THE LINDE GROUP

Furnace atmospheres no. 4. Brazing of metals.



02

Preface.

This expert edition is part of a series on process application technology and know-how available from Linde Gas. It describes findings in development and research as well as extensive process knowledge gained through numerous customer installations around the world. The focus is on the use and control of furnace atmospheres; however a brief introduction is also provided for each process.

- 1. Gas carburising and carbonitriding
- 2. Neutral hardening and annealing
- 3. Gas nitriding and nitrocarburising
- 4. Brazing of metals
- 5. Low pressure carburising and high pressure gas quenching
- 6. Sintering of steels

Passion for innovation.



Linde Gas Research Centre in Unterschleissheim, Germany.

With R&D centres in Europe, North America and China, Linde Gas is leading the way in the development of state-of-the-art application technologies. In these R&D centres, Linde's much-valued experts are working closely together with great access to a broad spectrum of technology platforms in order to provide the next generation of atmosphere supply and control functionality for furnaces in heat treatment processes. As Linde is a trusted partner to many companies in the heat treatment industry, our research and development goals and activities are inspired by market and customer insights and industry trends and challenges. The expert editions on various heat treatment processes reflect the latest developments.

More Information? Contact Us!

Linde AG, Gases Division, Carl-von-Linde-Strasse 25, 85716 Unterschleissheim, Germany

heat-treatment@linde-gas.com, www.heattreatment.linde.com, www.linde.com, www.linde-gas.com

Contents.

Pretace	2
Passion for innovation	3
1. Introduction	6
2. Process	7
2.1 What is brazing?	7
2.2 Wetting and spreading	9
2.3 Designing a quality brazement	10
2.4 Capillary attraction and joint clearance	11
2.5 Brazing alloy	11
2.6 Cleanliness	14
2.7 Thermal brazing cycle	14
2.8 Troubleshooting common problems	15
3. Furnace and equipment	16
3.1 Continuous furnaces	17
3.2 Batch furnaces	18
3.3 Vacuum furnaces	18

4. Atmosphere generation, gas supply	20
4.1 Nitrogen supply	21
4.2 Argon supply	22
4.3 Hydrogen supply	22
4.4 Methanol supply	23
4.5 In-situ methanol cracking	23
4.6 Nitrogen and external atmosphere generators	24

26

	. Atmosp	here contro
--	----------	-------------

5.1 Atmosphere constituents and their functions	26
5.2 Atmosphere influence on wetting and spreading	27
5.3 Oxidation control	29
5.4 Carbon control	31
5.5 The atmosphere nitrogen potential	31
5.6 Hydrogen reactions	32
5.7 The atmosphere control system	32
5.8 Vacuum as atmosphere	33
5.9 Brazing of different alloys	36
5.9.1 Steel brazing	36
5.9.2 Stainless steel brazing	37
5.9.2.1 Atmosphere brazing	37
5.9.2.2 Vacuum brazing	37
5.9.3 Aluminium brazing	39
5.9.3.1 Atmosphere brazing	39
5.9.3.2 Vacuum brazing	4(
5.9.4 Copper and brass brazing	4(
5.9.5 Brazing of reactive metals	42
5.9.6 Brazing of ceramics and glasses	42
5.9.7 Brazing of cemented carbides	43

6. Safety

44

0.1 Salety awareness	44
6.2 Gases used in the process	44
6.3 Potential safety hazards and their sources	44
6.3.1 Explosions/flammability/fire	45
6.3.2 Toxicity and asphyxiation	46
6.3.3 Cold burn hazards	46
6.3.4 Pressurised piping and the gas expansion hazard	46
6.4 Control of safety hazards	46
6.4.1 General safety regulations and guidelines	46
6.4.2 Explosions/flammability/fire	46
6.5 Safe use of gases along the value chain	47
7. Appendix. Pressure unit conversions	48
8. Glossary	49
9. Acknowledgements	50
10. References	51

1. Introduction.

After furnace brazing of steel or other metal objects, numerous process parameters need to be controlled in order to achieve specific properties such as required joint strength and surface quality. The composition and function of the furnace atmosphere are among the most critical parameters, making atmosphere control one of the key success factors in metal brazing. In furnace brazing processes, the major function of the atmosphere is to create clean and oxide-free surfaces that guarantee high-quality brazing joints. Therefore, it is important to ensure a reliable supply of required gases and process gas blends, but also to integrate leading application technologies to enable precision control of furnace atmospheres and achieve the desired product specifications for brazed steel and metal alloy objects.

The purpose of this expert edition is to deliver a comprehensive, technical overview of furnace brazing processes and critical defining parameters in terms of the necessary equipment and furnace atmosphere in a structured, single document. By sharing valuable background information on this complex topic, this expert edition will give readers greater confidence when making business decisions. Additional expert editions from Linde Gas are available on subjects such as carburising and carbonitriding, and hardening and annealing (see the Preface for a full listing).

Each of the expert editions displays a similar content structure. The first part focuses on the process, in this case speaking about the basic principles of brazing processes as well as the related properties. The next section focuses on the different types of furnaces and the equipment required in the process. The furnace atmosphere generation and required gas supply is highlighted in the fourth section, while the interaction between furnace atmosphere and steel or metal surface and ways to control the atmosphere are described in the fifth section. As flammable, asphyxiating and toxic gases are used in brazing processes and since safety issues are an important concern for Linde Gas, these are addressed in the final section. Finally, definitions of key terms are included in the glossary.

2. Process.

2.1 What is brazing?

Brazing is a metal joining process that uses heat and a braze alloy, often called filler metal, to create a metallurgical bond between two or more separate pieces without melting or substantially modifying the material structure. The materials being joined, referred to as the base or parent materials, are positioned so only a small gap separates the pieces. A braze alloy is positioned close to the gap and upon melting, the braze alloy is drawn into the gap by capillary action. Thereby a solid joint is formed upon cooling. To be defined as brazing, the braze alloy liquidus temperature must be below the melting point of the base material but above 450 °C (842 °F).

The commonly used joining processes are brazing, welding and soldering. Some of the defining characteristics that distinguish each process are described below.

Characteristics of joining processes Soldering

- Solder alloy, called solder, has liquidus below 450 °C (840 °F)
- Forms bond with base material mainly by mechanical adhesion
- · Base metal remains solid
- Performed in air or nitrogen using a flux to break down surface oxides

Brazing

- Braze alloy, also called filler or filler metal, has liquidus above 450 °C (840 °F)
- Typical processing temperatures: 540–1620 °C (1000–2950 °F)
- Forms metallurgical bond with base material by dissolving a very small amount of surface material
- Base metal remains solid
- Performed in air by adding fluxes, or without the use of fluxes in inert, reducing or vacuum atmospheres

Table 1. Advantages and limitations of the furnace brazing process

Welding Weld al

- Weld alloy has liquidus above 450 °C (840 °F)
- Part of base metal melts to join with weld alloy
 Farme metally and with base metalling
- Forms metallurgical bond with base material

There are different brazing methods such as torch brazing, furnace brazing, induction brazing, dip brazing, and resistance brazing. In this document, the description is focused on and limited to furnace brazing. Advantages and limitations of the furnace brazing process are shown in Table 1.

Brazing allows diverse configurations of parts, dissimilar metals and non-metals of non-uniform thickness to be joined where other joining methods could not be economically used. Brazing is most commonly performed on metals, including those that are wrought (sheet, bar, tubing and extrusions), cast (sand, investment, die, shell and pipe), and powdered metal products. Joining of ceramics and glasses is also viable and is experiencing increased usage with advances in this technology.

Brazing is a widely accepted and standardised process for joining steel components, whether they are low-carbon, low-alloy or high-carbon steels, tool steels, or stainless steels. Cast irons are also successfully brazed if proper pre-cleaning is performed to remove graphite from the surfaces to be joined. Brazements are commonly used in the manufacture of automobiles, bicycles, and a wide variety of other vehicles, and in consumer products like frames, steel panels and shelving, tubular frame furniture, cutting tools, knives, reservoirs, electronic chassis, etc.

Advantages

5
Economical fabrication of complicated assemblies with many joints
Distortion and warpage are relatively low
High production rates can be readily accomplished using commercially
available equipment and process know-how
Dissimilar material combinations can be joined
Materials of varying thickness and cross-sectional area can be
accommodated
Complex geometries and multi-step joining procedures can be designed
Reproducible, high-quality results can be obtained
Brazing can be combined with heat treatment in the same cycle

The process is well recognised and documented in design handbooks

Limitations

Base metals hardened via heat treatment or cold working may lose these properties during brazing

The gap, or spacing, between the pieces largely determines the strength of the joint. Control of the gap is a critical design and production parameter

Parts must be held in a correct orientation and with the right spacing during heat-up and processing, and until solidification is complete Production of small quantities may not be cost-effective

Calculating the mechanical properties of an assembly can be difficult



Figure 1: Examples of brazed parts. Heat exchangers: (a) courtesy of Mahler GmbH and (b). Different automotive and other parts courtesy of Mahler GmbH: (c) and (d)

Aluminium brazing to manufacture automotive radiators, heat exchangers for refrigerators and industrial applications, and household goods is a mature technology. The development of brazing technology for aluminium in the 1970s has advanced the use of aluminium radiators in automobile production, where their decreased weight offers reduced vehicle fuel consumption and significantly reduces the environmental impact.

Copper is an alternative to aluminium in heat exchangers. High thermal efficiency and strength are copper's advantages. The copper alloys used in the past have been adapted to soldering, which involves joining at a temperature below 450 °C (840 °F), and if used at elevated temperature, these alloys have softened. The development of alloys that can be joined at temperatures above 450 °C (840 °F) and still maintain their strength during brazing has resulted in a new brazing process called CuproBraze[®].

Ceramics and composites are difficult materials to form or machine into complex shapes, so joining expands the engineer's ability to design complex components. Brazing is the leading method for joining ceramics, glasses and metals. Especially in electronics production, there are numerous examples of very advanced brazing applications for joining a great variety of materials. As an example, a variety of seals such as metal-metal, ceramic-metal and ceramic-ceramic are needed for solid oxide fuel cells to increase the reliability and life of the cell stacks. These seals are expected to function in the most severe environments with temperatures in the range 600–900 °C (1110–1650 °F) and under thermal gradients. Silicon carbides and silicon nitrides can be bonded to other components of similar or different compositions. Even diamond is brazed onto base metals, for instance in some rock drills.

There are numerous examples of brazed cemented carbide products such as cutting tools, drill tips, rock drill parts, dies, etc.

For further details on brazing of different metals and materials, see section 5.9 "Brazing of different alloys".

Some brazing applications are exemplified in Figure 1.



 Y_{sv} – Surface tension at the solid/vapour interface Y_{tv} – Surface tension at the liquid/vapour interface Y_{st} – Surface tension at the solid/liquid interface

Figure 2: Mathematical balancing of surface tensions for a drop of braze alloy on a metal substrate



Figure 3: Schematic showing relationship of contact angle to wetting a) Effective wetting b) Poor wetting or de-wetting

2.2 Wetting and spreading

A braze joint is formed when the braze alloy (filler metal) is drawn into the space between two surfaces that are close and parallel. This movement is via capillary action and occurs in three steps: adhesion, wetting, and spreading of the braze alloy. The surface tensions acting on a drop of braze alloy are illustrated in Figure 2.

Wetting can be analysed by balancing the horizontal components of the surface tensions by using what is known as Young's Equation:

 $\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos \Theta$ (Eq. 1)

The contact angle θ provides a measure of the quality of wetting. To have good wetting, the wetting angle, θ , must be substantially smaller than 90°. θ <60° is in practice required for good wetting and for a proper joint to form. Equation 1 shows that θ <90° corresponds to the condition $\gamma_{SV} > \gamma_{SL}$.

A decrease of the angle $\boldsymbol{\theta}$ resulting in improved wetting can be achieved by:

- Increasing γ_{sv}
- Decreasing γ_{SL}
- Decreasing γ_{LV}

Figure 3 shows the specific situation for brazing. When:

 $\theta \leq 90^{\circ}$, there is wetting

 $\theta \ge 90^\circ$, there is no wetting or de-wetting.

The wetting properties vary with different materials in the following way [1]:

- Difficult to wet: Titanium, zirconium, ceramics, glass and titanium carbide
- Fair wetting: Aluminium, cast iron, tungsten, tungsten carbide, molybdenum, tantalum, and alloys with more than 5% of metals forming refractory oxides
- Good wetting: Copper, nickel, cobalt alloys, steels and precious metals.

A wetting of a filler metal on the surface of the base material is only possible when at least one of the components in the filler metal is able to alloy with the components of the base material.

10

Table 2. Comparison of common braze joints

Feature	Butt Joint	Lap Joint	Butt-Lap Joint	Scarf Joint
Strength of Joint	Lowest	Good	Moderate	Moderate
Ease of Set-up	May be difficult with thermally mismatched materials.	Braze alloy is easy to place. Easy self-jigging or self-aligning fixturing.	Depends largely on complexity of component. Might be self-jigging or may require fixturing.	Requires fixturing to maintain gap and alignment.
Advantages	Ease of preparation. Low stress concentration. Single thickness of material.	Load is transmitted in shear rather than as tensile stresses.	Single thickness. Placement of braze alloy may be controlled. Can control location of stress concentration points.	Load-bearing capacity between that of the butt and lap joints. Single thickness.
Disadvantages	Load transmitted as tensile stress.	Double thickness of material due to overlap. Stress concentration produced at edge of lap.	Requires more machining and preparation. May require fixturing. Complicates part fabrication.	Complicates part fabrication. Fixturing generally required.

2.3 Designing a quality brazement

The braze joint should be designed as part of the overall component design. The joint configuration plays a critical role in the mechanical and fatigue resistance, corrosion resistance, thermal and electrical properties and physical appearance of the final assembly. Certainly, consideration must be given to cost-effective manufacture.

Examples of common braze joints are shown in Figure 4, and some basic comparisons between the types of joints are illustrated in Table 2.





Butt joints – The smaller the available bonding area, the lower the strength of the joint. In a butt joint, the only available bonding surfaces are the cross-sectional areas of the pieces being joined, so the strength of the joint is limited. The major advantage of this configuration is the smooth contour and the clean appearance. The major disadvantage is low strength, which makes this type of joint uncommon. In addition, the fixture required to assist in joining the parts is very complex.

Lap joints – As the name suggests, the pieces overlap to produce a large bonding area, but this creates a change in the overall thickness of the assembly. Jigging and braze alloy placement are relatively easy in this configuration, and the orientation of the component can often be controlled during the brazing process, preventing the parts from moving relative to each other. Lap joints are either of the type single-lap or double-lap configuration.

Butt-lap joints – Butt-lap joints combine the properties of the two methods by machining a precision contour through the thickness of the base materials to provide mating surfaces. The increased amount of contacting surface offers increased mechanical strength. The profile minimises stress concentration and therefore reduces the risk of crack initiation. This type of joint provides precision features for controlled gap spacing. The added production steps of machining, cleaning and set-up increase the manufacturing cost.

Scarf joint – Scarf joints are an attempt to combine the smooth surface of the butt joint with the increased strength of the lap joint. In a scarf joint, the faying surfaces are machined to a precision angle to increase the contacting surface area. The advantage obtained by maintaining a single thickness through the joint must be evaluated against the difficulties in machining, alignment and braze alloy placement. Scarf joints have higher load-bearing capability than butt joints because the stresses are transmitted off-axis and the bond cross-sectional area is greater.

2.4 Capillary attraction and joint clearance

The joint gap is of great importance for establishing a high-strength joint. Generally, joint strength will increase with decreased joint gap.

The correct dimensioning of joint gaps (gap width) and cleanliness of the brazing surfaces are crucial factors for determining the capillary attraction as illustrated in Figure 5. Excessively large gaps and improperly cleaned surfaces reduce the capillary pressure and lead to brazing gaps being only partially filled. The high capillary pressure in gaps smaller than 0.05 mm is exploited for brazing operations in protective gas atmospheres or vacuum. For mechanised brazing with fluxes, the gap range is between 0.05 and 0.2 mm. Up to a gap size of 0.2 mm, the capillary attraction is enough to assure adequate penetration and filling of the gap with filler metal. Wider gaps are difficult to fill and are therefore not suited for mechanised brazing. The range up to 0.5 mm is still suited for manual brazing. For gap widths exceeding 0.5 mm, the low level of capillary pressure prevents reliable and uniform filling of brazing gaps with filler metal [2].



