Brazing of Aluminium Alloys with Higher Magnesium Content using Non-Corrosive Fluxes

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Abstract

For just as long as aluminium has been used for brazing heat exchangers, there has been a trend to down-gauging components for weight savings. The most common alloying element to achieve higher strength alloys for the purpose of down-gauging is magnesium. While magnesium additions are helpful in achieving stronger alloys, the consequence is a decrease in brazeability.

This article discusses the mechanism of brazing deterioration with the addition of magnesium and proposes the use of caesium compounds as a way of combating these effects.

Introduction

Aluminium brazing using non-corrosive fluxes is the leading process for manufacturing automotive heat exchangers. Recently, this process has become more wide spread in the stationary Heating, Ventilation, Air-Conditioning and Refrigeration (HVAC&R) industry, both for domestic and commercial applications. The standard brazing process involves joining of components with a brazing alloy, typically an aluminium-silicon filler alloy. Al-Si brazing alloys have melting ranges from 577°C to 610°C, which is appreciably lower than the melting point range of the base aluminium alloys used for heat exchangers (630°C – 660°C). Fluoride-based non-corrosive fluxes of the system KF-AlF_3 are used to displace the surface oxide film during the brazing process. A commonly used non-corrosive flux of the general formula $K_{1-3}AlF_{4-6}$ is known under the trademark name NOCOLOK® Flux[i] with a melting range between 565°C and 572°C. The flux works by melting and disrupting the oxide film on aluminium, protecting the surfaces from re-oxidizing during brazing thus allowing the Al-Si brazing alloy to flow freely.

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[i] NOCOLOK is a registered trademark of Solvay Fluor GmbH, Germany

A consistent and on-going trend across all heat exchanger manufacturing sectors is towards lighter weight, accomplished by down-gauging of components. Also corrosion resistance is a key factor - particularly when there is no additional post brazing coating or treatment. These often contradictory trends call for aluminium alloys having higher and higher post brazed strength. While alloys from the 7xxx (alloyed with Zn) and 2xxx (alloyed with Cu) series can be precipitation hardened to the highest strengths of any aluminium alloys, their corrosion resistance without any additional coating is low and their solidus temperatures are below the melting range of currently used flux and filler metal combinations, and therefore they are not suitable for heat exchanger manufacturing by brazing.

The most common alloys used for aluminium brazing are from the 3xxx series (alloyed with Mn). After being subjected to the high temperature during the brazing cycle, these alloys have relatively low post-braze mechanical strength. Higher strength is offered by alloys from the 5xxx series (alloyed with 2 to 5 wt% Mg) where post brazed strengthening is achieved by solid solution hardening or by the 6xxx series (alloyed with Mg and Si) which can be precipitation hardened. A more comprehensive survey of mechanical properties of brazeable aluminium alloys is presented in [1]. It is worth observing that the brazing cycle itself could be considered as a thermal treatment for obtaining the precipitation hardening effect providing the cooling rate from the brazing temperature is sufficiently fast [2]. An example of such an alloy designated for specific use for aluminium brazed heat exchangers is described in detail in [3].

As well as increasing post-braze mechanical strength, the addition of Mg to certain alloys allows for improved machinability. Machining is necessary for heat exchanger components such as connecting blocks and threaded fittings.

There is however a certain limitation with the above mentioned alloys. They all contain magnesium. During the brazing cycle Mg negatively influences the process of oxide removal and it is generally accepted that Mg levels only up to 0.3% can be safely brazed with the standard brazing flux. This negative influence can be mitigated with the use of caesium containing compounds. The mechanism of Mg interference with the brazing process and the positive role of Cs additions to the flux in combating the effects of Mg are the subjects of the current paper.

Effects of Mg on the brazing process

To illustrate the effects of Mg on the brazing process, Bolingbroke et al [4] chose the angle-on-coupon method. In this technique, an aluminium angle is laid on top of a cladded aluminium coupon where the legs of the angle are raised using stainless steel wire (see Fig. 1). Brazeability is thus measured as a function of the length of the fillet formed. In this set of experiments, the coupon base alloy is 3003 with Mg additions ranging from 0.1 to 0.58 w%. Only the coupon was fluxed at pre-defined loads ranging from 2 to 10 g/m^2. The results of the Mg content on brazeability are shown in Fig. 2.

