NEW ALLOY DEVELOPMENTS IN ALUMINIUM BRAZING SHEET

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ABSTRACT As part of the overall target in the automotive industry to decrease weight and production costs, the heat exchanger market has to develop more effective designs and thinner materials on an on-going basis. In turn this places demands on the material supplier to develop higher strength alloys, which enable down-gauging for lighter-weight structures, or the use of high pressure cycles for increased cooling efficiency. This increased performance must be achieved with brazing and corrosion performance equivalent to, or superior to, the existing material, and also at a cost effective price.

In order to meet these market demands, Hoogovens Aluminium has developed new families of improved alloys suitable for Vacuum and/or Controlled Atmosphere Brazing (CAB). These alloy improvements have resulted from fundamental investigations, such as the understanding of corrosion mechanisms and the improvement of brazability and formability, as well as specific programs, such as the development of higher strength alloys with Long-Life corrosion performance. This paper will overview the latest alloy developments at Hoogovens Aluminium in the field of Long-Life Aluminium Brazing alloys.

Keywords: *Aluminium Alloys, Brazing sheet, Mechanical properties, Long-Life properties*

1. INTRODUCTION

Brazed aluminium components, produced by either Vacuum Brazing or CAB, have become the common choice in all major engine cooling and climate control systems such as condensers, evaporators, radiators, and oil coolers.

Brazing sheet is typically a two or three layered aluminium system comprising of a core alloy responsible for supplying the required strength and corrosion resistance, and a clad alloy responsible for supplying the material for joining. In most cases the core alloy is an AA3000 type alloy, and the clad a low melting point AA4000 type alloy.

Over the last few years the customer requirements for brazing materials have become more demanding. High strength materials, combined with excellent corrosion performance, are required to enable down-gauging for weight saving, or the use of higher pressure cycles for increased cooling efficiency. Alloy development must take into account the required performance criteria and balance and optimise the key material characteristics of strength, formability, corrosion resistance, and brazability.

Both non-heat-treatable (NHT) and heat-treatable (HT) Aluminium alloys are used for the different and numerous heat exchanger components, e.g. engine and transmission cooling, charge air coolers, climate control, etc.

In the NHT alloys, strain hardening by cold deformation increases the strength achieved through solid solution and dispersion hardening. The NHT alloys can be supplied in the "H" temper if the alloy is supplied in the hardened condition, or in the full annealed soft "O" temper if good formability is required. The brazing process obviously also softens the NHT alloys.

The HT alloys can also be strengthened by cold deformation, and can be supplied annealed, but have the additional potential benefit of extra strength through precipitation hardening. Brazing is carried out at temperatures of around 600°C, which is capable of dissolving soluble alloying elements. If the subsequent cooling rate from the braze cycle is sufficient then these alloying

elements can be retained in solid solution enabling subsequent appreciable strength increases by the mechanism of precipitation hardening. These HT alloys can therefore be naturally age hardened at room temperature (T4 temper), or can be artificially aged, typically at 150°-200°C for a few hours , to achieve maximum properties (T6 temper).
This paper will discuss some of the alloy developments and results for both NHT and HT core alloys over the last few years at Hoogovens Aluminium.

2. STANDARD CORE ALLOYS

Typically AA3003, AA3103 and AA3005 are used in applications where high formability is required and severe corrosion is not expected. For Vacuum and CAB brazing specific alloys are available. The CAB alloys generally contain <0.3% Mg as higher levels poison the standard flux by forming a higher melting point compound which inhibits fluidity of the molten cladding alloy. For example, alloy AA3005 is often used in Vacuum brazing as it has higher strength compared to AA3003 and AA3103, but is not suitable for CAB brazing.
Hoogovens Aluminium has also developed special Zn containing core alloys for fins. These alloys have a lower corrosion potential (sacrificial anode) to protect the tubes in a tube/fin system.
Heat treatable 6000 alloys, e.g. 6063, are commonly used for Vacuum brazing, but not CAB due to the high Mg content. Hogal-3570 (Hogal = Hoogovens Aluminium) is a heat treatable alloy that can be used in both CAB and Vacuum brazing although for the CAB process a higher flux concentration is required. These standard heat treatable alloys give high strength after brazing, but low corrosion resistance compared to the Long-Life alloys discussed later. Table 1 shows typical standard core alloy chemistries and properties (for 0.4mm gauge material).