Figure 5: Capillary pressure dependent on gap width (courtesy of SAXONIA Technical Materials GmbH)

Table 3 gives some approximate recommendations for allowable joint gaps for various braze alloy systems at ambient temperature. However, the joint gaps can vary a lot depending on geometry, joint length, specific alloy composition, etc.

Table 3. Preferred gaps for different brazing filler metals [3]. The gaps given are just for guidance as they may vary with conditions

Brazing filler-metal system	Joint clearance, mm (in.)
Al-Si alloys	0.15-0.61 (0.006-0.024)
Mg alloys	0.10-0.25 (0.004-0.010)
Cu alloys	0.00-0.05 (0.000-0.002)
Cu-P	0.03-0.13 (0.001-0.005)
Cu-Zn	0.05-0.13 (0.002-0.005)
Ag alloys	0.05-0.13 (0.002-0.005)
Au alloys	0.03-0.13 (0.001-0.005)
Ni-P alloys	0.00-0.03 (0.000-0.001)
Ni-Cr alloys	0.03-0.61 (0.001-0.024)
Pd alloys	0.03-0.10 (0.001-0.004)

There are several other factors that influence the brazing success such as the braze alloy viscosity and specific gravity, the tendency of the filler metal to alloy with the parent metals, joint length, brazing temperature and base metal reactions [1,2,3].

The strength of a professionally and successfully brazed part subjected to tensile stress across the joint will be decided by the base material strength and not by the joint. Tensile tests of bars of a precipitationhardening alloy have proven this. The tests were performed in the as-brazed condition and after additional aging to give precipitationhardening effect of the base metal. The tensile strength of the brazed bars was substantially greater after aging [4], which proves that joint strength was not the limiting factor for the overall strength.

2.5 Brazing alloy

The brazing alloy, often called filler metal, is the material used to bridge the gap between the two pieces being joined. Forming an effective bond requires the braze alloy to wet, spread, and be drawn in to the joint where it metallurgically bonds with the mating surfaces. If some of the braze alloy is soluble in or reacts with some constituent of the parent material, it is called alloying. The molten braze alloy may dissolve the base metal, forming an effective bond (see Figure 6).



Figure 6: Diffusion zones after brazing (courtesy of SAXONIA Technical Materials GmbH). Upper part of picture before brazing; lower part of picture after brazing

Or, the braze alloy and base materials can interact metallurgically to form intermetallics or precipitates. The molten braze alloy can penetrate the base metal grain boundaries, or surface irregularities of the joint surfaces. Any of these effects will normally contribute to producing a strong joint. There is an exception for those cases where brittle intermetallics form due to reactions between the braze alloy, the base metal, and the atmosphere. The risk of creating unwanted precipitates increases with increased time at brazing temperature.

Braze alloys come in a wide variety of forms, including powder, foil, paste, and solid metal pre-forms. Paste is a blend of brazing alloy powder in a solvent and binder suspension agent and is commonly used because of its flexibility of application, wide availability, and low cost. It is important to supply sufficient paste to the joint to accommodate the thermal expansion of the work pieces being joined and allow for loss of the vaporised brazing paste solvents at elevated temperature. Braze alloy pre-forms are solid forms of braze alloy as rings, sheets, shims and wire. Pre-forms can be put into place as part of the assembly process and may allow complete assembly of a component prior to brazing. Pre-forms may offer a cleaner application and be less labour-intensive than pastes, but they can be difficult to place correctly in the assembly.

Most braze alloys melt over a temperature range, not at a discrete "melting point" such as for a pure metal. This melting range is an important parameter for selecting the appropriate filler. The lower temperature is called the solidus. This is the onset of melting. The upper temperature where the filler is completely liquid is called the liquidus. For braze alloys with eutectic composition, the solidus and liquidus are the same temperature. This is called the eutectic temperature, illustrated in Figure 7 by the binary phase diagram for the silver (Ag) – copper (Cu) system.



Figure 7: Binary phase diagram of Ag and Cu; Eutectic point is at 780 °C (1435 °F) with a composition of 72 wt% Ag and 28 wt% Cu (courtesy of SAXONIA Technical Materials GmbH)

The braze alloy must be fully liquid at the brazing temperature to flow and enter the joint through capillary action. Brazing temperature therefore, as a general guideline, should be 20–30 °C (68–86 °F) higher than the braze alloy liquidus.

Braze alloys from the silver, copper or nickel families can be used for steel brazing. Copper-base filler metals are generally preferred because of their low cost and the high joint strengths produced. The solidus of copper-base filler metals is typically in the range 1095–1100 °C (2000–2010 °F), which sets a requirement of a brazing temperature above this

temperature range. This can be used to advantage by combining brazing with a heat treatment cycle, for instance hardening.

Silver-base alloys have lower solidus compared to the copper-base filler metals. Silver-base alloys are accordingly used when the brazing temperature must be below a certain temperature in order not to impair the base material properties obtained in a foregoing heat treatment or to reduce thermal-induced stresses, for example when joining cemented carbides to steel.

Careful consideration of how the brazing and heat treatment will interact can reduce the number of processing steps. For example, low-alloy pre-heat-treated metals may use silver-based fillers with liquidus temperatures below the steel transformation temperature to retain their heat-treated properties. Alternatively, brazing and heat-treating can occur concurrently if copper-zinc or certain silver-based filler alloys are used with their solidus temperature above the steel austenitising temperature. Brazing of hardenable high-carbon steels is either done prior to hardening or as a step in the hardening process. For hardenable tool steels with tempering temperatures in the range 550–650 °C (1020–1200 °F), it is possible to perform brazing and tempering concurrently by selecting a silver-base filler metal with sufficiently low solidus.

Brazing is one of the easiest ways to assemble stainless steel components; however, the chromium content of stainless steels makes them much more difficult to wet than carbon steels. Copper, nickel and silver-based braze alloys are the most commonly used filler metals. Nickel-brazed joints are, in contrast to silver- and copper-brazed joints, suitable for high-temperature service, even in combination with corrosive environments. Exercise care when selecting the braze alloy since diffusion of certain elements may have a negative impact on corrosion and mechanical properties. Nickel-base filler metals may form brittle intermetallic compounds with the base metal. This is because the filler metal component boron (B) may react with nitrogen to form boron nitrides (BN), and the component silicon (Si) may react with the metal to form silicides. The brittle compounds are formed at the centreline of the joint and are sometimes referred to as centreline precipitates.

Copper and brass encompass a wide range of chemical compositions and most of their alloys are readily brazed. Since copper alloys are generally hardened by cold work, brazing temperatures often decrease the strength of the base metal. Braze alloys such as silver and copper are commonly used and may be self-fluxing or fluxless.

Table 4 gives an overview of types of filler metals, their properties and applications.

Table 4. Major classes of braze alloys (filler metals) [2, 3, 5, 6]

Alloy (filler metal) family and type	ISO 17672 designation	AWS designation	Brazing temper- ature, °C (°F)	Forms	Base materials joined	Major applications
Al-Si, eutectic	Al 105-415	BAISi	555-645 (1030-1195)	Pre-forms, wire, rods, foil, powder, RS foil (a)	Aluminium to aluminium alloys, steel to aluminium, aluminium to beryllium	Car radiators, heat exchangers, honeycomb aircraft structures, structural parts
Cu-X, solid solution	Cu 087-141	BCu	1095–1150 (2000–2100)	Pre-forms, wire, rods, foil,	Copper to copper alloys, copper to mild steel,	Heat exchangers, structural parts, automotive parts
Cu-Zn, peritectic	Cu 470–773	RBCuZn	910–980 (1670–1800)	powder, RS foil	copper to stainless steel, most ferrous metal combinations	
Cu-P, eutectic	CuP 178-389	BCuP	690–925 (1275–1700)	Pre-forms, wire, rods, foil, powder, RS foil	Copper to copper, copper to silver/ oxide powdered metal composites	Electrical contacts, bus bars, heat exchangers
Cu-Ag, eutectic	Ag 125-485	BAg	620-980 (1150-1795)	Pre-forms, foil, powder	Most ferrous and non-ferrous metals, except aluminium and magnesium	Most widely used utility filler metals
TM-Si-B(b), eutectic (Ni/Fe + Cr)-Si-B	Ni 600-810	BNI	930–1205 (1705–2200)	Powder, tape(c), RS foil	AISI 300- and 400-series steels and nickel- and cobalt-base super alloys; carbon steels; low-alloy steels; and copper	Aircraft turbine components, automotive parts, heat exchangers, honeycomb structures, moulds, other tools, etc. Honeycomb structures,
(Ni, Pd)-Si-B	Co 900	None		Powder, tape, RS foil	AISI 300-series stainless steels, cemented carbide, super alloys	cemented carbide/ polycrystalline diamond tools, orthodontics, catalytic converters, aircraft
(Co, Cr)-Si-B		BCo	1175-1245 (2145-2275)	Powder, tape, RS foil	Cobalt-base heat- resistant corrosion- resistant super alloys	engines, honeycomb marine structures
Au-Ni, solid	Au 295-827	BAu	890-1230	Pre-forms, wire,	Nickel-base heat-	Honeycomb structures,
Cu- (Ti, Zr)-Ni eutectic and peritectic		None	(1035-2245)	Cladded strip, RS foil	Titanium/zirconium- base alloys	Titanium tubing, aircraft engines, honeycomb aircraft structures, aircraft structural parts, chemical reactors

a) May be produced as rapidly solidified, ductile, amorphous/microcrystalline foil.

b) This group includes alloys based on transition metals (TM) such as nickel, iron and cobalt.

c) Brazing filler metal is carried on a plastic-bonded tape.

2.6 Cleanliness

Wetting is negatively affected by the presence of surface oxides and contaminants such as dirt, grease, lubricants and detergents. Poor cleanliness results in lack of wetting, incompletely filled joints, and low joint strength. The furnace atmosphere can remove limited amounts of surface oxidation by integrating sufficient quantities of reducing gases such as hydrogen. However, it is not advisable to use the brazing furnace, especially not a vacuum furnace, as a cleaning machine. Vaporised dirt may in such cases condensate on cold furnace parts and create furnace functionality problems.

Mechanical cleaning may be performed by wire brushing or blasting. Grinding or machining requires the use of chemical cleaning to remove the machining fluids. Chemical cleaning methods will be determined by the type of surface contaminants likely to be found on the surface. Degreasing agents will remove hydrocarbon deposits from cutting oils, while aqueous cleaners work well to remove water-based machining fluids. Plasma cleaning and blasting with CO₂ pellets would not leave any residues if developed to be technically and economically viable cleaning methods.

2.7 Thermal brazing cycle

A typical brazing process cycle is pre-heat (optional) including holding, ramp to temperature, brazing, cool down and exit, as illustrated in Figure 8.



Figure 8: Schematic of a typical brazing process cycle

Pre-heating is done up to a temperature which is below the filler metal solidus. Part thickness and the amount of fixture determine the pre-heat and holding time. Enough time should be allowed for the temperature to stabilise.

The parts should heat quickly but uniformly. The heating rate is therefore limited by the risk of creating distortion due to thermal stress build-up. For parts with complicated geometries, large dimensions, big differences in dimensions, or crack-sensitive materials, more than one holding step and associated ramp may be required.

Brazing time should be the minimum time that allows the braze alloy to flow through the joint at the coldest part of the work piece. Often one to two minutes is enough to create a sound joint. Theoretical predictions as well as actual measurements show that joint filling by the molten braze alloy occurs virtually instantaneously in a time of the order of 0.1 second [7]. Extended processing times can lead to excessive interactions between the filler and base metal, grain growth, and recrystallisation. However, in some cases a longer processing time is beneficial when the braze alloy interaction will lead to a modified braze alloy with increased melting temperature, which may be beneficial if the component will be brazed a second time.

Cool-down and exit:

A controlled cool-down allows the joint to solidify. Cooling under a protective atmosphere down to a temperature of about 150 °C (300 °F) for steels will avoid discoloration of parts exiting the furnace.

2.8 Troubleshooting common problems

Listed below are some of the more common brazing problems and possible solutions.

Table 5. Common brazing problems and possible solutions

Problem or symptoms	Possible cause	
Furnace-brazed parts exit furnace gold or straw	Parts are exiting the furnace at too high a temperature. Parts temperature should be less than	
in colour, generally uniform in appearance.	150 °C (300 °F) when exiting.	
Braze joint is good.		
Furnace-brazed steel parts exit furnace with	Parts may be exiting the furnace at too high a temperature. Also, check for air leaks in high	
blue or black colouration, either uniform or not uniform. Braze joint may or may not be good.	temperature zone possibly at muffle flanges or water leakages in the cooling jackets.	
Vacuum-brazed parts are discoloured with or	Air infiltration in the backfill gas and/or contamination from an external or internal source.	
without poor braze joint quality.	Check to make sure that the parts have been thoroughly cleaned and dried prior to processing,	
	Leak-check the backfill lines to the furnace. If the base material contains nitrogen as a	
	strengthening agent, it will not braze well using filler metals with boron, even if the furnace is	
	clean.	
Cracking	Strength of base metal may be too high. If possible, use metal in annealed condition. Modify joint	
	design to avoid stress concentration points.	
Porosity in braze joint	Porosity occurs when gases become trapped, particularly in blind joints. Modify design or	
	assembly so gases may vent properly.	
Disbonding	Check joint design. Cross-sections should be similar in size and part thicknesses must be	
	comparable. Verify parts are not shifting during heat-up with resultant oversize gap.	
Discolouration	The most common causes:	
	→ Improper pre-braze cleaning	
	→ Cleaning residue left from aqueous cleaning system	
	\rightarrow The presence of oxygen at too high a temperature in the heating or cooling portion of the cycle	
	→ Residual lubricants or machining fluids	
Discolouration from vacuum furnace	Contaminated quenching gases or too high a vacuum level in vacuum furnace	
	Furnace opened before parts were cooled below 150 °C (300 °F)	
	Water leak from heat exchanger	
	Faulty door seal	
	Out-gassing of parts	
Discolouration from pusher, belt or humpback	Insufficient hydrogen percentage	
furnaces	Verify quality of furnace atmosphere (dew point and oxygen level)	
	Air infiltration from entrance or exit	

3. Furnace and equipment.

Table 6. Comparison of common types of protective atmosphere and vacuum brazing furnaces

Characteristic	Continuous furnace	Batch furnace	Vacuum furnace
Scheduling/Production rates	Continuous production	Production in batches	Production in batches*
Operator required in attendance?	Operator is required to continuously load and possibly unload parts from belts or trays.	Operator is required to load and unload furnace and to start and finish process. Operator presence	Operator is required to load and unload furnace and to start and finish process. Operator presence
		may be required if hydrogen is in	may be required if hydrogen is in
		use.	Use.
Capital cost	Moderate to high	Moderate	High
Can produce reducing environment	Yes	Yes	By dissociation
Can produce oxidising environment	Yes	Yes	No
Can produce very low oxygen environments	Most cannot	Most cannot	Yes
Environmental issues	Emissions of CO and excess heat	Emissions of CO and excess heat	Minor emissions from oil vapours from vacuum pumps
Can handle long parts and complicated assemblies	With difficulty	Effectively	Effectively
Can be shut off or idled for off- production	Furnace would be idled during off-production (reduced atmosphere and temperature)	Yes, but mostly maintained at temperature	Yes, can be completely shut off
Cleanliness of final product	Clean	Clean	Very clean

* There are semi-continuous vacuum furnaces, for instance for aluminium brazing, but batch vacuum furnaces dominate.

A thorough knowledge of the product, material requirements, production volumes and schedule is vital when a company is purchasing a furnace or looking for a commercial brazing company. The types of brazing furnaces are generally classified as continuous, batch or vacuum furnaces and are compared in Table 6.