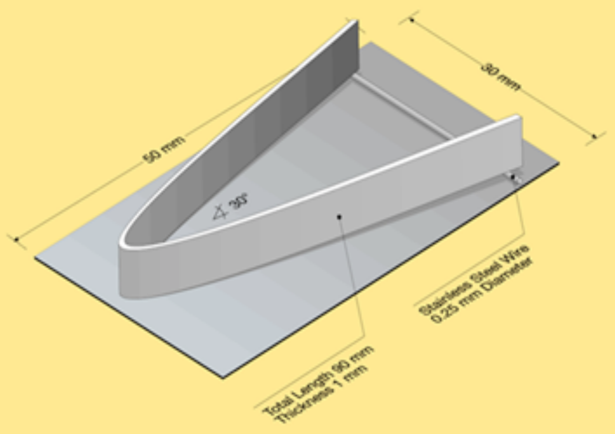


Fig. 1: Experimental set up for brazeability measurement [4].

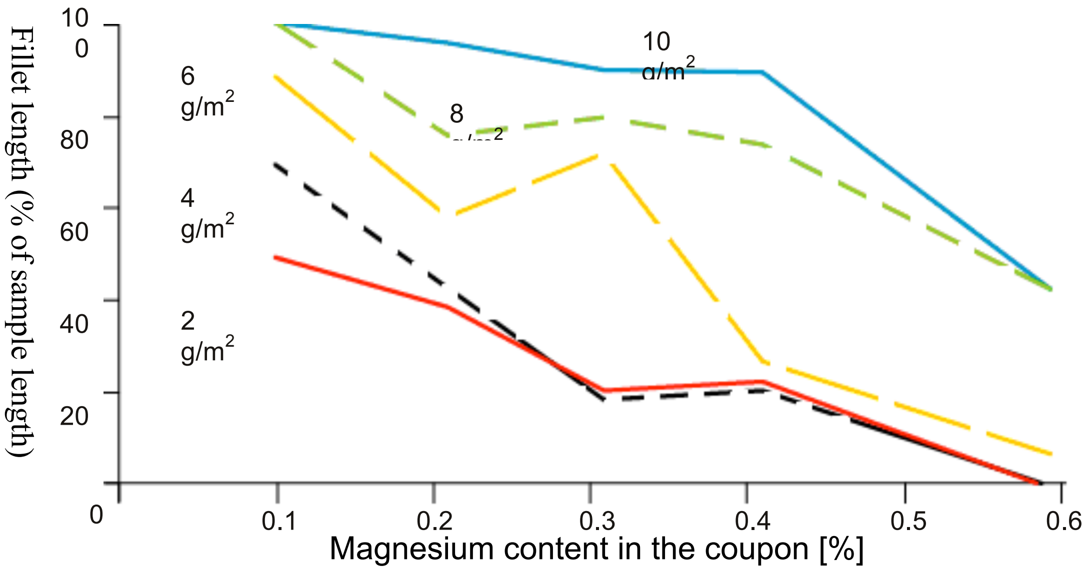


Fig. 2: Brazeability as a function of magnesium content [4]

Fig. 2 shows that increasing the flux load can reduce the negative influence of magnesium.

The solid state diffusion is time-temperature dependent and becomes rapid above 425°C. Thus brazing at higher heating rates should reduce the negative influence of Mg. The influence of heating rate on brazeability is shown in Fig. 3.

