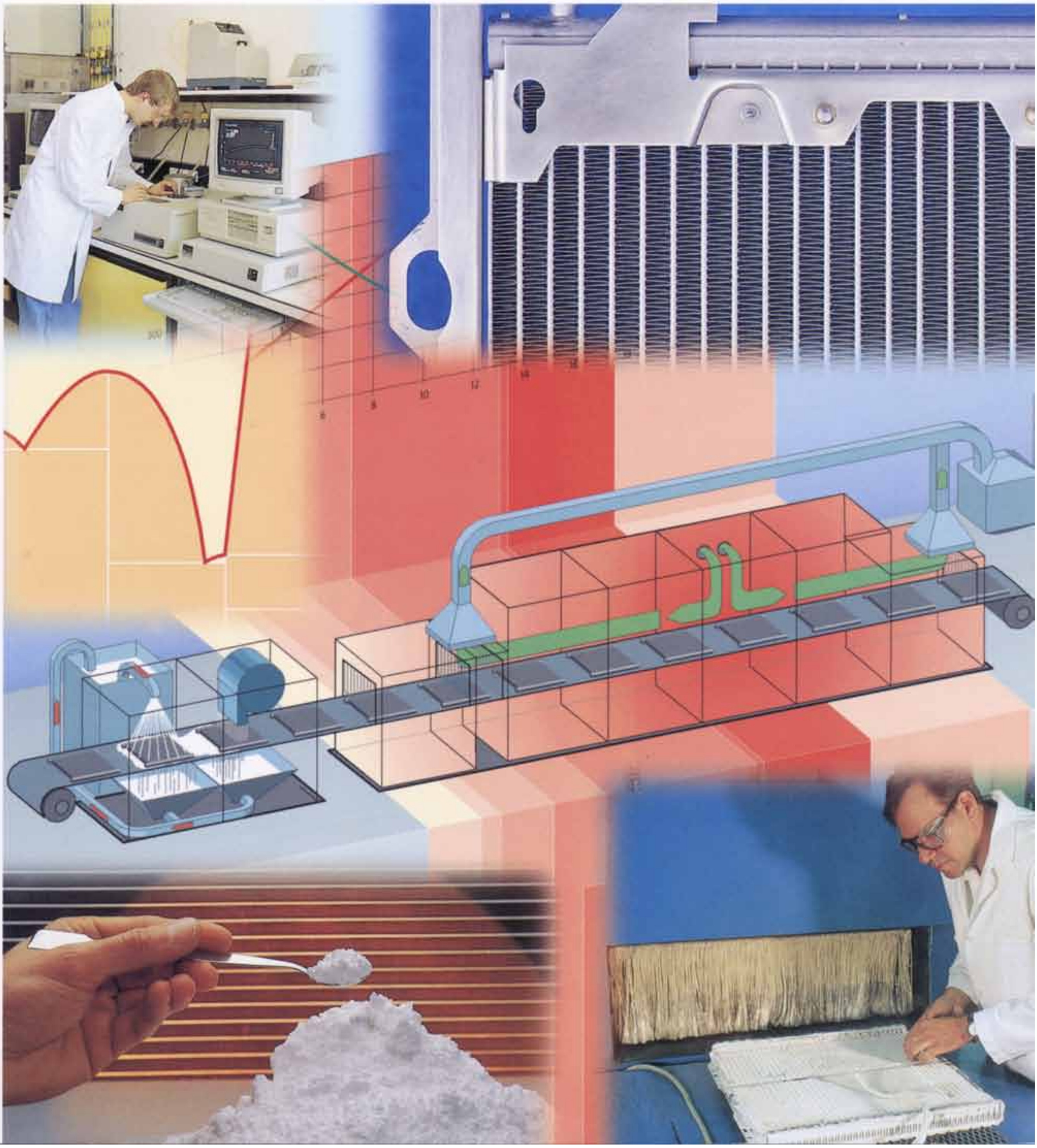
苏威
氟及衍生物有限公司

NOCOLOK® 钎剂钎焊工艺
The NOCOLOK® Flux Brazing Process



引　言

在汽车热交换器，如水箱、冷凝器、蒸发器和加热器散热部件的生产中，铝钎焊现已是被乐于采用的工艺。由于其良好的防腐性、可塑性和热导性，使铝成为制造上述热交换器的理想材料。

铝钎焊是指用钎料连结部件，这种铝钎料(Al-Si)的熔点低于部件材料的熔点。钎料通常置于需要连接部件的焊接面附近或里面。安装后部件加热至钎焊合金熔融而部件不熔的温度。冷却后，钎料就会与部件接面间形成金属结合。

在汽车热交换器生产应用中，这种填充金属是以薄片或复合合金的形式提供的。在钎焊时，当低熔点的包层 Al-Si 合金熔融流动时，钎料芯就作为结构材料，使冷却后与部件形成金属结合。

