Aluminium Brazing with Non-corrosive Fluxes State of the Art and Trends in NOCOLOK® Flux Technology

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Presented at the 6th International Conference on Brazing, High Temperature Brazing and Diffusion Bonding (LÖT 2001), Aachen, Germany (May 2001) – Revised Text

Abstract

This paper summarises the general development and the current status of aluminium brazing with non-corrosive fluxes. Based on the most common manufacturing practices, present-day brazing operations are described.

Numerous improvements to aluminium brazing technology have been made in recent years. The most significant developments and trends are addressed, particularly process reengineering (e.g., cleaning, flux application), cost savings (e.g., water, flux, energy), and aluminium alloy improvements (e.g., high strength, good formability, and long-life).

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Introduction

Since the early 1980's, Controlled Atmosphere Brazing (CAB) with non-corrosive fluxes has evolved as the leading technology for manufacturing aluminium heat exchangers in the automotive industry. Today, more than 400 CAB furnaces are in operation throughout the world using the NOCOLOK® process.

This technology offers the benefits of a flux for successful oxide removal, working at atmosphere pressure while avoiding the disadvantages of post braze treatments and corrosion susceptibility. The non-hygroscopic and non-corrosive potassium fluoroaluminate flux does not react with aluminium in the molten or solid state and the post braze flux residues have a very low water solubility [1].

The process in most brazing operations includes the following *steps:*

- Component Forming and Assembly
- Cleaning and Flux Application
- Brazing

The process *sequence* in brazing operations is dependent on:

- Heat Exchanger Design
- Cleaning Method
- Flux Application Method

Success or failure in CAB production relies on several factors. The starting point is good *product fit-up.* Parts to be metallurgically joined must have intimate contact at some point along the joint. An adequate (but not excessive) quantity of filler metal must be available to fill the joints. Capillary forces pull the filler into the joints. The *gap tolerance* is 0.1 to 0.15 mm for non-clad components. When clad products are used, intimate contact is recommended; the clad layer(s) will act as a gaping tool.

Another essential for reliable brazing results is a *uniform flux coating* on all surfaces involved in the joint formation. The main focus for achieving this task is on the *cleaning and fluxing procedure.*

Equally important are the *furnace conditions,* i.e. *temperature profile, temperature uniformity,* and *atmospheric conditions.*

1. Cleaning and Flux Application

Cleaning and flux application procedures depend on product designs and personal choice. Heat exchangers are classified in two groups:

a) *no internal brazing* required
b) *internal brazing* required

No internal brazing is necessary with the following types:

- Radiators (welded tubes)
- Parallel Flow Condensers [PFC] (extruded tubes)
- Serpentine Evaporators
- Heater Cores (welded tubes)
- Intercoolers (extruded tubes)

Internal joint formation (and therefore internal flux application) is needed on these types:

- Radiators (folded tubes)
- Condensers (folded tubes)

- Heater Cores (folded tubes)
- Oil Coolers
- Plate Evaporators
- Intercoolers (with turbulators)

For the majority of brazed heat exchangers, assembly is followed by cleaning and subsequently by flux application. However, when internal surfaces need to be fluxed, the production sequence may follow a different order, determined by when and how the flux is applied.

- *Cleaning Methods*:

The purpose of cleaning is to remove fabricating oils and lubricants as well as other contaminants from the surfaces. The cleaning procedure must allow for adequate flux retention and render the surfaces suitable for brazing. Cleaning results have great influence on the brazing results, post braze product appearance and corrosion performance.

The following cleaning methods are commonly utilised:

- *Aqueous Cleaning:*

Aqueous cleaning of high volume assemblies is usually by spray. The parts travel on a belt through a multi-chamber cabinet, and are spray-cleaned by an aqueous solution, spray-rinsed with warm and cold water (2 - 3 x). The excess water is then blown off with air.

In most cases, the cleaning solution contains a mild alkali ingredient and detergents (acid-based cleaning solutions seem less common). The cleaning solution not only removes lubricants from the surfaces, but also has a mild "etching" action (i.e. producing a microscopic roughness). This etching action renders the surface of aluminium wettable by lowering the surface tension.