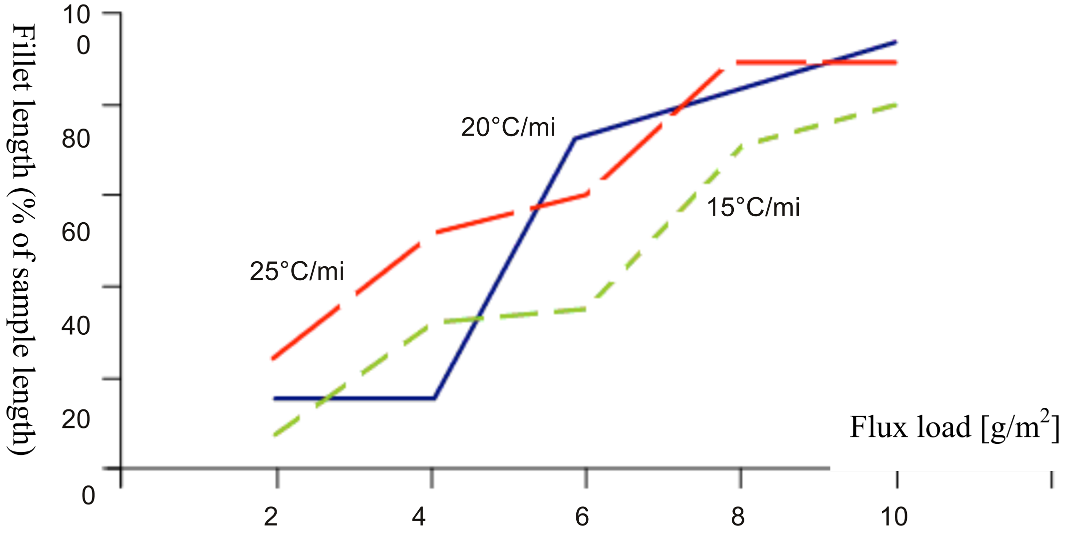


Fig. 3: Brazeability of 3003 alloy + 0.31 wt% Mg as a function of heating rate and flux load [4]

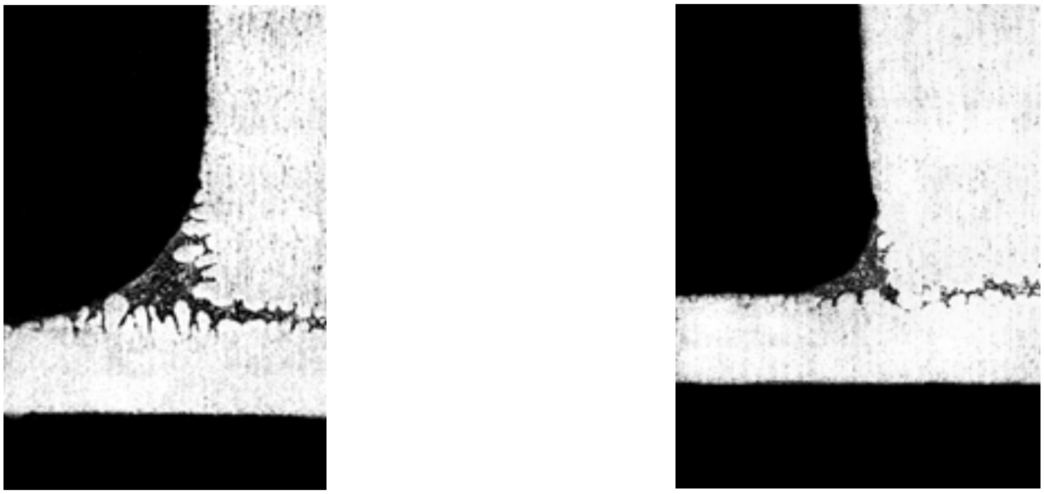
The influence of heating rates when kept within the values attainable for the CAB process is rather weak. Increasing the flux load is more effective in combating the negative influence of Mg for CAB processes.

In flame or induction brazing, where the heating rates are about two orders of magnitude higher than in the CAB process, alloys with Mg concentration even as high as 2% can be successfully brazed.

It should be noted that when one speaks of the brazing tolerance to Mg, it is always the **total sum of the Mg concentrations in both components**:

$$[\mathrm{Mg}]_{\mathrm{component\ 1}} + [\mathrm{Mg}]_{\mathrm{component\ 2}} = [\mathrm{Mg}]_{\mathrm{total}} \qquad (1)$$

The effect of magnesium content on the appearance of the brazed joint is shown in Fig. 4.



