INFLUENCE OF ALLOYING ADDITIONS ON CORROSION BEHAVIOUR OF ALUMINIUM BRAZING SHEET

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ABSTRACT The trend in industry is to use thinner aluminium brazing sheet without compromising corrosion and mechanical properties. To follow this trend more fundamental knowledge of the corrosion mechanism is needed. This paper details a preliminary study carried out to give a more fundamental understanding of the corrosion mechanism of so-called Long Life alloys as produced by Hoogovens Aluminium. In these alloys a sacrificial layer, obtained by Si diffusion from the clad layer, is deployed to obtain outstanding corrosion performance. The sacrificial layer is characterised by a band of dense precipitates. The effect of the alloying elements Si, Mg and Cu in the core alloy on the effectiveness of the sacrificial layer was investigated. A Si level of 0.5 wt.% in the core alloy prohibits the formation of a band of dense precipitates. Mg enhances the amount of precipitation in the band of dense precipitates, which makes the sacrificial layer more effective for obtaining Long Life properties. Cu is believed to be mainly in τ-AlMnCu precipitates. The Cu-containing alloys had a more noble corrosion potential and had a higher resistance to pitting corrosion.

Keywords: *aluminium alloys, brazing sheet, precipitates, corrosion, Long-Life properties.*

1. INTRODUCTION

The trend in the industry for the use of ever thinner aluminium sheet, remaining good corrosion properties, leads to extensive research on the corrosion properties. In thin aluminium sheet, e.g. brazing sheet used in radiators, pitting corrosion (resulting in perforation) can be a severe problem. In the so-called *Long-Life* brazing sheet of Hoogovens Aluminium, a sacrificial layer is used to obtain outstanding corrosion resistance[1,2]. The sacrificial layer is obtained by Si diffusion from the clad layer into the core.

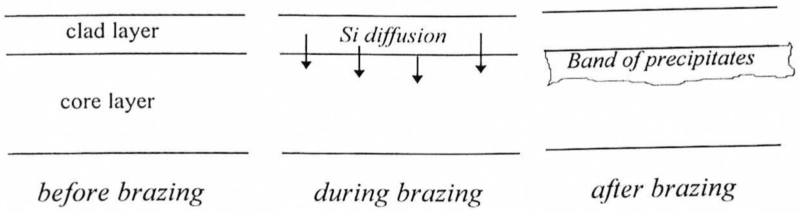

Figure 1: A sketch of the formation of the band of precipitates (BDP), which is characteristic for the sacrificial layer.

The diffusion of Si stimulates the precipitation of α-AlMnSi particles. This leads to a high density of these precipitates just beneath the clad/core interface, usually called the band of dense precipitates (BDP). This BDP is characteristic for the sacrificial layer. The sacrificial layer transforms the corrosion mechanism from the extremely harmful pitting corrosion to a lateral corrosion attack, which is less harmful. The actual mechanism by which this sacrificial layer wo is unknown. In this study the first results of a research program on the influence of various allo elements in the core alloy on the corrosion performance are given.

2. EXPERIMENTAL PROCEDURE

For the core alloy of the brazing sheet, eight different alloys have been cast. All all contain 1.1wt % Mn and 0.1wt% Fe. The Si content is 0.05 or 0.5wt%, the Mg content 0 0.35wt% and the Cu content is 0 or 0.7wt%. The possible combinations of these quantities alloying elements lead to eight core alloys, which are labelled as given in Table I.

The clad alloy for all brazing sheet was a standard AA4045 alloy. The clad thickness w about 10% of the total thickness of the brazing sheet. A normal production route, simulated on scale, was used for processing the brazing sheet down to 0.38mm in H24 temper. For the braz procedure a common cycle as applied by most aluminium-radiator manufacturers was chosen.

Table I: Chemistry of the eight core alloys (with 1.1%Mn and 0.1%Fe as a base)

Alloy	Si (wt.%)	Mg (wt.%)	Cu (wt.%)
1	0.05	0	0
2	0.50	0	0
3	0.05	0.35	0
4	0.50	0.35	0
5	0.05	0	0.70
6	0.50	0	0.70
7	0.05	0.35	0.70
8	0.50	0.35	0.70

After a 30 days natural ageing period, the alloys were subjected to the Salt Water Acetic A Test (SWAAT) according to ASTM G85c. This test is a standard test to establish the corros performance of brazing sheet. The samples are coated on the core-metal side, whereas the oth side is exposed. The number of days elapsing until the sample is perforated, is taken as a meas for the corrosion resistance. This test is believed to be a representative for the corros environment of the brazing sheet used in radiators[3]. The commercial Long-Life alloys will eas withstand 20 days SWAAT exposure.