The cleaning efficiency in aqueous cleaning is a function of:

- Concentration (Cleaning Solution)
- Time and Temperature
- Contact Pressure (usually 1–2 kg/cm^2)

An alternate cleaning method often used is:

- *Thermal Degreasing:*

With the use of special "evaporative/ vanishing oils/ lubricants", a heat exchanger can be degreased simply by heating. These lubricants volatilise when heated to approximately 200 – 250°C. The heat exchanger surface temperature should not exceed 300°C, to avoid the formation of high temperature oxide (see also Product Dehydration).

An important consideration is that this degreasing method leaves the heat exchanger "non-wettable", i.e. a uniform flux distribution in wet fluxing can be difficult. When a product is thermally degreased, the flux slurry requires the addition of a surfactant (wetting agent) to lower the surface tension of the water, thus ensuring more uniform flux distribution.

- *Other Cleaning Methods:*

In some small volume manufacturing, solvent cleaning is used. However, health safety and environmental issues are critical with many of these chemicals. Vapour degreasing has been phased out almost completely world-wide.

Some consideration has been given to totally eliminating the cleaning step under certain conditions. However, the question of how much residue (contamination) is acceptable must be resolved before such decision can be made.

2. Flux Application Methods

There is a wide variety of different fluxing methods including:

- Low Pressure Spray
- Flooding (Cascade)
- Dipping or Submerging
- High Pressure (atomised) Spray
- Brushing (Paste Application)
- Dry or Electrostatic

3. Wet Flux Application

The most common flux application method in CAB is by spraying an aqueous suspension. Constantly agitated flux slurries with concentrations of approximately 10 – 35% solids are pumped from tanks to fluxing booths. All aluminium surfaces involved in the brazing process are coated with the slurry, resulting in a uniform flux layer. Excess flux slurry is removed with a high-volume air blow; the excess is then collected, recycled and reused in the fluxing booth.

Capillary effects throughout the unit can result in non-uniform flux distribution. Flux slurry tends to be held in fin/ tube joints, fin louvers etc. This excess is difficult to blow off with only one curtain or knife air system. Slurry also collects on the bottom surface of units in the shadowed area that doesn't see direct air impingement. The excess in those areas is wasted flux, as a uniform 5 g/m^2 load is sufficient to ensure good brazing. If wettability is poor on the headers, flux load tends to be low. The relatively plain header surfaces generally hold less flux slurry. Most fluxers are designed with two flux slurry concentrations to ensure sufficient coverage in the header area by applying a 10 to 15% higher slurry concentration.

Excess flux slurry can be blown off by installing a second tandem overhead blow-off system or additional air knifes for cutting off droplets from the bottom and side surfaces. Reducing excess slurry on the core in the fluxer (slurry is recyclable) is more economical than removing dried flux from a drier (due to hot air currents in the drier), which is not recyclable.

- *Product Dehydration:*

When wet fluxing is utilised, the heat exchangers are dried prior to brazing in a separate dry-off oven. Product entering the brazing furnace must be completely dry from water introduced via aqueous cleaning or flux slurry coating. This can easily be confirmed initially by weighing the product as it exits the dry-off oven, running a second and third time through the oven, and weighing after each run. If the product weight has stabilised, drying is acceptable. If further weight loss occurs, more time in the drier or higher temperature will be necessary. However, the surface temperature of the parts in the drier should not exceed 250°C. High temperature oxide is formed at about 300°C.

Oxide thickness increases with temperature, time at temperature and particularly in the presence of moisture. Oxide formation will affect clad fluidity[2]. There is only a small drop in brazeability when the oxide thickness increases from 40 to 220 Angstroms at 5 g/m^2 flux load. However, there is an appreciable drop in clad fluidity as the oxide thickness increases from 40 to 100 Angstroms at 2 g/m^2 flux. A reduction in brazeability can even be noted as the oxide thickness is increased from 40 to 60 Angstroms.

Proper flux loads should be maintained since low flux load appears to be quite sensitive to even small changes in oxide thickness.

4. Dry/ Electrostatic Flux Application

Over the past five to ten years, some users of CAB technology have successfully implemented dry flux application methods. Based on the principles of powder paint technology, an application technique alternative was introduced in the brazing industry.

