

Furnace atmospheres no. 2.

Neutral hardening and annealing.



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.

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1. Introduction.

In order to achieve specific properties and the desired surface quality after heat treatment of a steel object, numerous process parameters need to be controlled. A most critical parameter is the composition, function and control of the furnace atmosphere. In annealing/hardening processes, the major function of the atmosphere is to provide the right oxidation and carbon potential in order to produce oxide-free surfaces with no decarburisation. 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 to achieve desired product specifications of steels and metal alloy objects.

The purpose of this expert edition is to deliver a comprehensive overview of annealing and hardening processes with critical influencing parameters in terms of the required equipment and furnace atmosphere in a deep technical way. This expert edition should deliver valuable background information on a complex topic in a structured, single document in order to achieve a higher confidence level in the readers' business decisions. Hardening is normally described separately from annealing. However, since the furnace atmosphere requirements are similar for both processes, they are treated together in this booklet.

Each of the expert editions has a similar content structure. The first part focuses on the process, speaking about the basic principles of different annealing and hardening processes as well as the related properties. The next section focuses on the different types of furnaces and the required equipment in the process. The furnace atmosphere generation and required gas supply are highlighted in the fourth section; the interaction between furnace atmosphere and steel surface and how to control the atmosphere is described in the fifth section. As flammable, asphyxiating and toxic gases are used in annealing and hardening processes, safety issues need to be addressed in the last section; this is an important concern of Linde Gas.

2. Process.

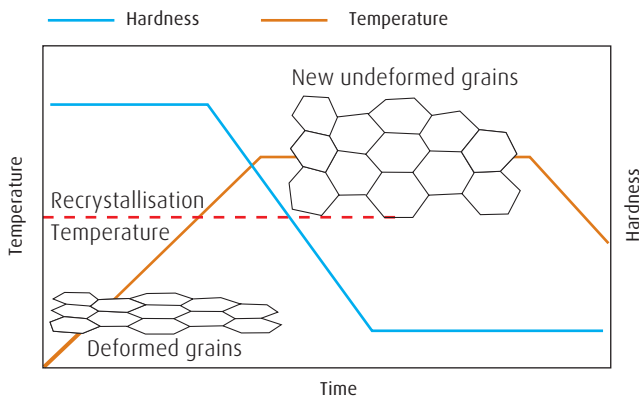


Figure 1: The left part of the figure shows how the crystal grains are very elongated and deformed. The hardness is high. When heating to a high enough temperature, new crystal grains are formed. The hardness is then lowered.

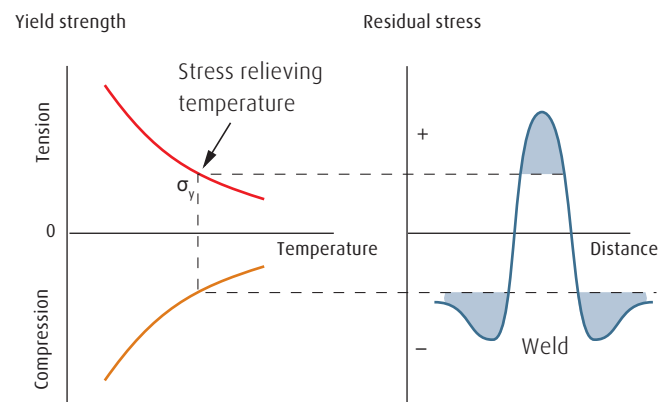


Figure 2: The yield stress of a metal falls with increased temperature (left part of figure). Around a weld there is a residual stress state as shown in the right part of the figure. During stress relieving, the temperature is increased so that stresses within the shadowed areas are revealed due to plastic deformation.

2.1 Annealing processes

In this booklet, we use the term annealing for heat treatment processes which require a neutral (or inert) controlled atmosphere, and where the aim is to produce certain (non-martensitic) microstructures and properties.

2.1.1. Recrystallisation

Recrystallisation annealing is typically done between cold deformation passes, such as in cold rolling of strip, or in wire drawing. During annealing, new undeformed crystal grains are formed. These new grains then consume the deformed crystal grains. The driving force for recrystallisation is given by the stored plastic deformation (dislocation density). Both the nucleation rate and grain growth increase with the degree of deformation. A certain critical degree of deformation is required for recrystallisation to occur. Grain growth rate increases exponentially with increased temperature, whereas nucleation rate increases with lowered temperatures. After annealing, the hardness of the metal is lowered.

During the processing of tube, plate, strip and wire, many intermediate annealings may be required between passes of cold rolling, drawing, or any other cold deformation process in order to soften the material to enable further cold deformation before the strip, wire or tube has reached the final thickness. As the last annealing is done near, just before, or even just after the final cold deformation, thus before the final delivery status, it follows that there is often a bright surface quality requirement on the annealed product. The term bright annealing is then used. Bright annealing is especially required for thin products where oxides or other surface defects may be cold rolled or pressed into the product and cause loss of mechanical properties.

Typical temperatures for recrystallisation annealing of different alloys are given in Table 1. Higher temperatures and/or a longer time at temperature will give a coarser grain size and lower hardness. For specific combinations of degree of deformation, temperature, and time, abnormal grain growth may occur. The result will be abnormally large grains, which is normally detrimental for performance properties.

Recrystallisation annealing is sometimes done as a final treatment to give the alloy/product certain bulk and surface properties. Quench annealing of austenitic Cr/Ni steels is one such example. (See also the section Solution annealing and precipitation hardening.)

2.1.2. Stress relieving

The purpose of stress relieving is, as evident from the process name, to relieve stresses in order to avoid warping or distortions of the parts when in use or at later production stages. Stress relieving is carried out typically on welded parts (see the principle in Figure 2) and on cold deformed or machined parts. Stress relieving is performed at a lower temperature than recrystallisation annealing; compare Tables 1 and 2. Recovery is a process that decreases the internal energy in the metal by dislocation rearrangement (but not annihilation of dislocations as after recrystallisation). There is no notable change in hardness and no visible change in microstructure as viewed in a light or scanning microscope. Its practical importance is that internal residual stresses are removed. If not performed, these stresses may be released uncontrollably and cause distortion or even failure of a ready-made product. Internal stresses also can cause stress corrosion, specifically in austenitic stainless steels and in brass.

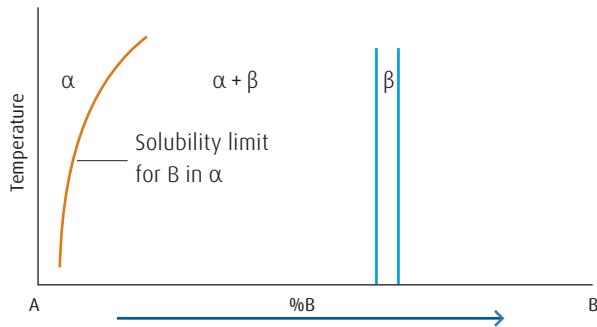


Figure 3: Schematic phase diagram for an alloy of the elements A and B. The element B goes into solid solution in the A-rich α -phase up to a concentration determined by the solubility limit line.