The microstructure of the samples before and after SWAAT were investigated by means light microscopy and Electron Probe Micro Analysis (EPMA). The corrosion potentials have be measured according to ASTM G69.

3. MICROSTRUCTURE

3.1. Grain structure

The grain structure of alloy 1 (no addition) and alloy 3 (Mg addition) are shown in Fig Although all eight alloys show elongated grains, they can be divided into three groups. The fi group of alloys 1, 2 and 5 exhibits very large grains (abnormal grain growth ?). The third group alloys 3, 6 and 8 exhibit smaller, but still elongated grains. The second group of alloys 4 and show grain sizes which are between those of the two other groups.

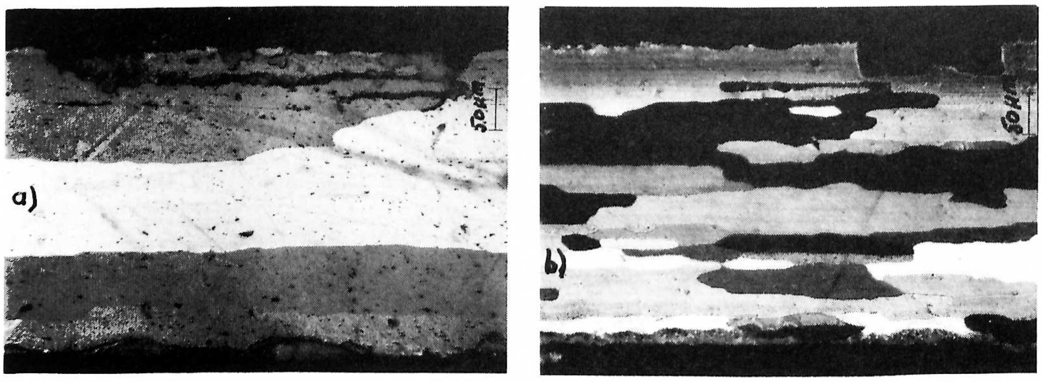

Figure 2: Grain structure of the alloys exhibiting elongated grains. a) alloy 1 as a typical example for the group with very large grains. b) alloy 3 as a typical example for the group with relatively smaller grains.

3.2. Precipitates in the core

Cross sections of the brazing sheet were polished and etched for precipitates in a dilute HF solution. The precipitate density in the core alloys with high-Si content is much higher than for the core alloys with lower Si contents (Fig. 3). This observation is in agreement with the fact that Si reduces the solubility of Mn in aluminium alloys. The low-Si core alloy with Mg showed lower density of precipitates than the one without Mg. Copper does not seem to have a large influence on the density of precipitates. If both Cu and Mg are added there is also a lower density of precipitates. In the high Si alloys the effect of Mg addition is just opposite; a significantly higher density of precipitates is observed in these alloys. Again, Cu does not seem to have a large influence on the density of precipitates.

The density of the precipitates is also reflected in the conductivity of the core alloys as shown in Table II. In these types of core alloys, the precipitates are mainly Mn-containing ones (Al_6Mn, α-AlMnSi or τ-AlMnCu)[4]. If Mg and Si are present, then also Mg_2Si particles will precipitate. Thus, in general, in these alloys precipitation leads to a decrease of Mn in solid solution. As conductivity is very sensitive to variation of elements in solid solution, especially Mn, the density of precipitates is reflected in the conductivity.

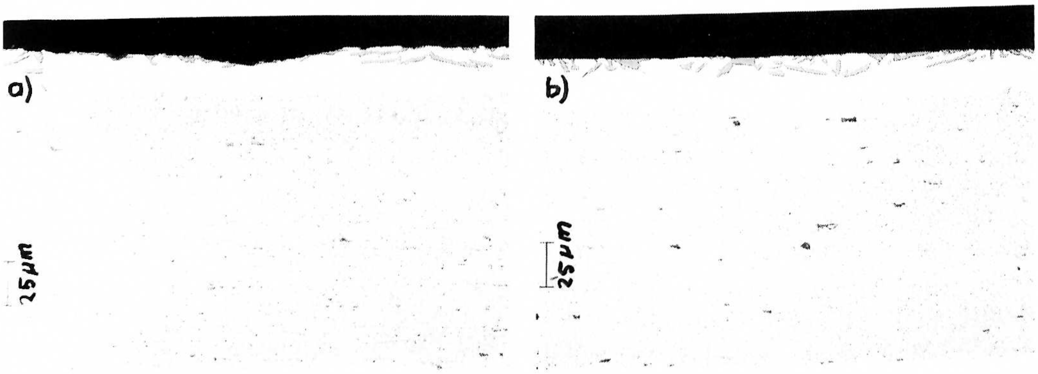

Figure 3: Light-microscopy photos of alloy 6 (Si and Cu additions), showing no band of precipitates after HF-etching and of alloy 7 (Cu and Mg additions) showing a distinct band of precipitates after HF-etching.