0.1 wt% **0.4 wt%**

Fig. 4: Effect of Mg content on appearance of brazed joint [4]

At 0.1 wt% in the base coupon, the fillet is large and joining is complete. At 0.4 wt% Mg in the base coupon, the fillet volume is smaller.

Mechanism of magnesium interaction with the brazing process

According to M. Yamaguchi et al [5], when magnesium diffuses to the surface during brazing, a chemical reaction takes place with the flux resulting in the generation of $KMgF_3$.

The authors suggest the following equations to explain some of the chemical interactions between magnesium and $K_{1-3}AlF_{4-6}$ flux:

- $3\,MgO + 2\,KAlF_4 \rightarrow MgF_2 + 2\,KMgF_3 + Al_2O_3$ (a)
- $3\,MgO + 2\,KAlF_4 \rightarrow 2\,MgF_2 + K_2MgF_4 + Al_2O_3$ (b)
- $3\,MgO + 2\,K_3AlF_6 \rightarrow 3\,K_2MgF_4 + Al_2O_3$ (c)

By performing XRD (X-ray Diffraction) phase identification on products brazed with Mg containing alloys, A. Gray et al [6] confirmed the presence of K_2MgF_4, spinel oxide (Al_2MgO_4) and possibly $KMgF_3$. These magnesium containing compounds have a characteristic needle like morphology as shown in Fig. 5.

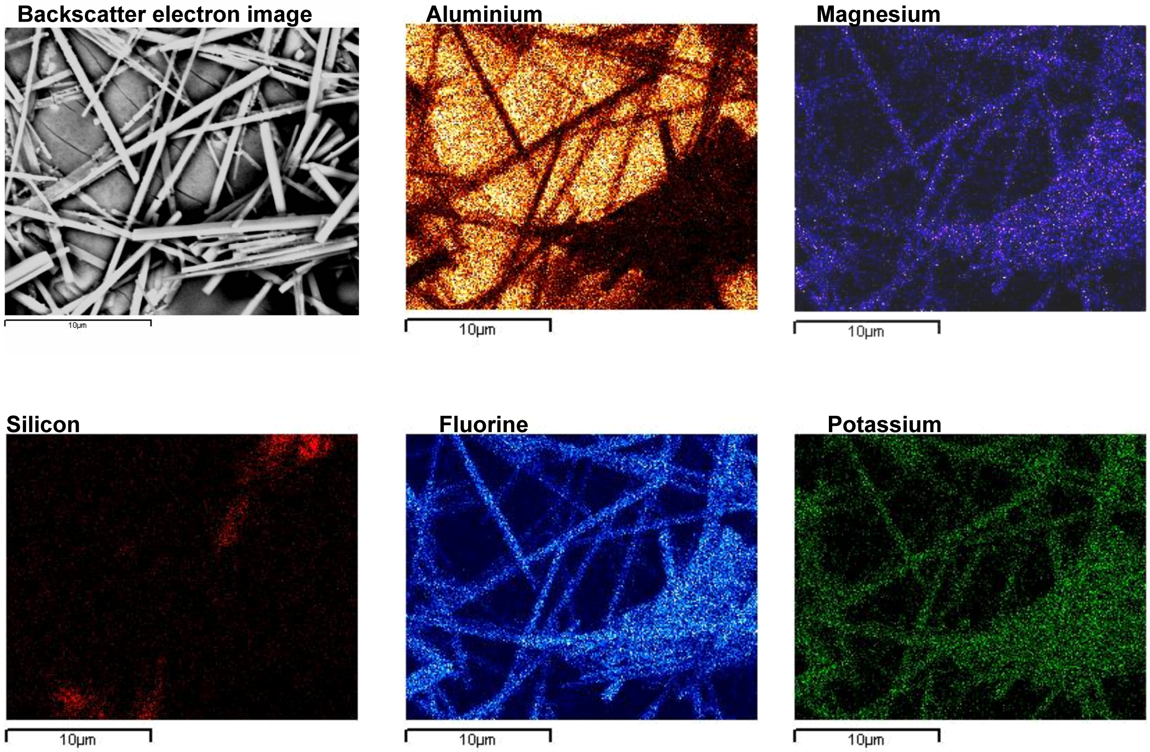


Fig. 5: Morphology of magnesium containing compounds as seen by Scanning Electron Microscope [6]