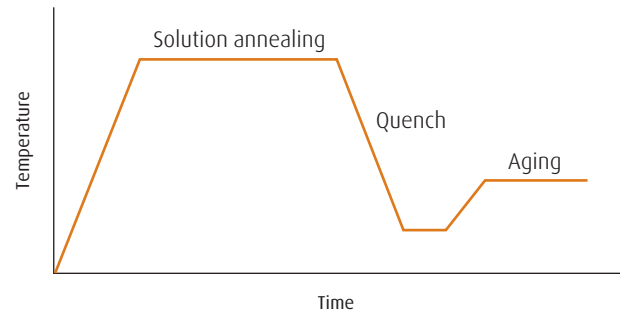


Figure 4: Precipitation hardening. The first step, solution annealing, brings the main alloying element into solid solution. After the quench, the alloying elements are “frozen” in solid solution. The third step, aging, is heating to a temperature which allows diffusion and formation of precipitates.

Table 1. Recrystallisation annealing temperatures

	Temperature	
	°C	°F
Low-alloy steel	650–700	1200–1300
Austenitic stainless steel	950–1150	1740–2100
Ferritic stainless steel	650–1050	1200–1920
Duplex stainless steel	950–1175	1740–2150
Cu-alloys	250–825	480–1520
Al-alloys	260–480	500–900
Ni-alloys	750–1200	1380–2200
Ti-alloys	650–900	1200–1650

Table 2. Typical stress relieving temperatures

	Temperature	
	°C	°F
Low-alloy steel	550–650	1020–1200
Tool steel/High-speed steel	600–750	1110–1380
Al-alloys	200–350	390–660
Ni-alloys	480–1200	900–2190
Cu-alloys	150–350	300–660
Ti-alloys	480–815	900–1500

Examples where stress relieving is used are:

1. after welding,
2. after castings,
3. after rough machining,
4. before final grinding or machining of steel parts later subjected to low temperature surface hardening such as nitriding and nitrocarburising,
5. after any deformation of parts in alloys subjected and sensitive to stress corrosion.

Based on these examples, it is understandable that stress relieving is performed to a greater extent by the manufacturing industry as compared to recrystallisation annealing, which is done more in steel and metal mills.

2.1.3 Solution annealing and precipitation hardening

Solution annealing is a heat treatment process to bring one or several alloying elements into solid solution. The principle utilised is that the solubility of the alloying elements increases with increased temperature. This is illustrated in Figure 3, where the solubility of the element B in the A-rich α -phase increases with increased temperature.

After bringing the alloying element into solution at the solution annealing temperature, there is normally a rapid quench (shown in Figure 4) to keep the solute in solution. After this process step, the alloy is normally soft.

Solution annealing, sometimes called quench annealing, is performed on austenitic Cr/Ni steels to bring chromium into solid solution, which is needed to yield corrosion protection and make the steel “stainless”.

For nonferrous alloys, solution annealing is seldom used as a separate, single process but in combination with a subsequent aging process. The combination solution annealing + aging is called precipitation hardening. There are also some steels, PH (Precipitation Hardening) and maraging steels, which utilise precipitation hardening to produce strength and toughness.

Table 3. Examples of temperatures for solution annealing and aging [1]

Alloy	Solution treatment temperature		Aging temperature		Aging time h	
	°C	°F	°C	°F		
Aluminium						
	Al-Cu	515–535	910–995	160–190	320–375	10–30
	Al-Cu-Mg	495–510	920–950	170–190	340–375	8–16
	Al-Cu-Li	530–860	990–1000	170–190	250–375	12–24
	Al-Mg-Si	520–560	970–1040	160–205	320–400	1–18
	Al-Zn-Mg	465–515	870–960	120–155	250–315	3–24
Copper						
	Cu-Ni-Sn	700–860	1292–1580	350	662	1–6
	Cu-Be	780–1000	1436–1832	300–480	572–896	1–3
	Cu-Ni-Cr	900–950	1652–1742	760	1400	1–2
PH* steels						
	17.4 PH	1040	1904	480–620	896–1148	1–4
	17.7 PH	955	1751	510–595	950–1103	1

*PH=Precipitation hardening

After solution annealing and rapid quenching, the solute is supersaturated in the matrix. By bringing the alloy up to aging temperature, which is low in comparison to solution temperature, the supersaturated solute can precipitate to very small microscopic intermetallic oxides, carbides etc. For the A-B system in Figure 3, the aging process will result in precipitation of the phase β . The alloy hardness is then increased by precipitation hardening. This is an important hardening mechanism for aluminium, copper, nickel and titanium alloys.

2.1.4. Isothermal annealing

Low-alloy (case hardening) steels with low carbon contents, < 0.3 wt-% C, are widely used in the automotive industry for gears and other transmission parts. Uniform machinability, is an important requirement. To yield such good machinability it is common practice to conduct isothermal annealing. The process is performed in two steps, normally in continuous furnaces. The first step is austenitising at 930–940 °C (1706–1724 °F) followed by rapid cooling to 610–680 °C (1130–1256 °F). The second step is holding for several hours at this temperature. This treatment produces a ferritic/pearlitic microstructure with good chip breaking properties for good machinability.

2.1.5. Soft annealing

Soft annealing is used for steels with a fairly high carbon content, > 0.35 wt-% C. The carbon is contained in hard platelets of cementite (iron carbide). This microstructure causes great problems in machining. To produce a microstructure with improved machinability, the steel is heated to a temperature in the range 700–775 °C (1292–1427 °F) or in the range 820–880 °C (1508–1616 °F) for tool and high-speed steels. Holding at this temperature for 2–6 hours is followed by slow controlled cooling. The process transforms the hard abrasive cementite platelets into round, almost spherical cementite, thus improving machinability.

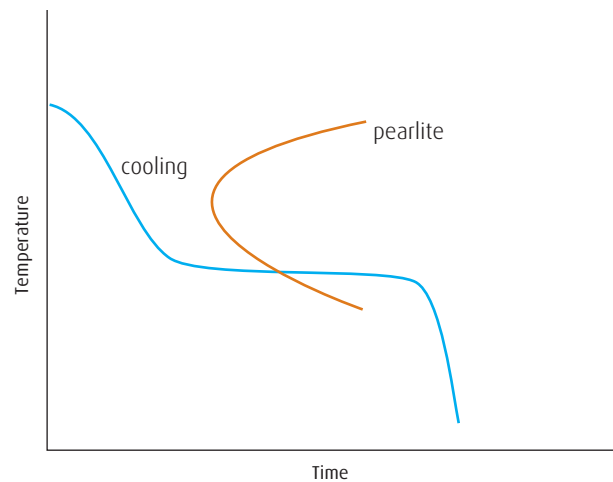


Figure 5: After austenitising, the steel is cooled down to a temperature where a ferrite/pearlite microstructure is formed isothermally. After full transformation, cooling to room temperature is performed.

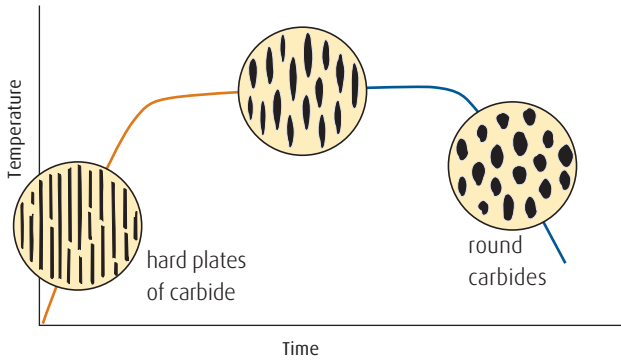


Figure 6: In high carbon steels, the cementite may be in a lamella form (black in the figure). This is unfavourable for machinability. By soft annealing, the lamellas are transformed into round spheroidised form, which is easier to machine.