ALLOY	Si	Cu	Mn	Mg	Zn	Proof Strength (MPa)	SWAAT LIFE
AA3103	≤0.50	≤0.10	0.9-1.5	≤0.3	≤0.20	35	3 days
AA3003	≤0.6	0.05-0.20	1.0-1.5	-	≤0.10	35	3 days
AA3005	≤0.6	≤0.30	1.0-1.5	0.20-0.6	≤0.25	50	3 days
Hogal-3570	0.45-0.65	0.40-0.60	0.70-0.90	0.30-0.40	≤0.20	70(T4)	3 days
AA 6063	0.20-0.6	≤0.10	≤0.10	0.45-0.9	≤0.10	75(T4)	2 days

Table 1: Typical chemistry (wt%) and post-brazed properties of Standard core alloys.

3. LONG LIFE VARIANTS

Hoogovens Aluminium has developed special chemistries which together with well designed thermo-mechanical processing give excellent mechanical properties combined with significantly improved corrosion performance compared with the more conventional 3000 type alloys. These alloys are termed "Long-Life" alloys and have typically over 5 times higher corrosion resistance than alloys such as 3003, 3005 and 6063 (compare tables 1 and 2).
The enhanced corrosion performance is obtained by the formation of a sacrificial layer during the braze cycle [1,2,3]. The sacrificial layer is formed when Si diffuses from the clad into the core during brazing. The diffusion of Si stimulates the precipitation of α-AlMnSi as the solubility of Mn is locally decreased. This results in a very dense band (20 to 60μm thick) of precipitates just below the surface of the material, i.e. the sacrificial layer, which transforms the corrosion mechanism. If the sacrificial layer/precipitate band is not present, then in SWAAT corrosion testing the corrosion attack proceeds in an accelerated intergranular/pitting manner. When the precipitate band is present, the sacrificial nature of the band deflects the corrosion attack in a lateral manner, i.e. along the direction of the band parallel to the original filler-core interface, preventing through thickness penetration.
In addition to the sacrificial layer, the grain structure of the Long-Life alloy prior to, and after brazing is critical, and for this reason the alloys are supplied in the H24 temper. This controls the

recrystallisation during brazing so that coarse elongated grains are still present in the final product. As grain boundaries are enhanced paths for corrosion attack, the so-formed 'pancake' grains minimise the available grain boundary area thereby improving the corrosion performance. The typical morphology of the lateral corrosion attack and the required elongated grain structure in Long life alloys, are shown in Fig. 1.

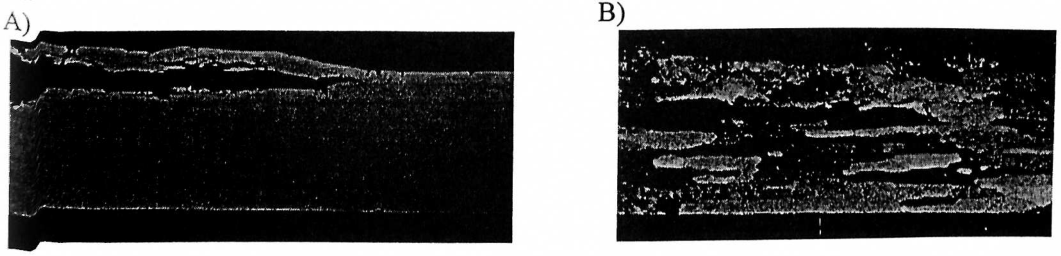

FIG. 1: A)Typical morphology of lateral corrosion in Long -Life alloys. B) Elongated grains, from H24 material, necessary for optimum corrosion performance.