Processing requirements of the base material and the filler alloy with respect to temperature and atmosphere are the most critical aspects of furnace selection. If oxygen, nitrogen or hydrogen cannot be tolerated, vacuum processing will offer the highest quality. Ceramics and reactive metals such as titanium, molybdenum, vanadium, beryllium and tantalum must be processed in a non-oxygen-bearing inert argon or helium atmosphere or in vacuum.

Critical production information includes the number, weight and shape of parts. Other important information includes if the parts arrive at the brazing departments in batches or if they should be brazed as part of a continuous production line. Continuous equipment offers some flexibility for changes in atmosphere and/or temperature. For batch equipment, the entire furnace must undergo the process cycle even if only a few parts are in the load. An operator must be continuously present to load and unload parts from a continuous furnace, while for a batch furnace, an operator need only be present to start and finish the process. If flammable gases are used, then an operator must always be present, but may be involved with other activities.

If the material does not require the use of vacuum, then continuous and batch atmosphere furnaces often offer a lower capital cost solution. Each facility must determine which furnace offers the best cost of operation. If utility costs are high or are restricted, batch equipment may offer a significant advantage. Reliability of vacuum equipment has improved substantially over recent decades, and the current generation of equipment is easier to install, program and maintain, which leads to low operational costs. Vacuum brazing in addition offers lower running costs for utilities like electricity and gas. Stricter environmental legislation and directives may in the future lead to costs for cleaning and recycling of effluents, which will reinforce the economic benefits of vacuum brazing.



Figure 9: Parts exiting a continuous atmosphere brazing furnace riding on a mesh belt (courtesy of Mahler GmbH)



Figure 10: Mesh belt furnace (courtesy of Mahler GmbH)



Figure 11: Schematic layout of a humpback continuous furnace (courtesy of Mahler GmbH, Germany)

3.1 Continuous furnaces

Continuous brazing is suitable for production with a steady flow of incoming parts. The parts move through the furnace, either as individual components or in trays or baskets. Mesh belt, humpback or pusher furnaces are generally used. A furnace is typically brick- or fibre-lined with a metallic muffle to assure control of the atmosphere and to minimise the amount of contamination residing in the insulation. A continuous furnace offers consistent part quality, readily integrates into the manufacturing material flow, and is easily adaptable for automation. Figure 9 shows individual parts entering a continuous atmosphere furnace on a mesh belt and Figure 10 shows a typical small, mesh belt furnace.

In a continuous furnace, the parts to be brazed are transported on a conveyor. The temperature profile is determined by the speed of the conveying mechanism. To allow rapid heating to temperature, the heat input in the first section of the furnace must be high. A short dwell time at the brazing temperature is followed by a cool-down, fast enough to avoid formation of precipitates and intermetallics which may cause embrittlement. The cooling section of the furnace must be long enough

for the parts to reach a low enough temperature, typically below 150 $^{\circ}$ C (300 $^{\circ}$ F) for steels, to avoid oxidation upon exiting the furnace.

The ratio of time spent during heat-up versus time at brazing temperature is fixed due to the ratio of lengths of each of the furnace zones.

Parts may travel on a mesh belt fabricated of metal, or of carbon composite for very high temperature applications. Most belts remain level through the furnace. Humpback furnaces (Figure 11) are the exception. The belt in a humpback furnace travels up an incline, flattens through the high heat processing section, and then descends through the cooling chamber. The distinctive profile gives the humpback furnace its name. The low density of hydrogen gas allows it to accumulate in the elevated section of this furnace, thereby minimising the hydrogen consumption. Nitrogen is introduced at the entrance and exit to buffer the hydrogen-processing chamber from disturbances from air ingress caused by product movement in and out of the unit. Removing product that has fallen from the belt or trays that get jammed is more difficult in a humpback than in a flat belt or pusher furnace.



Figure 12: Two-chamber front-loading CuproBraze batch brazing furnace with purging/ cooling vestibule and a convection heating chamber (courtesy of SECO/WARWICK Corporation)



Figure 13: Temperature and pressure cycles in vacuum brazing

3.2 Batch furnaces

As indicated by the name, every batch or load is processed separately. Depending on how the furnace is loaded, it is called a pit furnace (loaded from the top), a bell furnace (loaded from the bottom), or a box or retort furnace (loaded from the side, see example in Figure 12). As with continuous furnaces, a metallic lining is used to isolate the atmosphere from the insulation and potential contamination. This lining may be called retort, muffle or inner cover depending on the type of furnace being discussed. The furnaces are sealed using either a gasket or seal made of sand or oil to keep the oxygen and moisture levels low.

A typical batch furnace cycle would include the following steps: Step 1: The cycle begins by loading and closing the furnace.

Step 2: The load is heated to an intermediate temperature to allow any surface contamination to off-gas and allow the load to come to a uniform temperature.

Step 3: If the atmosphere is inert, it may be introduced at this point. If a flammable atmosphere will be used, the chamber may be filled with an inert gas that will later be replaced with the flammable atmosphere. Some furnaces will allow introduction of a flammable atmosphere into a furnace containing air if the furnace is above the auto-ignition temperature of the atmosphere and the furnace was designed to be gassed up in this manner.

Step 4: The furnace will ramp to temperature, hold at the selected brazing temperature, and then ramp down to cool the load. During the cool-down, flammable atmospheres must be purged from the furnace for safety.

Step 5: The load may be removed when it is below a temperature that will cause discoloration.

3.3 Vacuum furnaces

Brazing is a major vacuum heat treatment process and the associated product value probably exceeds that of any other vacuum heat treatment process [8]. Vacuum brazing is particularly used in the aerospace and electronics industries for joining of metals and alloys that easily react with oxygen, nitrogen and other gases, and for parts that cannot tolerate the presence of fluxes or other impurities. Complex assemblies with blind passages, such as stainless steel heat exchangers, are increasingly brazed in vacuum. Such parts are almost impossible to braze with atmosphere flux brazing. The steps in vacuum brazing are schematically shown in Figure 13 and include:

Step 1: The load is charged into the furnace. A vacuum pump (rough pump) removes much of the air that entered the furnace with the load. Another pump (normally a diffusion pump) reduces the pressure further.

Step 2: Inert gas (nitrogen) is let into the furnace and the pressure is increased to a pressure in the range 0.9-1.5 bar to allow for convection heating (if the furnace is equipped with a fan for improving convective heating). If there is no fan, then the low pressure is maintained. Heating in that case will only be by radiation.

Step 3: Heating of the load begins. The heating rate should allow the parts to heat uniformly to minimise distortion. The parts are held for a soak period at a temperature below the filler alloy solidus temperature to assure that the whole load uniformly reaches the braze temperature before going to step 5.

Step 4: At the end of the holding time, vacuum pumping is activated to give a low pressure. This is to lower the atmosphere oxygen partial pressure and to efficiently remove all volatile species originating from vaporised brazing paste vehicles and dirt on the parts. Step 5: The temperature is increased to the brazing temperature. The braze alloy starts to melt and is drawn into the joint.

Step 6: The pressure is increased if the base alloy has alloying elements that tend to vaporise. The soak time at brazing temperature should be just long enough to assure melting of all braze alloy in the entire load; too long may lead to embrittlement. The properties of the final braze joint are influenced by the time at temperature. Grain growth, penetration of alloy along grain boundaries, precipitation of carbides of intermetallic compounds, and diffusion of alloying elements between the braze alloy and base metal must be considered.

Step 7: In this step, the temperature is lowered until the braze alloy is completely solidified.

Step 8: Fast cooling down to room temperature is achieved by introducing inert gas into the furnace up to a certain elevated pressure. The use of nitrogen with 1–6 bar pressure is common. Furnaces for 10 bar and higher are developed for higher cooling capacities. The proper cooling rate depends on the risk of distortion and if there are certain requirements on the cooling rate for obtaining the best material properties.

Vacuum heat treatment means that the occurrence of gaseous molecules is so rare that there are no net reactions such as oxidation or carburising with the metal surface. There is a cleaning action from the vacuum caused by vaporisation. If the vapour pressure or partial pressure of a certain element at the actual temperature is higher than the actual vacuum pressure, then that element will vaporise. This is mostly a beneficial effect because dirt or oxides remaining on the metal parts will vaporise. Parts exiting the furnace after a vacuum brazing cycle therefore are mostly cleaner than upon entering. An important effect of vaporisation and degassing is that the braze joints will be free from pores. Joint strength accordingly is improved by vacuum brazing. In some cases, vaporisation can be negative if alloying elements in the base metal are vaporised. Running with increased pressure, "partial pressure", can counteract this. In addition, this also yields a better cleaning effect.

Oxygen, water and hydrocarbons are the most common contaminants in vacuum atmospheres. Oxygen can be introduced as air through vacuum leaks, from contaminated back-fill gas, or from dissociation of surface oxides. Water is generally inadvertently introduced from the water-cooled heat exchange system. Water contamination often begins as extremely small pinhole-sized leaks that only open at elevated temperatures, making it difficult to locate these leaks before they begin causing considerable brazing problems. Occasionally, water is introduced with the parts either from incomplete drying after cleaning or hygroscopically attached to the part surface or to the furnace interior. To assure the highest quality vacuum conditions, vacuum furnaces should have all doors closed and be kept under vacuum to minimise moisture and air infiltration when not in use. Discoloration of vacuum-brazed parts may also be caused by hydrocarbons originating from residual lubricants on improperly cleaned parts, or more commonly, from pump oil that migrates backward (backstreams) into the vacuum chamber.



Figure 14: Batch vacuum furnace for brazing (courtesy of Kepston Limited)

Leak testing of vacuum furnace systems should be done when required because of discoloration of brazed parts and as a regular quality control. Helium or the lower-cost alternative nitrogen/hydrogen mixtures are used for leak testing. The principle used is that helium or nitrogen/ hydrogen gas is sprayed around sealings and couplings on the outside of the vacuum furnace and a He or H₂ sensor is placed at the vacuum pump outlet. The use of the small-molecule gases helium or hydrogen makes the leak detection more efficient because these gases will detect and penetrate leaks much better than pure nitrogen, which is a large-molecule gas. Helium is preferred over hydrogen because it is non-flammable.

For leakage tests of brazed parts, high-pressure nitrogen can be used with the pressure registered. A drop of pressure with time indicates a leak.

4. Atmosphere generation, gas supply.

The furnace atmosphere is supplied to a furnace in one of two basic ways. The first, here referred to as in-situ generation or synthetic atmospheres, is by supplying gases, such as nitrogen, hydrogen or argon, in separate lines directly to the furnace, where they are mixed to create the correct composition. The second, called external generation, is to react components (typically a fuel and air) in an external generator to produce the furnace atmosphere. These two methods can be combined. In-situ methods can create widely varying atmosphere compositions and the flow can also be adapted to needs at any time, whereas separate external gas generators produce a fixed atmosphere composition and the output flow rate can be varied only within restricted limits.

Specific advantages related to the use of in-situ atmospheres are:

- Flow rate can at any time be adapted and minimised to meet the true need of the furnace and the process
- Gas mixture can be adapted to any ratio according to the need of the alloy and the process
- Short start-up and conditioning
- · Maintenance and supervision are minimised
- Gas production reliability is improved compared to the use of generators
- Quality and productivity can be improved by using the flexibility of mixing and flow rate

To make a good atmosphere, it is usually necessary to combine at least two different gases. For instance, N₂/H₂ atmospheres are produced by feeding N₂ and H₂ through separate flow meters to the furnace. N₂/ CO/H₂ atmospheres are produced from methanol, which dissociates to CO and H₂ in the furnace and is diluted with nitrogen to the correct composition. The most common combinations are shown in Table 7, where the Linde designations for the different systems are also shown. From the table it is clear that a certain atmosphere composition can be obtained in different ways. For instance, an N₂/H₂ atmosphere can be produced not only from combining the pure gases (N₂ and H₂) but also from cracked ammonia or by nitrogen dilution of cracked ammonia. N₂/ CO/H₂ atmospheres can be produced from N₂ + methanol, from endogas, from a combination of N₂ + endogas and so on.

Table 7. Synthetic atmospheres based on composition

Composition	Supply alternative	Linde designation
100% nitrogen	Gaseous supply in cylinders or bundles	GAN
	Liquid nitrogen supply	LIN
	Cryogenic on-site supply	CRYOSS®
	PSA on-site supply	ADSOSS®
	Membrane on-site supply	MEMOSS®
100% hydrogen	Gaseous supply in cylinders or tube trailer	Hydrogen
	On-site supply	
	Liquid hydrogen supply	
100% argon	Gaseous supply in cylinders or bundles	Argon
	Liquid argon supply	LAR
100% helium	Gaseous supply in cylinders	Helium
Nitrogen/hydrogen mixture	$N_2 + H_2$	HYDROFLEX®
	N ₂ + cracked ammonia	HYDROFLEX
Argon/hydrogen mixture	$A_{\Gamma} + H_2$	HYDROFLEX
Nitrogen/hydrocarbon mixture	N_2 + natural gas (+ H_2)	CARBOFLEX®
	N_2 + propane (+ H_2)	CARBOFLEX
Nitrogen/carbon monoxide/hydrogen mixture	N ₂ + methanol	CARBOFLEX
	N_2 + endogas	CARBOFLEX

4.1 Nitrogen supply

There are five major supply forms for nitrogen (see Figure 15):

Gaseous nitrogen in cylinders or bundles

For cost reasons, this option is relevant only for limited gas consumption.

Liquid nitrogen

The liquid nitrogen is supplied by truck to a vacuum-insulated container (see Figure 15a) at the customer site. This is the most common supply method that is cost-efficient for a flow from 10 up to about 250 m³/h. Nitrogen supplied in liquid form has a high purity, with typical $O_2 + H_2O$ contamination levels of 5 ppm. The liquid nitrogen supply form has the advantage that the amount of nitrogen supplied to the furnaces can be varied within wide limits. The customer takes only the amount needed at any time.

Nitrogen produced on-site with cryogenic technology

Cryogenic on-site production, Figure 15b, yields high-purity nitrogen, typically with 5 ppm oxygen and moisture content. It is relevant for flow rates from 250 to 2000 m^3/h .

Nitrogen from adsorption (PSA) units installed on-site

Nitrogen produced on-site using the PSA (Pressure Swing Adsorption) technique, Figure 15c, has a purity of 99 to 99.99%. Flow rates from 10 up to 2000 m^3/h can be accommodated. ECOVAR[®] is a family of PSA on-site production units supplied by Linde Gas.

Nitrogen produced on-site with membrane technology

Nitrogen produced at the customer site using the membrane technique has a purity of 90–99%, or differently expressed contains up to 1 vol% oxygen. Flow rates from 5 up to 1000 m^3 /h can be accommodated. The cost for membrane nitrogen is lowered if a certain impurity level of oxygen can be accepted.

The on-site production methods are combined with a liquid nitrogen tank supply or a gas cylinder supply. This extra supply is for back-up purposes and to meet instant needs of higher flow rates than is possible with the on-site supply unit.







Figure 15: Nitrogen supply methods. a) Storage tank and vaporiser for liquid nitrogen, b) Cryogenic nitrogen production with CRYOSS[®], c) PSA (Pressure Swing Adsorption)



Figure 16: Different supply forms for hydrogen. a) Cylinder bundle with hydrogen, b) Hydrogen tube trailer, c) Liquid hydrogen truck with production facility in the background

4.2 Argon supply

Argon is supplied either as gas in cylinders or as liquid in a tank like the nitrogen tank shown in Figure 15. Purities are the same as for the corresponding nitrogen supply methods, thus 5 ppm of $O_2 + H_2O$.

4.3 Hydrogen supply

Hydrogen is alternatively supplied by:

- a) Gaseous delivery from cylinders, cylinder bundles or a tube trailer
- b) On-site production by electrolysis of water, steam reformation of natural gas, ammonia dissociation or methanol dissociation
- c) Liquid hydrogen supply

Examples of different supply methods for hydrogen are shown in Figure 16.



Figure 17: Methanol tank installation. The liquid nitrogen tank is seen in the background

4.4 Methanol supply

Methanol is stored in tanks of varying size depending on the rate of consumption. Small consumers fill their tanks from barrels, while large consumers fill them from road tankers. An example of a methanol tank installation is shown in Figure 17. Nitrogen inerting of the methanol storage is common both to ensure safety and to eliminate the risk of humidity entering the methanol.

