C599/013/2003

Controlled atmosphere brazing of heat treatable alloys with cesium flux

H JOHANSSON
Valeo Engine Cooling AB, Mjällby, Sweden
T STENQVIST
SAPA Heat Transfer, Finspång, Sweden
H-W SWIDERSKY
Solvay Fluor und Derivate, Hannover, Germany

ABSTRACT

The age hardenable alloys which have been accessible for aluminium heat exchanger constructions in the past only found limited application in CAB-brazing due to their magnesium content. Current industry standard furnaces and fluxes are limited to at total magnesium content of ≤ 0.3 % (by weight) for the parts to be brazed. Current age hardenable alloys (commonly from the 6000-series) have magnesium contents between 0.4 and 0.7 % all resulting in total magnesium levels normal magnesium levels far above the current limit.

Nevertheless, many large heat exchangers need age hardenable aluminium alloys whose integrated parts after artificial ageing, can reach the mechanical values required to withstand the stresses, created in the vehicle.

This paper discuss and points out the possibilities to manufacture aluminium heat exchangers with magnesium joint percentages up to 0.6 wt-% and a set of aluminium alloys capable of meeting product demands.

KEYWORDS

Aluminium brazing, Heat exchangers, Cesium flux, Artificial ageing, Heat treatable Al-alloy, High strength

1 INTRODUCTION

To resist the significant stresses on a heavy duty (truck and off highway) radiator during normal operation the integrated parts often need to be made of age hardenable Al-alloys which can reach high tensile strength values after artificial ageing. This condition is valid for vacuum brazing material where alloys (from the 6000-series) with high Mg content can be used. After the brazing, which works as a solution heat treatment, followed by a rapid cooling, the parts can be artificial aged. Thus the targeted tensile values can be achieved.

Valeo Engine Cooling in Sweden has a long experience with vacuum brazed and age hardened radiators, using AA6063 as the core alloy in headers and fins. The non-heat treatable 3005LL alloy has been used in the tubes.

As the industry has moved from vacuum brazing to controlled atmosphere brazing (CAB) for improved reliability of fillet formation and continuos processing the ability to use 6000-series alloys has been eliminated due to their high magnesium content. The compounds formed between Mg and the flux reduce the possibilities of the flux to dissolve the aluminium oxide (1). The sum of the Mg content of the two materials that shall be brazed together can be used to estimate the brazeability. Based on a large number of brazing tests a limit using a standard flux has been established to <0.3 % Mg to achieve good joints.

It has been shown (2) that good brazing can be achieved in a laboratory environment for joint magnesium contents up to 0.6 wt-% with the addition of cesium to the standard flux. This level was not sufficient for the currently available 6000 series alloys.

The cesium forms a compound with the Mg which does not reduce the capacity of the flux to dissolve the oxide on the aluminium surfaces.

2 FLUX WITH A CONTENT OF CESIUM

Brazing of aluminium with the CAB-process requires a filler metal with slightly lower melting point than that of the base material, as well as a non-corrosive flux type $K_{1\text{-}3}AlF_{3\text{-}6}$ (potassium fluoro aluminates).

The flux acts by melting, spreading and then dissolving of the oxide film. The melting starts above 560°C and is completed at 575°C. As soon as the flux melts it starts to dissolve the oxide layer. The solvating process is going to continue until the oxide is gone. The filler metal melts at 577°C and consists of an aluminium-silicon eutectic.

The solvating of alumina dissociation:

$$\mathbf{Al_2O_3 \quad \Rightarrow \quad AlO_2^- \quad + \quad AlO^+}$$

When brazing of magnesium containing aluminium alloys is attempted, chemical reactions between the flux and the magnesium result in the formation of K_2MgF_4 and MgF_2. These products are stable and will neither react with nor dissolve alumina. Other elements in the alloys like manganese and silicon are inert to the flux, as well as others.

