained for a conventional, three-layer product.

2 Experimental Details

Sheets having size of approximately 8 by 20 cm$^2$ were cut from rolled modified copper-containing AA3xxx aluminium alloy (480 μm thick) clad with AA4343 (36 μm thick) on one side and AA4343 (36 μm thick) on top of copper-free AA3xxx (38.4 μm thick) on the other side. The sheets were degreased in acetone, dried and placed into a Controlled Atmosphere Brazing (CAB) furnace. The materials were heated up to 600°C, kept at that temperature for 2 min. and then cooled down with a specified rate. The process temperature was selected to be close to the liquidus temperature of the clad material and much lower than the solidus temperature of the core material.

Both as-rolled and brazed materials were etched down to certain depths using glow discharge optical emission spectroscopy (GDOES) argon ion sputtering. The applied power was 40 W and the argon pressure in the sputtering chamber was 650 Pa. The diameter of the sputtering crater was 4 mm. The depth distributions of the main alloying elements (Si, Cu, Mn) were used to identify the interfaces between the cladding layers and to define the required sputtering depth.

The polarization behaviour of both as-rolled and brazed materials (i.e. corrosion potential, pitting potential, cathodic and anodic reactivities) was determined as a function of depth using a Dualscope EC localized electrochemical cell and a conventional potentiostat (GillAC, ACM Instruments). The system utilizes a small reservoir cavity having reference and counter electrodes and a plastic pipette tip with a micron scale opening which ensures the contact with the working electrode. The diameter of the pipette tip was 1 mm in all experiments. The contact between the electrolyte inside the cell and the working electrode is achieved by a hanging droplet which is formed by an airtight system with a precise control of the solution pumping. The size and shape of the droplet are permanently controlled using a microscope and a digital video camera attached to the cell [4-7]. In all measurements an Ag/AgCl reference electrode and a Pt wire as a counter electrode were used. Potentiodynamic polarization scans were performed separately in the anodic (from OCP up to 300 mV vs. OCP) and cathodic (from OCP down to -250 mV vs. OCP) direction with a rate of 1 mV/s. Prior to each measurement, the OCP was allowed to stabilize for 5 min. A 0.1M NaCl (analytical grade) solution was used as the electrolyte. All experiments were conducted at room temperature and no aeration was applied to the electrolyte.

Zero resistance ammetry (ZRA) measurements were performed in a conventional 3-electrode cell using the same potentiostat. The measurements were conducted in either as-dissolved 0.1M NaCl or in 0.1M NaCl with pH 2.8 (adjusted with HCl) at room temperature. In each ZRA experiment, galvanic coupling was made between two pieces of the same material sputtered down to different depths by GDOES. Only
the sputtering craters were exposed to the electrolyte, while the remaining surface of each sample was covered by a protective lacquer.

The microstructure and surface morphology of the GDOES-sputtered surfaces for the as-rolled and brazed material were examined using optical microscope and scanning electron microscope (SEM, Quanta 200 ESEM FEG, FEI) equipped with an energy dispersive X-ray spectrometer (EDX, 80 mm$^2$ X-Max silicon drift detector, Oxford Instruments).

3 Results and Discussion

3.1 Elemental depth profiling by GDOES

Fig. 1 shows depth profiles of Si, Mn and Cu for the as-rolled and brazed multi-clad material. The drastic decrease in the concentration of Si and increase in the concentration of Mn after 7 min. of sputtering corresponds to the interface between the Al-Si AA4343 alloy and the AA3xxx interlayer. The increase in the concentration of Cu after about 16 min. of sputtering indicates the interface between the interlayer and the core material. Based on the thickness data for the individual layers, the sputtering rate is estimated to be 4.5 μm/min.

It can be noted that the surface regions of the AA4343 layer are enriched with Si, while in the deeper layers the concentration of Si is almost constant (around 6 %). After brazing the concentration of Si next to the surface is dramatically increased (up to 22 %) and the interfaces between the individual layers cannot be clearly defined. The concentration of Mn in the AA3xxx interlayer becomes smaller after brazing, and the surface of the AA4343 layer also gets enriched with Mn (up to 1 %).