3.3. Precipitates in the BDP

The low-Si alloys showed a band of dense precipitates (BDP) in the core just below the clad/core interface. The high-Si alloys didn't show this BDP. The influence of Cu and Mg in the core alloy on the BDP in the low-Si alloys is increasing the density of precipitates; Mg has a larger effect than Cu. The BDP is also thicker in the Mg containing alloy than in the Cu or Cu+Mg containing alloys.

Table II: Results of the investigation on the microstructure of the core alloys, the average SWAAT result, corrosion potential and the conductivity after brazing.

Core alloy	Si	Mg	Cu	grain structure*	density precipitates in core	BDP	SWAAT (days)	E_{corr} (mV)	Conductivity (%IACS)
1	-	-	-	1	low	yes	5	-727	37.9
2	+	-	-	1	high	no	4	-735	43.7
3	-	+	-	3	low	yes	17	-726	34.5
4	+	+	-	2	high	no	10	-742	42.8
5	-	-	+	1	low	yes	25^+	-665	32.6
6	+	-	+	3	high	no	22	-694	41.3
7	-	+	+	3	low	yes	25^+	-694	30.8
8	+	+	+	2	high	no	25^+	-698	40.6

* see section 3.1: 1= large grains, 2 = average grains size and 3 relative small grains.

4. CORROSION

4.1. Salt Water Acetic Acid Test (SWAAT)

The SWAAT results for the eight different brazing sheet with different core alloys are given in Table II. The copper containing alloys (nr.5-8) have a significantly better SWAAT performance than the non-copper (nr.1-4) containing ones. If there is no Cu in the core alloys, then the Mg containing alloys also show better SWAAT results than the non Mg-containing ones.

The brazing sheet with core alloy 1 exhibits a bad SWAAT result. In this alloy a band of dense precipitates (BDP) is observed (see section 3.3). This means that the BDP in alloy 1 does not provide good corrosion resistance and that core alloy 1 itself also has a low corrosion resistance.

As expected, adding Si as in alloy 2 and 4 does not improve the SWAAT result, i.e., the BDP is not formed anymore. Adding Mg, as in alloy 3, drastically improves the SWAAT results. This is probably caused by fine Mg_2Si dispersoids which enhances the nucleation of fine α–AlMnSi dispersoids in the sacrificial layer[5].

The fact that all Cu containing alloys withstand more than 25 days SWAAT exposure suggests a similar mechanism for the corrosion performance in these alloys. This can be Cu in solid solution, which is known to give good corrosion performance as long as it is homogeneously distributed in the alloy (no denuded zones), i.e., Cu shifts the corrosion potential of Al-alloys to more noble value[6]. In Ref. [12] it is assumed that Cu will be mainly in solid solution after brazing. Another possible explanation for the enhanced corrosion resistance is that in alloys with the Cu and Mn contents as in alloys 5-8, τ-AlMnCu precipitates are formed preferential to Al_6Mn and α-AlMnSi precipitates[4]. Recent TEM work[7] shows that after brazing the τ-phase is still present in large quantities. As the processing of the brazing sheet is close to the one in Ref.[7], it is more likely that the τ-phase is somehow responsible for the good corrosion resistance.

Photographs of cross-sections of some SWAAT samples after failure are shown in Fig.4. Two types of corrosion mechanism are shown. The first one in Fig. 4a is pitting corrosion. This type of corrosion is often observed in standard AA3xxx alloys. This kind of corrosion behaviour is most feared in brazing sheet used for radiator applications, because it causes leakage. Fig. 4b shows the beneficial use of a sacrificial layer. The sacrificial layer transforms the corrosion attack from pitting into a lateral corrosion attack and thus preventing or delaying leakage.

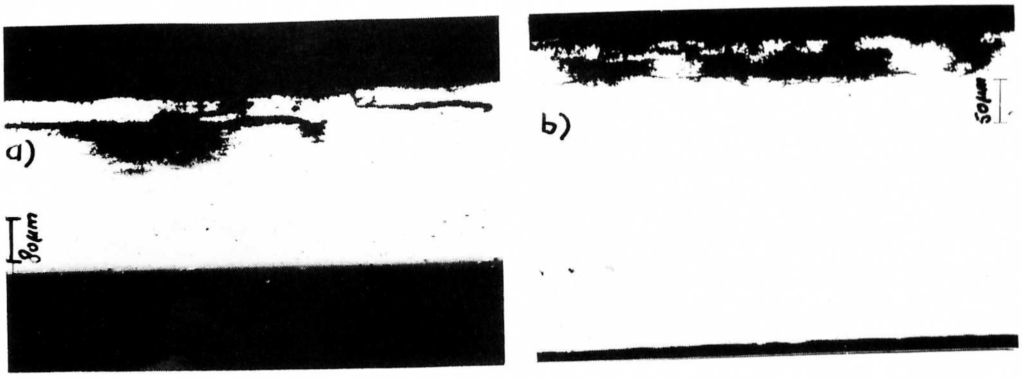

Figure 4: Two types of corrosion observed in the SWAAT tested samples. a) Pitting corrosion in alloy 2, typical corrosion behaviour normally observed in standard AA3xxx alloys. b) The beneficial usage of a sacrificial layer in alloy 3, obtained by Si diffusion from the clad into the core.