The reaction of the flux with the magnesium and the spontaneously formed MgO drives the melt point of the flux upwards, which reduces its activity. The poisoning effect of magnesium consuming the flux and producing stable compounds substantially lowers

the accessible amount of flux to remove the aluminium oxide. The remaining oxides will prevent the flux wetting and result in poor joint formations.
An increasing amount of Mg reduces the efficiency of the flux. The main reason is believed to be decrease of the $KAlF_4$ level in the flux. The effects of Mg are summarised below:

- Above 425 °C magnesium diffuses rapidly to the surface and form magnesium oxide (MgO) and the Spinel ($Al_2O_3 \cdot MgO = Al_2MgO_3$). These compounds have low solubilitiy in flux.
- Magnesium reacts with flux ($KAlF_4$ and K_3AlF_6) and form magnesium-fluoride (MgF_2) and potassium-magnesium-fluorides ($KMgF_3$, K_2MgF_4), e.g.:

  - $3\,MgO + 2\,KAlF_4 \rightarrow MgF_2 + 2\,KMgF_3 + Al_2O_3$
  - $3\,MgO + 2\,KAlF_4 \rightarrow 2\,MgF_2 + K_2MgF_4 + Al_2O_3$
  - $3\,MgO + 2\,K_3AlF_6 \rightarrow 3\,K_2MgF_4 + Al_2O_3$

These compounds have a limited solubility in the flux, since they change the flux composition and increase the melting point of the flux.

The melting point of the formed $KMgF_3$ is 1070°C, which also drives the melting point of the flux upwards.
To avoid the formation of above described magnesium compounds; a flux product containing cesium ($Cs_aK_bAl_cF_d$) from Solvay was used. The formation of the compounds as MgF, $KMgF_3$ and K_2MgF_4, which have an influence on the spreading, wetting and oxide dissolving characteristics as well as increasing the melt temperature of the flux, can be reduced with a little addition of cesium. The cesium reacts with the magnesium and forms the compounds $CsMgF_3$ and /or $Cs_4Mg_3F_{10}$ which counteracts some of the undesired reactions described above. This means that the driving force to form the cesium compounds must be higher than the driving force to form the magnesium fluoride compounds. The Cs-containing components melt at a lower temperature when compared with the K-containing compounds, and they do not interfere as much with the aluminium brazing.

3 THE NEW AGE HARDENABLE ALLOYS

3.1 Material selection and theory

The material selection was a vital part for the project. This section summarises the alloy choices and some data for these materials.
The high demands on the finished radiator required age hardening alloys for all parts; the tubes, the fins, the header, and side support. Several age hardening systems exist in aluminium, but only alloys using Mg and Si can be survive in a 600°C brazing operation. Age hardening utilise the precipitation of minute particles containing Mg and Si. Thus both Mg and Si must be in solid solution within the aluminium matrix before the ageing process. Fortunately the brazing process works as a solutionising treatment, but care has to be taken that the cooling rate after brazing is fast enough to avoid unwanted precipitation during that phase. The critical temperatures are between 400°C

and 200°C, where the cooling rate must be faster than 1°C/s to obtain a reasonable strength response (3)(4).

A solutionised material will strengthen in ambient temperature, which is called natural ageing, but the process is slow (5 to 14 days before a reasonable strength level is reached). Artificial ageing, i.e. age the material in a furnace at 150°C to 200°C is faster, normally some hours. If aged too long the material will start to soften; this is called “overageing”. Thus there is a maximum, “peak”, strength. At lower temperatures, i.e. during service, the ageing process is too slow to overage an already aged radiator during its lifetime. The resultant strength will depend on the ageing time and temperature; the lower the temperature, the higher the peak strength but the time to reach the peak is longer. In production the process must be optimised, in order to get sufficient strength of the material in the shortest time. The sufficient strength is not necessary the peak strength.

Age hardenable tube and header material with the limited Mg level suitable for the project was commercially available at the start of the project. The existing FA7850 tube material, presented two years ago (4) was the first selected.

The material first considered for the header and the side support was the existing alloy FA7827 (3). However that material had not been used in artificially aged radiators and it was disregarded as the tensile strength after brazing and ageing would likely be too high for the tab header bending. Sapa Heat Transfer therefore modified the FA7827, reducing the Mg level, which gives a softer alloy called FA7870.