The benefits of electrostatic application are directly related to the problems of wet application:

- No need to mix slurries
- No need to monitor slurry concentration
- No need for a surface wettability concept (i.e., surface treatment or wetting agent)
- No separate drying step required to remove moisture
- No waste water effluent

Particularly when dry fluxing is used in combination with thermal degreasing (i.e. evaporative oils and lubricants), the objective is to completely eliminate or significantly reduce water consumption in the process.

In dry flux application, the following difficulties have been described by users when operating with conventional flux qualities:

- Powder fluidisation and material transport is difficult. Vibration or stirring is necessary to improve on these characteristics.
- Inconsistency of flux flow and non-uniformity of applied flux.
- Adhesion of deposited flux is inferior when compared with wet application.
- High humidity causes physical adsorption of moisture to the fine powder dust in the booth. This can result in agglomerations.
- Recovering, recycling and reusing flux requires special attention.

Some operations electrostatically apply flux before they thermally degrease the units. The thin layer of residual lubricants seems to improve powder adhesion [3].

Special flux qualities with adjusted particle distribution are commercially available, and contribute to improved electrostatic application.

5. Post Braze Flux Residue

It is generally accepted that the presence of flux residues on a heat exchanger enhances its corrosion resistance [4] [5] [6]. However, it has always been difficult to quantify the level of corrosion resistance enhancement. In corrosion testing of flat panels or coupons coated with flux residue, there is no doubt that there is a beneficial effect. With heat exchangers on the other hand, the general trend shows a longer corrosion life, but factors such as uniformity of flux residue coverage and variations in flux load sometimes confuse the corrosion test data.

There is no indication of interactions between flux residue and coolants, refrigerants[7], turbine oils, and polyalcylene glycol lubricants.

6. Filler Metal Alloys

Commercial filler metals are *aluminium silicon alloys* containing from 6.8% to 13% silicon.

Alloy AA	Si [8]	Start Melting	Fully Molten	Braze Range
4343	6.8-8.2%	577°C	613°C	593-610°C
4045	9-11%	577°C	591°C	588-604°C
4047	11-13%	577°C	582°C	582-600°C

Table 1: Filler Metal Alloy Characteristics

The solidus (or the point at which melting begins) is 577°C for all filler metal alloys. However, melting occurs in a range. The temperature above which the filler metal is completely molten is called the liquidus. In between the solidus and the liquidus, the filler is partly molten, existing as both solid and liquid. Before the filler metal becomes fully liquid and starts to flow, more than 60% of the clad material must melt. This requires a minimum (threshold) temperature for each filler metal alloy in the brazing process. (Note: AA 4047 cannot be used for furnace brazing. It is too liquid at brazing temperature and will flow down. It may even be drawn out of the joints by gravity forces. Applications for 4047 are induction and flame brazing.)

Recent developments for filler metal alloys are focused on the control of fluidity and flow pattern[9] [10]. By adding specific trace quantities of alloying elements (e.g., Li, Na), brazing characteristics improve. These effects appear to be related to reduced surface tension. Under certain conditions, brazing can be accomplished with reduced flux loads or with no flux at all[11]. It has not yet been determined if the alloying of additional elements to the filler metal is feasible on a high volume scale.

- *Core Alloy Dissolution/ Erosion:*

During the brazing cycle, silicon from the clad alloy diffuses into the core and causes dissolution of base metal. This condition results in a reduction in thickness of the core. The extent of erosion is increased by:

- higher silicon levels in the clad,
- longer than recommended braze cycles,
- excessive peak brazing temperatures,
- excessive thickness of the clad alloy, and
- a design which allows pooling of the braze metal.

In some instances, filler metal erosion can be so severe that the entire thickness of the base metal (tube or fin) is consumed, resulting in total failures.

The most common factors leading to excessive erosion are not design-related; rather, they are linked to the process. Brazing beyond the recommended maximum peak temperature and/or dwelling at brazing temperature are the leading causes of erosion.

7. Brazing Alloys and Brazing Sheet

The core alloys in common use for heat exchanger manufacturing include, but are not limited to: AA 3003, AA 1100, AA 1145, AA 1070, AA 3005, AA 3105, AA 6951, AA 1050, AA 1435, AA 3102, AA 6063.