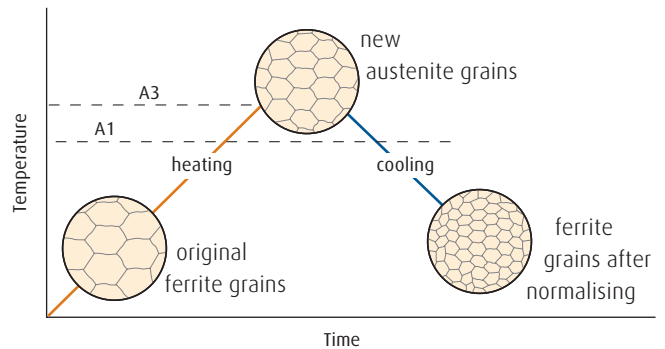


Figure 7: The large crystal grains shown in the left part of the figure could be a result of hot forging or rolling. Normalising means that a refined grain size is formed principally as a result of austenite grain formation upon heating above A3 and ferrite/pearlite grain formation upon cooling below A1.

2.1.6. Normalising

After hot forging, hot rolling, casting, etc. of mild steel, the microstructure is non-uniform and contains large crystal grains. Such a microstructure gives poor strength and toughness. Machinability could also be impaired. The large crystal grains shown in the left part of Figure 7 could be a result of hot forging or rolling. Normalising means that a refined grain size is formed principally as a result of austenite grain formation upon heating above the A3 temperature and ferrite/pearlite grain formation upon cooling below the A1 temperature.

Heating to a temperature in the austenitic region, 800–920 °C (1472–1616 °F), with 10–20 minutes' soak produces new austenite grains from the parent ferrite/pearlite microstructure. Upon cooling at a controlled rate, a new ferrite/pearlite microstructure, which is finer and more uniform than the original, is produced. With a fast final cooling, high mechanical strength can be obtained. Normalising therefore is often the final annealing operation for products like tubes and strip. Normalising is also applied before cold drawing of welded tubes as normalising yields an even microstructure with good cold drawing properties.

2.2 Hardening and tempering processes

Neutral hardening is a heat treatment procedure for steels with the aim of producing a martensitic microstructure. Neutral hardening is a final heat treatment and is mostly performed on ready-made parts. For some low-alloy steels, hardening and tempering are already done in the steel rolling mill.

Hardening involves the steps of heating up to a temperature above A3, where the steel is austenitic, followed by a fast quench. (After hardening there is normally a tempering process, see Figure 8a.) The austenite will transform upon quenching to the hard microstructure martensite if the

quenching rate is fast enough. Fast enough means that the cooling curve has to pass to the left of the ferrite, pearlite and bainite transformation "noses" in the TTT (Temperature, Time, Transformation) diagram schematically shown in Figure 8b.

A martensitic transformation occurs without long-range diffusion (movement) but by small displacements of the C (carbon) and Fe- (iron) atoms less than the interatomic spacing. (Martensitic transformations also occur in the Ti, Ni and Cu-alloy nonferrous systems, but the practical importance is negligible in comparison to the importance of hardening of steels.) The transformation is immediate and not dependent on time. Transformation from austenite to martensite starts at a specific temperature, M_s , and ends at the temperature M_f , which is lower than M_s , see Figure 8b.

M_s = Martensite transformation start

M_f = Martensite transformation finish

The M_s and M_f temperatures decrease with increased total concentration of carbon and alloying elements in the steel. For medium-carbon alloy steels, the following empirical formula can be used to estimate M_s [2]:

$$M_s = 520 - 320 \times (\text{wt}\% \text{C}) - 50 \times (\text{wt}\% \text{Mn}) - 30 \times (\text{wt}\% \text{Cr}) - 20 \times [\text{wt}\% (\text{Ni} + \text{Mo})] - 5 \times [\text{wt}\% (\text{Cu} + \text{Si})]$$

For high-carbon and high-alloy contents, the M_f temperature is below room temperature. Upon quenching, the austenite will therefore not transform completely to martensite, but a certain amount of retained austenite will remain after hardening. Figure 9 shows how the concentration of carbon in the steel affects the amount of retained austenite.

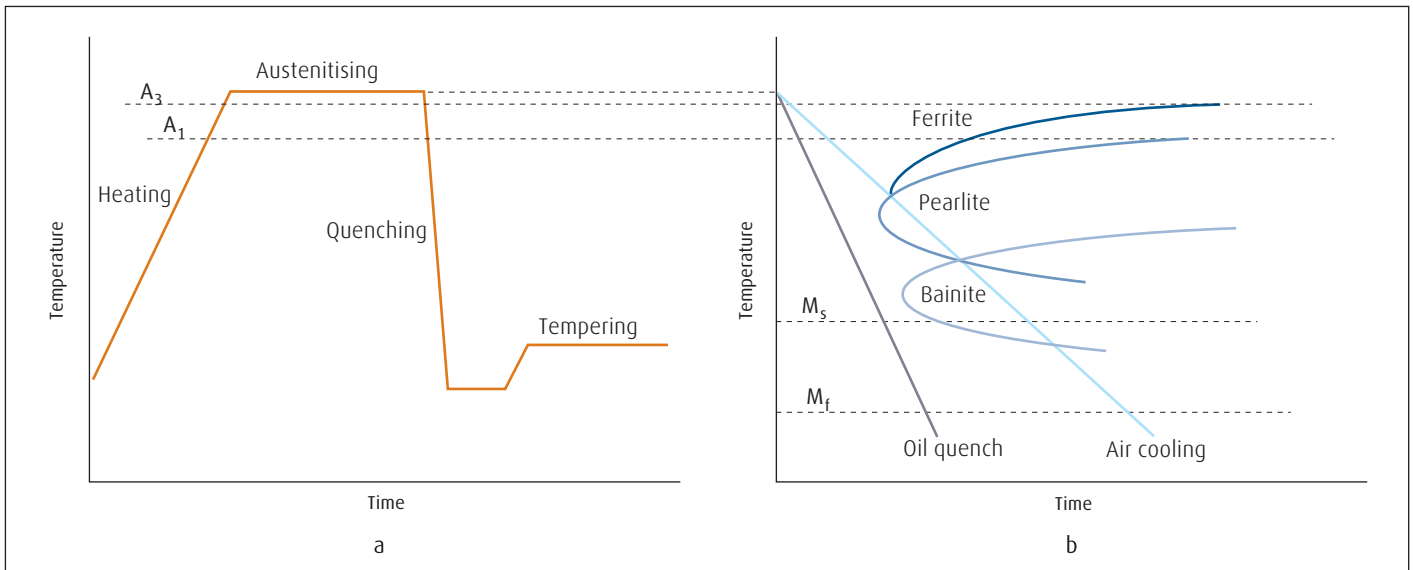


Figure 8: a) Temperature-time cycle and b) its relation to the TTT diagram.