H. Johansson et al [7] also determined that at temperatures above 425°C the magnesium diffusion to the surface is very rapid resulting in the formation of magnesium oxide (MgO) and spinel oxides (Al_2MgO_4). These oxides have very low solubility in NOCOLOK® Flux. Subsequently these magnesium oxides react with the flux resulting in the formation of magnesium fluoride (MgF_2) and potassium magnesium fluorides ($KMgF_3$, K_2MgF_4, see equations a), b), and c)). These reactions change the flux chemical composition causing its melting range to rise. The melting point of these magnesium fluorides is very high, which in turn drives the melting point of the flux upwards, thereby decreasing the activity of the flux. The above factors also cause a decrease in the flowing characteristics of the flux thus lowering its overall effectiveness. Therefore the desired key point to limit the flux poisoning effect would be to reduce the formation of magnesium oxides and potassium magnesium fluorides.

Caesium fluoroaluminates

Magnesium is an extremely reactive element and therefore even a small amount of oxygen will cause its oxidation. In standard brazing furnaces most often the level of oxygen in the furnace atmosphere at the temperature ranges below brazing could be relatively high. Thus the formation of magnesium oxides seems to be inevitable. On the other hand, one can think about neutralizing or inhibiting the formation of the poisoning potassium magnesium fluoride compounds mentioned earlier. The formation of those compounds can be reduced in the presence of caesium fluoroaluminate compounds.

Caesium fluoroaluminates exist in several compositions and crystallographic states such as $CsAlF_4$, $Cs[AlF_4 (H_2O)_2]$, Cs_2AlF_5, $Cs_2AlF_5 H_2O$, Cs_3AlF_6. The Cs compound commonly used for aluminium brazing contains mainly $CsAlF_4$ and is also known as CsAlF - Complex.

Cs acts as a chemical scavenger for Mg. During the brazing process, caesium reacts with magnesium to form compounds such as $CsMgF_3$ and/or $Cs_4Mg_3F_{10}$ [8]. These compounds melt at lower temperatures than the filler metal. As such these compounds do not significantly interfere with aluminium brazing and allow the flux to retain much of its oxide dissolution and wetting capability.

The caesium fluoroaluminate complex has a low melting range (420 - 480°C), a high water solubility (~20 g/l at 20°C), and contains between 54 - 59 % of elemental caesium. Though there are literature references for using the pure Cs-complex as a brazing flux [9], the chemical characteristics present practical problems when one would like to replace standard NOCOLOK® Flux with pure caesium fluoroaluminates complex. The low melting range means that under normal CAB process conditions the flux would essentially dry out by evaporation before reaching the brazing temperature (~ 600°C). Furthermore, the high content of Cs makes it prohibitively expensive as a replacement for standard NOCOLOK® Flux.

However the Cs complex does find a use in several applications such as flame and induction brazing and as a key component of flux paste formulations for specialty alloys. In some processes, mainly flame brazing of copper and aluminium, this complex is the state of the art [10].

Aluminium and copper form a low melting eutectic (546°C). This means that it is not possible to braze copper and aluminium in a CAB process using standard filler metal alloys having a melting range from 577°C to 605°C. It is however possible to join aluminium and copper by flame brazing, but it requires high degree of temperature control and a lower melting filler alloy is recommended. Zinc-aluminium alloys are commonly used for such applications. Lower melting range filler alloys require lower melting range fluxes and since flux consumption for flame brazing is relatively low, it is economically feasible to use a caesium fluoroaluminate complex such as $CsAlF_4$.