Aluminium producers are now offering so-called "Long Life Alloys". These are modified AA 3XXX series alloys, offering superior strength and corrosion resistance. Most of these alloys have not been designated by the Aluminum Association and are known only by their manufacturers' designations. Some examples of long life alloys are: X800, X900, HE45, K315, K319, MD267 etc.

A general trend in the industry is to use thinner gauges for the design of heat exchanger components. Thinner gauges not only save on material (i.e. costs) but also on weight and space. Based on this development, there is strong demand for higher strength alloys with good formability.

- *Long Life Alloys:*

Historically, Al-Mn based alloys such as AA 3003 and AA 3005 have been used for the manufacturing of heat exchanger components. However, these alloys are susceptible to inter-granular corrosion that is accelerated by the diffusion of silicon along grain boundaries from the cladding alloy during brazing.

The automotive industry has stipulated that their heat exchangers last a minimum of 10 years. This encouraged the development of more corrosion resistant alloys.

Long life alloys utilise the feature of silicon diffusion from the cladding to form an intermediate layer between the cladding and the core alloy. This generates a dense band of precipitate that acts sacrificially to the core alloy, restricting corrosion to within this layer, and overcoming inter-granular attack.

Long life alloys are now widely used in many heat exchanger components.

- *Magnesium Containing Alloys:*

For added strength and machineability, certain alloys contain Mg. Most notably are the 6000 series alloys (up to 1% Mg). These are used for fittings and machined components as well as some long life alloys (up to 0.3% Mg).

During the braze cycle, Mg diffuses to the surface and reacts with the surface oxide to form MgO and $MgO{:}Al_2O_3$ (spinel). These oxides have reduced solubility in the molten flux. Furthermore, Mg and/or MgO can react with the flux forming compounds such as MgF_2, $KMgF_3$ and K_2MgF_4. All of these serve to poison the flux, significantly reducing its effectiveness (i.e. resulting in smaller joints or no joint formation at all).

The limit to the amount of Mg tolerated in furnace flux brazing is 0.5%; while around 1% Mg is tolerable for flame brazing. It should be noted that the brazing tolerance to Mg is the total sum of the Mg concentrations in both components to be joined:

$$[Mg]_{component\ 1} + [Mg]_{component\ 2} = [Mg]_{total}$$

Improved brazing results have been reported with magnesium-containing aluminium alloys (up to 0.6% Mg) when the flux formulation contains some cesium (i.e. approximately 2%)[12]. Cesium reacts as a buffer for magnesium by forming $CsMgF_3$ and $Cs_4Mg_3F_{10}$, which reduces the flux inhibition. These compounds melt at lower temperatures and interfere less with aluminium brazing[13].

- *Flux Pre-coated Brazing Sheet/ Components:*

The concept of a brazing sheet which is supplied with a flux coating is very plausible. Such material would significantly change the way heat exchangers are currently manufactured in that the flux application step would be eliminated.

Several patent applications have recently been filed on this premise [14] [15] [16]. Its greatest challenge is the best way to make the flux adhere to the metal surface. Throughout the forming process of the components, uniform coverage and strong adhesion are equally important. The latter is the origin of yet another concept. Flux coating technologies have been developed for (pre-)formed components, which are primarily adapted for heat exchangers with internal brazing required, i.e. plate evaporators[17]. Flux application with a binder system allows coating of specific surface areas with a precise flux amount. It also reduces flux fall-off during assembly.

Binders used for pre-fluxing must evaporate during the process without interfering with the brazing performance or leaving any contamination on the surfaces. Exhaust treatment may need to be adjusted to the presence of binder fumes.

- *Clad-less Brazing:*

There are several suggestions for brazing technologies where the filler metal is generated during the brazing cycle from a coating layer on a plain aluminium sheet or on extrusion material.

One method involves a mixture of flux with silicon powder, the NOCOLOK® Sil Flux process[18]. At brazing temperature, the silicon powder diffuses into the aluminium substrate and generates Al-Si filler metal for joint formation. Sil flux can be applied with a binder to specific component surfaces, e.g. extruded tubes. In this case, the filler metal would be supplied from the tube and a clad fin sheet is not necessary.