A new alloy for the fins was called for. Two primary characteristics were needed in this material, age hardening properties, and it also had to be sacrificial to the tube material. Looking at the FA7850 tube material and the outstanding non-heat treatable FA6815 fin alloy the FA7868 was designed. The alloy has been described previously (5).

3.2 Material data

The chemical compositions of the materials are shown in Table 1. For comparison some standard and other common alloys are included. Table 2 shows the normal delivery tempers and the associated strengths. Their natural ageing strengths are shown in Figure 1.

Table 1. Typical chemical compositions, wt-%

Part	Alloy	Si	Fe	Cu	Mn	Mg	Zn	Ti	Zr
Tube core	FA7850	0.8	0.3	0.3	0.6	0.3	—	0.18	—
Fin	FA7868	0.8	0.3	—	0.6	0.3	0.7	—	0.15
Header core	FA7870	0.65	0.3	0.3	—	0.25	—	0.18	—
Reference	AA6063	0.5	0.3	—	—	0.7	—	—	—
- “ -	AA3003	0.2	0.5	0.1	1.2	—	—	—	—
- “ -	3005LL vb	0.1	0.2	0.3	1.2	0.5	—	—	—
- “ -	FA6815	0.8	0.3	—	1.6	—	1.5	—	0.15
- “ -	FA7827	0.65	0.3	0.3	—	0.45	—	0.18	—

Table 2. Delivery temper and the corresponding strength

Part	Alloy	Temper	$R_{p0.2}$ (MPa)	R_m (MPa)	A_{50mm} (%)
Tube	FA7850	H24	min 150	175 – 225	min 8
- " -	AA3003	H14	min 115	140 – 180	min 3
- " -	3005LL vb	H24	min 150	185 – 235	min 8
Fin	FA7868	H14SR	min 150	170 – 220	min 0.5
- " -	FA6815	H14SR	min 160	180 – 220	min 0.5
Header	FA7870	O	min 40	80 – 120	min 20
- " -	AA6063	O	min 35	75 – 115	min 20
- " -	AA3003	O	min 35	95 – 135	min 20
- " -	FA7827	O	min 40	80 – 120	min 20

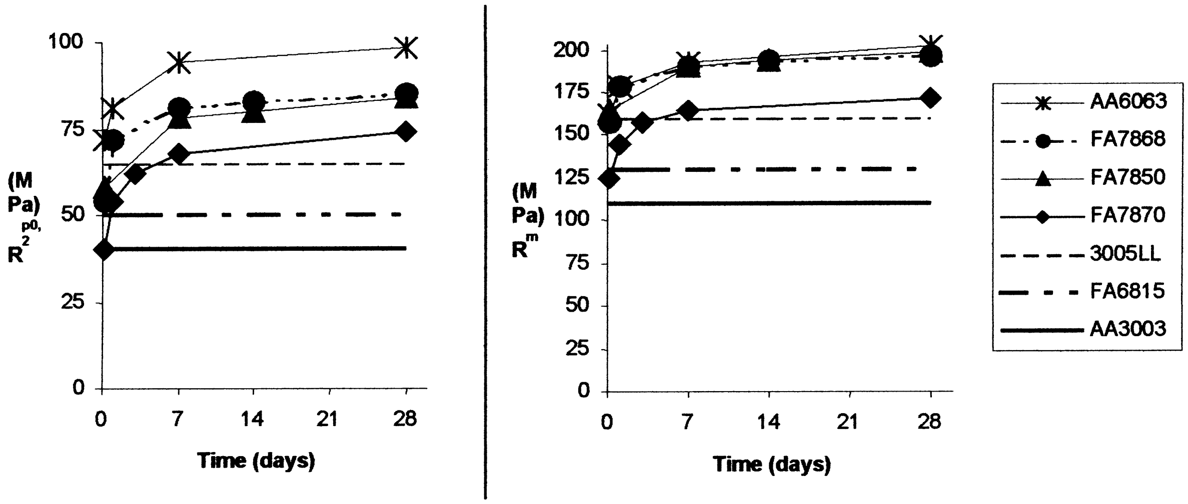

Figure 1. Tensile strength ($R_{p0.2}$ and R_m) after natural ageing of the selected alloys and some references

Obviously in this case it is more interesting with the artificially aged strengths, however they are dependent on the ageing parameters. This is illustrated in Figure 2. Note the strength level, yield strengths above 150 MPa is readily available.