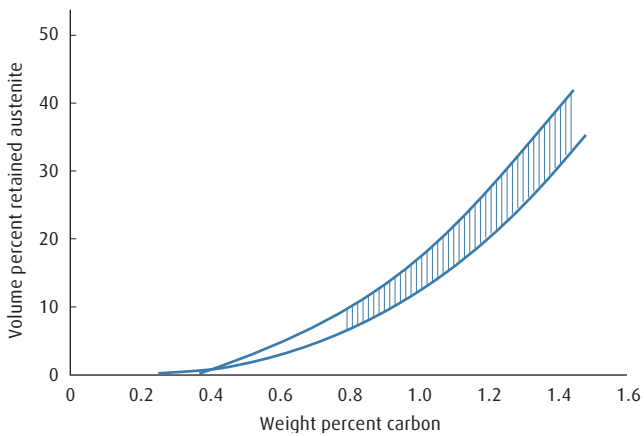


Figure 9: Retained austenite after hardening as a function of steel carbon concentration [3].

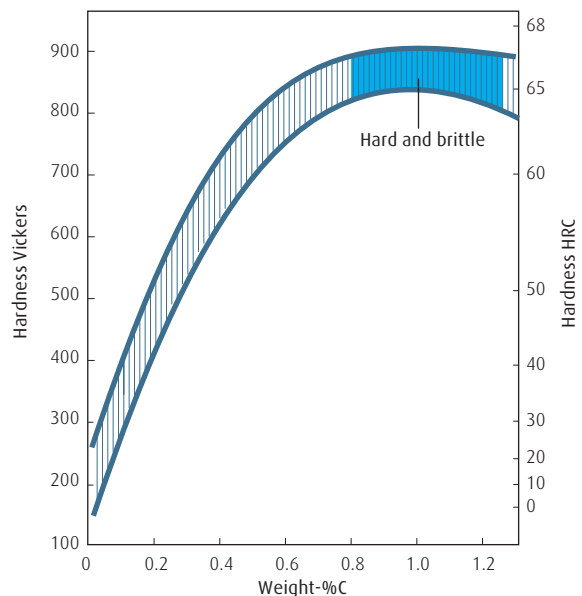


Figure 10: Hardness of hardened steels as a function of carbon content.

The hardness of martensite and of hardened steels increases with increased carbon concentration, see Figure 10. The reason for the hardness drop at carbon concentrations above approximately 0.8% C is that the retained austenite concentration increases. Retained austenite has a low hardness compared to martensite. (It is possible to transform the retained austenite to martensite and thereby to increase hardness by cooling to cryogenic temperature. This is described in other Linde brochures about Sub-Zero Treatments.)

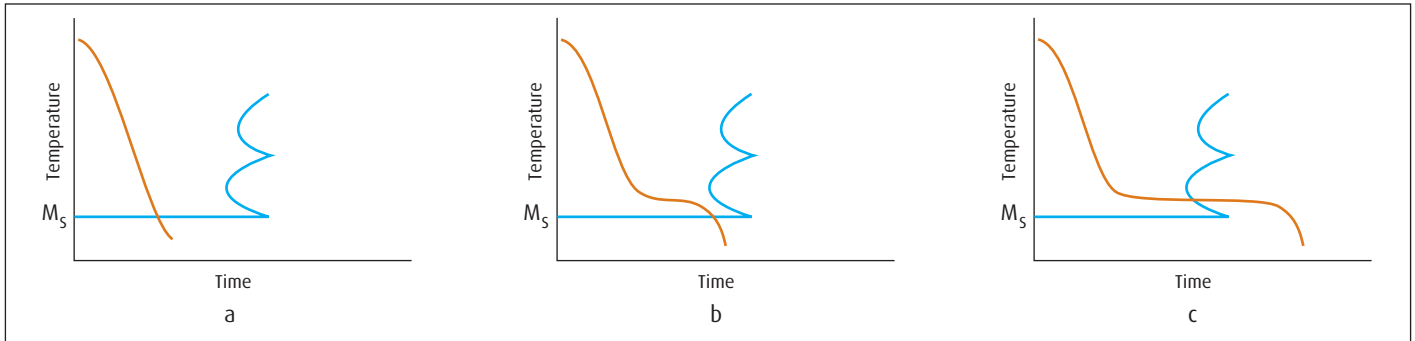


Figure 11: Temperature sequences for a) direct hardening, b) martempering or isothermal hardening and c) austempering.

The hardenability of a steel describes its ability to transform to martensite upon quenching and is related to the total concentration of alloying elements in the steel. High-alloy content yields high hardenability and vice versa. High hardenability means that the steel can transform to martensite even when quenched with modest cooling rates such as cooling in still air. With reference to Figure 8b, this means that the ferrite, pearlite and bainite “noses” are pushed to the right, letting the cooling curve pass to the left of the noses. Conversely, a low hardenability steel requires a high cooling rate in extreme cases by forced water circulation.

The hardening process is mostly performed as direct hardening as illustrated in Figure 11a. This means that cooling is performed directly after austenitising and that the cooling is uninterrupted and continues until the parts have the same temperature as the cooling medium. The cooling medium is mostly a mineral oil for atmosphere furnaces and gas for vacuum furnaces.

In some cases, hardening is conducted as isothermal hardening (also called martempering) as illustrated in Figure 11b. Cooling is initially interrupted at a temperature above the end cooling temperature. High temperature quench oils may be used as isothermal quench baths. More often, salt baths are used, because the bath temperature is too high for most mineral oils. Isothermal hardening is performed on high-alloy tool steels in order to reduce distortions and to avoid quench cracks upon quenching.

Austempering, Figure 11c, is a process normally described under hardening although the process produces a bainitic microstructure. Salt quench baths are mostly used for this. The holding time in the austempering quench bath is long, typically of the order of several hours for complete isothermal transformation of austenite to bainite.

The as-hardened martensitic structure is brittle because of high hardness and high micro stresses. Therefore, hardening is generally followed by a tempering heat treatment to improve ductility. Tempering involves heating up to a temperature in the range 150–650 °C (300–1200 °F). Upon heating, the internal micro stresses are lowered and the carbon in the martensite is precipitated as transition carbides. Strength and toughness are adjusted by choosing different tempering temperatures. Increased tempering temperature for low- and medium-alloy steels results in reduced hardness and increased ductility. High-alloy tool steels and high-speed steels develop secondary hardening due to precipitation of fine dispersion of carbides. This is illustrated in Figure 12.

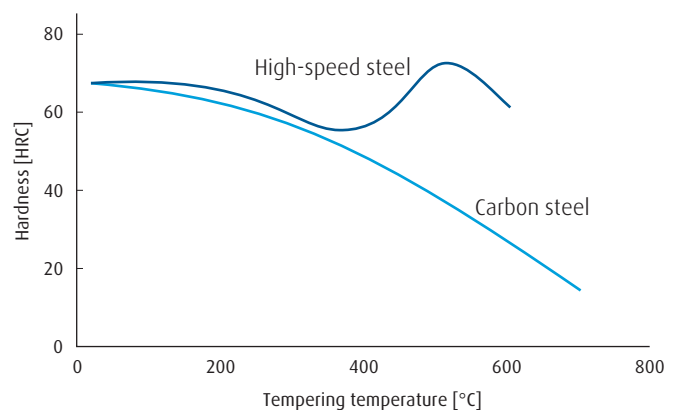


Figure 12: Principal tempering curves for a low-alloy and a high-speed steel.

