2001-01-1763

Brazeability of Aluminum Alloys Containing Magnesium by CAB Process Using Cesium Flux

J. Garcia and C. Massoulier
Valeo Engine Cooling, Branch Laboratory, France

Ph. Faille
Valeo Engine Cooling, Reims Division, France

ABSTRACT:

The increasing durability requirements for aluminum heat exchangers involve the use of higher levels of magnesium in the core material in order to increase the strength of its components. The challenge is to braze these aluminum alloys by the preferred CAB process.
During the CAB process magnesium diffuses out, forming a Magnesium Oxide and Magnesium Fluorides and the use of conventional flux becomes ineffective for disrupting it. When wetting occurs, the brazed joint is discontinuous and the presence of leaks becomes more probable.
It was found that using a modified aluminum flux that includes some cesium in its composition for aluminum controlled atmosphere-brazing process, it is possible to obtain strong brazed joints on the heat exchangers. Additionally, the inclusion of cesium in the flux makes possible to braze aluminum alloys with higher levels of magnesium providing stronger and more durable heat exchangers assemblies.
In this work, it was tested the cesium flux on plate to plate specimens, on mock-ups in our CAB laboratory furnace, and in complete heat exchangers in the standard production line. The results and future work with cesium flux are presented.

INTRODUCTION

The brazing of aluminum alloys in controlled atmosphere furnaces, requires a filler metal with slightly lower melting point than that of the base material, as well as a non corrosive flux type $K_{1-3}AlF_{3-6}$ (Potassium Fluor Aluminates). The flux residues are not required to be removed after brazing because the flux is insoluble to water and they are non corrosive.
The flux acts by melting, spreading and then dissolving the oxide film. Melting starts at 562°C and is completed at 575°C. As soon as the flux melts it starts to dissolve the oxide layer, but the solvating process will continue until the oxide is gone, even if the filler alloy has melted. The filler metal melts at 577°C and it consist of an Aluminum-Silicon eutectic. According to Sichen and al [1], the solvating is based on the alumina dissociation:

$$Al_2O_3 \rightarrow AlO_2^- + AlO^+$$

They found that although a considerable amount of alumina was solved into the flux, no difference in melting point could be detected by a DTA analysis. Bertling [2] confirmed by thermodynamic calculations that the flux - Al_2O_3 solvating process did not result in any reaction products. Consequently, they conclude that the flux does not react with pure aluminum in its solid or liquid state.
However, brazing of magnesium containing aluminum alloys involves chemical reactions between the flux and magnesium. Field and Steward [3] have reported the formation of K_2MgF_4 and MgF_2. These products are stable and will not react with nor dissolved alumina. The elements Manganese and Silicon present in the alloy are inert to the flux like aluminum. The reaction of the flux with Magnesium and the spontaneously formed MgO drives the melting point of the flux upwards, which reduces its activity. Childree [4] suggested that the poisoning effect comes from the magnesium consuming flux by producing stable compounds, this means that the amount of flux available for the oxide removal is substantially reduced, therefore, remaining Al or Mg oxide on the brazing sheet will prevent the surface from wetting and that will results in poor brazed joints.
Yamaguchi at al. [5] studied the effect of Mg for a flux containing $KAlF_4$ and 30 % wt $K_2AlF_5.H_2O$, named FL-7. They found that the efficiency of the flux decreased with increasing amount of Mg. The reason was believed to be the decreasing $KAlF_4$ concentration due to the following reaction:

$$\mathbf{KAlF_4 + Mg \rightarrow KAlF_4 + KMgF_3 + K_3AlF_6 \rightarrow KMgF_3 + K_3AlF_6}$$

The melting point of the formed $KMgF_3$ is 1070°C, which also drives the melting point of flux upwards, thereby decreasing the activity of the flux.
The key issue to solve the brazing problem becomes to avoid the formation of the above described Magnesium compounds. Solvay Fluor and Derived products [6] has patented several fluxes containing Cesium, which forms chemical compounds that do not interfere with the aluminum joining process. These fluxes have the following characteristics:

<u>Cesium fluoraluminates</u>: They exist in several compositions and crystallographic phases, mainly: $CsAlF_4$, $Cs[AlF_4(H_2O)_2]$, $CsAlF_5$, $CsAlF_5 \cdot H_2O$, Cs_3AlF_6

- Melting range: 430 – 450°C
- Tends to dry out under CAB conditions when used for aluminum alloys to be joined with AlSi filler metal
- High water solubility (> 45 g/l at room temperature)
- High water solubility of the post-brazed flux residue (> 25 g/l at room temperature)

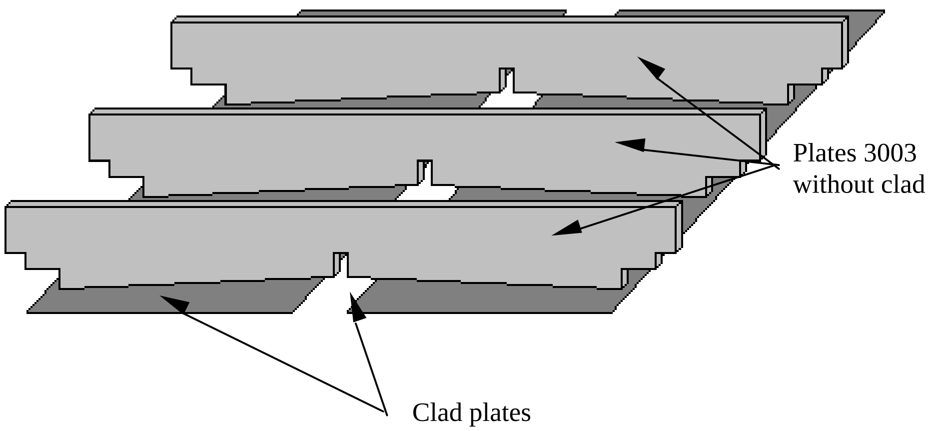
- Very expensive due to high Cesium raw material costs