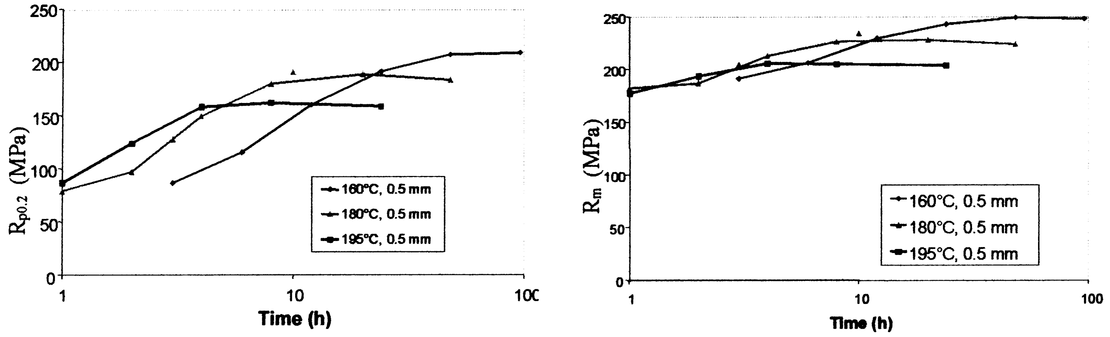

Figure 2. Tensile strength ($R_{p0.2}$ and R_m) after artificial ageing of FA7868

Table 3. Tensile strength after artificial ageing, laboratory tests

Part	Alloy	Ageing		$R_{p0.2}$ (MPa)	R_m (MPa)	A_{50mm} (%)
		Preageing time	Parameters			
Tube	FA7850	4 h	195°C/1.5 h	69	174	17
- " -	- " -	24 h	195°C/3 h	103	179	12
- " -	3005LL vb	—	—	62	155	17
Fin	FA7868	24 h	195°C/1.5 h	160	216	10
- " -	AA6063	72 h	180°C/1.5 h	152	228	16
Header	FA7870	24 h	195°C/1.5 h	176	220	12
- " -	AA6063	72 h	180°C/1.5 h	138	210	15

The problem to solve is to achieve the same strength of CAB-brazed radiator as the old vacuum brazed design. Tensile strength tests were performed at Sapa Technology to using different ageing parameters, Table 3. The heat treatable FA7850 tube alloy has a higher strength than the 3005LL material, the fin alloys were comparable, and the new FA7870 header alloy was stronger than AA6063 with the chosen ageing parameters.
It is clear that any heat treatable alloy using artificial ageing is vastly superior to standard non-heat treatable alloys. It is a way to use the full potential of aluminium.

Fatigue tests have been performed on the new alloys, as well as on the corresponding alloys for vacuum brazing. Each pair of materials, for each product, had similar fatigue properties.

3.3 Tensile tests after brazing in production furnaces

Samples both for vacuum and CAB-alloys have been manufactured in standard coupons and subjected to a tensile test machine. Different thicknesses have been used to closer represent normal application of the materials, but for the fin material a thicker gauge was used for rigidity during the experiment. The samples have been subjected to their respective brazing process and then been cooled with a cooling rate over 1.5°C/s.
The ageing temperature and time has been 180°C/ 1,5 hours for the vacuum alloys and 195°C/ 2 hours for the CAB alloys. Table 4 below shows there are only small differences in tensile test results. The high value for the 3005LL alloy could be explained by an ageing process, as Si from the braze cladding and Mg from the core may combine and age the material.