3. Furnace and equipment.

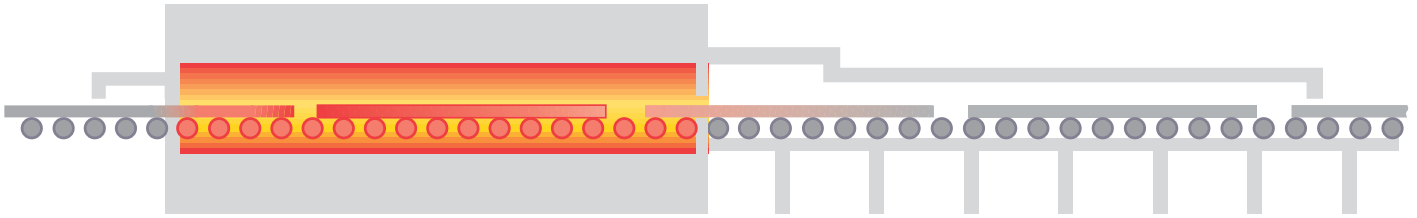


Figure 13: Schematic view of a roller hearth furnace.

Annealing is done both in steel and nonferrous milling plants, usually in connection with cold deformation, such as rolling. In the manufacturing industries, annealing furnaces have a wide range of sizes and designs from a small box furnace in a tool room, to a big continuous isothermal annealing furnace in the automotive transmission workshop, and from an advanced vacuum furnace in the aerospace industry to air-filled furnaces for lower-demand industries.

The main difference between annealing and hardening furnaces is the design of the cooling section. The cooling section in annealing furnaces is designed to give a controlled cooling rate to result in the required properties of annealed products. For hardening, a rapid quench is required after heating to austenitising temperature. Hardening furnaces are therefore equipped with quenching equipment. A few examples of furnaces used are described below.

3.1 For annealing

The most common continuous annealing furnace is the roller hearth furnace, which is used for continuous annealing of tubes, bars, strip, and wire coils, see Figure 13.

The products run on rollers through the furnace. In order to minimise disturbances from air entering the furnace, there is an option, especially for wire and strip coils, to have charging vestibules at the inlet side, which are evacuated or purged with nitrogen before the coils are transferred into the heating zone of the furnaces. As illustrated in Figure 13, the cooling section often has a longer length than the heating section.

Pusher furnaces are common for isothermal annealing, for instance of forgings to improve machinability. These furnaces have a forced convection cooling section between the heating and the isothermal soak sections.

Wire annealing is often carried out in tubular strand furnaces. The wires are fed through several parallel tubes, which are mounted through the furnace. Strips are also continuously annealed in vertical or horizontal furnace lines.

3.2 For hardening

Roller hearth furnaces are also used for hardening, for instance of bearing rings, which are transported by the rollers. At the end of the furnace there is a quenching bath usually containing agitated mineral oil. For small parts like bolts, nuts, etc., the conveyor furnace is commonly used, see Figure 14. The parts are transported through the furnace on a movable conveyor. At the end of the conveyor, the parts fall down into the quench bath. A second conveyor transports the quenched parts further for washing and tempering.

Other examples of continuous hardening furnaces are shaker hearth, rotary retort and pusher furnaces.

The integral sealed quench or multi-purpose furnace, Figure 15, is the "work horse" for batch load hardening in the manufacturing industries. The heating chamber is separated from the quench chamber by an internal door. The parts are loaded in baskets, which are loaded into the heating chamber. After austenitising is completed in the heating chamber, the intermediate door opens and the load is transferred down into the oil quench bath on an elevator.

Bottom loaded bell type furnace lines with integrated units for quenching are not so common but have advantages for hardening long products. Box and pit furnaces are used in hardening, but are accompanied by separate quench baths, which means that the load has to be transferred in air from the furnace to the quench.

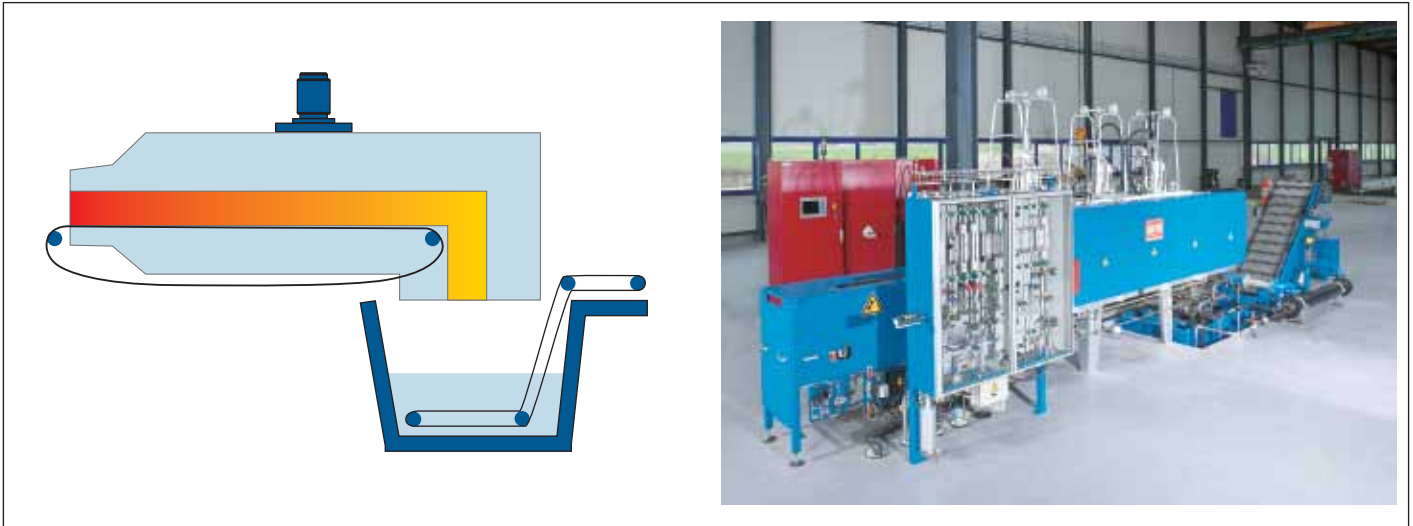


Figure 14: Conveyor furnace for hardening: cross section and installation (Courtesy of Safed, Fours Electrique Delmont S.A.).