In Composite Deposition technology (CD process)[19], the filler metal for joint formation is derived from a composite powder, a compound consisting of potassium fluoroaluminate flux and Al-Si alloy. The CD powder is "deposited" selectively and accurately on heat exchanger components prior to assembly and brazing.

The common challenge for all clad-less approaches is the development of a reliable coating procedure.

8. Furnace Conditions

Specifications for acceptable CAB furnaces (with the use of 5 g/m^2 uniform flux load) are:

- *Furnace Atmosphere:*
  - *Oxygen level* below 100 ppm
  - *Dew point* below –40°C
- *Brazing Temperature* and *Time*:
  - Ideally a uniform 600°C ± 5°C (heat exchanger surface temperature)
  - Ideally 3 minutes ± 0.5 min from 580°C heat-up to 605°C on cool-down

Currently, many production sites work with flux loads of 3 g/m^2. As flux coating goes down, furnace atmospheric conditions become more critical. Most CAB furnace manufacturers produce furnaces which routinely operate in the 20 – 50 ppm oxygen and dew point levels of –45 to –50°C (i.e., 92 – 67 ppm H_2O). A low dew point will keep the formation of hydrogen fluoride according to equation (1) to a minimum[20]:

$$3\ KAlF_4 + 3\ H_2O \rightarrow K_3AlF_6 + Al_2O_3 + 6\ HF \qquad (1)$$

A suitable treatment for the furnace exhaust (i.e. dry scrubber) is required.

- *Furnace Curtains*:

Furnace curtains are installed in the muffle or at the ends to maintain a positive nitrogen pressure in the furnace. This is required to prevent the ingress of outside atmosphere, i.e. high moisture and oxygen from back-streaming, into the furnace. Higher dew point and oxygen in the furnace require higher flux load on the parts to handle the degraded atmosphere. Curtains must be kept in the recommended condition; they should not be "sculptured" to accommodate product height.

- *Muffle Mesh Belt:*

The furnace mesh belt has a considerable surface area. It exits the muffle and returns to the entrance outside the furnace atmosphere. During this time, it substantially cools and picks up moisture, which is driven off inside the muffle, thus contributing to degrading the furnace atmosphere. A higher dew point not only creates a potential necessity for higher flux load; it can also be a factor in increased muffle corrosion at the entrance of the furnace.

- *Muffle Integrity:*

Holes or leaks in the muffle allow the potential of outside atmosphere being drawn by the Venturi effect into the muffle. If air is drawn in from outside, moisture and oxygen levels will increase.

- *Flux Build-up:*

Molten flux has a very low surface tension and can easily drip down from the aluminium surfaces of heat exchangers and fixtures, especially when the flux load is high. These flux droplets solidify under the conveyor belt in the furnace zone where the temperature is below the flux freezing point (usually between the brazing and the cooling zone). A second source for flux powder residue is re-condensed $KAlF_4$ vapour. The quantity of $KAlF_4$ vapour generated during the brazing cycle depends on time at temperature.

Under normal production conditions, there will always be some flux build-up on the conveyor belt and, eventually, some build-up on the furnace bottom. If this build-up exceeds a certain height, the conveyor belt can be deflected. Therefore, the flux build-up on the muffle bottom must be removed during regular maintenance cleaning operations.

Summary

Controlled atmosphere brazing using non-corrosive flux is the dominant process for making aluminium heat exchangers for the automotive industry.

There are several factors determining the success of aluminium brazing:

- Product Fit-up and Assembly
- Component Cleanliness
- Flux Application
- Furnace Atmosphere
- Brazing Temperature Uniformity
- Brazing Time at Temperature

Recent developments in brazing technology focus on improvements in aluminium alloy composition (i.e. higher strength, good formability and higher corrosion resistance).

Research and development activities throughout the industry have resulted in concepts for:

- new flux qualities more suitable in dry/ electrostatic flux application and for furnace brazing of Mg-containing alloys (up to 0.6%)
- clad-less brazing technologies
- pre-fluxed brazing sheet/ components
- reduction of consumables (e.g. flux, water)

Future developments for flux brazing technology will include manufacturing more heat exchanger types and extended product ranges, some of which are currently still produced with other processes and materials.

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