Table 4. Comparison o tensile values between artificially aged vacuum and CAB alloys

Part	Alloy	Thickness (mm)	$R_{p0.2}$ (MPa)	R_m (MPa)	A_{50mm} (%)
Tube	FA7850	0.5	85	174	16
- " -	3005LL vb	0.5	78	166	12
Fin	FA7868	0.5	109	188	15
- " -	AA6063	0.5	137	208	13
Header	FA7870	1.6	175	222	14
- " -	AA6063	1.6	130	210	14

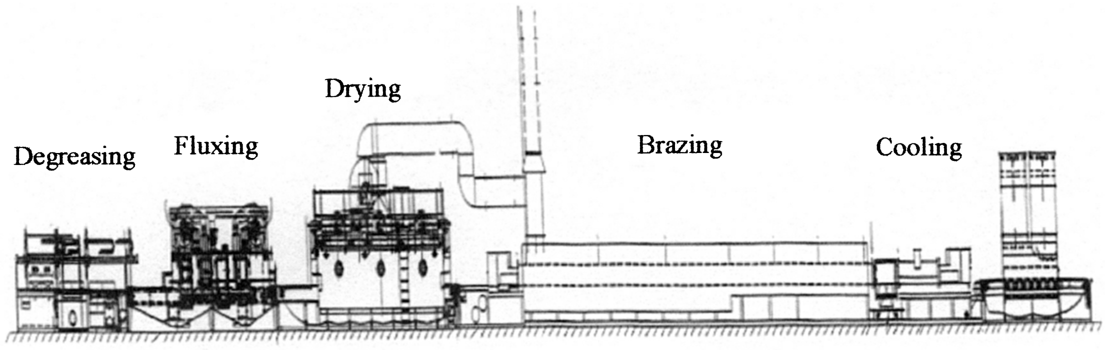

Figure 3. Block schema for the CAB-brazing process

4. CAB-BRAZING AND BRAZING RESULTS

4.1 The brazing process

Aluminium brazing with non-corrosive fluxes in a CAB-furnace include following steps given in Figure 3. After the forming of the components and their assembling they are cleaned by deagresing in the first step of the furnace line. The following steps are fluxing and drying before brazing. The final step is the cooling, and the cooling rate is very important to reach high mechanical strength of the components. The cooling rate should be over 1°C/s for age hardenable alloys.

4.2 CAB-brazing of Mg containing alloys with cesium flux

The Mg contents of the new age hardenable alloys have been adapted so that their sums applicable for joints tube/fin and tube/header do not exceeded the limit value of 0.6 % above.

J. Garcia et al have reported (2) that a standard flux with a Cs content of 2 % is enough to get good brazing results. During all tests in this project a flux with this Cs content has been used. Garcia has reported that a flux with higher Cs content do not improve its capacity to reduce the negative Mg effect or reinforce its capacity to break up the oxide or improve the wetting capacity. A higher Cs content only raises the costs.

Before the fluxing of the truck radiator cores, the flux was diluted into different concentrations. One lower concentration was used for the core (tube/fin) varying between 6-10 % and one higher for the tube to header joints, varying between 12-25 %. Many tests have been made and totally 150 cores were brazed with concentrations within these intervals.

Several joints from most of these brazed cores have been metallurgical examined. Fillet sizes and the occurrence of pores have been evaluated and compared with joints from corresponding vacuum brazed cores. The results from these examinations have pointed out that joints, which have been brazed with the Cs flux above a concentration of 10 % respectively 25 % and the new age hardenable alloys have fulfilled the demands of qualitatively good joints in production processing.

5. THE METALLURGICAL EVALUATION OF THE BRAZING RESULTS

5.1 Production evaluation

To assure that the conclusions of the laboratory testing could be applied in high volume manufacturing, a series of production trials were performed. In these trials the current CAB alloys, 3000 series, were replaced one by one with the new alloys to evaluate their individual effects on brazing results. These trials were conducted in the current high volume production equipment and in representative batch sizes. The remaining results presented here are based on the final trial where FA7850, FA7868, and FA7870 with 2 % cesium enhanced flux were utilized.