<u>Cesium Complexes</u>: $Cs_aK_bAl_cF_d$

- Melting range: 545 – 570°C
- Amount of Cesium complexed into Nocolok is tailored to work under CAB conditions with AlSi filler metal
- Solubility in water: 2.5 g/l at room temperature
- Low solubility of the post-brazed flux residue (> 2 g/l at room temperature)
- Reasonable pricing due to minimum Cesium amount needed.

For reasons of cost and more appropriate conditions for CAB process (melting range is closer to the filler metal melting point), it was decided to use the Cesium complexes for this work.
Solvay Fluor and Derived products [6], propose the following mechanisms to explain the role of cesium flux:
As explained above, when brazing magnesium containing alloys by CAB process, the magnesium diffusion adversely affect the good flux spreading, wetting and oxide dissolution properties because of the formation of MgF_2, $KMgF_3$, K_2MgF_4 and spinell type compounds as $MgAl_2O_4$. These compounds increase the melting point of the flux blocking the oxide dissolution power of the virgin flux, the spreading and wicking properties of the flux. Cesium reacts like a scavenger of magnesium by forming $CsMgF_3$ and/or $Cs_4Mg_3F_{10}$, which minimizes the inhibiting factors of the flux activity. It means that the driving force to form the Cesium compounds is much higher that the driving force to form the Magnesium fluoride compounds. The formed components melt at lower temperatures than the filler metal and they do not interfere with the aluminum brazing.

<u>*Figure 1. Schema of the brazing probe:*</u>



This probe is placed on a stainless steel support coated with a substance called "STOP OFF" before brazing in order to avoid the adhesion between the plates (see figure 2).

TESTING TECHNIQUES

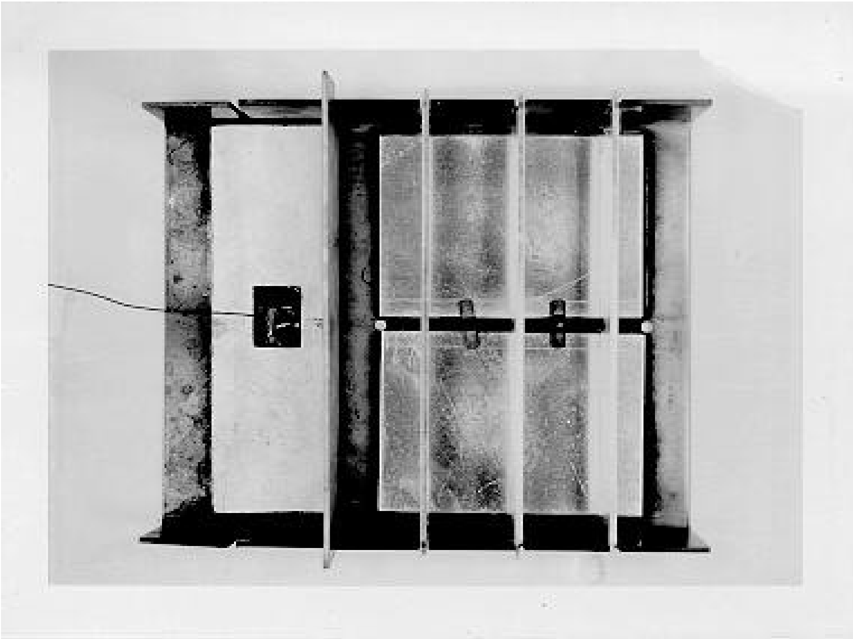
The evaluation of the braze quality using cesium flux was performed by three methods with different sample specimens:
A. Plates to plate specimens.
B. Mock-ups built with sections of the heat exchanger components.
C. Production radiators.
The first two types of samples were brazed in a laboratory furnace, and the complete parts were brazed in the production furnace.

The first series of tests were carried out on plate sample specimens in order to determine the optimal amount of Cesium providing an acceptable compromise braze quality/flux cost.

A. Plate to plate specimens:

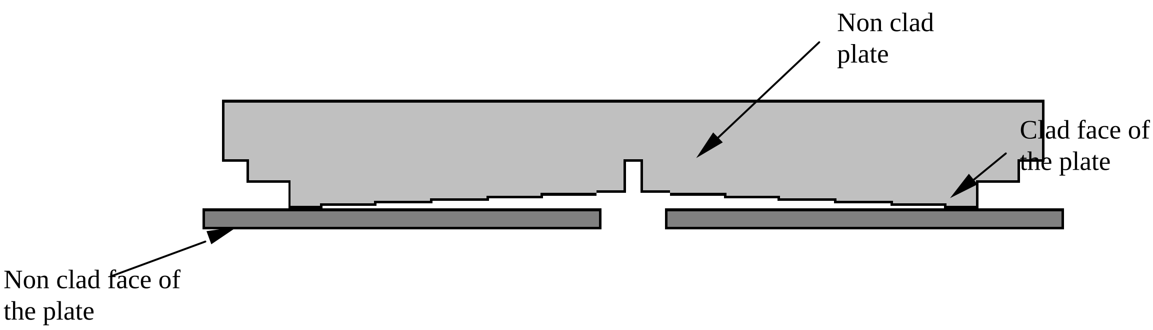
This kind of sample allows us to evaluate the brazeability of the aluminum materials. The principle is to promote the flow of the filler metal by capillary and to obtain long fillets extended as much as possible from the edges to the center of the probe according to the brazeability of the materials. The idea is to maintain a constant angle between the clad and the part to be brazed.
Our brazing specimen is composed of two plates of the material to be evaluated, placed one besides the other and three plates of non clad 3003 alloy placed perpendicularly to the clad material establishing the contact among them (see figure 1).