The methanol storage installation should comply with local safety regulations. This could for instance mean that the tank must be surrounded by a barrier or wall to eliminate the risk of spreading methanol spills. Due to the high level of toxic risk, a locked entrance to the methanol storage location is also advisable.

There are three different means of passing the methanol from the storage tank to the furnace. The first is by applying pressure to the nitrogen by pressurising the methanol storage tank with nitrogen. This method is straightforward but has the drawback that nitrogen may dissolve in the methanol, causing problems with gas bubbles and unsteady flow. The second method is by positioning the methanol container at such a high level that gravity will feed the methanol to the furnace. In practice, this method is limited to cases with small methanol containers. The third and preferred method is to use a pump to feed the methanol.

4.5 In-situ methanol cracking

A carbon monoxide/hydrogen (CO/H_2) atmosphere can be produced by in-situ cracking of methanol according to the reaction:

 $CH_3OH \rightarrow CO + 2 H_2$

By mixing cracked methanol with nitrogen, it is possible to produce a wide range of $N_2/CO/H_2$ compositions, thus also those obtained by endo-, exo- or monogas generators.

The injection of methanol has to be carried out properly in order to obtain the correct cracking products. If cracking occurs at too low a temperature, there will be a risk of soot formation. Therefore, methanol should be introduced into the furnace at a place where the temperature exceeds 800 °C (1470 °F). At lower temperatures, other cracking reactions may produce CH_4 , CO_2 , H_2O and soot. The cracking of methanol can be improved by disintegrating the liquid methanol stream into droplets. This can be accomplished by introducing the methanol into the fan area of the furnace, as shown in Figure 18. Another way is to use a special atomising spray nozzle.

When introducing methanol into thick-walled furnaces, it is important that the time for the liquid methanol to pass the temperature interval of 250–800 °C (482–1470 °F) is as short as possible. Below 250 °C (482 °F), the methanol will not readily crack, but will vaporise. Furnace regions at that temperature can in some cases be used successfully for vaporising methanol. In certain furnaces such as low-height conveyor furnaces and bell furnaces, it is advantageous to have a separate methanol vaporiser



Figure 18: Methanol injection into the fan area of a furnace



Figure 19: Examples of methanol vaporiser installations in a) a conveyor and b) a bell furnace

as shown in Figure 19. A methanol vaporiser is a good solution in all cases where the methanol cracking occurs within a limited volume such as in small furnace rooms.

Injectors and gas inlets should be located away from exhaust gas outlets, sample gas outlets as well as away from any oxygen probe.



Figure 20: Schematic principles of a) exo- and b) endogas generators and c) an ammonia cracker/dissociator

4.6 Nitrogen and external atmosphere generators

By causing air to react with a hydrocarbon (propane or natural gas), it is possible to produce the generator atmospheres commonly known as RX, DX and HNX atmospheres, or endogas, exogas and monogas respectively. Cracked ammonia (DA) is also made in a type of gas generator. Figure 20 shows the principle design of these generators. Each generator can vary the gas composition, but only within a range that is dictated by the combustion process. Thus, the output flow rate can be varied only within restricted limits, in turn limiting the types of materials that can be heat treated within that atmosphere.

Typical generator atmosphere compositions are given in Table 8. The compositions given are those at the outlet of the external gas generators. These atmosphere compositions will change when the gas enters the hot furnace because of the reaction with air and oil vapours that are present. The composition will also change because a new chemical equilibrium composition will be established determined by the furnace temperature itself. This has particular importance for dried exogas, which has a non-equilibrium composition after the drying step. When the exogas is brought to the high temperature in the furnace, water will be produced through the reaction

$$CO_2 + H_2 \rightarrow H_2O + CO$$

The resulting atmosphere inside the furnace will accordingly have a considerably higher water content than the exogas coming out of the generator.

Endogas is produced in a reaction between air and a hydrocarbon, commonly natural gas and sometimes propane. These gases are mixed and fed via a blower into a retort heated to approximately 1000 °C (1830 °F). The retort is filled with a nickel catalyst to enable a complete reaction between the hydrocarbon and the oxygen in the air. The air/ hydrocarbon ratio is chosen so that the hydrocarbon mainly reacts to form CO and H₂ according to the principal reactions:

$$C_3H_8 + 7.2 \text{ Air} \rightarrow 3CO + 4 H_2 + 5.7 N_2$$
 with propane as the hydrocarbon

١O

 $CH_4 + 2.4 \text{ Air} \rightarrow CO + 2 H_2 + 1.9 N_2$ with methane as the hydrocarbon.

Endogas is a reducing atmosphere with a controllable carbon concentration.

For exogas production, a higher air/hydrocarbon ratio is used, which results not only in CO and H_2 but also in H_2O and CO_2 production. The reaction between air and hydrocarbon is exothermic and does not require a catalyst. Air/natural gas ratios vary typically from 7 to 9. The resulting exogas is dried to lower the water vapour concentration. Exogas is the cheapest generator gas but the least reducing atmosphere with the lowest carbon activity of all generator atmospheres. Consequently, it can be used for heat treatment and brazing of copper and of steels for which no carbon control is required.

25

Table 8. Typical atmosphere compositions

Method	Vol% of the o	ol% of the different atmosphere constituents					
	N ₂	H ₂	СО	CO ₂	H ₂ O	CH ₄	
Exogas (from natural gas, dry)	Balance	7	6	7.5	0.5	0.25	
Endogas (from natural gas)	Balance	40	20	0.4	0.1	0.15	
HNX (monogas)	Balance	7	5	0.1	0.1	0.1	
DA (dissociated ammonia)	25	75					

Monogas is a high-purity atmosphere with low concentrations of water vapour and carbon dioxide. It is obtained by cleaning exogas thoroughly with respect to these oxidising gases. The equipment needed for this is costly and requires extensive maintenance. The resulting atmosphere composition is typically 2–20 vol% CO + H_2 , the rest being nitrogen. It is reducing and has a controllable carbon concentration.

An ammonia cracker consists of a heated retort, in which ammonia dissociates to a 25 vol% nitrogen/75 vol% hydrogen gas mixture by the reaction

 $2 \text{ NH}_3 \rightarrow \text{N}_2\text{+} 3 \text{ H}_2$

It is important to regularly maintain the ammonia cracker to assure proper dissociation of the ammonia. Otherwise, there is the risk that un-cracked ammonia leaves the cracker and causes unwanted nitriding of parts in the furnace.

5. Atmosphere control.



Figure 21: Schematic illustration of atmosphere/metal interaction (left) and expressions for oxygen, carbon, nitrogen and hydrogen activities in the atmosphere (right)

In a neutral atmosphere, there are no net reactions between atmosphere and metal. The same atmosphere may be neutral towards one alloy but active towards another alloy. There are several possible reactions that may occur between the gas species in the furnace atmosphere and the metal surface. However, it is possible to reduce the problem of atmosphere control to control of the elements oxygen and carbon present in the atmosphere. As indicated in Figure 21, the atmosphere composition control is based on analysis with respect to O₂, CO, CO₂, H₂O and H₂. The atmosphere carbon concentration can, as an example, be controlled by analysing the atmosphere's CO and CO₂ concentrations.

5.1 Atmosphere constituents and their functions

To avoid the negative effects of oxidation, carburising, decarburising or nitriding, the atmosphere must be neutral with respect to the alloy concerned. Neutrality implies that no net reactions occur between the metal/alloy and the atmosphere elements oxygen (0) and carbon (C). Reactions with nitrogen (N) and hydrogen (H) must be considered in certain cases. Figure 21 shows that these four elements may be

present in the furnace atmosphere as the gas molecules oxygen (0_2) , hydrogen (H_2) and nitrogen (N_2) , but preferentially as elements in multi-atom gaseous molecules such as carbon monoxide (CO), carbon dioxide (CO_2) and water vapour (H_2O) . In industrial practice, it is often easier and more reliable to analyse and control the concentrations of the multi-atom species CO, CO₂ and H₂O instead of directly analysing the O₂ and C concentrations.

The furnace atmosphere can principally be divided into a neutral gas and an active gas. The neutral gas generally is nitrogen. The active gas is usually a blend of carbon monoxide (CO), hydrogen (H_2) and hydrocarbon (C_nH_m) . The active gas can be reducing, oxidising, carburising or decarburising with respect to the heat-treated alloy. As seen in Table 9, the reducing effect of hydrogen (H_2) is balanced by the oxidising effect of water vapour (H₂O). The reducing and carburising effect of carbon monoxide (CO) balances the oxidising and decarburising effect of carbon dioxide (CO₂). Keeping a constant balance between oxidising and reducing or carburising and decarburising species is the basic principle utilised for atmosphere control.

Table 9. Atmosphere constituents and their action

Active gases				Neutral or inert gases
Reducing	Oxidising	Carburising	Decarburising	
H ₂ **	H ₂ O	CO	H ₂ O	N2*
СО	CO ₂	C _n H _m ***	CO ₂	Ar
	02		02	Не

' Nitroaen is neutral to most metals but is actively nitriding in the case of titanium, zirconium, stainless steels and some other metals with high affinity to nitrogen. These alloys must therefore be treated in argon, hydrogen or vacuum ** Hydrogen is reducing in the case of oxides and is neutral to most metals, but is reactive to form hydrides with certain metals like titanium and zirconium. *** C_H_m stands for a hydrocarbon: Most common is methane, CH₄.

Truly inert atmospheres are made up only of the noble gases argon and helium. Nitrogen can be regarded as inert to most alloys such as steels and copper alloys. However, it is not inert in contact with metals that have a high affinity to nitrogen. Such alloys will be nitrided, resulting in an increased nitrogen concentration in a surface layer of the alloy. Stainless steels and titanium are the most important examples of such alloys. Argon or possibly helium must be used in those cases.

The neutral or inert part of the atmosphere should:

- purge oxygen or other disturbing gases from the furnace
- eliminate air ingress to the furnace by maintaining a positive pressure inside the furnace
- carry and bring the active gas into contact with the metal surfaces
- dilute the atmosphere concentrations of flammable constituents to assure safety.

The active gas should:

- enable the controllability of the atmosphere
- · contribute to good wetting and a quality brazement
- maintain reducing conditions with respect to the metal oxides that may form during brazing
- maintain a neutral carbon activity (for steel brazing) to avoid decarburising or carburising
- react with flux vapours and eliminate their detrimental effect on the brazing result.

For safety and economic reasons, the amount of active gas is generally kept to the minimum amount required.

Controlled atmospheres used for high-temperature brazing fall into three broad categories: vacuum, reducing and neutral atmospheres, as shown in Figure 22.



Figure 22: Joining atmospheres

Reducing atmospheres not only prevent the formation of surface oxides during brazing, but can also reduce and eliminate residual surface oxides which were present before brazing or which formed during the lowtemperature stages of the heating process.

Vacuum is in this context considered a controlled atmosphere. Vacuum acts like an inert gas in the way that there are no gas species that can cause detrimental oxidation or other reactions with the base and filler metals. Vacuum is active in that the remaining surface residues on parts to be brazed are removed by vaporisation and the vapours are pumped out of the furnace. At high enough temperature and low enough pressure, oxide removal by dissociation is possible. Clean surfaces ensuring good brazeability are achieved in this way.

In addition to the chemical action, the atmosphere also influences heat transfer during heating and especially during post-braze cooling. The atmosphere composition, type of gas, pressure and the flow velocity of the gas will influence the heat transfer rate.

5.2 Atmosphere influence on wetting and spreading

An atmosphere with low oxygen and moisture levels will allow the filler metal to melt and flow into even very tight joint clearances. Oxygen or moisture present in the joining environment will negatively interfere with wetting. As the oxygen and moisture levels rise, they impede filler to flow and degrade the joint quality and strength. With reference to Figure 2, the atmosphere influences mainly the surface tension γ_{sv} (solid/vapour) and to some extent γ_{tv} (liquid/vapour) but not γ_{sL} (solid/liquid). Wetting is improved by establishing a clean, metallic and oxide-free base metal surface, which has the effect of increasing the surface tension γ_{sL} .

Area of spread is a way to measure wetting. A solid braze alloy is placed on a strip of base metal. The assembly is put into a furnace and the temperature is increased until melting and wetting occurs. After cooling, the diameter of the solidified braze alloy is measured. Figure 23 shows principally how wetting, measured as the area of spread, significantly decreases with increasing oxidising power of the atmosphere. Too reducing conditions (= low value of the ratio H_2O/H_2) may lead to excessive wetting. Hence the wetting angle Θ approaches 0°, leading to excessive braze alloy flow, to the point that it flows out of the joint and creates discoloration. The effect is sometimes called flashing. The oxidising/reducing power of the brazing atmosphere, measured by the H_2O/H_2 ratio, accordingly must be controlled within certain limits. The "process window", indicated in Figure 23, is specific for each braze alloy/base metal combination, for a high quality brazement to be the end result.



Figure 23: Principal variation of "Area of spread" for copper on steel in atmospheres with various $\rm H_2O/H_2$ ratios

Table 10. Atmospheres for brazing, compositions in vol% (adapted from [3])

In situ gas mixing							
Atmosphere	Vol%				Braze allo	У	Base metal
	H ₂	N ₂ /Ar	C0	CH ₄	_		
Nitrogen		100			Al/Si,		Aluminium,
					Cu/Sn/Ni	/P	copper
Nitrogen + hydrogen	1-75	25-99			Cu/Ag, Cu	/P, Cu/Zn, Cu, Ni	Copper, brass, carbon and low-alloy steels, stainless steels
Nitrogen + methanol or nitrogen + endothermic/ exothermic gas	2-20	70-97	1-10	0.5-5.0	As above		Copper, carbon and low-alloy steels
Nitrogen + natural gas		99.5-95			As above		Carbon and low-alloy steels
Hydrogen	100				As above		Steels, stainless steels, brass
Argon + hydrogen	1-75	25-99	_		As above		Titanium, zirconium, nitrogen-containing steels
Vacuum							
Vacuum > 2.5 mbar					Cu/Ag, Cu	/P	Соррег
Vacuum 0.5–2.5 mbar					Cu/Ag, Cu	/P	Copper, low-carbon steel
Vacuum 0.001–0.5 mbar					Cu/Ag, Cu	/Р	Copper, low-carbon steel, low-alloy steel
Vacuum <0.001 mbar					Cu/Ag, Cu	/Р,	High-alloy steel,
					Ni, Ag, Au	, Al/ Si, Ti	aluminium, titanium
Vacuum					Various		Be, Mo, Nb, Ta, V, Zr, ceramics, carbides
Externally generated atn	nospheres						
	Vol%						
Atmosphere	H ₂	N ₂	CO	CO ₂	H ₂ O	Braze alloy	Base metal
Exothermic gas, lean	5	75	5	5	0.5	Cu/Ag, Cu/P, Cu/Zn	Copper, low-carbon steel
Exothermic gas, rich	15	75	10			As above + Cu	Copper, low-carbon steel
Endothermic gas	40	40	20	0.3	0.7	As above	Copper, low- and high-
						+ Cu	carbon steels, low-alloy steels
Monogas	7	87	5	0.5	0.5	Cu/Ag, Cu/P, Cu/Zn	Copper, brass, carbon and low-alloy steels
Dissociated ammonia (NH ₃)	25	75				As above + Ni	Copper, brass, carbon and low-alloy steels, stainless steels

For wetting of ceramics and glass, it may be necessary to add oxidising gases such as air, water vapour or carbon dioxide in order to promote wetting by achieving what is called reactive brazing.

Braze alloy suppliers can give guidance on the atmosphere compositions that work best with their products. Additionally, reactions with the base material, availability of the specified atmosphere and furnace compatibility must be taken into consideration. For example, a furnace must be configured for flammable atmospheres before hydrogen or carbon monoxide additions can be introduced. Disregarding these precautions can produce unsafe working situations. Further information on this topic is presented later on in section 6 "Safety". Table 10 presents a few examples of commonly used atmospheres for some combinations of base metals and braze alloys.