NOCOLOK® Cs Flux

As a more practical means of obtaining better brazeability of Mg containing alloys, a mixture of standard NOCOLOK® Flux and caesium fluoroaluminates is used. The positive influence of Cs on brazing magnesium containing alloys was previously reported in a patent for a product where potassium fluoroaluminates were mixed with caesium fluoroaluminates [11]. However, this patent covered a rather wide ratio of potassium fluoroaluminates to caesium fluoroaluminates.

The influence of actual elemental Cs content on brazeability was investigated by Garcia et al [12]. Brazeability was determined by the length of the joint obtained in a system with a gradual increase in gap clearance (similar in concept to the one shown in Fig. 1). In their work they used 6063 alloy with a Mg content of 0.66 wt%. Their major finding is presented in Fig. 6.

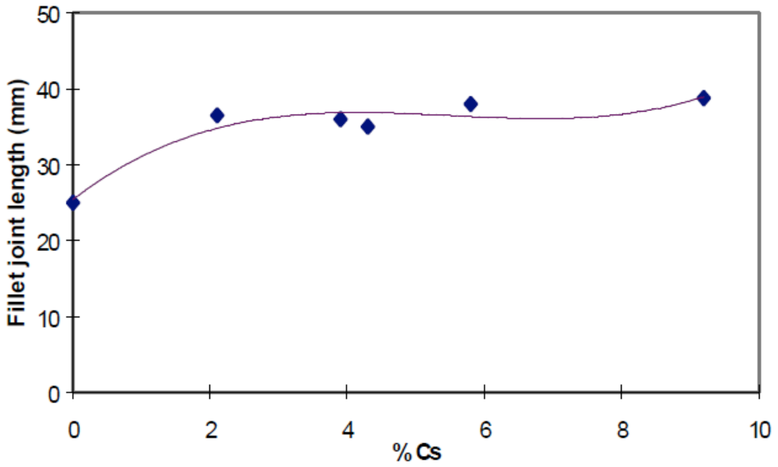


Fig. 6: Brazeability of AA6063 alloy as a function of caesium content at flux load of 5 g/m^2 [12]

As seen in Fig. 5, even a relatively low concentration of Cs in the flux mixture improves brazeability of an alloy containing 0.66 wt% Mg. An increase of Cs concentration above 2 wt% does not lead to further improvement in brazeability. In his work Garcia et al also confirmed that faster heating rates, though positive do not significantly influence brazeability.

This work led to another important finding. By brazing small sample radiators in an industrial type furnace, Garcia et al established a practical threshold for Mg content. The flux containing 2 wt% Cs is effective for brazing aluminium alloys with 0.35% to 0.5 % Mg. At lower levels of magnesium no difference between the standard flux and the 2 wt% Cs flux was observed. Brazing samples containing 0.66% of magnesium yielded leak free parts - but the brazing ratio for fins was not fully satisfactory.

This work led to the standardization of Solvay's NOCOLOK® Cs Flux at 2 wt% Cs. By using this minimal but effective Cs concentration in the mixture, the chemical and physical characteristics are similar to the standard flux.

Summary

- Magnesium is very often added to aluminium alloys to increase strength and machinability.
- The addition of magnesium negatively influences the brazing process due to the formation of smaller fillets and the presence of porosity in the joints. This is due to (a) magnesium diffusing to the surface during the brazing cycle and forming Mg containing oxides which are more difficult to remove by the molten flux and (b) by poisoning the action of flux through the formation of K-Mg-F compounds.
- The above effect can be made less pronounced when standard NOCOLOK® Flux is mixed with a caesium aluminium fluoride complex. At a concentration of 2 wt% Cs one can observe a positive effect on aluminium alloys containing magnesium. Increasing the Cs content above 2 wt% does not yield any further increase in brazeability.
- NOCOLOK® Cs Flux works effectively for alloys containing roughly 0.3 to 0.5 wt% Mg. Depending on specific design and process conditions, Cs containing fluxes can also offer benefits for alloys containing 0.3 wt% or even less Mg. For concentrations higher than 0.5 wt% of Mg, the effectiveness of Cs compounds in non-corrosive fluxes gradually decreases.
- Pure caesium aluminium fluoride complex is effectively used for flame brazing where a lower melting point flux is required.

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