Figure 2. Mounting schema:

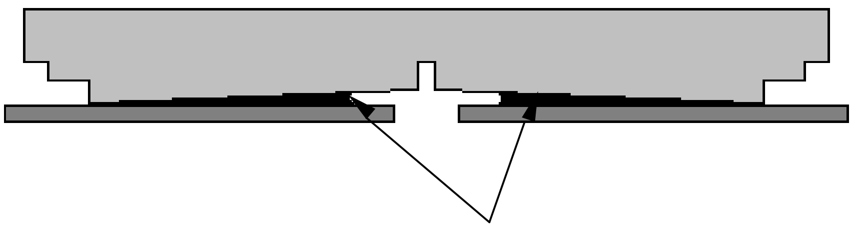


In order to prepare the braze specimens, we proceeded to check the surface condition, and clean the plates with organic solvents. After the samples are thermally degreased and then fluxed and weighted to determine the exact amount of flux deposited on the samples surface. It follows the plates mounting, brazing and cooling. The figure 3 shows the appearance of the specimens before and after brazing.

Figure 3. Probe before brazing:



Probe after brazing:



A.1 Tests with plate to plate brazing probes:

The tests included three parameters: flux concentration, heating rate cycle, and type of flux. The tests were made on AA6063 alloy with 10% AA4045. The table 1 shows the chemical composition of this alloy.

Table 1. Chemical composition of the alloy AA6063.

Element →	Si	Fe	Cu	Mn	Mg	Cr	Zn	Other	Al
Nominal, wt %	0.2-0.6	0.35	0.1	0.1	0.45-0.9	0.1	0.1	0.15	Rem.
Analysis, wt %	0.48	0.22	<0.01	0.042	0.66	<0.01	<0.01	0.15	Rem.

Once the registered temperature of 600°C was reached, we proceeded to remove the brazing mounting from the furnace.

For every test we obtained six brazed joints. The table 2 shows the experimental plan.

Table 2. Experimental plan:

Parameters	Attributions	Level	% Cesium
A	Nature of the flux	Nocolok® 100 Nocolok® Cs Flux Nocolok® Cs Flux 1 Nocolok® Cs Flux 2 Nocolok® Cs Flux 3 Nocolok® Cs Flux 7	0 2.1 3.9 5.8 4.3 9.2
B	Flux load	3 g/m² 5 g/m²	
C	Heating rate (Cycle)	Short = 60°C/min Moderated = 18°C/min	

A.2 RESULTS.

Table 3 and figures 4 and 5 show the results:

Table 3. Brazing test results:

% Cs	Flux load →	3 g/m²				5 g/m²			
	Cycle →	Short		Moderated		Short		Moderated	
	Fillet joint length →	mm	%	mm	%	mm	%	mm	%
0	Nocolok® 100	31.0	100	22.5	100	34.0	100	25.0	100
2.1	Nocolok® Cs	-	-	-	-	44.2	130	36.5	146
3.9	Nocolok® Cs1	36.5	118	29.0	129	38.5	113	36.0	144
5.8	Nocolok® Cs2	29.0	94	30.5	135	36.5	107	38.0	152
4.3	Nocolok® Cs3	-	-	-	-	44.9	132	35.0	140
9.2	Nocolok® Cs7	-	-	-	-	41.8	123	38.8	155

Figure 4. Brazeability of AA6063 alloy in function of the cycle, flux load = 3 g/m²