5.2 The brazing ratio tube/fin

The brazed core has been cut in five sections according to Figure 4 before analysing of the braze ratio for the tube and fin joints. Good brazed joints have been compared in relation to the total number of possible joints and a braze ratio tube to fin has been calculated. The demand has been a ratio over 90 %.

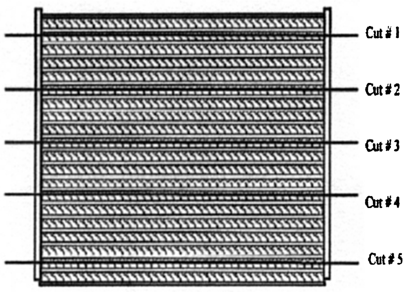

Figure 4. Core cut in five sections for calculation of the brazing ratio tube/fin

5.3 The metallurgical analysis of the fillets

In Figure 5 the six areas are marked from which samples have been taken and analysed with respect to the tube to fin joints, side plate to fin, and tube to header joints. Joints both from top and bottom (with reference to the belt of the furnace) have been analysed.

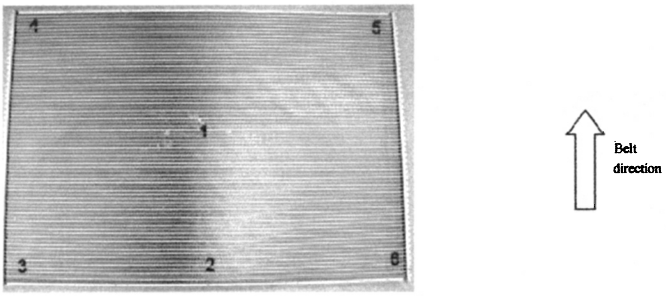

Figure 5. Heavy duty core with marked analyse areas

Options

5.4 The number of analysed joints of a core

A great number of joints have been evaluated with respect of the brazing qualities of a core. The table 5 below show the typical result from a core analyse.

Table 5. Typical results from a heavy duty core

Joints	**Analysis**	**Remarks**
Tube/header over the bellow	All 80 very good joints	Only small pores
Tube/header over the bellow	31 good joints of 32	1 joint with a little column
Tube/Fin	625 joints analysed	2 % of the joints were unbrazed
Side plate/fin	108 joints analysed	Some of the joints were eroded

5.5 The joint sizes

The size of the joints has been measured in a metal microscope. In the Figure 6 the fillet length A and the fillet height B have been marked.

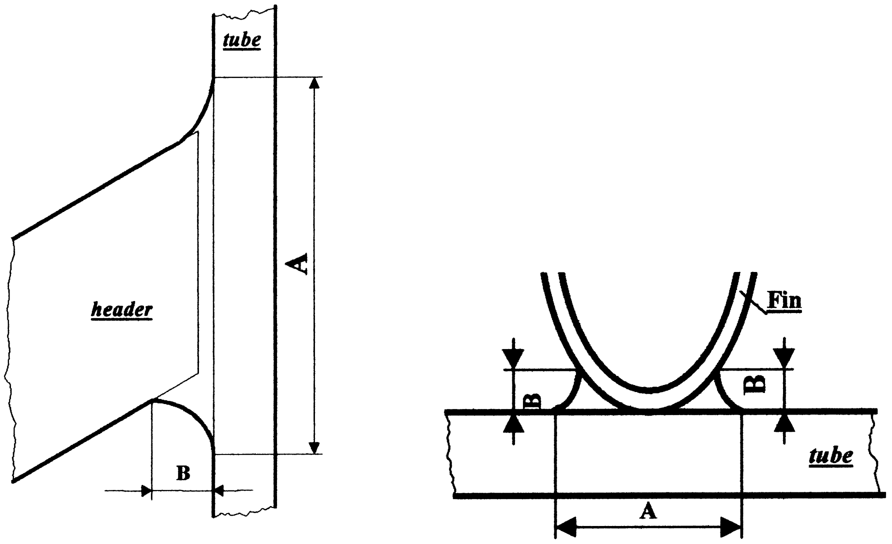

Figure 6. Fillet length and fillet height for joints tube/header and tube/fin

A typical result from a measurement of the joints from a heavy duty core is given in table 6 below. Every number is the mean value over ten joints.