The reasoning in the following paragraphs on the atmosphere control of oxygen potential, carbon and nitrogen activities is valid only in thermochemical equilibrium. This means that all reactions in the gas, between gas and metal, and in the metal are fast enough to reach chemical equilibrium. The assumption of chemical equilibrium between gas and metal is approximately valid in practice for heat treatment at a high temperature, say above 800 °C (1472 °F), for a long enough time at heat treatment temperature, of the order of at least 10 minutes, and in N₂/CO/H₂ atmospheres.

For N_2/C_nH_m (C_nH_m being a hydrocarbon such as methane, CH_4 , or propane, C_3H_8) atmospheres, the equilibrium assumption is no longer valid. Because of the slow reaction rate, atmosphere control must then be based upon empirical results and kinetics.

5.3 Oxidation control

The oxidation of a pure metal, Me, is expressed by the chemical equilibrium reaction

$$Me + 1/2 O_2 \rightarrow MeO$$
 (A)

with the equilibrium constant

$$K_{A} = 1/P_{0}^{1/2}$$

(Assuming that the activities of metal and metal oxide can be approximated to unity).

The oxygen partial pressure value, P₀₋, above which oxidation occurs, and below which the metal stays non-oxidised, is well known for each metal. For each metal oxide, that pressure is a function of temperature and the explicit value is found in chemistry handbooks, tables or databases. Oxygen equilibrium partial pressures are often shown in a diagram referred to as the Ellingham or Richardson diagram. A faster, more precise and modern way is to calculate the oxygen equilibrium pressure with the help of modern databases and computer programs. As an example, Figure 24 displays the equilibrium oxygen partial pressure as a function of temperature for the metal oxides of copper, iron and chromium calculated using the Thermo-Calc program [9]. The three metals, copper, iron and chromium, are profoundly different as regards their sensitivity to forming oxides. Copper is a fairly noble metal that is resistant to oxidation, whereas chromium oxidises at extremely low oxygen partial pressures. The demands on the atmosphere with respect to reducing power are accordingly increased in the order: copper \rightarrow steel \rightarrow stainless steel. Consequently, the atmosphere oxygen partial pressure must be adjusted in relation to the heat-treated or brazed metal to yield a bright surface.



Figure 24. Relation between oxygen partial pressure (atm) and temperature for metal/metal oxide equilibrium for copper (Cu), iron (Fe) and chromium (Cr) (calculated by Thermo-Calc [9])

The partial pressures of oxygen needed to oxidise metals at brazing temperatures are very low, ranging from approximately 10^{-6} atm (=1 ppm) to 10^{-30} atm (= 10^{-24} ppm). These very low values are unrealistic as measurable values in the sense that there are no free oxygen molecules to be measured at partial pressure of the order 10^{-30} atm. (The oxygen content of the brazing atmosphere, even using cryogenic-purity nitrogen as the source, may exceed the acceptable level of oxygen to avoid oxidising the surface.) However, although there are no free oxygen molecules present, there are substantial and measurable amounts of oxygen bonded in the molecules CO, CO₂ and H₂O. By measuring and balancing the atmosphere ratios of CO₂/CO or H₂O/H₂ it is therefore possible to maintain the atmosphere oxygen control.

As hydrogen (H_2) and carbon monoxide (CO) are added to a brazing atmosphere, they react with the oxygen and create water vapour and carbon dioxide, respectively, according to the following reactions:

$\mathrm{H_2} + \mathrm{1/_2O_2} \rightarrow \mathrm{H_2O}$	(B)
$(0 + \frac{1}{2})_{2} \rightarrow (0)_{2}$	(C)

Chemical equilibrium in these reactions means that the atmosphere oxygen partial pressure, $P_{0_{2'}}$ can be expressed either by

$$P_{0,}$$
=Constant× $(P_{H,0}/P_{H,})^2$

or by

$$P_0 = Constant \times (P_{co} / P_{co})^2$$

where P denotes partial pressure and is at atmospheric pressure equal to the quantity vol% divided by the factor 100. Quantitative expressions for the equilibrium constants may be found in Linde Gas Expert Edition no. 2 [10].

30





From these expressions it follows that the atmosphere oxygen control can alternatively be realised by using:

- Direct measurement of the oxygen pressure
- Analysis of CO and CO₂
- Analysis of H₂ and H₂O

At brazing temperatures, it is often preferred and easiest to measure the water concentration (as dew point) for determining the oxygen partial pressure. Therefore, by using the relation between oxygen partial pressure and water vapour concentration, Figure 24 can be redrawn, to show oxidation equilibrium as a function of the concentration ratio H₂O/ H₂ as shown in Figure 25. This type of diagram has to be made up for a specific hydrogen concentration. The figure gives examples for 1, 5, 25 and 100% hydrogen respectively. The water concentration is measured as dew point. An example is drawn in the diagrams with lines for the dew point –50 °C (–58 °F) and brazing temperature 1000 °C (1830 °F). At the dew point, -50 °C (-58 °F), only the 100% hydrogen atmosphere will theoretically be clearly reducing towards Cr_2O_3 (the two lines cross each other below the Cr_2O_3 curve). The 25% hydrogen atmosphere is just on the border to be reducing (on the curve). 5% and 1% hydrogen atmospheres will be oxidising (the lines cross each other below the Cr_2O_3 curve).

One method to reduce the oxygen level accordingly is to increase the proportion of hydrogen in the atmosphere. Another way is to increase the total gas flow rate in order to dilute the water concentration to a low enough level. The addition of flux is a third way.

Brazing without flux has great benefits, because cleaning from flux residues is omitted. However, in the case of aluminium brazing under controlled atmospheres, a flux must be added because the stability

of the surface oxide layer is too high as to be removed only by active atmospheres.

As illustrated in Figure 23, too low oxygen potential may result in too good wetting (flashing) and too high oxygen potential in poor or no wetting. Oxidation also may lead to discoloration.

5.4 Carbon control

Atmosphere carbon concentration control is important in steel brazing to avoid decarburising or carburising. Like calculating the oxygen potential, the carbon potential can be calculated for a furnace atmosphere from the knowledge of the CO + CO₂, CO + H₂ + H₂O or CO + O₂ atmosphere concentrations. These gas constituents are controlled by atmosphere analysis using infrared analysis of CO₂, dew point analysis for H₂O or oxygen probe analysis for O₂. Using chemical equilibrium formulas, we can express the atmosphere carbon activity, a_c , in the following alternative ways:

$$a_{c} = K_{H} \times (P_{C0}^{2}/P_{C0_{2}})$$

$$a_{c} = K_{H} \times (P_{C0} \times P_{H_{2}}/P_{H_{2}0})$$

$$a_{c} = K_{H} \times (P_{C0}/P_{0_{2}}^{1/2})$$

Expressions for the equilibrium constants K_{ν} , K_{\parallel} and $K_{\parallel\parallel}$ are found in Linde Gas Expert Edition no. 2 [10]. These expressions are the basis for atmosphere carbon concentration control systems. Instead of carbon activity, the carbon potential is commonly used. The atmosphere carbon potential is defined as the carbon concentration expressed in weight percent of pure iron equilibrated with the atmosphere. (See also Linde Gas Expert Edition no. 1 [11].)

It is possible to generate the carbon potential from any CO/H_2 atmosphere with knowledge of CO_2 , dew point or millivolt value from an oxygen probe. However, oxygen probes may not operate well at brazing temperatures. It is important to observe that the proper atmosphere carbon potential is affected by alloying elements in the steel and corrections will be necessary for steels with high alloy concentrations.

Improper carbon potential control can have the same consequences as improper oxygen potential control as the carbon potential is directly related to the oxygen potential. A too low carbon potential results in decarburising, which normally is negative for the hardness and the strength of the steel. A too high carbon potential leads to carburising, which may lead to an increase in surface hardness and in extreme cases leads to soot deposits that deteriorate the brazeability.

5.5 The atmosphere nitrogen potential

When brazing metals sensitive to nitrogen pick-up such as molybdenum, titanium, beryllium, niobium, tantalum, vanadium and zirconium or stainless steels, nitrogen gas is no longer neutral but may cause detrimental nitriding. The nitriding reaction:

$$N_2 \rightarrow 2N$$
 (D)

means that a nitrogen molecule, N₂, splits into two nitrogen atoms, 2N, which dissolve in the metal. This reaction can be disregarded in most cases, but not when brazing stainless steels, where chromium attracts nitrogen and remarkable amounts of nitrogen may dissolve in the steel as shown in Figure 26. In theory, the surface nitrogen concentration is approximately proportional to the square root of the atmosphere nitrogen concentration as long as nitrogen is going into solid solution in austenite. This corresponds to the curve marked y in the left part of the diagram. For a certain nitrogen activity, a knick point is seen in the diagram at about a nitrogen activity corresponding to $\sqrt{(P_{N_2})} = 0.3$ and $\sqrt{(P_N)} = 0.8$ respectively. $\sqrt{(P_N)} = 0.3$ corresponds to a nitrogen concentration in the atmosphere of approximately 10 vol%. Above this nitrogen activity, there is a change in the slope of the theoretical curve corresponding to ε -nitride formation. In practice, the obtained nitrogen surface concentrations are lower than theoretically predicted. This is because residence time is so short that equilibrium is not reached. At any rate, the risk of detrimental nitriding must be considered when brazing stainless steels, titanium, and other metals that easily form nitrides. The use of argon, hydrogen, mixtures thereof, or vacuum is then recommended. Too high nitrogen potential will for certain stainless steels lead to deteriorated corrosion resistance and to hardness increase. Titanium and zirconium may become brittle if brazed in a nitrogencontaining atmosphere.



Figure 26: Theoretically calculated equilibrium surface nitrogen concentrations as a function of atmosphere nitrogen activity after brazing of two stainless steels at 1050 °C (1920 °F) of a) an austenitic 18% Cr / 8% Ni stainless steel type AISI 304 and b) a ferritic 13% Cr steel type AISI 405 (calculated by Thermo-Calc [9])



Figure 27: Principal atmosphere controlling zones in a continuous brazing furnace equipped with a HYDROFLEX[®] nitrogen/hydrogen system for brazing

5.6 Hydrogen reactions

Hydrogen brazing is common and generally results in excellent brazements. However, in some cases hydrogen can cause unwanted reactions. Brazing of oxygen-bearing copper (not deoxidised) in hydrogen gas can lead to a reaction with the oxygen to form water vapour. Due to the high pressure of water vapour formed and enclosed in the copper, blisters and embrittlement may be a detrimental result.

Certain high-strength steels with an ultimate tensile strength above 1050 MPa [12] can be sensitive to what is generally referred to as hydrogen embrittlement. The embrittlement does not appear during normal mechanical tensile tests, but during static mechanical loading or during slow strain rate tensile tests. Hydrogen concentrations in the steel as low as 2–2.5 ppm can drastically reduce the steel ductility. The embrittlement is caused by atomic hydrogen in highly supersaturated solution. Molecular hydrogen can form at voids or slag inclusions and thereby facilitate crack propagation. Molecular hydrogen is, however, not the cause of embrittlement [12].

Titanium, zirconium, tantalum and some other metals have such a high affinity to hydrogen that metal hydrides are formed. Generally, this leads to embrittlement.

5.7 The atmosphere control system

When the gases enter the furnace, they will react in different ways: with each other, with vapours from the braze paste, with surface contaminants on the parts, with air entering the furnaces through leaks or by drag-in with the parts, etc. The resulting atmosphere composition needs to be controlled to ensure that high-quality brazements are formed. Based on the principles earlier described, an atmosphere control system for realising this must have: 1) a gas analysing system and 2) a flow and gas mixture control system that maintains the atmosphere composition within set limits. In a continuous furnace, these atmosphere composition set points can be different in different zones of the furnace as depicted in Figure 27. In a batch furnace, the atmosphere composition set points correspondingly can change with process time.

With reference to the letter notations A, B, C, etc., in the upper part of Figure 27, there are the following atmosphere requirements in the different zones:

A: The atmosphere should provide support in eliminating hydrocarboncontaining vehicles in the brazing paste or surface contaminants in order to avoid the formation of soot deposits. This can be done by burning off the hydrocarbons in an atmosphere that is slightly oxidising with respect to the hydrocarbons. This principle cannot be used for brazing of for instance stainless steels, for which the requirements are very strict with respect to the reducing power of the atmosphere. Instead, the use of 100% very dry hydrogen will facilitate the vaporisation of hydrocarbons.

B: When the temperature exceeds approximately 500 °C (930 °F), the oxidation rate is noticeable. The atmosphere accordingly must be reducing to avoid oxidation and preferably also to reduce surface oxides that were formed earlier.

C. The atmosphere should maintain reducing conditions and in the case of steels also maintain carbon neutrality.

D. Upon cooling, the risk of oxidation is increased because the oxygen equilibrium pressure over oxides decreases with decreased temperature (see Figure 24). The atmosphere must therefore be highly reducing in this zone.

33

E. In this section, it is enough to have a neutral and oxygen-free atmosphere because the rate of oxidation is at this low temperature decreased to such an extent that atmosphere control based on equilibrium is no longer functioning at temperatures below about 150 $^{\circ}$ C (300 $^{\circ}$ F).

The atmosphere analysis and control is for the system shown in Figure 28 based on dew point analysis in the hot zone and oxygen control in the cooling zone. The result of the analysis is registered in the control cabinet and compared with a set point value for each zone. The difference between the actual value and the set point is the control parameter for the flow control in the flow train. With the closed loop control system, shown in the figure, the brazing quality is ensured through proper atmosphere composition control in the different furnace zones. In the hot brazing zone, this is achieved either by changing the total flow of nitrogen + hydrogen or by changing the mixing ratio of nitrogen/hydrogen. In the cooling zone, the oxygen concentration set point is maintained by controlling the nitrogen flow into that zone. The flow rate is minimised at any time based on the requirement that the atmosphere composition is within set limits at each moment.

Manual analysis is an alternative to automated atmosphere composition and flow control. It is less costly than the automated systems and serves well in cases where brazing and atmosphere conditions are stable and constant. Gas flow rate and mixing are then set to the values that yield the atmosphere analysis set point.

It is possible to achieve different atmosphere compositions along a continuous furnace by proper location of the gas inlets with respect to the type of gas and flow. An example is shown in Figure 28, which shows a concentration profile that is possible to achieve by the injection of proper amounts of nitrogen and hydrogen respectively at the proper locations in a continuous brazing furnace. A high reducing power is created in the hot part of the furnace, where it is needed, by injecting all hydrogen there. At the furnace inlets and outlets, a non-flammable atmosphere is obtained by the dilution with nitrogen at these points.

5.8 Vacuum as atmosphere

Vacuum brazing is used when the primary function of the atmosphere is to minimise oxidation during the brazing process cycle. This is accomplished by eliminating the atmosphere from the vacuum furnace. So, in simple terms, vacuum replaces any protective atmosphere in the brazing process. Nitrogen, argon and sometimes hydrogen and helium are important gases in relation to vacuum heat treatment.

After the first vacuum pumping, nitrogen may be introduced up to about atmospheric pressure. A second vacuum pumping will lower the impurity, primarily the oxygen concentration. Although the gain in lowering the impurity level is highest after the first vacuum pumping, it is possible to reduce it by repeating the backfilling/vacuum pumping sequences.

In furnaces designed with convection, the heating is done in a neutral gas, normally nitrogen or argon, at a pressure slightly above atmospheric



Figure 28: Adaptation of gas inlet locations of nitrogen and hydrogen that results in a concentration gradient along a continuous furnace

pressure. This pressure is maintained up to a temperature at which the oxidation rate starts to be appreciable. The vacuum then is improved.

During brazing of alloys containing metals that easily vaporise, there is sometimes a need to run the process at a certain elevated pressure. The backfill gas, mostly nitrogen, is then added to maintain the pressure at the desired level.

An important function of industrial gases in vacuum brazing is to remove or "break" the vacuum after braze joint formation at the brazing temperature, allowing the parts to cool at a controlled or expedited rate. Instead of a continuous supply of industrial gases to the furnace, the vacuum-brazing furnace therefore requires a discontinuous supply of protective gas provided almost instantaneously at elevated pressures and significant flow rates.