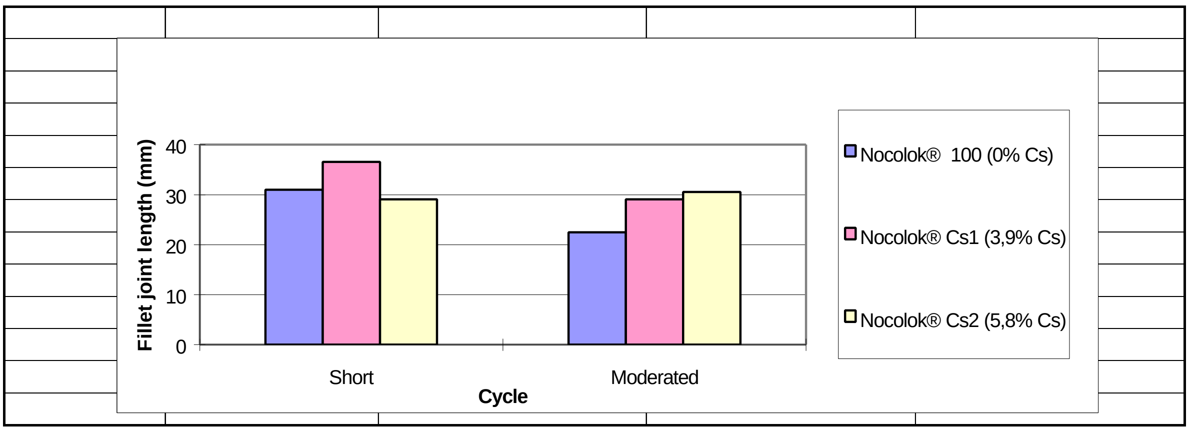
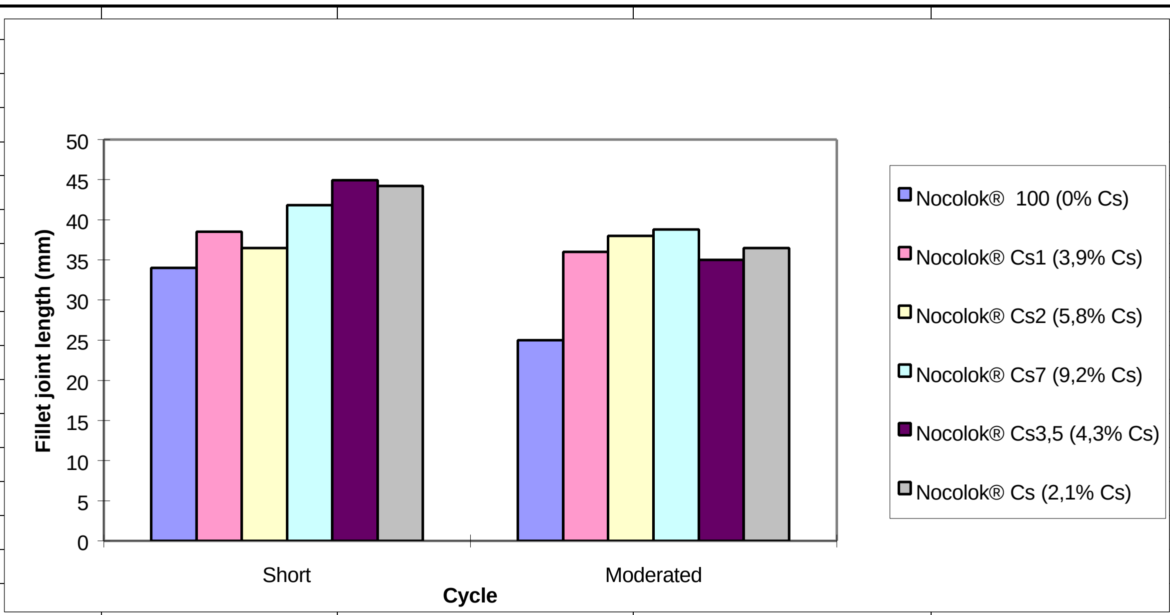


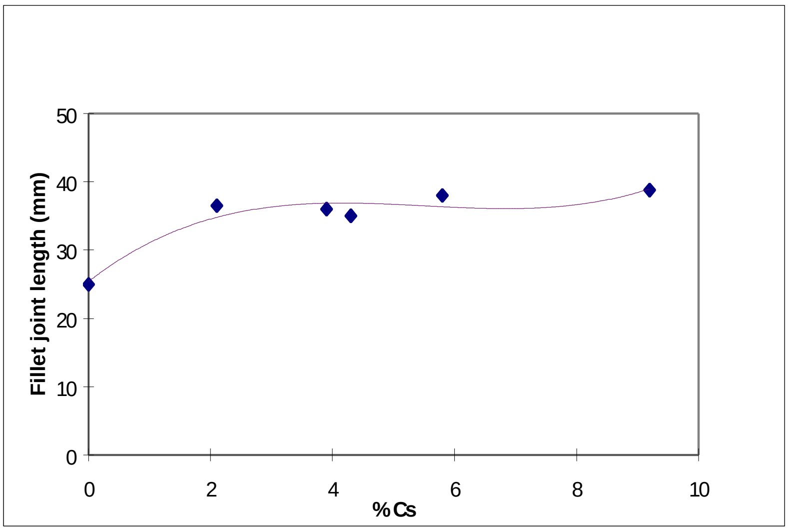
Figure 5. Brazeability of AA6063 alloy in function of the cycle, flux load = 5 g/m²



A.3 DISCUSSION.

- For both cases of flux loading, it was observed that the short cycle performed better. This can be explained by the time for the magnesium to diffuse. More the cycle is long, more brazing problems appear because the magnesium will have more time to diffuse.
- For the moderated cycle, all the flux Nocolok® CsX are equivalent in brazeability for the flux load 5 g/m², and all of them much more performing than the flux Nocolok®. It means that the Cesium in the flux substantially improve the brazeability of AA6063 alloy.
- Concerning the flux Nocolok® Cs1 and Nocolok® Cs2, it can be seen than for the short cycle the flux Nocolok® Cs1 is most performing and for the moderated cycle the flux Nocolok® Cs2 is the best, and that in all cases all Cesium fluxes are more performing than the flux Nocolok® 100. The figure 6 shows the influence of the Cesium concentration in the flux on the brazeability of AA6063 alloy :

Figure 6. Brazeability of AA6063 alloy in function of the % Cesium, flux load = 5 g/m² for moderated cycle



A.4 CONCLUSION:

- The tests performed with plate to plate brazing specimen show that the use of Cesium flux improves significantly the brazeability of alloy AA6063.
- The brazeability of AA6063 alloy increases with the Cesium content in the flux, but the differences in the brazeability found for a flux containing only 2.1 % of Cesium and the one containing 9.2 % Cesium are not so important.
- Given that the cost of the flux is function of the cesium content, it can be concluded that an optimization for the compromise: braze quality/cost, can be provided by the flux named Nocolok® Cs which contains 2.1 % of Cesium.