In order to expose different layers of the material for the further electrochemical investigation, the as-rolled sample was sputtered with different time intervals, based on the survey GDOES profile (Fig.1a). The same sputtering time intervals were also chosen for the brazed sample.

![Figure 1: GDOES profiles of the as-rolled (a) and brazed (b) multi-clad material.](image)
3.2 Analysis of microstructure and local chemical composition

SEM images of the surface of as-rolled and brazed multi-clad material after approximately 8 min. and 16 min. of GDOES sputtering are shown in Fig. 2 and 3. For different depths of the material, numerous intermetallics having various sizes and shapes can be observed. Based on the size, two types of particles can be distinguished for the brazed material: relatively big (a few μm) precipitates and smaller (less than 1 μm) particles. The EDX analysis performed on the bigger intermetallics reveals the presence of Al, Si, Mn and Fe. In the smaller particles, Al, Si, Mn, Fe and Cu can be found. Based on the detailed microstructural investigation of similar multicladd materials published previously [7, 8], the first group of particles can be referred to as α-Al(Fe-Mn)Si particles, while the second group is Al₂Cu and α-Al(Fe-Mn)Si particles. On the surface of the brazed material (not shown), a few μm big Al-Si precipitates can also be seen.

Figure 2: SEM images of the surface of the as-rolled multi-clad material after approximately 8 min. (a) and 16 min. (b) of GDOES sputtering

Figure 3: SEM images of the surface of the brazed multi-clad material after approximately 8 min. (a) and 16 min. (b) of GDOES sputtering
3.3 Electrochemical measurements

Fig. 4 (a, b) shows potentiodynamic polarization scans obtained in 0.1M NaCl solution for the surface of the as-rolled material sputtered by GDOES for 16 min. This sputtering time corresponds to the interface between the copper-free 3xxx intermediate layer and the core material. The anodic scans exhibit pitting at around -600 mV and the corrosion potential falls in the region between -700 and -650 mV. For the cathodic polarization curves, the discrepancy between the measured corrosion potential values is higher than for the anodic curves. In general, a relatively big scatter in the measured corrosion and pitting potentials can be explained by the short time (5 min.) of OCP stabilization. Potentiodynamic polarization scans obtained for the surface of the brazed material, sputtered by GDOES for the same period of time, are shown in Fig. 4 (c, d). It can be seen that after brazing the corrosion potentials remain almost the same, while the pitting occurs at slightly more positive potential values (between -600 and -500 mV).

![Figure 4: Potentiodynamic polarization scans obtained in 0.1M NaCl solution for the surface of the as-rolled material sputtered by GDOES for 16 min before (a, b) and after (c, d) brazing. Potentials are measured vs. Ag/AgCl reference electrode.](image)

Fig. 5 shows ZRA results for the copper-free 3xxx intermediate layer galvanically coupled with the core material before (a) and after (b) brazing. The measurements were performed in 0.1M NaCl solution with pH 2.8 (adjusted with HCl). Prior to each measurement, the OCP was allowed to stabilize for 3 h. For the as-rolled material (Fig. 5a), positive current reached after about 30 minutes indicates that the interlayer becomes anodic with respect to the core material. On the other hand, for the brazed material (Fig. 5b) the interlayer initially stays cathodic with respect to the core material, but after about 2 hours of measurements it shows anodic behaviour.
Such a notable change in the electrochemical properties of the considered interface region can be explained by the changes in the depth distribution of the main alloying elements (in particular, Si, Cu and Mn) during brazing. As can be seen from the survey GDOES profiles (Fig. 1), brazing leads to a significant increase in the concentration of Si at the considered depth. At the same time, the profile of Cu becomes more even and the concentration of Cu only slightly changes in the depth range between 50 and 100 μm.

**Figure 5:** ZRA results for the interface between the copper-free 3xxx intermediate layer and the core material before (a) and after (b) brazing, in 0.1M NaCl solution with pH 2.8.

### 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.

In general, the obtained results reveal that:
- A combination of local micro-capillary measurement and GDOES is an effective approach for the electrochemical investigation of multi-clad Al structures.
- Brazing of the multiclad material leads to significant changes in the depth profiles of the main alloying elements and the microstructure. That, in turn, leads to changes in the electrochemical properties of the cladding layers.

### 5 References