For radiators one of the most accepted corrosion tests is the SWAAT test (ASTM G85-A3). The minimum requirement for the so-called Long-Life alloys is >10-12 days SWAAT resistance [4], and Scott [5] has stated that one day of SWAAT is equal to one year of field exposure.
Typical chemistries and properties (for 0.4mm gauge material) of Long-Life alloys produced by Hoogovens Aluminium are shown in Table 2.

ALLOY	Si	Cu	Mn	Mg	Zn	Proof Strength (MPa)	SWAAT LIFE
Hogal-3190	**≤0.40**	**0.2-0.5**	**1.0-1.5**	**0.40-0.70**	**≤0.25**	**55**	**>20 days**
Hogal-3532	**≤0.3**	**0.5-0.7**	**0.65-1.00**	**0.1-0.3**	**≤0.10**	**50**	**>20 days**
Hogal-3534	**≤0.3**	**0.5-0.7**	**0.65-1.00**	**≤0.02**	**≤0.10**	**48**	**>20 days**

TABLE 2: Typical chemistry (wt%) and post-brazed properties of Long-Life alloys

4. NEW HIGH STRENGTH ALLOYS

Higher strength alloys are required due to the trend to lower gauges and to higher performances. This demand has led to recent alloy development programmes at Hoogovens Aluminium [2]. New alloys have been developed both for NHT and HT application, and are discussed below.

4.1. NEW HIGH STRENGTH NHT ALLOYS

A new series of NHT alloys (patent pending) have been developed in the laboratory for both Vacuum and CAB brazing. This alloy family has a relatively high Cu addition (typically 0.9 to 1.1%), low Si content (typically <0.1%), combined with specific tailored additions of Zr, Cr and Ti. This alloy type has been shown to obtain post brazed 0.2% yield stress values of > 65MPa, and typically 75MPa, combined with Long-Life properties (SWAAT > 15 days). A significant improvement in properties of 20% and over has been gained compared with the traditional Long-Life alloys described above.
The increased strength of these alloys has been optimised by specific combinations of Cu, Cr, Zr and Ti. The increased Cu content enhances strength by increased solid solution hardening. Significant strength increases are also obtained by tailored additions of Cr, Ti and Zr.
If, for example, Cr is used on its own then strength is increased. However with increasing Cr content above 0.2% there is a decreasing advantage in respect of the higher strength gained. Casting trials have indicated that with increased Cr concentrations there is a greater chance for the formation of coarse Cr containing intermetallic compounds. These compounds have been analysed to be

predominantly Cr-Mn rich in composition, and the chance of their formation increases with higher Mn and Cr levels. The formation of these coarse particles is obviously detrimental to mechanical properties as they decrease the effective Mn and Cr for strength purposes, and are also detrimental for formability and corrosion resistance.

If Zr is used as an alloying addition on its own then a slightly reduced strength increase compared to Cr is obtained. A critical factor is that a combined Cr and Zr addition has an additive effect on the mechanical properties as clearly shown in Fig. 2.

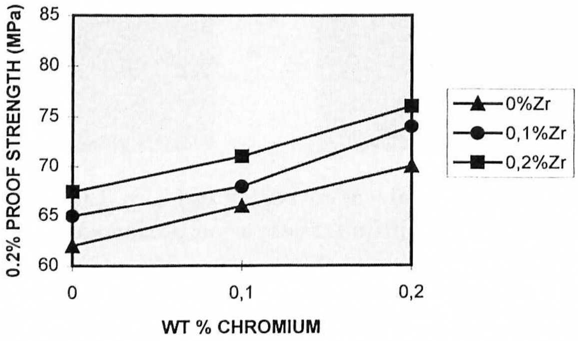

FIG. 2: Additive increase in post brazed mechanical properties with combined Cr and Zr additions (Base composition 1%Mn, 0.9%Cu, 0.35%Mg, 0.09%Si).