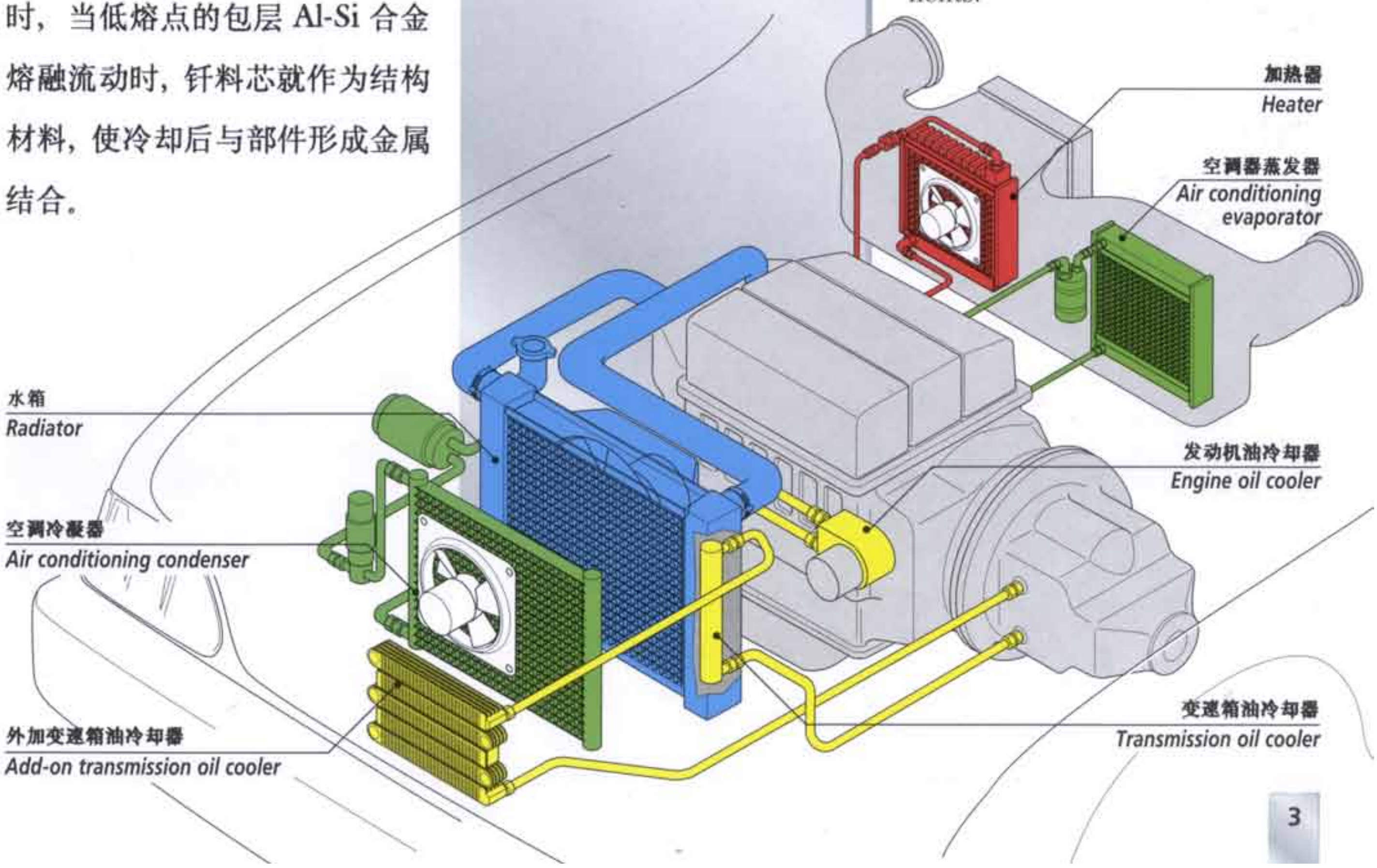
Introduction

Aluminum brazing is now the preferred process for the production of automotive heat exchangers such as radiators, condensers, evaporators and heater cores. Good corrosion resistance, formability and high thermal conductivity make aluminum an ideal material for the construction of these heat exchangers.

Aluminum brazing involves joining of components with a brazing alloy, that is an aluminum alloy (Al-Si) whose melting point is appreciably lower than that of the components. This brazing alloy is usually placed adjacent to or in between the components to be joined and the assembly is then heated to a temperature where the brazing alloy melts but not the components. Upon cooling, the brazing alloy forms a metallurgical bond between the joining surfaces of the components.

In automotive heat exchanger applications, this filler metal is supplied via a thin sheet or clad on a core alloy. The core provides structural integrity while the low melting point Al-Si cladding alloy melts and flows during the brazing process, to provide upon cooling a metallic bond between the components.

铝热交换器在汽车上
有多方面的应用
There are many automotive applications for aluminum heat-exchangers



在铝钎焊中通常是需要使用钎剂除去铝表面形成的氧化膜。钎剂必须在钎焊时除去氧化膜造成的障碍以使填充金属自由流动并防止表面重新氧化。多年来，有许多钎剂和钎焊工艺曾经应用于铝钎焊中，但有一种当今为全球所推崇的工艺就是 NOCOLOK® 钎剂钎焊工艺。

钎焊工艺的历史

含氯钎剂钎焊

在最早期钎焊铝热交换器工艺中是采用含氯钎剂钎焊的。这种钎剂是添加有少量氟化物的氯盐混合物。钎焊时部件浸入熔融的盐浴中，此时盐作为钎剂，然后把部件均匀加热至钎焊温度。采用这种技术钎焊后热交换器上留下了易于吸潮的腐蚀性残余物。

钎焊部件需要进行复杂的后处理，包括水洗、浸洗和受浸过表面的钝化以防止进一步的腐蚀。

以往在炉钎焊技术中同样引用含氯钎剂，用量范围为 150 ~ 300 g / m²。为减少后处理的程度，必需严格控制炉内保护气氛（例如，露点 ≤ - 40 ℃）以减少钎剂的用量。

It is usually necessary to employ a flux in brazing aluminum to remove the native oxide film present on all aluminum surfaces. The flux must be capable of displacing the oxide film barrier during brazing to allow the filler metal to flow freely and must prevent the surfaces from reoxidizing. Many fluxes and brazing techniques have evolved over the years, but one process that is now recognized worldwide is the NOCOLOK® flux brazing process.

Chronology of Brazing Processes

Chloride flux brazing

The earliest brazed aluminum heat exchangers employed a chloride flux, a mixture of chloride salts with minor additives of fluorides. The units were immersed in a molten salt bath where the salt acted as a flux and a means of raising the unit to brazing temperature. However, this technique left a hygroscopic corrosive residue on the heat exchanger.

The brazed unit required extensive post braze treatment in the form of water washing, pickling and passivation of the pickled surface to prevent further corrosive action.

Furnace brazing techniques were also employed using chloride flux loadings in the range of 150 g/m² – 300 g/m². To reduce the extent of post braze treatments, stringent furnace atmosphere requirements were imposed (eg. dew point ≤ –40 °C) to reduce the

1. 用动态扫描测热法进行精确的熔点测定
1. *Precise Melting Point Determination using Differential Scanning Calorimetry*

2. NOCOLOK®-钎剂粉末
2. *NOCOLOK®-Flux Powder*

虽然如此仍然需要进行后处理以除去腐蚀性残余物。后处理造成的成本增加和环境污染成为钎焊铝制品广泛应用的一大障碍。

真空钎焊

工业界的注意力随即转向无钎剂钎焊工艺，即真空钎焊。这种技术免除钎焊后处理的需要，但在炉内保护气氛（露点≤－60 ℃）、表面清洁和设备上就要求更为严格。在这种工艺中保持气体纯度既困难亦昂贵。因此，铝钎焊的注意力又重新转回有钎剂的钎焊工艺中。

NOCOLOK® 钎剂钎焊

目的在于开发一种崭新钎剂，它既拥有钎剂的优点又克服钎焊后需要处理以及具有腐蚀性的缺点。这种钎焊方法是使用一种不吸潮、无腐蚀性的氟铝酸钾钎剂。它可成功地清除铝表面上的氧化膜；在熔融和固态均不与铝发生反应；其残余物不溶于水。这种钎剂及其钎焊工艺用就叫 NOCOLOK® 钎剂钎焊工艺。

flux loadings. Post braze treatments however were still required to remove the corrosive residue. The cost and pollution of post braze treatments presented a barrier to a wider application of brazed aluminum products.