Table 6. Typical results from the analysis of the fillet sizes in a radiator core

Section	Fillet sizes (mm)					
	Tube/fin		Side plate/fin		Tube/header	
	A	B	A	B	A	B
1. Bottom	1.46	0.26	–	–	–	–
2. Bottom	1.46	0.24	–	–	–	–
3. Top	1.12	0.18	2.21	0.42	2.21	0.46
3. Bottom	1.46	0.24	2.67	0.56	3.06	0.74
4. Top	1.03	0.16	2.39	0.46	2.20	0.44
4. Bottom	1.30	0.21	2.52	0.57	3.25	0.83
5. Top	1.15	0.18	2.26	0.45	2.09	0.44
5. Bottom	1.32	0.22	2.49	0.52	3.16	0.82
6. Top	1.16	0.18	2.25	0.46	2.06	0.43
6. Bottom	1.39	0.21	2.58	0.63	3.22	0.80
Total Top	1.12	0.18	2.28	0.45	2.14	0.44
Total Bottom	1.40	0.23	2.57	0.57	3.17	0.80

6 OTHER VALIDATIONS

6.1 Radiator performance

The cooling air pressure drop, the coolant pressure drop and the heat rejection have been fulfilled according the current specifications. This result is also the same as for the corresponding vacuum brazed radiator.

6.2 Corrosion test

One CAB-brazed radiator has been SWAAT corrosion tested according to the ASTM-norm G85 during 7 days.

No leaks have been detected after the test. The tubes were without any corrosion attacks and the headers and side plates had only shallow attacks. The fins were less attacked (depending on a lower potential difference between tubes and fins) than for the corresponding vacuum brazed radiator.

6.3 Pressure pulsation tests

Three CAB-brazed heavy duty radiators have been tested in a pressure pulsation test with clean water as liquid. The test has been performed in three steps according to a Valeo norm, see Table 7 below. The tests were run until failure.

Table 7. Demands for a pressure pulsation test

Step	Temp (°C)	Low pressure (kPa)	High pressure (kPa)	Frequency (Hz)	No of cycles
1	95	30	170	0.5	100.000
2	95	30	200	0.5	50.000
3	95	30	250	0.5	to leak

No remarks have been noted during the steps 1 and 2. Weibul diagrams based on the number of attained cycles in step 3 have been developed. The mean values below, table 8, is based on eleven vacuum and three CAB brazed radiators

Table 8. Number of cycles L_{50} acc. to step 3 fetched from Weibul diagrams

Number of radiators	Vacuum brazed rad. cycles	CAB brazed rad. cycles
11	61.500	
3		71.500

Comparing with corresponding vacuum brazed radiators the result is somewhat better.

6.4 Temperature cycling tests

Several CAB-brazed radiators have been tested in temperature cycling tests acc to a Valeo product standard. The demands have been fulfilled. The test was run until failure and the CAB products survived longer than the vacuum.

7 CONCLUSION

This work has confirmed that age hardenable aluminium alloys with relatively high contents of magnesium can be brazed in high volume production equipment with good results if a standard flux with 2 % content of cesium was used. It has also confirmed that the new alloys FA7868, FA7850, and FA7870 can be heat treated to the same levels as currently used with the 6000 series.

Performed tests have showed that a well-adjusted brazing temperature and set time play an important role at the brazing with a cesium-containing flux. Notice that a flux with a Cs content melts between 558°C and 566°C whereas at standard flux melts between 562°C and 575°C. Consequently, all the important parameters had to be observed to get a successfully brazing result.

ACKNOWLEDGEMENTS

The authors would like to thank M. Moore, Valeo EngineCooling AB for his assistance with technical estimations and proofreading of this paper
We want specially give C. Massoulier, Valeo our appreciation of her excellent work with the initial Cs flux trials (se ref. 2 below).
We also want to mention the very good co-work with I.S.M.C.M – Laboratoire de Physique des Matériaux – who performed the fatigue tests.

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