The additive effect of a combined addition on the mechanical properties is not the only advantage. Another significant benefit is that a higher total Cr + Zr addition can be made without the risk of the formation of the detrimental coarse Cr intermetallics described above compared with Cr additions alone. Higher mechanical properties can therefore be obtained with a combined Cr and Zr addition.

Ti additions are also very effective in increasing strength. Casting trials, by use of 'wedge mould testing', have been carried out to optimise casting conditions (temperature, solidification rates etc.) to maximise the total allowable additions of Zr, Cr and Ti. The strength and performance of the alloy can be optimised in this manner. A typical chemistry and post brazed property range is shown in Table 3 (for 0.4mm thickness, H24 temper before brazing).

Si	Cu	Mn	Mg	Zr	Cr	Ti	Proof Strength (MPa)	SWAAT LIFE
<0.10	0.90-1.10	1.0-1.20	0.35-0.50	0.10-0.15	0.10-0.20	0.05-0.15	70-80	>20 days

TABLE 3: Typical chemistry (wt%) and post-brazed properties of a new NHT alloy.

The alloys have excellent Long-Life corrosion properties. The fact that most of the Cu in the alloys is retained in solid solution after brazing (which explains good mechanical properties) is a benefit for corrosion protection as Cu shifts the corrosion potential to a more noble value [6]. Benedictus et al [7] propose an additional explanation for the good corrosion performance of Cu containing alloys, i.e. the presence of Cu also in τ-phase precipitates (AlMnCu), which are present in a significant volume fraction both before and after brazing. The presence of the τ-phase appears to change the corrosion potential to an even more noble value enhancing the corrosion performance.

4.2. NEW HIGH STRENGTH HEAT TREATABLE ALLOYS

Hoogovens Aluminium has also developed two new Heat Treatable Brazing Alloys (one for Vacuum, one for CAB) which combine a very high strength with excellent Long-Life corrosion properties [2]. The alloys have a T4 0.2% proof strength of up to 110 MPa, which is 100% higher than existing Long-Life alloys of the 3005/Hogal-3190 type, and these properties can be achieved with typical industrial braze cycles.

The new alloys, which are currently undergoing customer trials, are designated Hogal-3571 and Hogal-3572, and are for Vacuum and CAB brazing respectively. Patents for these alloys are pending. Chemical compositions of the alloys are shown in Table 4.

Alloy	Brazing Process	Si	Mn	Mg	Cu	Fe
Hogal-3571	Vacuum	0.30-0.70	1.00-1.40	0.30-0.70	0.60-0.90	≤0.40
Hogal-3572	CAB	0.30-0.70	1.00-1.40	0.10-0.35	0.60-0.90	≤0.40

TABLE 4: Typical chemical compositions (wt%) of the new high strength brazing alloys Hogal-3571 & Hogal-3572

The high strength properties are obtained since the new alloys contain sufficient Mg and Si to form Mg_2Si hardening precipitates during natural ageing after brazing. The relatively high Cu content also contributes to strength through solid solution strengthening, and also enhances the ageing response [8]. The natural ageing response of the alloys is shown in Fig. 3, and typical properties after an air quench following the braze cycle are shown in Table 5.

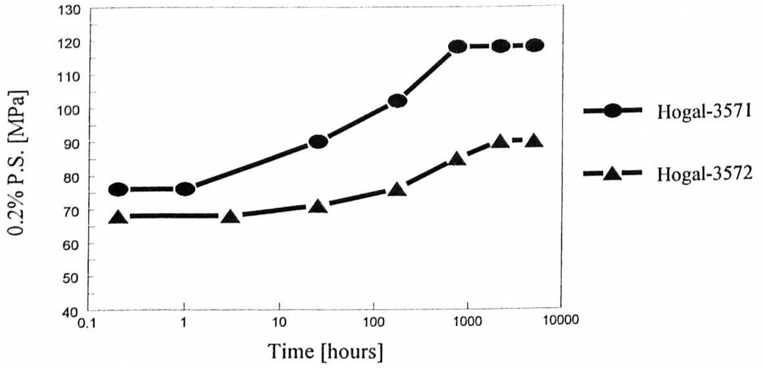

FIG. 3: Natural ageing response for the alloys Hogal-3571 and Hogal-3572 (Air quench after brazing).