Vacuum brazing

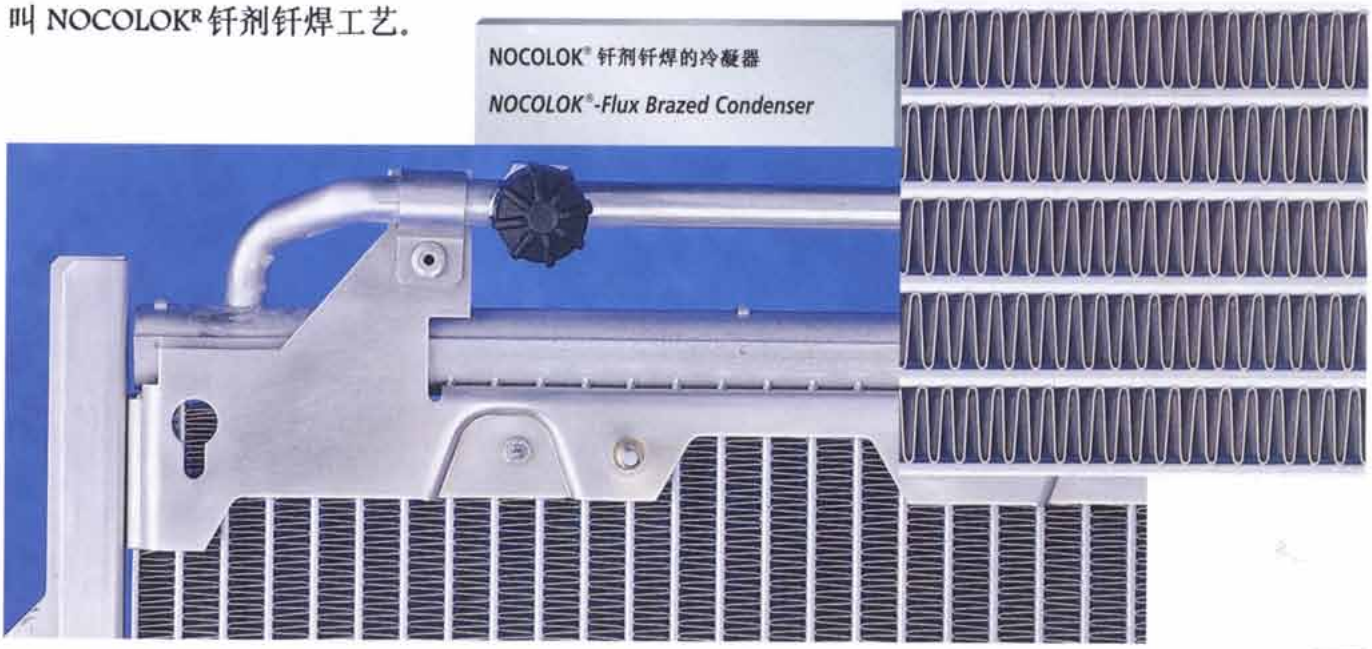
The industry's attention was then directed to fluxless brazing processes i.e. vacuum brazing. This technique indeed eliminated the need for post braze treatments but presented much tighter tolerances with respect to furnace atmosphere (≤-60°C dew point), surface cleanliness and fit-up. In this process, the maintenance of atmosphere purity was difficult and expensive and attention was soon redirected to processes employing a flux.

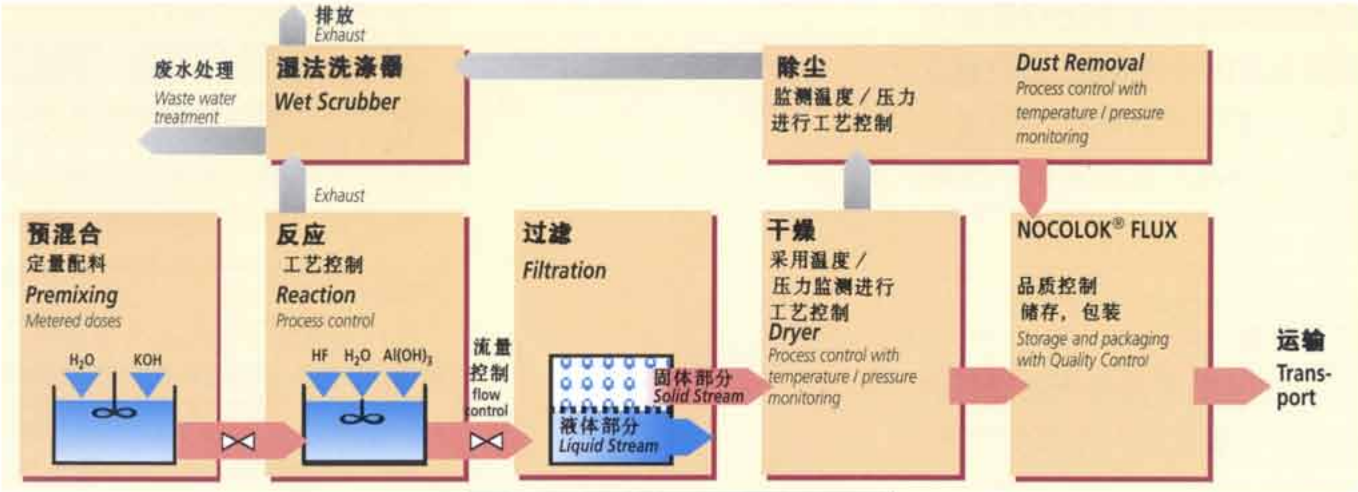
NOCOLOK® flux brazing

The objective was to develop a process which would offer the benefits of a flux while avoiding the disadvantages of post braze treatments and corrosion susceptibility. A brazing method was thus developed using a non-hygroscopic, non-corrosive potassium fluoroaluminate flux which successfully removes the oxide film on aluminum, does not react with aluminum in the molten or solid state and whose residue is insoluble in water. This flux and the process for using it is called the NOCOLOK® flux brazing process.