Further tests in this work were done using the flux containing about 2 % Cesium.

B. Mock-ups with sections of the heat exchanger components (see figure 7).

The mock-ups had the following dimensions:
Length = 100 mm
Width = 90 mm
Height = 52 mm

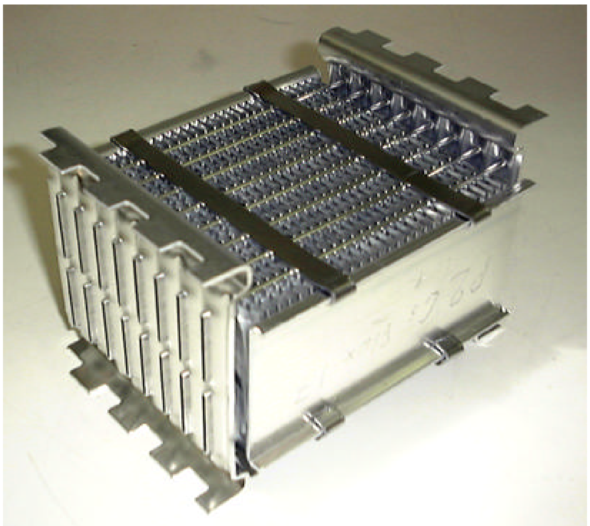
Materials:

The table 4 shows the characteristics of the materials used for the mock-ups.

Table 4. Main characteristics of the materials used for the components of the mock-ups

Component	Quantity	Material	Clad	Temper
Tubes	16	Modified AA3003 (0.35 % Mg)	AA4343 10 %	H24
Fins	9 Rows	Modified AA3003 (0 % Mg)	No clad	H14
Headers	Stamped in two rows	Modified AA6060 (0.45 % Mg)	AA4045 5 %	O

Figure 7. Photo of the mock up



B.1 Tests and results with Mock ups:

The table 5 shows the summary of the tests and the brazing results.

Table 5. Summary of the tests and brazing results

Test	Flux %			Temperature, °C		Furnace	Heating rate, °C/min	**Observations**
	Type	Core	Tube/header	Consign *	Brazing**			
1	Std	7	25	625	594	Laboratory	58	No leaks, good fin/tube brazing.
2	Std	7	25	600	592	Prototypes	31	No leaks, good fin/tube brazing.
3	Cs	10	30	625	587	Laboratory	52	No leaks, good fin/tube brazing
4	Cs	4	15	620	582	Laboratory	58	One tube/header leak, bad fin/tube brazing; too low brazing temperature.
5	Cs	4	15	620	588	Laboratory	51	No leaks, good fin/tube brazing
6	Cs	4	4	620	588	Laboratory	55	Several leaks, good fin/tube brazing. The flux concentration was too low.

* Consign is the programmed temperature for the furnace operation.
** Brazing is the temperature registered by the data pack/thermocouple system used for the temperature profile control.