To create a vacuum within a closed container, or vessel, the molecules of air and other gases that reside inside must be removed. This is done by means of a pumping system, which includes the pumps and furnace, together with the associated piping, valves, vacuum gauges/ instrumentation and other components of the vacuum system. Vacuum systems fulfilling this can be classified by the pressure range achieved by their pumping system, as shown in Table 11.

Table 11. Classification of vacuum systems (see Appendix regarding conversions between pressure units)

Quality of vacuum	Pressure ra	inge	Number of oxygen molecules per m ³	
	Ра	mbar		
Atmospheric pressure	10 ⁵	10 ³	5.6x10 ²⁴	
Rough	$10^2 - 10^5$	1-10 ³	5.6x10 ²¹	
Fine	$10^{-1} - 10^{2}$	10 ⁻³ -1	5.6x10 ¹⁸	
High	10 ⁻⁵ -10 ⁻¹	$10^{-7} - 10^{-3}$	5.6x10 ¹⁴	
Ultra-high	<10 ⁻⁵	<10 ⁻⁷	<5.6x10 ¹⁴	

Note: the number of molecules is given for the lower pressure limit

Different vacuum pumps are required to reach the various vacuum levels. The systems are generally configured with three pumps: a positive displacement mechanical pump (often called a roughing pump), a booster pump, and a diffusion pump. The roughing pump is used in the initial pump-down from atmospheric pressure to approximately 3 Pa $(2x10^{-2} \text{ mbar})$. The booster pump is a mechanical pump placed in series with the roughing pump and designed to "cut in", or start at around 9.5 kPa (95 mbar). It is designed to provide higher pump-down speeds in the pressure range of 1.3 kPa (13 mbar) to 0.1 Pa (10^{-3} mbar) . In this intermediate pressure range, the roughing pump is losing efficiency while the diffusion (vapour) pump is just starting to gain efficiency. Finally, the diffusion pump is a type of vapour pump and is used to help achieve even lower system pressures. The diffusion pump is capable of pumping gas with full efficiency at inlet pressures not exceeding 3 Pa (3x10⁻² mbar) and discharge (or fore line) pressures not exceeding 65 Pa (0.65 mbar). The diffusion pump cannot operate independently; it requires a separate pump to reduce the chamber pressure to or below the diffusion pump's maximum intake pressure before it will operate.

In general, the effects of evacuating the atmosphere from a vacuum furnace can be summarised as follows [13]:

A. The effects of evacuating a vessel from 100 kPa (1000 mbar), atmospheric pressure, to 130 Pa (1.3 mbar):

- 1. Removing air with possibly high relative humidity
- 2. Slow change in the composition of the gas remaining:
 - Initially, air is the major component of the gas (certain other contaminants such as oils, grease and water exist on cold surfaces such as vessel walls).
 - b. Eventually, almost all the air is pumped out, the grease and water will continue to evaporate, and their partial pressure will constitute a much larger portion of the total pressure. This is called outgassing.
- B. The effects of evacuating a vessel from 130 Pa (1.3 mbar) to 10 mPa (10^{-4} mbar) :
 - 1. The remaining gases in the vessel have a decreased ability to conduct heat.
 - 2. The voltage required to start a discharge decreases, so arcing is more likely to occur. This will happen only if metal vapour has condensed on furnace interior surfaces.
- C. The effects of evacuation from 10 mPa (10^{-4} mbar) to 0.1 mPa (10^{-6} mbar):
 - 1. Decreasing molecular density

- a. The mean free path of movement of gas molecules becomes greater. Therefore, molecules collide with the sides of the vessel as often as they collide with each other.
- b. Sliding friction increases.

A primary concern in vacuum brazing is the vaporisation of the material being processed. The risk of vaporisation means that vacuum brazing offers a narrower choice of brazing filler metals compared to atmosphere brazing. The vapour pressure of an element is the pressure where the solid and vapour are in equilibrium with each other. It increases with temperature. Figure 29 shows the variation of vapour pressure as a function of temperature for a number of metals. As seen from the figure, cadmium, zinc, magnesium, bismuth, manganese and chromium are elements with high vapour pressures. These elements accordingly vaporise more easily during vacuum. Vaporisation leads to negative effects both because of loss of material from the alloy processed, but even more importantly due to the fact that vapours can easily condense on cold parts in the furnace, causing problems for functionality and maintenance. Brass, which has zinc as the major alloying element, is an example of an alloy which is not suited for vacuum brazing because the zinc would vaporise. The only way to avoid vaporisation is to use a pressure above the vaporisation pressure, although this is counteractive with respect to keeping the best vacuum for a good brazing result.

In vacuum, there is no reducing gas that can reduce metal oxides. Instead, oxides can be removed by dissociation. The oxides will decompose into their constituent elements when heated to sufficiently high temperatures with a vacuum level under the required pressure for oxide dissociation. The pressures that will lead to dissociation are the same as the oxygen equilibrium partial pressures as was shown in Figure 24. That diagram is redrawn in Figure 30 to show the dissociation pressures for some common alloying elements present in base or filler metals. As the metal and the oxygen in the metal oxide dissociate, the oxygen recombines into gaseous form and is evacuated through the vacuum pumping system.

Vacuum is a relative state and does not imply freedom of gas molecules. At an ultra-high vacuum of the order 10^{-5} Pa (10^{-7} mbar) there are still about 1015 gas molecules per cubic metre. Consider a furnace originally filled with air. After pumping down to a vacuum of 10^{-5} Pa, assuming that 21% of those molecules are oxygen as in air, the oxygen partial pressure, P_{0_2} will be about 10^{-11} atm. From a theoretical equilibrium point of view, this is an oxidising atmosphere towards many metals at normal brazing temperature according to Figure 30. If the furnace is purged with nitrogen before the vacuum pumping, then the resulting oxygen partial pressure is reduced to about 10⁻¹⁶ atm. Still, this is oxidising towards metals like chromium. Repeated nitrogen purging and vacuum pumping could reduce this further. That is, however, not the practice, so how could vacuum brazing result in complete bright parts? A major reason is that the rate of oxidation is very slow in vacuum. If, as an example, the oxygen partial pressure is of the order 10^{-24} atm, it means that there are just five free oxygen molecules per m³. Thus, the available oxygen molecules are rapidly consumed, and oxidation processes are therefore stopped. Another reason is that oxygen concentrations are lower than



Figure 29: Vapour pressure curves for metals as a function of temperature (calculated by Thermo-Calc [9]). If the pressure in the vacuum furnace is below the vapour pressure curve for a certain element, then that element will vaporise. Example of the vacuum/ temperature combination 100 Pa/1000 °C indicated in the diagram: Mn, Al, Cu, etc. are stable but Pb, Bi, Ca, etc. will vaporise

predicted with the foregoing simplified assumptions because oxygen is consumed in the oxidation process primarily by the oxidation of graphite. The graphite used for heating elements, charging bricks and furnace chamber will consume oxygen via CO formation. An additional proposed mechanism that may lead to reduction of the chromium oxide passive layer on stainless steel is that carbon dissolved in the stainless steel reduces the oxide according to the reaction

 $MO + C \rightarrow M + CO$

where M denotes the metal and C denotes carbon dissolved in the steel.

Hydrogen has positive effects on reducing power toward oxides and on cooling rate when used as cooling gas. A negative effect is that hydrogen may react with graphite used as heating elements and other parts inside the furnace. Nitrogen, which is the cheapest and most common gas for purging, backfilling and cooling, should not be used when there is a risk of detrimental nitriding reactions with the base alloy or filler metal.



Figure 30: Dissociation pressures (oxygen equilibrium partial pressures) for some metal oxides (calculated by Thermo-Calc [9])

36

5.9 Brazing of different alloys

5.9.1 Steel brazing

Brazing in controlled atmosphere is most common, vacuum brazing being used only in very special cases. A requirement for steels is that the atmosphere in addition to being non-oxidising should also offer carbon control to avoid decarburising. Suitable atmospheres that offer carbon control are nitrogen/methanol, nitrogen/endogas or rich exothermic gas. Most steel brazing uses atmospheres that blend nitrogen with 5 to 30% hydrogen because hydrogen-containing atmospheres produce excellent brazements and because nitrogen/hydrogen systems are easier to set up and maintain.

Nitrogen/hydrogen systems can be run with a very low atmosphere dew point if the brazing furnace is leak-tight and disturbances from air ingress are minimised. This makes the atmosphere reducing towards metal oxides but also results in a low or negligible decarburising effect. The decarburising rate is lowered with lowered dew point.

Atmospheres like endogas and exogas with high amounts of the active components CO, CO_2 , H_2 and H_2O are more difficult to control with respect to decarburising because the carbon control must be based on balancing the atmosphere concentration ratio:

 $(vol\% CO)^2/(vol\% CO_2)$

٥ſ

 $(vol\% CO \times vol\% H_2)/(vol\% H_2O)$

respectively.

The atmosphere carbon potential corresponding to a certain concentration ratio varies with temperature. If the ratio is maintained to carbon neutrality at a specific point in a continuous furnace, this temperature dependence results in the atmosphere being decarburising for positions with higher temperature and carburising for positions with lower temperature.

If the ratio gets a value corresponding to decarburising, then the decarburising rate will be greater than for the low dew point nitrogen/ hydrogen atmosphere because of the high concentration of the decarburising components CO₂ and especially H₂O. This can be illustrated with an example referring to Table 12. The water vapour concentration of endogas (from methane) is 0.41 vol% for the case that the atmosphere is controlled to have a carbon potential of 0.4%C at the temperature 1050 °C (1920 °F). A typical nitrogen/hydrogen atmosphere has no defined carbon potential but a water vapour concentration of 0.01 vol% thus 1/40 of the endogas water content. The decarburising rate can be assumed to be proportional to the water content (and proportional to the difference between the atmosphere and the steel carbon activity). This means that if the endogas composition given in Table 12 is used for brazing of a 0.6%C steel, it will lead to a decarburising rate 40 times faster than for the nitrogen/hydrogen atmosphere with a dew point of -40 °C (-40 °F).

It is not possible to maintain such a low dew point as -40 °C (-40 °F) if there is substantial ingress of air into the furnace. Despite the shortcomings just described, it will in such cases be advantageous to use nitrogen/methanol or endogas, as such atmospheres have a higher buffering capacity because of their high concentrations of CO and H_2 compared to nitrogen/hydrogen systems with typically 5–10% hydrogen.

Table 12. Comparison of endogas and nitrogen/hydrogen atmosphere compositions with respect to water content

Endogas with o	arbon potential 0.4%	C				
Temp.°C	Vol% CO	Vol% H ₂	C-pot., %C	Vol% H ₂ O	Vol% CO ₂	$P_{0,}$, atm
1050	20	40	0.4	0.41	0.1	1.5x10 ⁻¹⁸
Nitrogen/hydr	ogen atmosphere wit	h dew point –40 °C (–	40 °F)			
Temp.°C	Vol% CO	Vol% H ₂	C-pot., %C	Vol% H ₂ 0	Vol% CO ₂	P _{0,} , atm
1050	0	5	0	0.01	0	1.3×10^{-19}



Figure 31: Locations of gas inlets and analysing points for a HYDROFLEX® atmosphere control system



Figure 32: Corrugated steel sheets with chevron pattern and braze alloy foil [14] (courtesy of Swerim AB)



Figure 33: Heat exchangers loaded for brazing [14] (courtesy of Swerim AB). The load to the left marked NA at the top was brazed in argon vacuum. The load to the right marked CA at the top was brazed in argon/hydrogen vacuum

With the HYDROFLEX atmosphere control system, it is possible to maintain a constant atmosphere composition, thereby assuring a stable quality of brazed parts. The HYDROFLEX atmosphere control system can be made to meet different cost- and functionality-related requirements. In all cases, the atmosphere composition is regulated by adjusting the inlet flows of nitrogen and hydrogen to yield the required dew point and oxygen concentration of the atmosphere as depicted in Figure 31. The ratio of H_2O/H_2 , which is a measure of the oxygen potential, is the control parameter for the hot zone and free oxygen is analysed in the cooling zone. The closed loop atmosphere control allows both the nitrogen/hydrogen mixture and the total flow to vary with oxygen potential in the hot zone. In the cooling zone, free oxygen (ppm) is in closed loop control with the nitrogen flow.

5.9.2 Stainless steel brazing 5.9.2.1 Atmosphere brazing

The atmosphere for stainless steel brazing should be reducing to the chromium oxide. For that, hydrogen with a very low dew point is required to promote wetting (see Figures 24 and 25). Atmospheres of 100% hydrogen or blended with up to 25% nitrogen (alternatively cracked ammonia) are effective for most stainless steel brazing. If nitrogen pick-up is to be avoided, then a 100% hydrogen system or an argon/hydrogen system must be selected. Carbon control is generally not an issue with the low carbon content in stainless steels. Hydrogen brazing, meaning brazing in dry 100% hydrogen, has several benefits:

- It is the atmosphere with the highest reducing power, leading to shiny and oxide-free high-quality brazements.
- The atmosphere buffering capability (the ratio H_2/H_20) increases with increased share of hydrogen. Increased buffering capacity makes the atmosphere less influenced by air ingress and leads to less gas being needed to maintain the atmosphere quality.

- Ammonia handling is eliminated.
- Nitrogen pick-up is eliminated.

A HYDROFLEX atmosphere control system for pure hydrogen as described in Figure 28 assures quality and minimises the gas consumption.

5.9.2.2 Vacuum brazing

Vacuum brazing for stainless steels is increasingly used for complex assemblies like heat exchangers. Either nitrogen or argon is used as backfill and cooling gas. Vacuum is effective in stopping the chromium oxide from forming at the elevated vacuum brazing temperatures. Vacuum brazing results in very good wetting of the base alloy by the filler metal.

Stainless steels with higher manganese contents (AISI 200 series) require more extensive cleaning and preparation because manganese forms an oxide that is difficult to reduce (see Figure 30). Some stainless steels, particularly the non-stabilised grades of austenitic stainless steel, can be sensitised to intergranular corrosion when processing occurs between 425 and 815 °C (800–1500 °F). Extended times in this temperature range should therefore be avoided. When brazing martensitic stainless steels, a primary guideline is to ensure that the brazing and the heat treatment cycles are compatible both if carried out separately and concurrently.

Adding hydrogen to the backfill gas is a potential way to lower the oxygen partial pressure in vacuum brazing. This was done in a research project, reported in reference [14], with small heat exchangers as the application studied. Stainless steel sheets with a thickness of 0.3 mm were pressed into a corrugated chevron pattern. The heat exchangers were produced by building up alternating layers of steel and braze foil, with each new layer of steel turned 90° relative to the previous layer

(see Figure 32). Thus, the apexes from each corrugation of one sheet will, during brazing, form a joint with the apexes of the underlying/ overlying corrugation from another sheet. All sheets were put into place, and then held together during the brazing cycle. The braze filler metal was in the form of a 0.04-mm-thick foil.

Figure 33 shows the load of heat exchangers.

Brazing was done with a pulsating pressure between 0.005 and 0.5 mbar controlled by the supply of argon and argon/hydrogen mixture respectively. Figure 34 shows schematically the gas supply system to the vacuum furnace.

The heat exchangers brazed in the two different atmospheres (Ar vacuum and reducing Ar/H_2 vacuum) were pressure tested. The results of the pressure tests showed that brazing in the reducing Ar/H₂ vacuum gave an improvement of more than 10% over the vacuum-brazed samples in burst pressure performance.

The heat exchangers brazed in a reducing Ar/H_2 vacuum atmosphere were cleaner in appearance than those brazed in Ar vacuum, as shown in Figure 35. The brazed joint surface was rough when brazed in vacuum and smoother when brazed in a reducing atmosphere, as seen in Figure 35 b) and d). However, no observable difference regarding the degree of wetting between the two brazing atmospheres was observed when the sectioned joints were studied using light optical microscopy.

It was observed that the last solidified phases in the samples brazed in vacuum were coarser than those formed under brazing in reduced atmosphere. This was true for all joints observed (approximately 45 joints).