NOCOLOK® 钎剂钎焊的冷凝器

NOCOLOK®-Flux Brazed Condenser





NOCOLOK®-Flux 生产工艺流程图

NOCOLOK®-Flux Process Flow Diagram

NOCOLOK®钎剂

生产

如流程图所示，NOCOLOK® 钎剂是在液相中以 $Al(OH)_3$，HF 和 KOH 为原料生产的。

通过采用精湛的工艺和一系列的严格的品质控制程序（Alcan 标准）生产出一种品质最高和稳定性最好的钎剂。

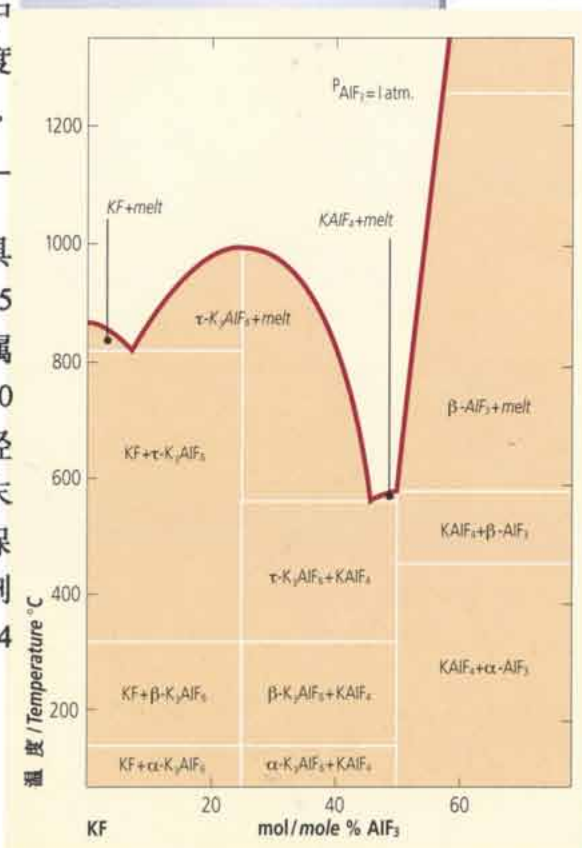
产品是一种精细的白色粉末。主要是氟铝酸钾盐的混合物，其总的分子式为 $K_{1\text{-}3}AlF_{4\text{-}6}$，其中可能存在一个结合水。在钎焊温度时，其组成相应于 $KF{:}AlF_3$ 相图。

特点

最终的低共熔点钎剂组分具有清晰确定的熔点范围，即 565 ℃至 572 ℃，低于 Al-Si 钎焊金属的熔点 577 ℃。粉粒大小在 2 ~ 50 μm 范围内。微粒中大的碎块经准确剔除。这一特性有利于在粉末处理过程中减少灰尘含量并且保持膏剂特性。NOCOLOK 钎剂不吸潮，只微溶于水（0.2 % 至 0.4 %）。

$KF\text{-}AlF_3$ 相图

$KF\text{-}AlF_3$ Phase Diagram



NOCOLOK® Flux

Production

NOCOLOK® flux is produced in the liquid phase using $Al(OH)_3$, HF and KOH as raw materials as indicated in the process flow diagram.

Stringent process tolerances and a variety of quality control procedures (Alcan Standards) produces a flux of the highest quality and consistency.

The result is a fine white powder consisting primarily of a mixture of the potassium fluoroaluminate salts of the general formula $K_{1\text{-}3}Al F_{4\text{-}6}$ where a water of hydration may be present. At brazing temperature, this corresponds to the $KF{:}AlF_3$ phase diagram.

Characteristics

The resulting eutetic flux composition has a clearly defined melting point range of 565 °C to 572 °C, below the melting temperature of 577 °C of the Al-Si brazing alloy. The particle size lies in the range of 2 µm to 50 µm. A larger fraction of fine particles is deliberately avoided. This feature reduces dust levels during powder handling and still maintains good slurry characteristics.

NOCOLOK® flux is non-hygroscopic and only very slightly soluble in water (0.2 % to 0.4 %).

因而该钎剂的储存期和适用期是无限的。钎剂在室温或钎焊温度下不与铝发生反应而仅在熔融（至少部分熔融）下才具有反应活性。钎剂在钎焊后留下极难溶于水的残余物，该残余物无需清除。

钎剂的作用

钎剂一旦熔融就会溶解铝表面的顽固氧化物，并防止重新氧化。钎剂湿润部件的焊接面，使填充金属利用毛细管作用自由地流入接合面。冷却后，钎剂在部件表面形成 一层附着力很强的粘膜。

钎焊工艺

钎剂应用

加钎剂前，安装好的热交换器例行通过清洗步骤去除残余的润滑油和成型油。

然后，在单独部件或装配后的单元上流洒，喷洒或浸渍调成含水膏状的NOCOLOK®钎剂。通常在膏剂中加入表面活化剂以帮助钎剂均匀地湿润和粘附。需不断搅拌以防止沉淀。膏剂的浓度通常是根据钎剂载量而定，在 5 % 至 25 % 范围内。

NOCOLOK® Flux

Right to the point!

The shelf and pot life of the flux is therefore indefinite. The flux does not react with aluminum at room temperature or at brazing temperature and only becomes reactive when molten (at least partially molten). The flux leaves a mainly water insoluble residue which need not be removed.

Role of the flux

Once molten, the flux works by dissolving the tenacious oxide present on aluminum, and prevents further oxidation. The flux wets the faying surface of the components to be joined allowing the filler metal to be drawn freely into the joint by capillary action. Upon cooling, the flux remains on the surface as a thin, strongly adherent film.

Brazing Process

Flux application

Prior to fluxing, the assembled heat exchanger typically goes through a cleaning step to remove residual lubricants and forming oils.

NOCOLOK® flux is then applied to individual parts or assembled units as an aqueous slurry by flooding, spraying or dipping. A surfactant is commonly added to the slurry to aid in wetting and uniformity of flux deposition. Agitation is required to prevent the flux from settling. The slurry concentration, typically in the range of 5 % to 25 %, regulates flux loading.