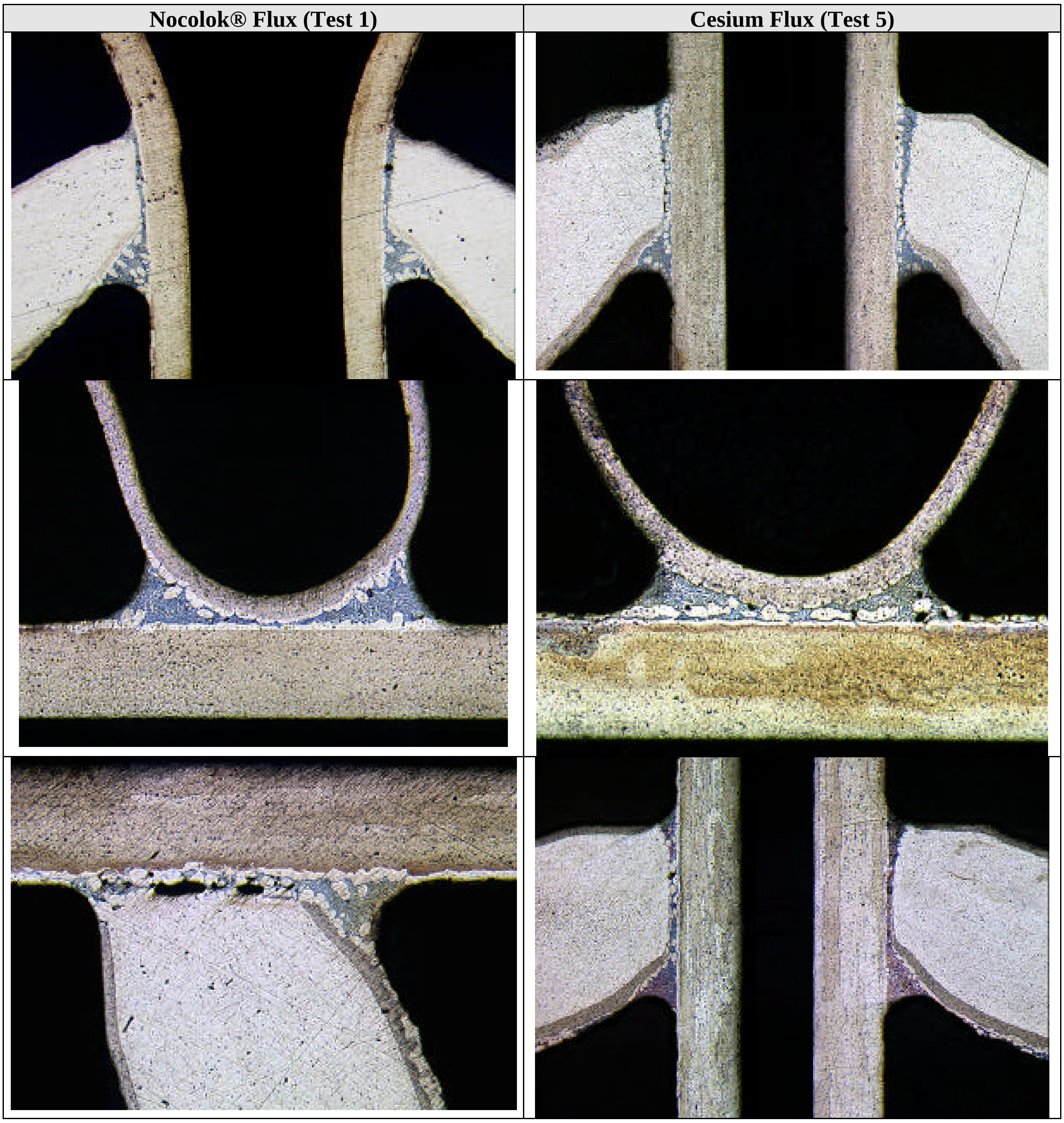
B.2 DISCUSSION

- The test results look to confirm the first studies made on plate to plate brazing specimens. It was observed an improvement by obtaining longer fillet joints.
- The flux concentration of 4 % on tube/header joints is not enough to braze these materials. Further tests with slightly higher concentrations are necessary to determine the flux concentration limit for the tube/header brazing in this configuration.

B.3 CONCLUSION

- The Cesium flux looks effective to braze aluminum materials with 0.35 to 0.5 % Mg.
- The 4 % flux concentration is enough to insure a good fin/tube (core) brazing.
- It is planned to perform additional tests in order to verify the influence of the different parameters such as temperature, furnace, flux concentration on tube/header joints, and flux nature.

Figure 8. Photo 2 through 7. Some examples of the brazing test results, using standard flux and Cesium flux.



C. Production radiators.

Materials:

The table 6 shows the characteristics of the materials used for the production radiators.

Table 6. Materials used for the components of production radiators

Material Reference	Number of radiators	Header	Fins	Sideplate	Tube
Low Mg*	50	AA6060 (Mg < 0.5 %) /AA4045, 10 %	AA3003	AA1145 10% / AA6060 (Mg < 0.5 %) / AA4343, 5 %	AA3003/ AA4045,10 %
High Mg**	15	AA6063 (Mg=0.66 %) /AA4045, 10 %	AA6063 (Mg=0.66 %)	AA1145 10% /AA6060 (Mg < 0.5 %) /AA4343, 5 %	AA3003/ AA4045,10 %

* Low Mg = Material with low magnesium content
** High Mg = Material with high magnesium content

C.1 Tests on production radiators.

All radiators were manufactured by CAB process (Controlled Atmosphere Brazing process). The table 7 shows the different test conditions.

Table 7. Test matrix on production radiators

Test Number	Material Reference	Number of pieces	Flux type	Flux concentration	
				Core	Tube/header
1	Low Mg	50	Nocolok®	10 %	28 %
2	Low Mg	3	Nocolok®	10 %	28 %
3	Low Mg	3	Cesium flux	10 %	28 %
4	Low Mg	3	Cesium flux	5 %	15 %
5	High Mg	3	Cesium flux	10 %	28 %
6	High Mg	3	Cesium flux	5 %	15 %

C.2 Test results

The table 8 and figure 9 show the braze ratio, or % of formed fin/tube brazed joints and the table 9 shows the visual remarks of the braze quality.

Table 8. Braze ratio or % of formed fin/tube brazed joints

Test Number	Material Reference	Flux Concentration, %	Flux Application	Flux load, g/piece	% Fin/tube brazed joints (Braze ratio)
1	Low Mg	Nocolok® (10/28)	Automatic spray	95	100
2	Low Mg	Nocolok® (10/28)	Manual	59	100
3	Low Mg	Cesium (10/28)	Manual	56	97
4	Low Mg	Cesium (5/15)	Manual	35	99
5	High Mg	Cesium (10/28)	Manual	56	84
6	High Mg	Cesium (5/15)	Manual	35	5

Figure 9. Braze ratio or % of formed fin/tube brazed joints in function of the material, type of flux and flux concentration.