Coarse phases are more susceptible to cracking than the finer phases, thus a risk leading to an earlier failure. Such cracking was observed in the samples brazed in vacuum, but in only three of all the joints. Coarser phases are formed at slower cooling rates, fine phases at more rapid cooling rates. In both brazing processes, the furnace was flushed with gas, during the cooling cycle. This gas atmosphere was pure argon following the vacuum braze and a 96% Ar/4% H₂ blend in the reduced







a) Brazed in vacuum



c) Brazed in reducing atmosphere



b) Brazed in vacuum



c) Brazed in reducing atmosphere

38

Figure 35: Macroscopic images comparing the brazing atmospheres (courtesy of Swerim AB). Reducing atmosphere c) and d) appear cleaner and smoother than vacuum atmosphere

39



Figure 36: Photomicrographs of joints in 2545MO stainless steels brazed with BNi-5 (courtesy of Swerim AB): a) showing large precipitates in the thin end of the joint and b) showing the thick end of the joint with precipitates and eutectic structure [15]

atmosphere. The hydrogen gas mixture will increase the cooling rate compared to pure Ar, which may be the reason for the finer structure for the 96% Ar/4% H₂ mixture. In the research report [14] some additional reasons for the finer structure are discussed.

Examples of braze joint microstructures for a highly alloyed austenitic stainless steel designated 254SMO are shown in Figure 36. The joint in Figure 35 a) was brazed with a thin brazing gap and the joint in Figure 35 b) with a thick brazing gap. Large precipitates are seen through the joint with the thick gap.

A new vacuum brazing process called AlfaFusion utilises a special stainless steel filler metal, which is claimed to yield both improved corrosion resistance as well as mechanical strength [16].

5.9.3 Aluminium brazing

Furnace brazing of aluminium can be performed in air or nitrogen or as vacuum brazing. Controlled atmosphere brazing (CAB) has grown more than vacuum brazing mainly due to its adaptability to high-volume serial production. Vacuum brazing is very demanding as regards brazing gap clearances, which must be within close limits to result in good brazements. Vacuum brazing has clear environmental advantages in the absence of hazardous and aggressive fluxes and in the cleanliness of the brazed parts.

Aluminium is brazed at temperatures between 555 and 645 °C (1030– 1195 °F). Any strengthening, whether by heat treatment or cold working, will be lost at these temperatures. Aluminium poses particular brazing challenges since aluminium oxide is an adherent and readily forms oxide, even at room temperatures.



Figure 37: Aluminium heat exchangers entering a CAB furnace (courtesy of SECO/WARWICK S.A.)

5.9.3.1 Atmosphere brazing

The aluminium strip used in making the heat exchangers is a compound material with a base alloy as the core and a thin cladding of a lowmelting alloy that serves as filler metal. Brazing under controlled nitrogen atmosphere (CAB) produces a quality joint and reduces the amount of flux required. The fluxing agent mostly used and specially developed for nitrogen brazing is the NOCOLOK[®] flux. The flux is applied as a liquid solvent onto the parts before brazing. A drying step is required before loading the parts onto the brazing furnace conveyor (see Figure 37). Successful brazing relies on the proper control of oxygen concentration and dew point in the atmosphere. Studies [17] have identified the relationship between oxygen concentration, dew point and flux load, and Figure 38 graphically illustrates this relationship. An oxygen concentration level of 400 ppm inhibited effective brazing. With an oxygen concentration below 50 ppm, a lowered dew point or an increased flux load increased the braze joint quality. One conclusion from the study is that it is possible to reduce the flux load and still have highquality brazements by lowering the atmosphere dew point.

The following real customer case illustrates the different steps taken when designing a good atmosphere control system for aluminium brazing. Oxygen analysis was first carried out at different positions in the customer's CAB furnace when in production. High oxygen concentrations were measured near the furnace inlet but also close to the outlet of the furnace. In the brazing zone, the oxygen level was much lower. Thus, it was clear that oxygen was entering the furnace through the openings and the atmosphere control system should eliminate or lower the effect of these disturbances. An atmosphere closed loop control system capable of keeping the oxygen concentration at the pre-set level was developed. A block diagram of the system is shown in Figure 39.

The HYDROFLEX atmosphere control system is an active flow rate control system based on the requirement that a certain set point for the oxygen concentration is maintained within the brazing furnace. The nitrogen flow rate is always minimised to maintain this oxygen concentration set point. If the actual O₂ concentration is higher than the set point, then the nitrogen flow rate is increased. If the actual O₂ concentration is lower than the set point, then the nitrogen flow rate is decreased. Flow rate adjustments are continuous and stepless by use of mass flow controllers. Separate set points for the O₂ concentration are used for idling, which results in a lower nitrogen consumption during that period. During idling, it is a requirement just to maintain good enough atmosphere conditions for enabling quick reconditioning time when starting production again. The complete system is contained in one cabinet and contains three major parts:

- Gas flow control system for the nitrogen
- O_2 analysing system (dew point meter is an option)
- Control panel

The system in Figure 39 maintains the set point for the O_2 atmosphere concentrations, in the actual case 200 ppm, by adapting the nitrogen flow rate. The nitrogen flow rate increases initially during start-up to get the oxygen concentration down as fast as possible to the set point value, typically 200 ppm. After a while, the flow is reduced to a minimum (=pre-set value) as long as the oxygen level is below set point.

The brazing results when using the closed loop atmosphere control were the same as during normal production with constant nitrogen flow. No leaking radiators were produced, and the overall fault rate was zero percent. This specific mesh belt furnace was originally running with a constant nitrogen flow of 40 m³/h, independent of the kind of radiator brazed. The flow distribution is shown in Table 13, which also shows the flow distribution after installing the atmosphere control system. With the control system in action during production, the average nitrogen flow was decreased to a level of $26 \text{ m}^3/\text{h}$, corresponding to a 35% reduction. A constant oxygen concentration level at about 100 ppm in the brazing zone was maintained during the whole cycle. Another result was that the personnel experienced a good overview of the atmosphere, being more aware of the quality of the total brazing production.

Table 13. Flow distribution before and after installation of the HYDROFLEX atmosphere control system

	<mark>Flow m³/h</mark> Zone 1	Zone 2	 Zone 3	Zone 4	Total flow Furnace
					volume
Before	8	14	14	4	13.8
After	6	8	18 (mean)	2	9.0
			15-35		
			regulating		
			interval		

5.9.3.2 Vacuum brazing

Vacuum brazing is performed without a flux. No post-cleaning is therefore required. An additional benefit with the absence of flux residues is that there is no corrosion associated with entrapped flux. The aluminium parts to be brazed are clad with a high-Mg-concentration braze alloy, which acts as the filler metal. Mg in the cladding alloy acts as an oxygen getter, thereby improving wetting. An example of parts loading for vacuum brazing is shown in Figure 40.

5.9.4 Copper and brass brazing

The atmosphere for copper and brass brazing is usually nitrogen-based, often with up to 15% hydrogen. One special consideration is that oxygen-containing copper cannot be processed in hydrogen-containing atmospheres due to the reaction between oxygen and hydrogen forming blisters or embrittlement.

CuproBraze is a lead-free brazing process for manufacturing of copperbrass automotive and heavy-duty industrial heat exchangers (see Figure 41). The brazing of radiators uses a non-toxic low-temperaturemelting alloy, CuSnNiP (5% Ni, 15% Sn, 5% P, copper balance) developed and produced by the company SAXONIA Technical Materials that works well in nitrogen-based controlled atmospheres [2]. The brazing alloy melts at 590 °C (1110 °F) and has a melting range of 20 °C (68 °F). The core material is specially designed to withstand the high temperature. A normal solder-joined radiator would be annealed at this elevated temperature. The process results in stronger joints and better high-temperature performance of the base alloy. An alliance of companies with their own homepage [18] has been formed to market this technology.

The paste, which has, depending on the application, a metal content of 70%–90%, is applied to the tubes, headers and fins prior to brazing by spraying, sprinkling, roller coating or brushing. The parts are then brazed in an atmospheric continuous mesh belt furnace or in a backfilled vacuum furnace under nitrogen protection. Normal brazing temperature



Figure 38: Relationship between brazeability of aluminium and atmosphere concentration of oxygen and dew point [17]



Figure 39: Principle schematic diagram for an atmosphere control system



Figure 40: All-purpose vacuum furnace Vector® (courtesy of SECO/WARWICK S.A.)



Figure 41: Copper radiators brazed for automotive applications (courtesy of SECO/WARWICK S.A.)

is approximately 650 °C (1200 °F). The atmosphere conditions should be a dew point lower than –40 °C (–40 °F) and an oxygen concentration level of less than 20 ppm.

After brazing, the copper-brass joint is significantly stronger than the solder metal.

The benefit with this process is that it makes it possible to manufacture high-performance products such as charge air coolers that are running under high pressure and elevated temperature. New regulations regarding environmental emissions enhance the use of heat exchangers with higher performance. Copper's higher thermal conductivity has a positive influence on the production capacity, as the heat exchangers are reaching brazing temperature faster.

5.9.5 Brazing of reactive metals

Metals such as titanium and zirconium which react readily with oxygen, nitrogen or hydrogen are preferably brazed either in a dry and clean inert argon or helium atmosphere or in a vacuum. Vacuum brazing at a temperature in the range 900–950 °C (1650–1740 °F) is increasingly preferred as the method which yields the best brazing result. The ease with which surface oxides are formed in ambient air makes it necessary to perform cleaning before brazing. Otherwise wetting will be poor. These metals also tend to form intermetallic brittle compounds with commonly used filler metals like the silver-base filler metals. Alternative

filler metals based on alloys from the elements Ti, Zr, Ni, Cu, and Be are used and still developed.

As for steels, it is important to select a brazing temperature and cycle to result in good base metal properties. Some titanium alloys are heat treated for instance by solution annealing and aging (precipitation hardening). It may in certain cases be possible to combine the brazing and the heat treatment cycle.

5.9.6 Brazing of ceramics and glasses

The greatest obstacles are getting the metal filler to wet the ceramic substrate. Improving the wettability can be accomplished in two ways:

- 1. By increasing the tendency of the ceramic surface to wet by assistance of surface modification techniques like metal coating.
- 2. By changing the chemistry of the braze alloy so it wets the surface. The most common method of accomplishing this is called "Active Metal Brazing". When joining ceramics and glasses, the braze alloys employed are still metallic. In active metal brazing, a metal (usually titanium) is added to the braze alloy to promote reaction and wetting with a ceramic substrate. The addition of the "active metal" results in increased reactivity and considerable improvement in wetting behaviour. The ceramic is wet by the formation of an intermetallic interfacial reaction product which can then form a joint with the braze alloy. Active metal brazing is normally performed in an inert or vacuum atmosphere. The braze alloy liquidus temperature.

Process	Ceramic/metal	Applications	Specific conditions	Typical strength (MPa)
W/Mo-Al ₂ O ₃	Al ₂ O ₃ (>97%)	Vacuum devices,	_	20–200 (bend)
MnO-SiO ₂		electronic packaging		
Active metal brazing	Al ₂ O ₃ , AlN, ZrO ₂ , SiC, Si ₃ N ₄ , Sialons	Vacuum devices, automotive parts	_	100–200 (bend)
Dxide joints from the Al ₂ O ₃ -CaO-MgO-MnO-SiO system	Al ₂ O ₃ , Sialons	Light sources, automotive parts, recorder heads	-	50–200 (bend)
Metal-metal oxide eutectic Cu/CuO	Al ₂ O ₃ , Aln	Electronic packaging		50–150 (bend)
Ceramic frit joints (Al ₂ O ₃ - CaO-MgiO ₂ frit)	Al ₂ O ₃ /Mo	_	H ₂ /N ₂ , 1500 °C (2730 °F), 2 min	150 (3-point bend)
Ceramic frit joints $(Al_2O_3$ - MnO-SiO ₂ frit)	Al ₂ O ₃ /Kovar	_	H ₂ /N ₂ , 1200 °C (2190 °F), 2 min	150 (3-point bend)
Active metal brazing (Ag-13%Cu-18%Ti filler alloy)	316 steel/RBSN	_	Vacuum, 900 °C (1650 °F), 5 min	< 45 (shear)
Active metal brazing (Ag-13%Cu-1.5%Ti filler alloy)	316 steel/PLS SiC (Ti-Mo interlayer)	-	Vacuum (3 mPa), 810 °C (1490 °F), 10 min	< 50 (shear)
W/Mn metallisation (Ag-Cu filler alloys)	Al ₂ O ₃ /Fe-Ni-Co	_		80 (4-point bend)
Active metal brazing (Ag-Cu-Ti)	ZrO ₂ /Steel	-	_	109–144 (shear)

Table 14. Examples of ceramic/metal joints and corresponding brazing approach [19]

Another obstacle is the difference in thermal expansion between dissimilar materials. Ductile interlayers, the use of a series of layers deposited upon the surfaces of the parts, are used to accommodate the differences in thermal expansion between the components and minimise the mismatch. Examples of brazing conditions for different ceramic/ metal joints are shown in Table 14.

5.9.7 Brazing of cemented carbides

Wetting of cemented carbides is more difficult than for metals but better than for ceramics, which makes brazing in hydrogen or vacuum the preferred brazing methods. Silver-base filler metals that contain nickel for improved wettability are preferred, but also copper-base filler metals are used. Brazing is performed at a temperature of approximately 770 °C (1420 °F) for silver-based filler metal and 980 °C (1800 °F) in the case of copper-based materials. Different thermal expansion between the cemented carbide, the braze alloy and the alloy to be joined to the cemented carbide causes thermal stresses that may have deteriorating effect. By using a three-layer foil with copper at the centre surrounded by a silver-bearing braze alloy, it is possible to minimise these thermal stresses as shown in Figure 42. The comparatively soft copper will act to lower the stresses in the surface of cemented carbide.



Figure 42: Schematic picture of a trifoil used for joining cemented carbide (courtesy of SAXONIA Technical Materials GmbH)

6. Safety.



6.1 Safety awareness

Safety is a key concern when working with industrial processes. Therefore, any person working in the heat treatment industry including brazing should be aware of the hazards from processes and equipment and apply appropriate safeguards to control the risk at an acceptable level.

In this section, The Linde Group wants to create awareness of potential safety hazards related to gas usage, their sources, and control options in heat treatment-related processes. Avoiding harm to people, society and the environment are important priorities for The Linde Group. This means that we expect all our people to behave and conduct themselves at all times in a manner that safeguards the health, safety and security of people, and protects the environment.

Products and services provided by The Linde Group to customers around the world are measured against high safety standards. But not only the "end" product or service, but rather the whole value chain is considered when it comes to safety issues – starting from gas production and gas supply to gas usage as well as the installation and commissioning of gas application technology.

Before we have a look at the whole value chain, we will focus on the gases used, the potential safety hazards and the related control options.

6.2 Gases used in the process

Gases used in the brazing process are mainly nitrogen, dissociated methanol and hydrogen. Hydrogen may be produced by dissociation of ammonia. Hydrocarbon gases are in certain cases used for carbon potential control.

6.3 Potential safety hazards and their sources

The main hazards related to the used gases and to methanol are:

- Explosions/flammability/fire
- Toxicity and asphyxiation
- Cold burn hazards
- · Pressurised piping and the gas expansion hazard

Some additional hazards related to the use of cold liquid gas are:

- Gas expansion risks
- · Embrittlement of the material in contact with the cold liquid

Some additional hazards related to the use of compressed gas are:

- Pressure increase from heating (fire)
- Leakages

Detailed information on these hazards is found in safety standards and regional and national safety regulations. Only hazards related to heat treatment, brazing specifically, will be further elaborated in this document.

Examples of hazards related to the use of heat treatment equipment are:

- Failure of energy supply
- Failure of atmosphere gas supply
- Flame failure control (burner(s) and pilot(s)) and consequently the
- spillage/ leakage of asphyxiating gases into the room
- Failure/disorder of control systems

45



Figure 43: The flammability triangle

- · Pressure of flow control devices; low- or high-temperature detectors
- Mechanical hazards such as moving parts, cranes, loading and unloading equipment, robots, trucks and forklifts, charging doors, rotating shafts, moving rolls or conveyors, hydraulic leaks, etc.

Hazards related to equipment will not be further elaborated in this document. The focus in the following description is on hazards connected with the use of gas.