在间歇炉中采用NOCOLOK®钎剂进行钎焊

NOCOLOK® Brazing in a batch furnace

通常也采用“吹落”步骤以除去在部件下侧积累过多的钎剂。目的是获得均匀的钎剂涂层而在任何位置上都避免沉积太多的钎剂。

干燥

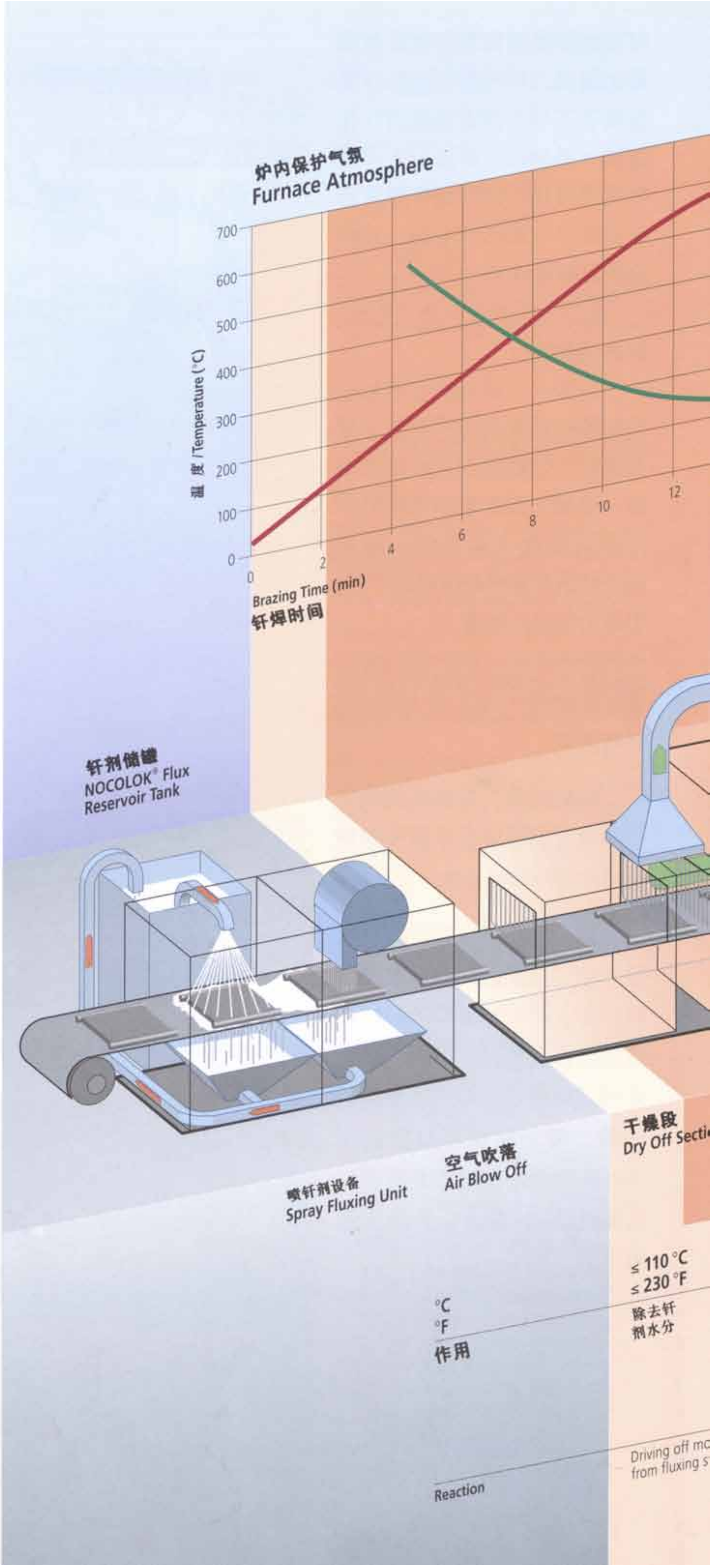
喷洒钎剂后，部件随即进行干燥，温度通常控制在 200 ℃左右。应小心防止热交换器过热，因为过热（即 250 ℃）可能导致铝表面形成高温氧化物．这些氧化物很难被 NOCOLOK®钎剂去除。这步骤的目的仅是为了在进入钎焊炉之前彻底去除钎剂所含的水分。由于钎焊只需要少量的钎剂（~ 5g / m^2），因而形成钎剂粘附已是非常充分。

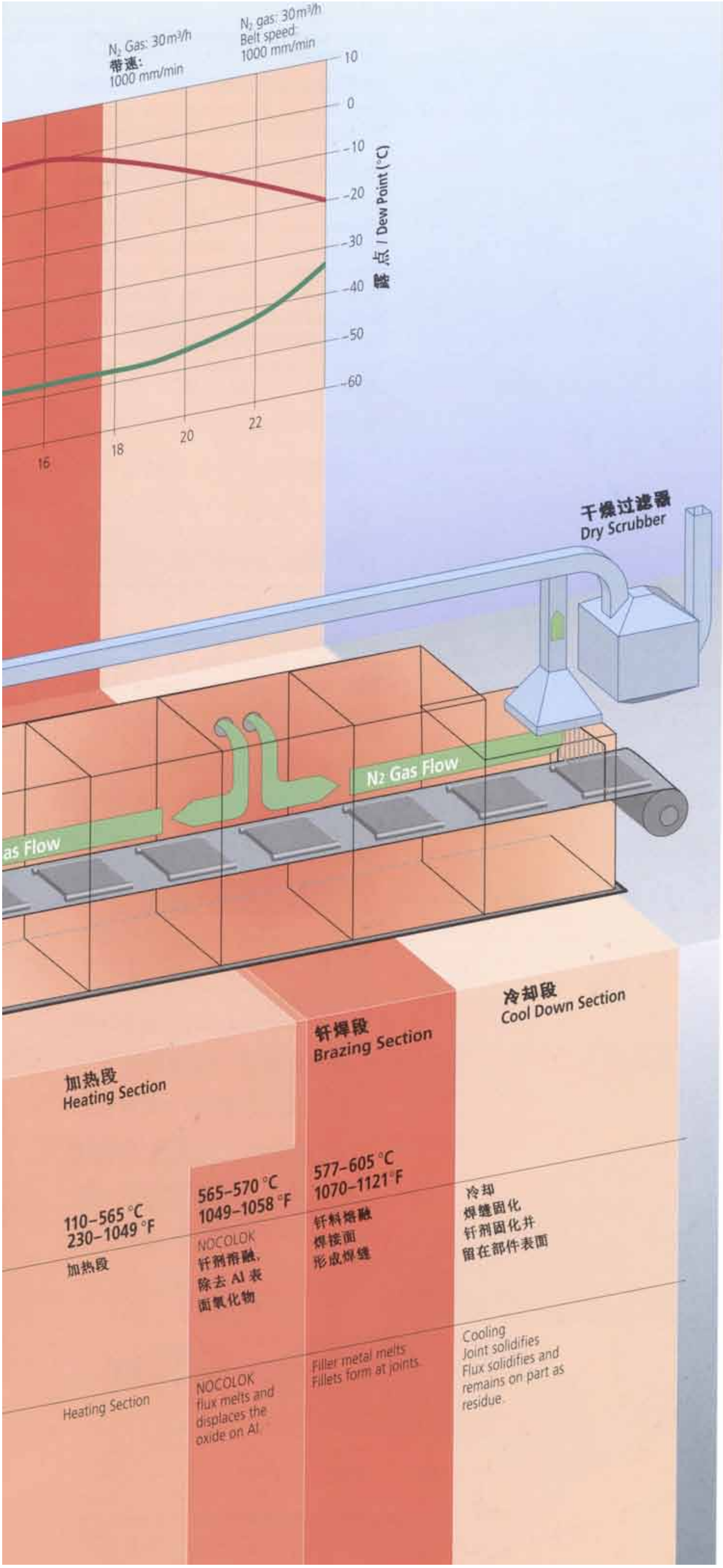
钎焊

NOCOLOK®钎剂钎焊是在惰性气体如氮气保护气氛下进行。既可在间歇炉内钎焊，亦可在更为常用的如图所示的连续隧道炉内钎焊。

氮气在炉中最为关键的钎焊段流入而流向炉的入口和出口处。以此防止炉外杂质气体的侵入。当部件进入关键的钎焊段时，炉内保护气氛已形成，例如露点 ≤ - 40 ℃而 O_2 的浓度 〈 100ppm ．这些是获得最佳钎焊效果所必需的条件。

在 530 ~ 560 ℃的温度范围内，微量的 $KALF_4$ 蒸发与所存在的湿气反应生成微量的 HF ．因此必须严格控制露点，不仅是提供钎焊气氛，而且是尽量减少 HF 的生成。





An air "blow-off" step is also typical to remove excess slurry accumulated at the downside of the fluxed part. The goal is to achieve a uniform coating of flux without significant accumulation in any one place.