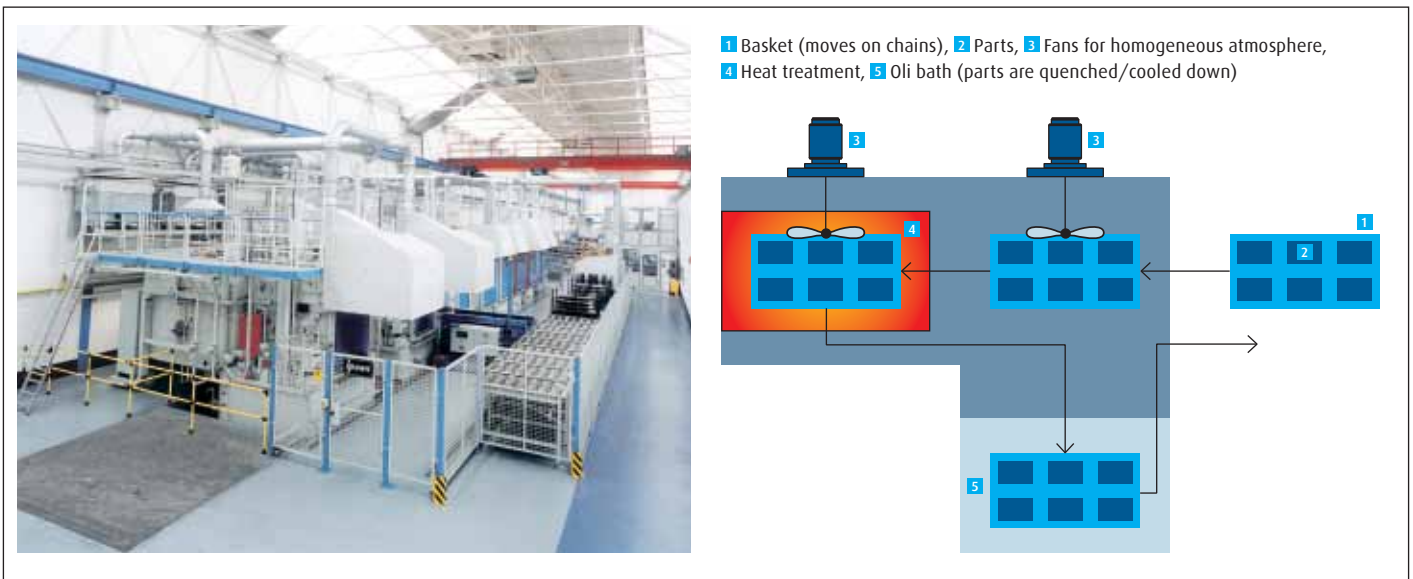


Figure 15: Example of a sealed quench furnace line and charging equipment (left) and cross section of a sealed quench furnace showing the heat chamber and the integrated oil quench bath (right) (Courtesy of Ipsen International GmbH).

3.3 Vacuum furnaces

Vacuum furnaces are increasingly used for annealing and for hardening. Earlier they were mainly used for high value parts such as tools, and aeronautic parts made of super alloys, tool and high-speed steels. Today they have come more and more into use for serial production in hardening of low-alloy steels. However, single-chamber furnaces are still more common, see Figure 16.

The heating cycle in a single-chamber furnace is performed under vacuum. After finalised heating, quenching is done with gas at high velocity and pressure. This means that after the completed vacuum cycle, the chamber is filled for a short time with gas up to an elevated pressure, typically 5 bar. The bottom loaded furnace shown in Figure 16d is used for heavy

parts and is fairly common for annealing and hardening of aeronautic parts. The furnace shown in Figure 16c has a “cold” quenching module separated from the heating chamber, which results in increased cooling capacity compared to a “hot” single-chamber furnace.

Also vacuum hardening for mass production of engineering parts made of medium- or low-alloy steels is possible. The multi-chamber vacuum furnace line shown in Figure 17 is designed for vacuum carburising, but a design on the same principle can be used also for a hardening line. Modern one-piece flow systems integrate heat treatment into the manufacturing work centre. The components are transported individually from each working step to the next working step following the “one-piece flow”-philosophy. A continuous product-flow is generated between soft-machining, heat treatment and hard-machining.



Figure 16: Single-chamber vacuum furnaces:
 a) Cross section of a single-chamber furnace with integrated high pressure gas cooling,
 b) single-chamber furnace (Courtesy of Ipsen International GmbH),

c) One-piece-flow system (Courtesy of ALD Vacuum Technologies GmbH),
 d) Vertical bottom loaded vacuum furnace (Courtesy of Ipsen International GmbH).



Figure 17: A continuous vacuum furnace hardening line (Courtesy of Ipsen International GmbH).

3.4 Atmosphere equipment

3.4.1 High-speed gas injection for improved gas homogeneity

It is essential that the furnace atmosphere is evenly mixed and circulated so that all part surfaces will experience the same effect from the atmosphere with respect to final carbon content and freedom from oxides. CARBOJET® high-speed gas injection is a patented technology from Linde Gas which allows for better gas convection in heat treatment furnaces without ventilators. By injecting small amounts of nitrogen at high velocities into one or several sections of the furnace, CARBOJET creates a movement in the furnace atmosphere to ensure homogeneous gas and temperature distribution. CARBOJET can be installed in both continuous and batch furnaces.

The system consists of one or several CARBOJET lances with piping and flow train. The number of lances is adapted to the furnace size and the existing gas consumption. The lances can be controlled manually or through a CARBOFLEX® control unit. The specially designed lances are made of heat-resistant material to ensure a long lifetime. In order to provide tailor-made solutions, Linde Gas adapts its CARBOJET systems to individual customer needs.

This solution has proven to be very successful in continuous annealing furnaces [4] but also in pit furnaces where significant savings on maintenance costs have been achieved, and a more homogeneous product quality and reduced soot formation have been established [5]. The CFD calculations shown in Figure 19 are made for a case of the installation of two CARBOJET lances in a 6-m-deep pit furnace. It demonstrates how the CARBOJET is able to steer the atmosphere circulation with uniform velocity from the top of the pit furnace to the bottom of the furnace. With the fan, very uneven flow velocities are achieved: they are high towards the top but low at the bottom. Uneven flow means uneven results.



Figure 18: High-pressure nitrogen inlet for the CARBOJET nozzle.