Alloy	Mechanical Properties		
	0.2%P.S. [MPa]	UTS [MPa]	Elong. [%]
Hogal-3571	118	247	11.6
Hogal-3572	90	212	15.1

TABLE 5: Post-braze properties (air-quenched) of the alloys Hogal-3571 and Hogal-3572, in the T4 temper after 30 days natural ageing.

The brazing cycle acts as a solution heat treatment cycle. The cooling rate after the braze cycle influences the mechanical properties, but Hogal-3571 and Hogal-3572 have been shown to be relatively non-sensitive to the cooling rate in the normal ranges applied in industrial brazing furnaces, which typically vary between 20 and 100°C/min. The results from several different controlled cooling rates (e.g.20, 60 and 90°C/min) from brazing are shown in Fig.4, and are compared with results ascertained for traditional HT alloys 6063 and 6060,as well as for Hogal-

3190 (Long-Life). The starting material was 0.4mm gauge in the H24 temper (i.e. Long-Life), and was brazed using a typical tube stock brazing cycle.

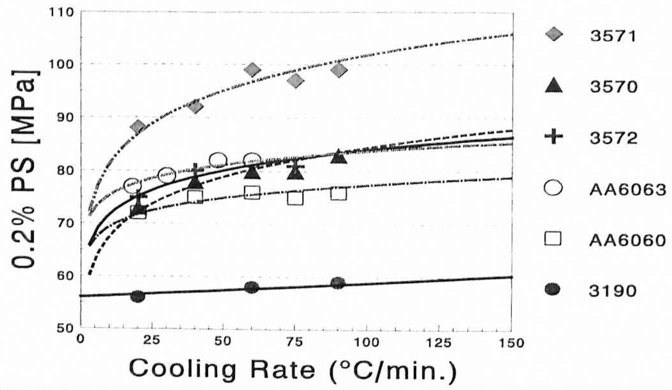

FIG. 4: Proof Strength (T4) vs Cooling Rate for various Hogal and AA alloys

Fig. 4 indicates that within the cooling rates that can be obtained during industrial practice the 0.2% proof strength of brazed Hogal-3571 in the T4 condition will be approximately 90 to 100 MPa. This is stronger than AA6063 and AA6060, and in addition the corrosion properties of the Hogal-3571 are far superior. Long-Life properties, i.e. SWAAT>10days, are obtained with Hogal-3571, whereas the 6000 alloys have very poor corrosion, lasting <3 days in SWAAT.

The Hogal-3572 CAB alloy achieves a T4 0.2% proof strength of approximately 80MPa, which is comparable to the 6000 alloys, but again is combined with superior Long-Life corrosion properties (SWAAT>15 days).

Both of the newly developed Long-Life alloys have superior mechanical properties compared to the existing Long-Life alloys (e.g. Hogal-3190), with Hogal-3571 having a proof strength up to 100% higher, and Hogal-3572 up to 60% higher than the present alloys available.

5. CONCLUSIONS

New material developments have to focus on new alloys with improved strength, formability, and corrosion performance as heat exchanger designers make lighter weight structures using down-gauged sheet. With this aim Hoogovens Aluminium has developed two new alloy systems:-

- Non Heat Treatable alloys with Long-Life corrosion properties and a post brazed strength increase of approximately 20% compared with standard Long-Life alloys.
- Heat Treatable alloys, Hogal-3571 and 3572, that also have Long-Life corrosion properties and achieve post brazed strength increases typically of up to and beyond 70% and 40% respectively compared to traditional Long-Life alloys at industrial cooling rates.

Due to this unique combination of strength and corrosion resistance these alloys have potential for down-gauging many parts of automotive heat exchangers, e.g. tube-stock, header stock, and evaporator-stock, which are up to now manufactured from standard 3000 and 6000 alloys.

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