Drying

After fluxing, the part is then dried, usually at about 200 °C. Care is taken not to overheat the heat exchanger as excess heat (i.e. >250 °C) may cause high temperature oxides to form on aluminum surfaces. These oxides are more difficult to remove with NOCOLOK® flux. The aim here is simply to remove water from the fluxing stage so that the component is completely free of adsorbed water prior to entering the brazing furnace. Since only a light flux loading is required (~5 g/m^2) the resultant flux adhesion is quite sufficient.

Brazing

NOCOLOK® flux brazing is carried out in an inert atmosphere such as nitrogen in either batch type furnaces or more commonly in continuous tunnel furnaces such as the one shown in the schematic.

Nitrogen is introduced in the critical brazing section of the furnace and flows towards the entrance and exit. This prevents the ingress of contaminants from outside the furnace. As the component enters the critical brazing zone, furnace atmosphere becomes established, i.e. the dew point is ≤−40 °C and the O_2 concentration is <100 ppm. These conditions are necessary for optimum brazing results.

In the temperature range of 530 to 560 °C, traces of $KAlF_4$ evaporate and in presence of moisture can react to form traces of HF. Therefore, the dewpoint is tightly controlled, not only to provide a good atmosphere for brazing, but to minimize HF generation.

钎剂残余物

冷却后，钎剂残余物留于部件表面，形成是厚度非常薄，为1 ~ 2 μ m的粘膜。钎剂残留层不吸湿无腐蚀性，不溶于水性溶剂。如需喷漆或转化为喷粉，则不需要进一步的表面处理。残余物是加强防腐的保护层。残余物薄层在热交换过程中不会出现碎裂。

Flux residue

After cooling, the flux residue remains on the surface as a very thin adherent film with a thickness in the range of 1 – 2 µm. The layer of flux residue is non-hygroscopic, non-corrosive and insoluble in aqueous media. No further surface treatment is required if painting or conversion coatings are desired. The flux residue is known to provide enhanced corrosion resistance. The residue is not subject to spalling during thermal cycling.

金属学资料

母材

铝合金是按其合金元素进行分类。下表列出铝协会的牌号：

Metallurgy

Core alloys

Aluminum alloys are classified according to their alloying elements. The Aluminum Association designations are listed in the table below:

精制铝合金牌号系列

合金系列	名称或主要合金元素
1xxx	含铝最小 99.00 %
2xxx	铜
3xxx	锰
4xxx	硅
5xxx	镁
6xxx	镁和硅
7xxx	锌
8xxx	其它元素
9xxx	不使用系列

Designation System for wrought aluminum alloys

Alloy-series	Description or major alloying element
1xxx	99.00 % minimum Aluminum
2xxx	Copper
3xxx	Manganese
4xxx	Silicon
5xxx	Magnesium
6xxx	Magnesium and Silicon
7xxx	Zinc
8xxx	Other Element
9xxx	Unused Series

每种 AA 合金的化学成分由铝协会注册，本手册列出部分实例如下：

The chemical composition of each AA alloy is registered by the Aluminum Association and a few examples are listed:

铝合金重量百分比成份极限举例*
Example of aluminum alloy composition limits in weight percent*

AA-合金编号 Alloy-Number	Si	Fe	Cu	Mn	Mg	Zn	Cr	其它/others 每样/each	其它/others 总量/total
1100	0,95	(Si + Fe)	0,05 – 0,20	0,05	–	0,10	–	0,05	0,15
1435	0,15	0,30 – 0,50	0,02	0,05	0,05	0,10	–	0,03	0,03
3003	0,60	0,70	0,05 – 0,20	1,00 – 1,50	–	0,10	–	0,05	0,15
3005	0,60	0,70	0,30	1,00 – 1,50	0,20 – 0,60	0,25	0,10	0,05	0,15
6063	0,20 – 0,60	0,35	0,10	0,10	0,45 – 0,90	0,10	0,10	0,05	0,15

*除给出范围外均为最大值/ Maximum, unless shown as a range

这些合金中的很多牌号可用于NOCOLOK®钎剂钎焊。如牌号为AA3003和AA3005的合金常用作NOCOLOK®钎剂钎焊热交换器的母材.

镁

为提高强度和机械性能，某些合金加有镁作为合金元素。然而用NOCOLOK®钎剂钎焊时镁的含量有一定的限制，含Mg大于0.5 %的铝合金的炉内钎焊性会降低。NOCOLOK®钎剂对含镁合金表面形成的镁氧化物的溶解有一定的限度。

再者，在钎焊时Mg会扩散到合金表面与钎剂进行反应，改变其组成，因而改变其性能。提高加热速度和加大钎剂的量，如在火焰钎焊应用中可以容许稍大的含镁量。

包层合金

如前所述，片状钎料是由母材在其一至两边包复低熔点的铝硅（Al-Si）合金组成。该包层厚度通常为钎料片厚度的5 %至10 %。

Many of these core alloys are compatible with NOCOLOK® flux brazing. Alloys such as AA 3003 and AA 3005 are commonly used as core materials for NOCOLOK® flux brazing heat exchangers.