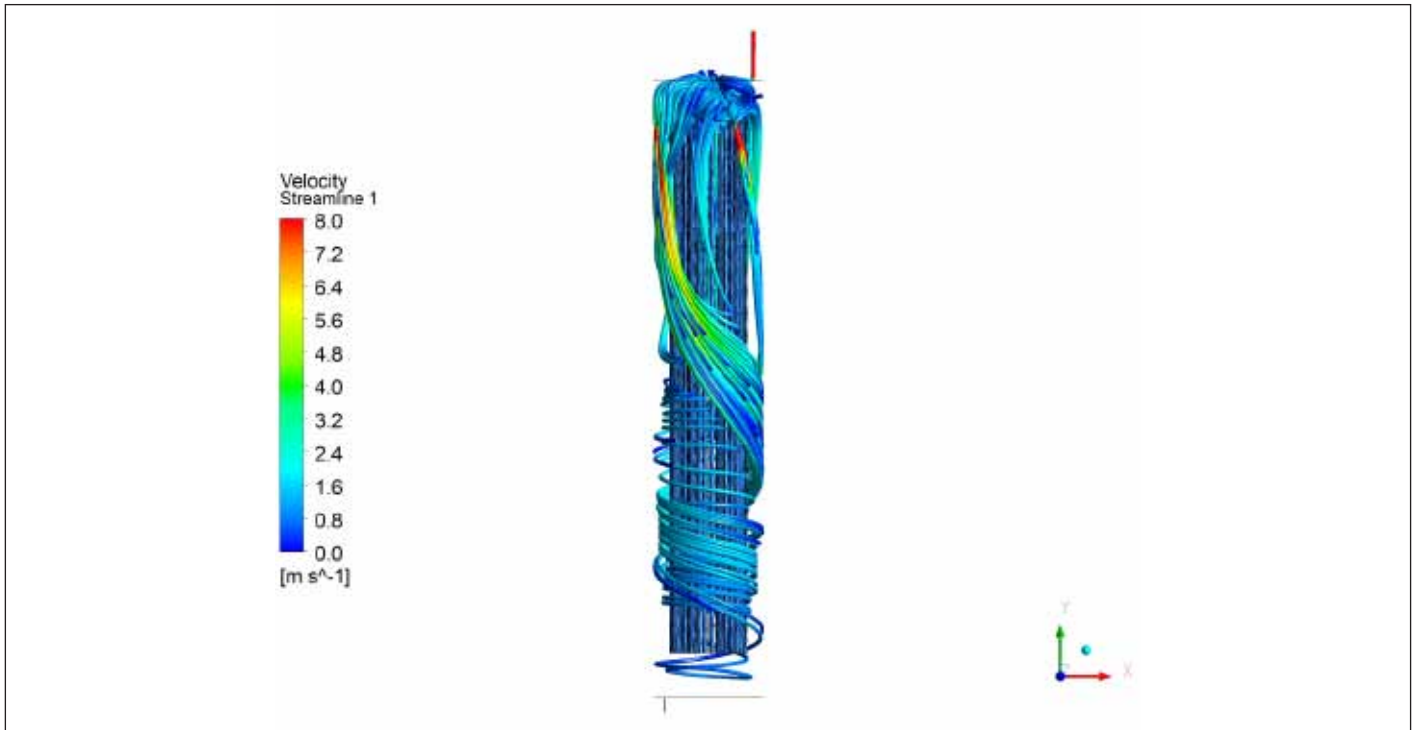


Figure 19: Flow patterns of CARBOJET in operation.

The lances are practically maintenance-free; furnaces where ventilators have been replaced by the CARBOJET high-speed injection system can therefore be operated for longer without shutdowns. Downtime caused by broken ventilators and disturbances of vibrating ventilators is completely eliminated. This leads to the additional advantage that the heating elements, retorts and brick lining will suffer less frequent damage.

In summary, the advantages of the high-speed gas injector are:

- homogenised product quality
- no ventilators are needed, maintenance-free technology
- increased utilisation of gases and reduced soot formation in heat treatment furnaces. The high-speed injection of gases also optimises the functionality of analysing equipment due to better gas mixing
- increased carbon transfer on material surfaces due to forced convection of the atmosphere

3.4.2 High-speed gas injection for improved cooling

A further development of the patented CARBOJET high-speed gas injection technique is CARBOJET cooling that typically is installed through the furnace roof (other installations possible) in the cooling section of a continuous annealing furnace in order to improve heat transfer. It is a system based on the installation of gas injection lances placed in several sections of the furnace. A control system regulates the gas flow to the lances with the help of the required gas flow train and piping.

The technique is suitable to improve situations like:

- Existing cooling insufficient
- Need to increase throughput due to increased demand
- Demand to shut down one furnace by increasing the output of the others to reduce overall costs
- Avoid/prolong the need to invest in a new furnace

Advantages obtained with the CARBOJET cooling technique include:

- Very little maintenance needed since there are no moving parts and the nozzles do not really wear
- High-speed nitrogen is the main gas component with no additional nitrogen consumption
- Increased throughput (faster process) due to increased heat transfer
- Higher flexibility
- Shorter cooling zones possible

3.4.3 Methanol injectors and pumps

The theoretical principles for using cracked methanol as a source for creating the atmosphere are described in the next section. The specially designed methanol injectors seen in Figure 20 are integrated parts of the CARBOTHAN® system.

The methanol pump is another integrated part of the CARBOTHAN system. To ensure steady supply, a double pump system is recommended. The gear pump has proven to be an adequate type of pump. It has to fulfil safety regulations.

3.4.4 Sample gas handling

It is most important that the sample gas is drawn from the furnace in a way that ensures that a representative furnace atmosphere sample is analysed. Figure 21 shows an example of a sample gas lance design that meets this requirement. It has an outer protective tube and a ceramic inner sample gas tube. The design is intended to avoid thermal stresses due to different thermal elongations of the metallic and ceramic tubes. There is a pin at the end of the lance that in case of a crack in the ceramic tube will obstruct it from falling into the furnace.



Figure 21: Sample gas lance.



Figure 20: Examples of methanol injectors.

4. Atmosphere generation, gas supply.

The furnace atmosphere is supplied to a furnace in two alternative basic ways. The first, here referred to as in-situ generation or synthetic atmospheres, is by supplying gases, such as nitrogen, hydrogen, and argon, 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 be adapted and minimised to 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 control
- Increased safety

In order to make a good atmosphere, it is usually necessary to combine at least two different gases. For instance, N_2/H_2 atmospheres are produced by feeding N_2 and H_2 through separate flow meters to the furnace. $N_2/CO/H_2$ atmospheres are produced from methanol, which dissociates to CO and H_2 in the furnace and is diluted with nitrogen to the correct composition. The most common combinations are shown in Table 4, 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 N_2/H_2 atmosphere can be produced not only from combining the pure gases (N_2 and H_2) but also from cracked ammonia or by nitrogen dilution of cracked ammonia. $N_2/CO/H_2$ atmospheres can be produced from N_2 + methanol, from endogas, from a combination of N_2 + endogas and so on.

Table 4. Synthetic atmospheres based on composition

Composition	Supply alternative	Linde designation
100% nitrogen	Gaseous supply in cylinders or bundles	Nitrogen
	Liquid nitrogen supply	
	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	
100% helium	Gaseous supply in cylinders	Helium
Nitrogen/hydrogen mixture	$N_2 + H_2$	HYDROFLEX®
	N_2 + cracked ammonia	HYDROFLEX
Argon/hydrogen mixture	$Ar + H_2$	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

An atmosphere supply system consists of three major parts: media storage, mixing and intake to the furnace.

4.1 Nitrogen supply

There are five major supply forms for nitrogen (see Figure 22):

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 22a) at the customer site. This is the most common supply method that is cost-efficient for a flow from 10 up to about 200m³/h. Nitrogen supplied in the liquid form has a high purity, with typical contamination levels of O₂ + H₂O at 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 22b, yields high purity, typically 5 ppm oxygen and moisture content. It is relevant for flow rates from 250 to 2000 m³/h.

Nitrogen from adsorption (PSA) units installed on-site

Nitrogen produced on-site using the PSA (Pressure Swing Adsorption) technique, Figure 22c, has a purity of 99 to 99.99%. Flow rates from 10 up to 2000 m³/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 m³/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 OSS unit.



Figure 22: Nitrogen supply methods. a) Storage tank and vaporiser for liquid nitrogen, b) Cryogenic nitrogen production with CRYOSS, c) PSA (Pressure Swing Adsorption); ADSOSS.



Figure 23: 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 22. 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:

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

Examples of different supply methods for hydrogen are shown in Figure 23.



Figure 24: Methanol tank installation. The liquid nitrogen tank is seen in the background.