4.2. The corrosion potential

Sometimes the corrosion potential of the core alloy is used to select a core alloy for good corrosion resistance. For brazing sheet, which is susceptible to pitting, the corrosion potential cannot be used as a criterion for SWAAT results. This is illustrated in Fig. 5a where the corrosion potentials of the alloys are given versus the SWAAT results. Although there is a general trend that a higher E_{corr} gives better corrosion performance, a correlation between the corrosion potential and the SWAAT result cannot be observed. Nevertheless the corrosion potential can be important if a radiator is assembled from different types of aluminium alloys.

The corrosion potentials of core alloy with chemistries as given in Table I can be estimated. It is known that Mg and Si in the quantities applied, do not significantly influence the corrosion potential[6]. On the other hand, Cu and Mn in solid solution will significantly influence the corrosion potential[8]. The Mn in solid solution can be estimated from the conductivity values of the core alloys[9] as given in Table II. Then with Ref. [10] the corrosion potential can be calculated. For core alloys 1-4 the values are in exact agreement with the measured ones (difference less than 1mV). The Cu containing alloys 5-8 show a large but constant difference of (38±1)mV between the calculated and measured corrosion potentials. Surprisingly, this value is equal to the difference in corrosion potential of an commercial pure Al-matrix and a binary Al-0.7%Cu alloy with all Cu in solid solution[10].

In alloys with chemistries as given in Table 1, the Cu will be in precipitates like the τ-AlMnCu[4,7]. Because Mg and Si seem to have no influence on the precipitation of the τ-phase[11] and the Mn and Cu levels are the same in alloys 5-8, it can be assumed that a difference in the calculated and measured corrosion potentials, due to the τ-phase in the alloys, is constant. Such a reasoning implies that the presence of the τ-phase in these alloys makes the corrosion pot more noble.

According to ref. [11,12], the existence of τ-phase precipitates after brazing is detrime the corrosion resistance. This is not in agreement with the results published in this paper, alloys with τ-phase precipitates still present after brazing showed the best SWAAT performa

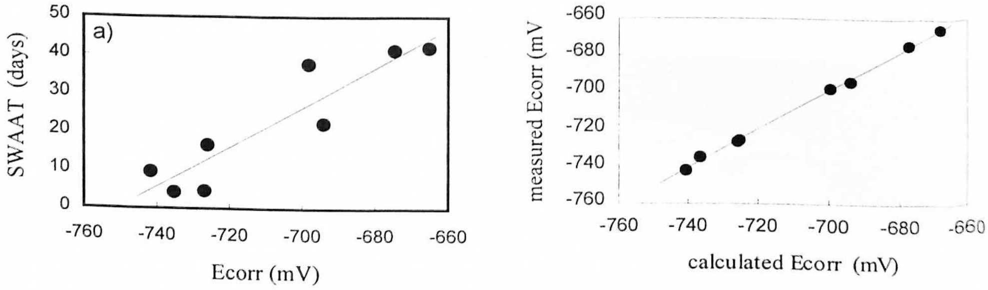

Figure 5: a) The measured corrosion potential versus the result of SWAAT. b) The mea corrosion potential versus the calculated corrosion potential. The calculated corrosion poten the core alloys with Cu have an offset of 38mV.

5. CONCLUSIONS

The influence of the alloying elements Si, Mg and Cu in the core alloy on the corr performance of brazing sheet has been investigated. In the core alloys with Si levels of 0.05 band of dense precipitates (BDP) is observed in the core alloy at the clad/core interfac occurrence of the BDP does not automatically mean a good corrosion resistance. For a corrosion resistance of the brazing sheet, Mg and/or Cu also have to be added to the core where the beneficial influence of Cu is larger than that of Mg on SWAAT performanc understanding how Mg and Cu influence the corrosion behaviour, further research is necessa

The measured corrosion potentials of the non Cu containing alloys is in good agreemen the calculated potentials. The corrosion potential of the Cu containing alloys show a differen (38±1)mV with the calculated ones. This is may be due to τ-AlMnCu precipitates. T precipitates then shift the corrosion potential to a more noble value. The τ-AlMnCu precip also seem to have a beneficial influence on the SWAAT result.

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