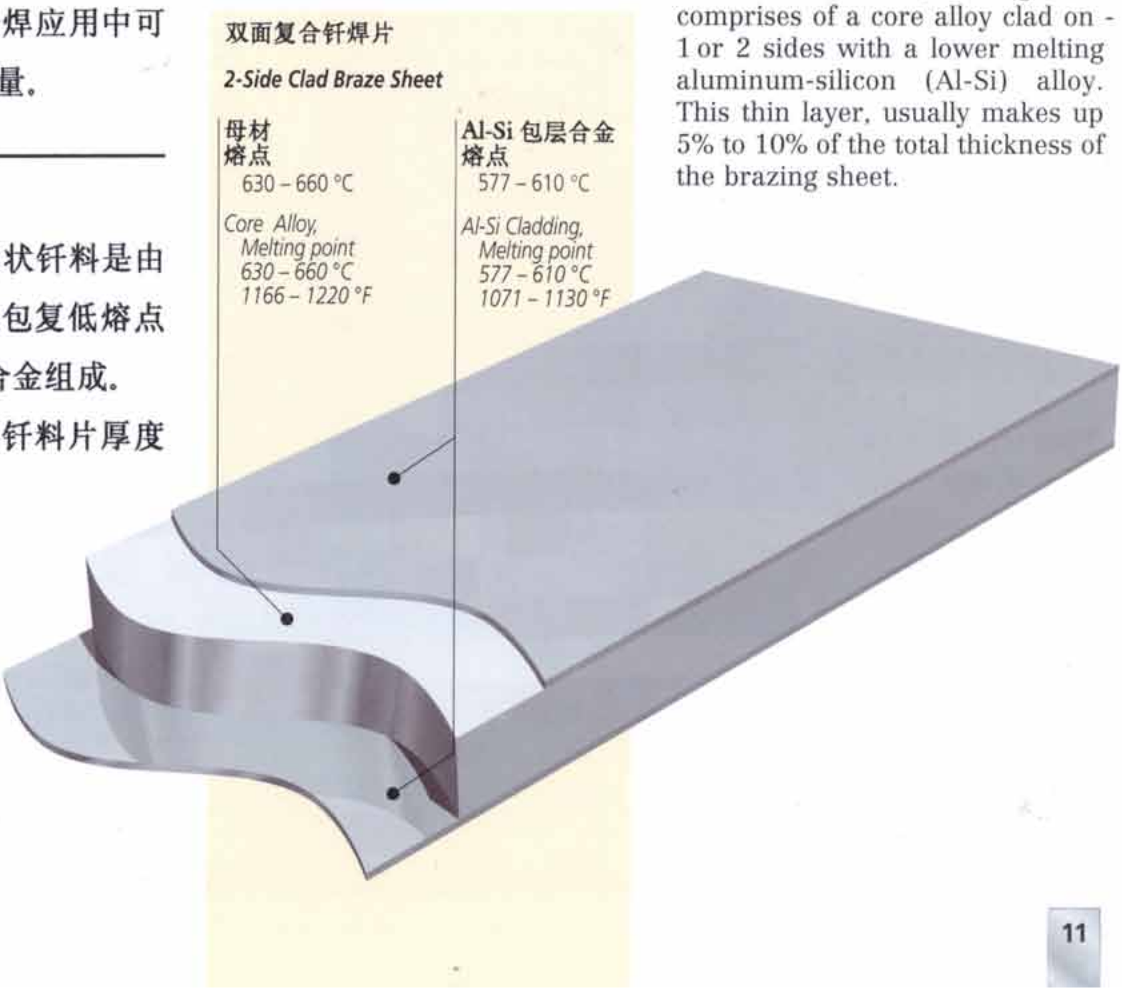
Magnesium

For added strength and machinability, certain alloys contain Mg as an alloying element. However, there is a limit to the amount of Mg that can be tolerated for NOCOLOK® flux brazing. There is reduced furnace brazeability of aluminum alloys containing greater than 0.5 % Mg. NOCOLOK® flux has a limited solubility for the magnesium oxides that form on the surface of Mg bearing alloys.

Furthermore, Mg can diffuse to the surface of the alloy during brazing and react with the flux, thereby changing its composition, and therefore its effectiveness. Rapid heat-up rates and heavier flux loadings such as used in torch brazing applications will tolerate slightly greater Mg concentrations.

Cladding alloys

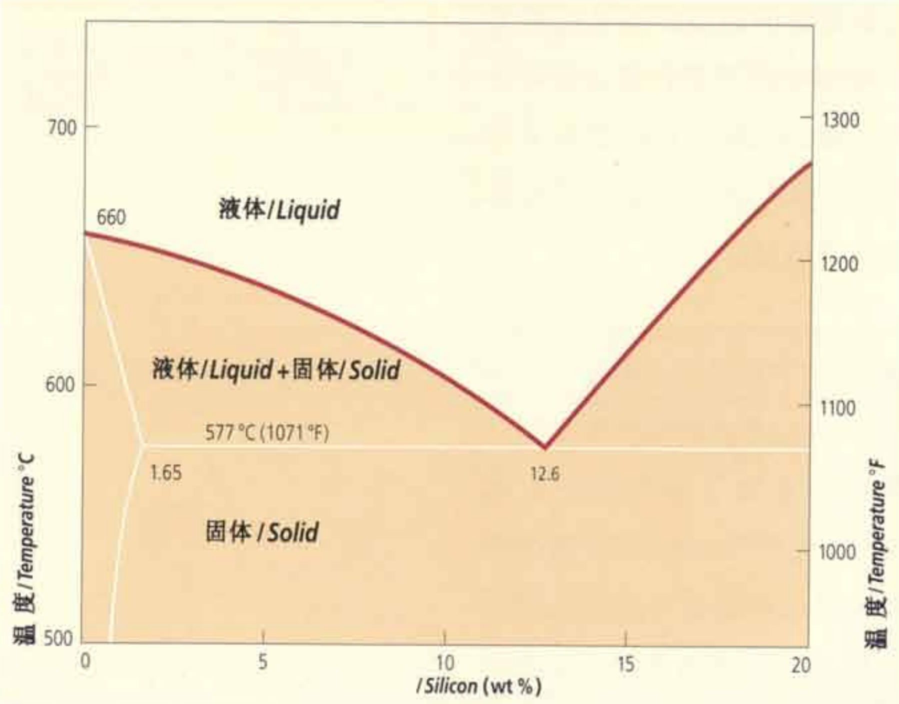
As described earlier, brazing sheet comprises of a core alloy clad on 1 or 2 sides with a lower melting aluminum-silicon (Al-Si) alloy. This thin layer, usually makes up 5% to 10% of the total thickness of the brazing sheet.



相图

Si 的加入降低了铝的熔点. 这种现象可用 Al-Si 相图中加以说明。

低共熔点化合物组成中, 如制出最低熔点合金的硅含量为 12.6 %. 该组分的熔点为 577 ℃. 在 Si 含量低的固相线或者熔融开始的点同样是 577 ℃. 而熔融产生一个大的范围而在此温度上填充物完全熔融称为液相线. 而固相线与液相线间的差成为制造不同填充金属合金的基础. 商品化的填充金属合金含有 6.8 % 至 13 % 的 Si.



铝硅相图的铝界限图

Aluminum End of Al-Si Phase Diagram

Phase diagramm

The addition of Si lowers the melting point of aluminum. This phenomena is illustrated with the Al-Si Phase diagram.

The eutectic composition, i.e. the amount of Si required to produce the lowest melting point is 12.6 %. The melting point at this composition is 577 °C. At lower Si levels the solidus or the point at which melting begins is also 577 °C. However, melting occurs in a range and the temperature above which the filler is completely molten is called the liquidus. In between the solidus and liquidus, the filler is partially molten, existing as both solid and liquid. The difference between the solidus and liquidus forms the basis for various filler metal alloys. Commercial filler metals may contain from 6.8 % to 13 % Si.

钎料

AA4343 是一种常用的填充钎焊合金. 但如需要填充大的焊缝或钎焊的环境要求较低的钎焊温度， AA4045 是一个很好的选择. 当然选择是基于特定的应用而言的.

Brazing alloys

AA4343 is a common filler metal brazing alloy. However, if larger fillets are desirable, or if in a situation where brazing is likely to occur at lower temperatures, AA 4045 is the preferred choice. The choice, of course, is dependent on the specific application.