Specific hazards concerning brazing are related to the use of filler metals and fluxes. Avoidance of cadmium-containing filler metals is one way to avoid such a hazard.

6.3.1 Explosions/flammability/fire

For ignition or explosion to occur, the following must be present: fuel, oxygen, ignition source (an exclusion here is acetylene which can violently decompose in the absence of oxygen). Flammability risk can be described in relation to the Safety Triangle shown in Figure 43. A triangle of this kind can be devised at a specific temperature and for a specific combustible gas in combination with oxygen. In the shaded area in the middle of this triangle, the gas mixture is flammable. This flammability region broadens as temperature decreases.

The flammable gases commonly found in these atmospheres are hydrogen, carbon monoxide, hydrocarbons, vaporised or dissociated methanol (dissociation produces hydrogen and carbon monoxide), and dissociated ammonia (forms hydrogen and nitrogen). The European safety standard EN 746-3 [20] gives a more definite description of the flammability range: "As a general rule, any gas mixture containing more than 5 volume percent combustibles $H_2+CO+CH_4$, of which methane (CH₄) is not more than 1 volume percent where the remainder of the mixture is non-flammable, is considered to be flammable. Any gas mixture that

contains more than 1 volume percent hydrocarbons (C_nH_m) or 2.5 volume percent ammonia (NH_3), where the remainder of the mixture is non-flammable, is also considered flammable. A flammable gas which contains 1 volume percent or less oxygen cannot itself form an explosive or flammable mixture."

The use of nitrogen to ensure safety during start-up and shutdown of furnaces may be illustrated in relation to Figure 43. When starting from an air-filled furnace, corresponding to the top left corner of the diagram, nitrogen is purged into the furnace until the oxygen concentration is lowered to point C. Fuel in the form of combustible gas is then added, which means that the composition is changed along the line C-S-100% fuel. This avoids entering the flammability region L-S-U. When shutting down, the furnace is first purged with nitrogen down to composition B before opening to air. Nitrogen is also used as a purging gas in alarm situations such as failure of electric power or if the furnace temperature falls below the safety temperature.

An explosion will occur if a flammable mixture of atmosphere gas and air has accumulated in a confined area and is suddenly ignited. This danger exists if flammable gases are being used at a process temperature below auto-ignition 750 °C (1382 °F). The destructive power of the pressure wave from an ignited flammable mixture depends on the amount of gas and the heat of combustion of the fuel gas, the combustion mode, and the configuration of the confinement space. The energy released is absorbed by the surroundings and in the worst case it destroys them. Possible ignition sources are:

- Surfaces with high temperature such as furnace inner walls, electric heating elements, and burners or burner tubes
- Sparks caused by friction or impact, for instance from fans or electric insulators as well as non-spark-free tools
- Catalysers such as soot, sulfur-containing gases, finely dispersed metal particles, chemical reactions between oxygen and fuel gases, electrostatic charging, and local overheating by soot fire
- · Pilot burners and other open burners, lit cigarettes or flame curtains
- Adiabatic heat from compression processes

6.3.2 Toxicity and asphyxiation

Carbon monoxide is highly poisonous and a concentration as low as 400 ppm is harmful. Carbon monoxide enters the blood and takes the place of oxygen in haemoglobin. Carbon monoxide uptake by the body is very fast, about 250 times faster than oxygen uptake, and even very small CO concentrations can be dangerous. Carbon monoxide has no odour, which makes the hazard more serious. Carbon monoxide has the same density as air and will therefore not disperse naturally. Heat treatment shops should therefore ensure that there is good ventilation in the work areas.

When the oxygen concentration in inhaled air is reduced from 21 vol% to 10 vol%, there is a serious hazard of asphyxiation. Oxygen deficiency can be caused by any asphyxiating gas, the most common being nitrogen. An example of this is when repair or inspection is required in a furnace that has been filled with nitrogen. Whenever entering confined spaces, a risk assessment needs to be carried out beforehand and a rescue plan needs to be in place.

The by-products of brazing filler metals and fluxes may produce harmful fumes.

6.3.3 Cold burn hazards

Direct contact with cryogenic liquefied gases such as liquid nitrogen or cold nitrogen vapour will produce effects on the skin similar to burns. Cold burn will also occur when exposed or insufficiently protected parts of the body come into contact with un-insulated pipes or vessels. The skin will stick fast by virtue of the freezing of available moisture, and the flesh will be torn on removal. The wearing of wet clothes should be avoided. Cold burns can be avoided by use of suitable protective clothing, including leather gloves, boots (trousers should be worn outside the boots), overalls and face shields or goggles as appropriate to the work being carried out. There is only the operation alternatively called cryotreatment or sub-zero treatment at which liquid gases, in this case liquid nitrogen, are applied directly in an operation in the heat treatment workshop.

6.3.4 Pressurised piping and the gas expansion hazard

The nitrogen supplied to the furnaces is under pressure. The gas supply should be locked out from the furnace and the pressure in the lines released in a controlled manner prior to performing maintenance on the system. Failure to do so can lead to unexpected releases of energy or the introduction of nitrogen into the furnace. Furthermore, any pipe section designed so that liquid can be trapped inside must be equipped with a safety valve.

6.4 Control of safety hazards

6.4.1 General safety regulations and guidelines

Parts of the international safety standard ISO 13577 [21], for example part 3 about "Generation and use of protective and reactive atmosphere gases", are still under development. It has not yet been possible to come to a completely unified agreement between countries on the exact text of the ISO standard, but there are some specific pages describing special requirements for Japan, the USA and the EU. The intention is that the new ISO standard, when published, will replace regional or national standards. However, the existing European and American standards [20, 22] as well as other national standards will for some time still serve as quidelines.

6.4.2 Explosions/flammability/fire

Measures to prevent oxygen forming flammable and inherently explosive mixtures with the furnace atmosphere are for instance

- Maintain a positive furnace pressure by proper gas flow to eliminate the ingress of air into the furnace
- Vacate the furnace atmosphere from the furnace by controlled combustion of the exit gas
- Use good natural ventilation, especially when controlled combustion of the exit gas cannot be ensured

Use flame curtains and pilot burners at the exhaust when a temperature below 750 °C (1382 °F) does not automatically ignite a flammable mixture. When using flammable gas mixtures, it is required that the furnace temperature is above the ignition temperature. A safety temperature with good safety margins is therefore used in industrial furnaces. In the European standard [20], the safety temperature is defined at 750 °C (1382 °F). The process temperature for brazing lies above this safety temperature. In the case of a temperature drop due to failure in energy supply or electric or burner heating, there must be a control system that automatically closes the valves for flammable gas and opens a valve for nitrogen supply.

When operating furnaces below the safety temperature, which is relevant at the inlet and outlet of continuous brazing furnaces, precautions must be taken to ensure that explosive mixtures are not created. A first precaution is to ensure that fuel concentrations are outside the flammability area. This can be realised either by establishing a non-flammable composition all along the furnace or by injecting nitrogen at inlets and outlets to lower the concentration of flammable gases. A further precaution is to avoid or minimise the amount of oxygen in contact with the flammable constituents.

Any commercially fabricated industrial furnace must comply with the industrial codes of the company where it will be installed. Several emergency safety functions should be integrated into the furnace and they should in an emergency be able to automatically and safely shut down the furnace. Typical situations would include furnace over-temperature or loss of heating, loss of atmosphere, electric system failure, and flame safety. The manufacturing plant should also train its employees on proper procedures for the unexpected or emergency situations that may arise. Hazard reviews and appropriate documentation are mandatory before starting the operation. Modifications to existing systems must be reviewed with respect to their impact on safety.

6.5 Safe use of gases along the value chain

Linde offers various gas supply solutions, which can be tailored to the customer's requirements. As safety is a key concern for Linde, the highest safety standards apply to all gas supply services, the installation of delivery systems and the commissioning of application technology equipment.

Starting with the gas supply to the customer, Linde takes care that every gas supply mode fulfils high safety standards. If the customer requests liquefied gas tank supply for instance, Linde takes the location, its foundations and floor surfaces, the gas tank itself and the gas supply route into safety considerations.

Regarding gas usage, in the case of oxygen for instance, the customer is instructed in safe gas handling. A risk assessment helps to support the customer in handling industrial gases safely.

Regarding the installation and commissioning of gas application technologies, the customer can expect that a robust equipment safety concept is in place. Furthermore, Linde's experts can start with a full review of the process landscape and a diagnosis of existing problems including safety risks regarding changes in the operating systems. A plan detailing how to overcome safety issues is created and implemented together with the customer.

The installation and commissioning process includes, where applicable, careful process diagnostics and tailoring of gas consumption to ensure the correct furnace gas atmosphere and distribution. The maintenance of safety-relevant components and a joint risk analysis and hazard review support this common goal. In addition, Linde experts can provide training on all aspects of the installed solution so that plant personnel can operate the system independently. Of course, Linde engineers can be called on afterwards if the customer requires further assistance.

7. Appendix. Pressure unit conversions.

	$Pa (=1N/m^2)$	Bar	Тогг	Atm
1 Pa (=1N/m ²)	1	10 ⁻⁵	7.50×10^{-3}	0.987 × 10 ⁻⁵
1 Bar	10 ⁵	1	750	0.987
1 Torr	1.33×10^{2}	1.33×10^{-3}	1	1.32×10^{-3}
1 Atm	1.01×10^{5}	1.013	760	1

Prefixes: k = thousand = 10^3 ;

³; Example: 1 kPa = 1 000 Pa

m = millionth = 10^{-6} ; M = million = 10^{6} ; Example: 1 mbar = 0.000001 bar Example: 1 Mbar = 1 000 000 bar

8. Glossary.

Braze alloy: An alternative term for the brazing filler metal.

Base metal: The name for the original pieces. The objective in brazing is to not melt the base metal.

Brazing: Joining of materials by allowing a filler metal to flow into a tight space, or gap, between the materials via capillary action. Bonding results from the intimate contact produced by dissolution of a small amount of base metal into the molten filler metal, without melting of the base metal. The term brazing is used when the filler metal has a liquidus temperature of 450 °C (840 °F) or higher. Brazing is amenable for metals, ceramics, composites and glass.

Capillary action: The physical phenomenon where a liquid gets drawn into a tight space, gap, crevice or joint due to the reduction in surface energy.

Diffusion: The degree to which the brazing filler metal penetrates the alloys with the base metal during brazing.

Eutectic: Term indicating the point where an alloy has a liquidus and solidus occurring at the same temperature.

Filler metal: The material used that becomes molten during the heating process and either 1) is drawn into the gap between the base metal parts by capillary action, or 2) was inserted into the gap as a pre-form, where it melts and stays. When the filler metal solidifies, the joint is considered brazed. The melting point of the filler metal is always lower than that of the base material.

Fillet: A region of brazing filler metal where the various parts of the assembly are joined.

Flash: A brazing defect where excess filler metal exits the joint. Excessive flash may need to be removed in subsequent processing steps for quality or cosmetic reasons.

Freezing: Solidification of the filler metal during cooling.

Flux: A chemical compound applied to the surface of a component to be brazed to prevent the formation of oxides and other undesirable substances; used to allow the brazing filler metal and base metal surface to remain relatively clean while being heated to brazing temperature.

Flow: The ability of molten filler metal to spread over a surface.

Flow-through: A term used to describe the motion of parts moving in a continuous furnace.

Gap: Another term for joint clearance.

Jig: Alignment of a braze joint or the fixturing to ensure that a joint will maintain the desired orientation and spacing during the braze process.

Joint: The area associated with joining of pieces either along an edge or at a junction. The term joint can be used for brazing, welding or soldering.

Liquidus: The lowest temperature at which a metal or alloy is completely liquid on heating.

Pre-form: The physical shape of the filler metal if it is not applied in paste form.

Setting the braze: A term used to describe an intermediate cooling step whereby the filler metal is allowed to cool to a semi-stable (liquid/solid) phase prior to the onset of rapid cooling.

Skull: An un-melted residue of filler metal.

Solidus: The highest temperature at which a metal or alloy is completely solid.

Spacer: Small spheres made of stainless steel or nickel that help fill the gap and allow the filler metal to bridge larger gaps or fill spaces that it would not normally fill.

9. Acknowledgements.

Linde is a trading name used by companies within The Linde Group. The Linde logo and the Linde word are trademarks of Linde AG. CRYOSS[®], ADSOSS[®], MEMOSS[®], HYDROFLEX[®], CARBOFLEX[®], ECOVAR[®] and CARBOTHAN[®] are registered trademarks of The Linde Group. Trademark registrations and their status may differ from one location to another. Copyright © 2019. Linde AG.

All other trademarks are the property of their respective owners.

This is an update of an expert edition published in 2009 [23]. The authors are grateful to SAXONIA Technical Materials GmbH, Hanau, for their technical insight and contributions to this expert edition.



51

10. References.

Authors: Michael Graf, Torsten Holm, Sören Wiberg

- 1. Schwartz, M., 2003. Brazing, 2nd Edition. *ASM International, Materials Park.*
- 2. Technical booklet "Principles of Brazing and soldering", 2nd Edition. October 2013. *Saxonia Technical Materials GmbH.*
- 3. ASM Handbook 6, Welding, Brazing and Soldering, 1993. ASM International, Materials Park.
- 4. Gundel, P., personal communication.
- 5. Hermanek, F.J. An introduction to brazing, brochure. *Alloy Metals, Inc.*
- 6. Brazing Handbook, 4th edition, 1991. *American Welding Society, Miami.*
- 7. Humpston, G. and Jacobson, D.M., 1993. Principles of Soldering and Brazing. *ASM, Materials Park.*
- Edenhofer, B., 1997. Steel Treatment Handbook, edited by G. Totten & M. Howes. *Marcel Dekker, Inc., New York.*
- 9. Engström, A. Thermo-Calc. http://www.thermocalc.se
- 10. Graf, M., Holm, T. and Wiberg, S., 2017. Furnace atmospheres no. 2. Neutral hardening and annealing. *Linde Gas Expert Editions.*
- 11. Graf, M., Holm, T., Malas, A., and Wiberg, S., 2016. Furnace atmospheres no. 1. Gas carburising and carbonitriding. *Linde Gas Expert Editions*.
- 12. Skogsmo, J.U. and Nordänger, S., 1997. Hydrogen embrittlement. *IVF 97823.*
- 13. Herring, D.H., January 2004. What is Vacuum? *Hot Topics in Heat Treatment and Metallurgy.*
- Oliver, J., Lille, C., Pettersson, R. and Nylén, M. Evaluation of Ni-brazed prototypes in stainless & tool steels (VAMP-13). Swedish Institute for Metals Research Report IM-2002-549.
- 15. Lille, C., Chèse, I. and Pettersson, R.F.A. Corrosion of Brazed Joints in Stainless and Tool Steels (VAMP 13). *Swedish Institute for Metals Research Report IM-2001-535.*
- 16. AlfaNova a revolution in heat transfer technology, September 2003. *Alfa Laval press release.*
- 17. Claesson, E., Engström, H., Holm, T. and Schölin, K., May 1995. Nitrogen Flow Optimization System for CAB (NOCOLOK) Furnaces. *VTMS Conference, England.*
- 18. http://www.cuprobraze.com/
- do Nascimento, R.M., Martinelli, A.E. and Buschinelli, A.J.A., 2003. Review Article: Recent advances in metal-ceramic brazing. *Cerâmica 49*, pp. 178–198.
- EN-746-3, 1997. Industrial thermoprocessing equipment Part 3: Safety requirements for the generation and use of atmosphere gases.
- ISO 13577-3. Industrial furnaces and associated processing equipment – Safety – Part 3: Generation and use of protective and reactive atmosphere (in development).
- 22. NFPA 86. Standard for Ovens and Furnaces, 2015.
- 23. Andersson, R., Holm, T., Wiberg, S., and Åstrom, A., 2009, Furnace atmospheres no. 4, Brazing of metals, *Linde Gas Expert Editions*.

Linde AG Gases Division, Carl-von-Linde-Strasse 25, 85716 Unterschleissheim, Germany Phone +49 89 31001-0, info@linde-gas.com, www.linde-gas.com