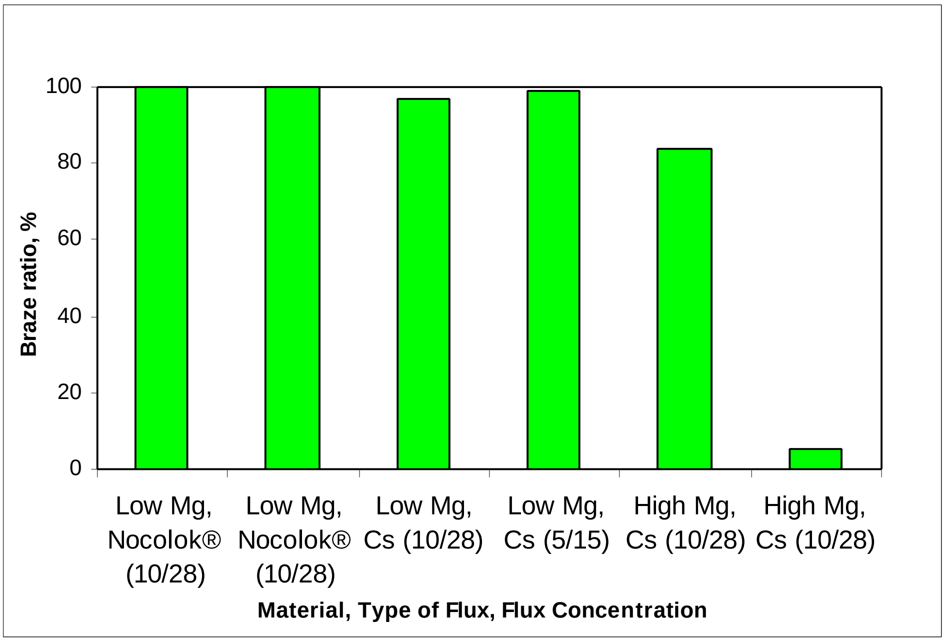
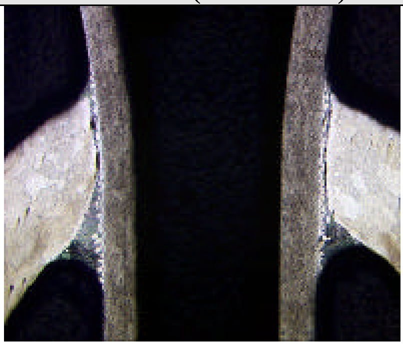
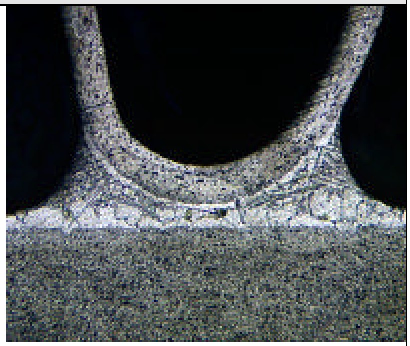
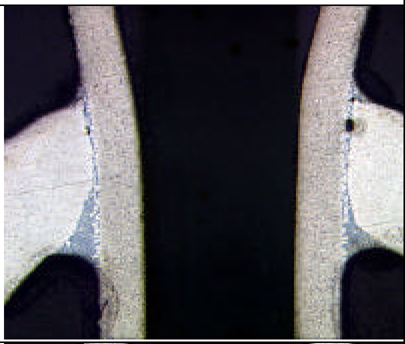
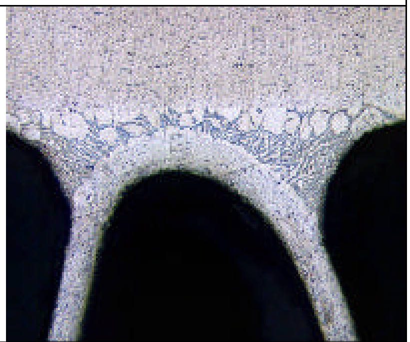
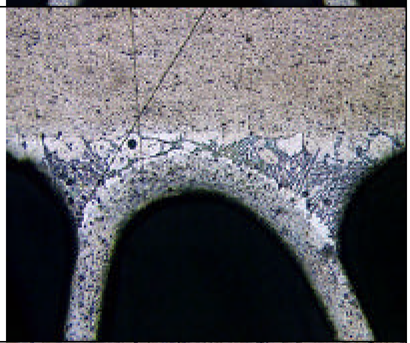
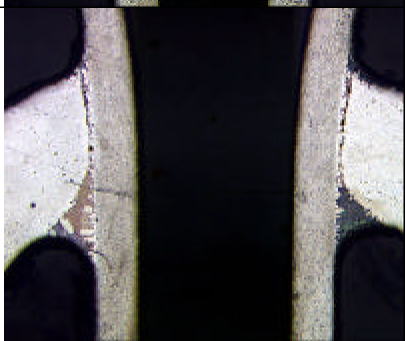
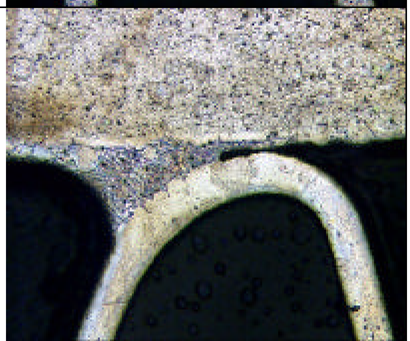
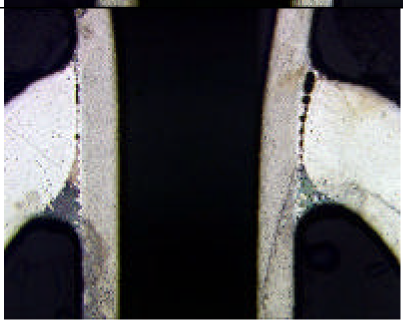
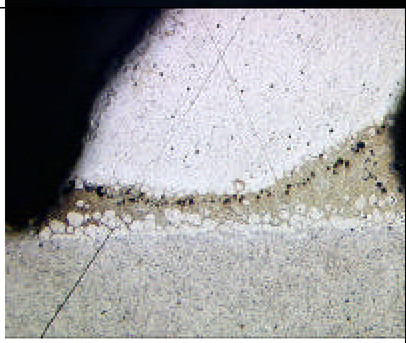


Table 9. Braze quality observations

Test #	Material	Flux	Tube/Header	Fin/Tube
1	Low Mg	Nocolok® (10/28)	Good joints without porosity	Good joints without porosity
2	Low Mg	Nocolok® (10/28)	Good joints with few porosity	Good joints without porosity
3	Low Mg	Cesium (10/28)	Good joints with few porosity	Good joints without porosity
4	Low Mg	Cesium (5/15)	The joints are continuous without porosity, but incomplete by 30 to 50 %	Good joints without porosity
5	High Mg	Cesium (10/28)	Joints relatively well brazed, but incomplete and with some porosity	Incomplete joints by 30 to 50 %
6	High Mg	Cesium (5/15)	The filler metal is well distributed, but there is significant porosity	Incomplete joints by 30 to 50 %

The photos 8 through 22 show some examples of the braze quality for tube/header and tube/fin joints.