铝钎焊包层合金

Aluminum Brazing Clad Alloys

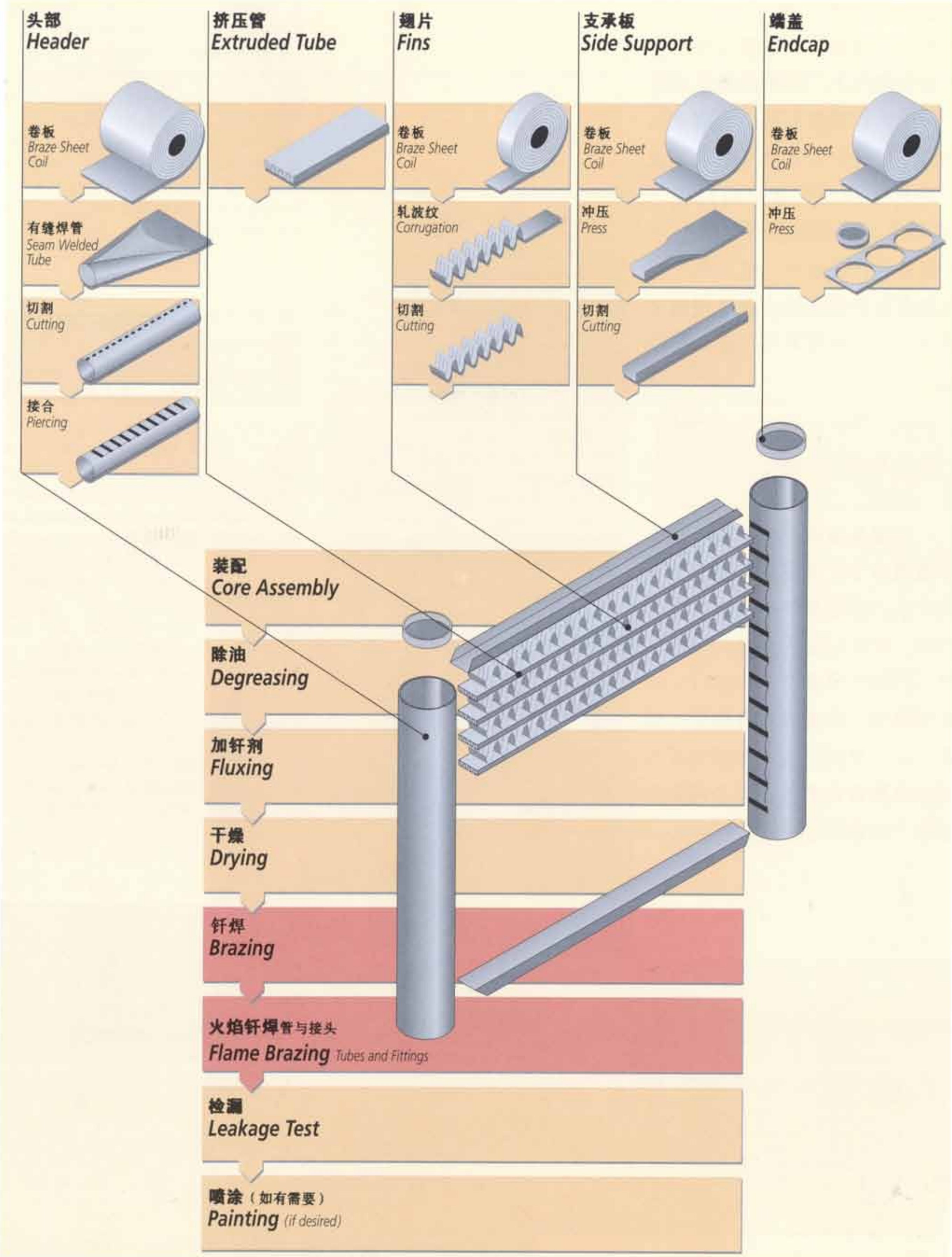
合金 *Alloy*		AA-4343	AA-4045	AA-4047
% Si 合金 *% Si Nominal*		7.5	10.0	12.0
固相熔点 *Start Melting*	°C °F	577 1071	577 1071	577 1071
液相熔点 *Fully Molten*	°C °F	613 1135	591 1095	582 1080
推荐钎焊温度 *Recommended Braze Range*	°C °F	593 – 621 1100 – 1150	588 – 604 1090 – 1120	582 – 604 1080 – 1120

生产

冷凝器典型生产工艺流程中的主要步骤展示如下:

Production

The main elements of a typical production process stream are depicted here for a condenser.



摘　要

NOCOLOK® 钎剂钎焊非常适合于大规模生产铝热交换器的焊接。钎剂及其残余物均为无腐蚀性和不吸潮。NOCOLOK® 钎剂便于采用流洒、喷洒及浸渍方法加到部件上，钎剂的载量亦易于控制。如欲提高部件的防腐蚀性能，钎焊后部件非常适合于直接进行喷涂或其它表面处理。NOCOLOK® 钎剂钎焊工艺适应于复杂的产品设计、连续生产以及拥有各种规格的合金选用使之成为汽车工业和其它工业的最佳选择。

氟化学的权威

苏威氟及衍生物以其在氟化学领域的专长而享誉世界。公司拥有这一领域最杰出的化学家和技师。公司以强大的应用技术优势，与用户紧密合作，随时应对任何挑战，解决用户所遇到的难题。公司更拥有极其丰富的氟及衍生物和特殊产品，以及遍布全球的市场和销售网络。

苏威氟化物一始终如一的品质，按照 DIN ISO 9001 的要求严格进行整个工艺控制和产品监测。苏威氟及衍生物有限公司为 Alcan International Ltd. 开发了 NOCOLOK 钎剂，该产品是在我们公司属下的德国巴特温普芬工厂生产。

Solvay fluorides – consistent quality according to DIN ISO 9001 through process control and product monitoring. Solvay Fluor und Derivate GmbH developed NOCOLOK® Flux for Alcan International Ltd. It is produced in our plant Bad Wimpfen/ Germany.

REG. NR. 2535-01

Summary

NOCOLOK® flux brazing is ideally suited for the large scale joining of Al heat-exchangers. The flux and its residue are non-corrosive and non-hygroscopic. NOCOLOK® flux is easily applied by flooding, spraying or dipping and the flux loading easily controlled. Brazed parts are ideally suited for painting or other surface treatments if enhanced corrosion resistance is desired. Complex product designs, continuous production, and a variety of alloy selections make the NOCOLOK® flux brazing process the preferred choice for automotive and other industrial applications.

Professional Fluorochemistry

A major name in fluorochemistry: Solvay Fluor und Derivate – the specialists. A name which stands for a team of outstanding chemists and technicians, all committed to the best in fluorochemistry. A name synonymous with powerful application technologies, prepared to take on any challenge, seeking to solve the problem at hand – where possible in close consultation with the client. A name encompassing the worldwide marketing and sale of an impressively broad range of

苏威
氟及衍生物有限公司

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NOCOLOK® Flux
Right to the point!

31/335/04 96/007/5000