Figure 10. Photo 8 through 22. Some examples of the industrial brazing test results, using standard flux and Cesium flux.

	Tube/header (cross section)	Tube/header (Lengthwise section)	Tube/fin
Low Mg, Nocolok®			
Low Mg, Cs (10/28)			
Low Mg, Cs (5/15)			
High Mg, Cs (10/28)			
High Mg, Cs (5/15)			

C.3 DISCUSSION

- The manual application of the flux reduces the flux distribution through the radiator core, which has an incidence on the braze quality of the product. However, during the industrial tests it was observed that the flux has the tendency to form a sort of gel very viscous that occurs faster for higher flux concentrations. This phenomenon does not allow the use of this flux under the actual industrial conditions. In despite of this situation, all the brazed parts were leaks free.
- In the other hand, the settling rate, wettability and other physical properties look similar than the standard flux.
- In regard to the brazeability of the tested materials, the flux Nocolok® for low magnesium materials gives correct results, the fin/tube and the tube/header joints are well formed. Independently of the flux concentration, the cesium flux did not provide significant improvements on low magnesium materials under the brazing conditions of the tests carried out.
- The use of cesium flux on high magnesium materials seems to give good brazed joints, but the reduction of the flux concentration involves a larger number of non brazed joints.
- The brazing tests were performed using a production-brazing program, it is evident that it would be necessary to modify some of the brazing parameters employed in these tests, in order to obtain much better results. In this work it was not possible to change some of the brazing parameters because of plant manufacturing constraints.

C.4 CONCLUSION

➢ Materials with Mg < 0.5 %

- The braze quality of the parts brazed with flux containing 2 % Cesium and those brazed with standard flux is equivalent.
- By reducing the flux concentration to 5/15 the braze quality is equivalent for the fin/tube and fin/sideplate joints, with an slight degradation on tube/header joints, but acceptable.

➢ Materials with Mg > 0.5 %

- The braze quality of the parts is not enough satisfactory, but is a good improvement because all the parts were leak free which is not the case when using standard flux.
- There were not found the « whiskers » (Magnesium fluorides crystallization morphology), normally present when using standard flux in the brazed joints.

GENERAL CONCLUSION

This work showed that the use of cesium flux to braze aluminum materials and to improve the braze quality of the parts with high magnesium content is possible.
The compromise cost/braze quality can be satisfied by using flux with only 2 % Cesium, however further tests are necessary in order to determine the brazing parameters compatible with the melting temperature of the cesium flux. In fact the cesium flux melts between 545 and 570°C meanwhile the standard flux melts between 562°C and 575°C. The heating rate, brazing temperature and time hold at the brazing temperature should play a significant role for brazing with cesium flux. This could be observed during the plate to plate tests at the beginning of this work.
Concerning the physical properties of the Cesium flux, most of them are similar to those of the standard flux with the exception of the gel formation phenomena. It is important to avoid it in order to be able to use this flux in production because it could block the nozzles during the flux spraying. It could be an intrinsic property of the material that we did not observe during the laboratory tests, but it is always possible to use an additive to reduce or eliminate the tendency of the flux to become more viscous.

AKWNOLEDMENTS

We would like to express our appreciation to L. Grussy for his important collaboration in this work. We thank Solvay for the flux samples they provide us and for their collaboration to achieve this work.

REFERENCES

[1] D. Sichen, I Arvanitidis, S. Seetharaman, ‘‘Flux reactions in Aluminum Brazing with Fluoride Fluxes’’, T 96/1042, Gränges Technical Report (1996).

[2] S. Bertling, ‘‘Alkaline Degreasing-Brazing’’, Technical Report, Swedish Institute for Metal Research, IM-XXXX, Stockholm, Sweden.

[3] D. J. Field and N. I. Steward, ‘‘Mechanistic Aspects of Nocolok® Flux Brazing Process’’, SAE Technical Paper Series, No. 870186, Detroit, Michigan (1987).

[4] D. L. Childree, ‘‘A New Al-Si-Li Filler Metal that Enhances Brazeability of High Strength Alloys in CAB and Vacuum’’, SAE Transactions: Journal of Materials & Manufacturing 105 (5), p. 248 – 256, Paper No. 960247 (1996).

[5] M. Yamaguchi, H. Kawase and H. Koyama, ‘‘ Brazeability of Al-Mg Alloys in Non Corrosive Flux Brazing’’, Furukawa review, No. 12, p. 139 – 144 (1993).

[6] Solvay Fluor and Derived Products. ‘‘ New Developments in non-corrosive fluxes for innovative brazing’’. U. Seseke-K, Technical presentation at the First International Congress Aluminum Brazing, at the Hotel Nikko, Düsseldorf, Germany on May 10 – 12, 2000.