4.4 Methanol supply

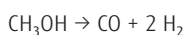
Methanol is stored in tanks of varying size depending on the rate of consumption. Small consumers fill their tanks from barrels, while large consumers fill them from road tankers. An example of a methanol tank installation is shown in Figure 24. Nitrogen inerting of the methanol storage is common both to ensure safety and to eliminate the risk of humidity entering the methanol.

The methanol storage installation should comply with local safety regulations. It could for instance mean that the tank has to 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 use cases with small methanol containers. The third and preferred method is by using a pump to feed the methanol.

4.6 In-situ methanol cracking

A carbon monoxide/hydrogen (CO/H₂) atmosphere can be produced by in-situ cracking of methanol according to the reaction:



By mixing cracked methanol with nitrogen, it is possible to produce a wide range of N₂/CO/H₂ 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. 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 CH₄, CO₂, H₂O 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 ventilator area of the furnace, as shown in Figure 25. 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 successfully be used for vaporising methanol. In certain furnaces such as low height conveyor and bell furnaces, it is advantageous to have a separate methanol vaporiser

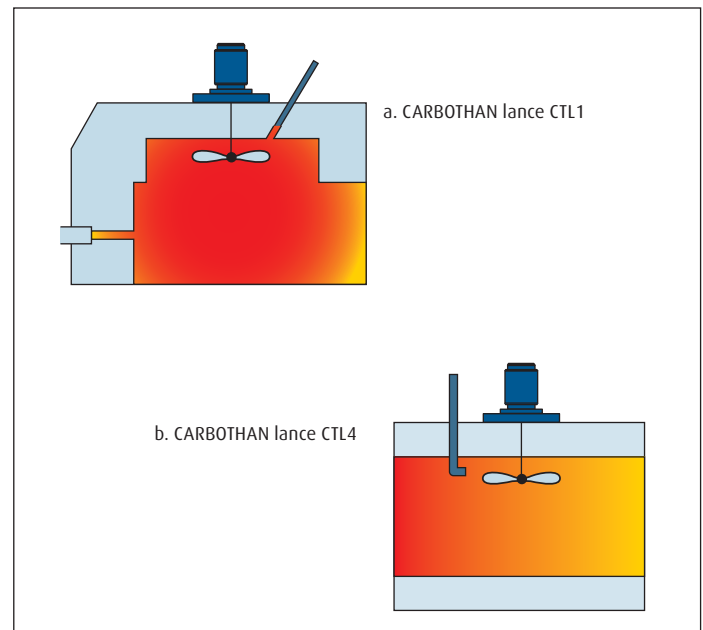


Figure 25: Methanol injection into the fan area of a furnace

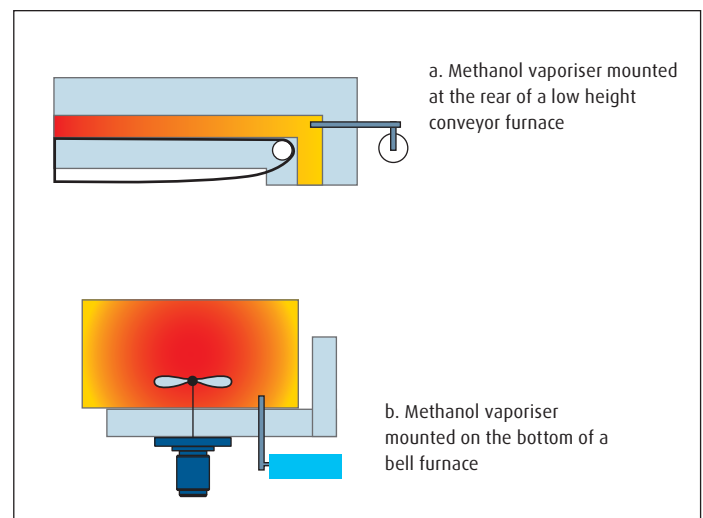


Figure 26: Examples of methanol vaporiser installations in a) a conveyor and b) a bell furnace.

as shown in Figure 26. 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.

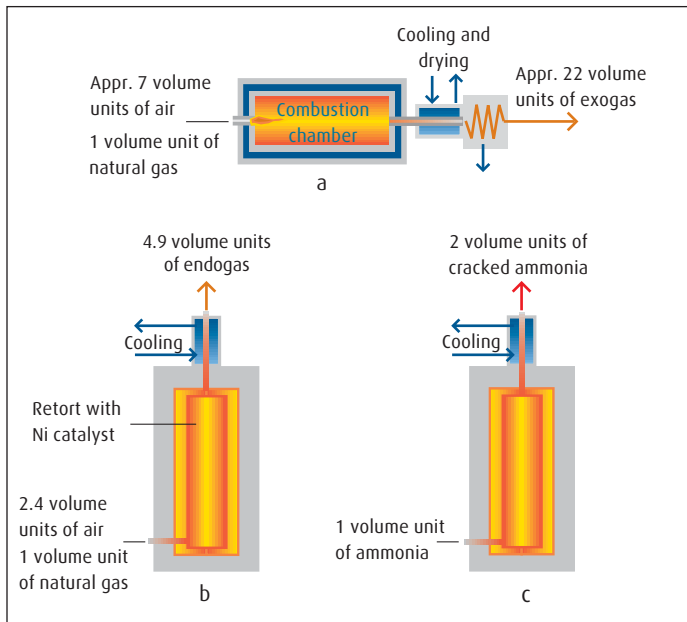
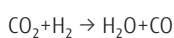


Figure 27: Schematic principles of a) exo- and b) endogas generators and c) an ammonia cracker/dissociator.

4.7 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 27 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 certain limits, in turn limiting the types of materials that can be heat treated within that atmosphere.

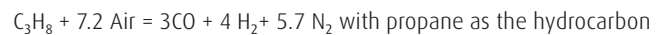
Typical generator atmosphere compositions are given in Table 5. The compositions given are those at the outlet of the external gas generators. These atmosphere compositions will change when the gas enters the hot furnace as a result of the reaction with air and oil vapours that are present. The composition will also change because a new chemical equilibrium composition will be established determined by the furnace temperature itself. This is especially the case 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



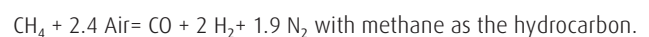
The resulting atmosphere inside the furnace will thus have a considerably higher water content than the exogas coming out of the generator.

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:



or



Endogas is a reducing atmosphere with a controllable carbon concentration.

The patented CARBOCAT® equipment that is available from Linde in certain parts of the European market is an in-situ generator in which endogas is produced directly inside the furnace chamber. Major benefits include the elimination of a cooling device for the gas, energy savings, floor space reduction and elimination of piping between generator and furnace. Several CARBOCAT generators can be installed in the same furnace. It is most economical when compared to external generators when there is a need for one or two CARBOCATs per furnace.

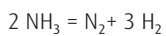
For exogas production, a higher air/hydrocarbon ratio is used, which results not only in CO and H₂ but also in H₂O and CO₂ production. The reaction between air and hydrocarbon is exothermic and does not require a catalyst. Air/natural gas ratios vary typically from 7 to 9. The resulting exogas is dried 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 of copper and of steels for which no carbon control is required.

Table 5. Typical atmosphere compositions

Method	Vol% of the different atmosphere constituents					
	N ₂	H ₂	CO	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 high-maintenance. The resulting atmosphere composition is typically 2–20 vol% CO + H₂, 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



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.

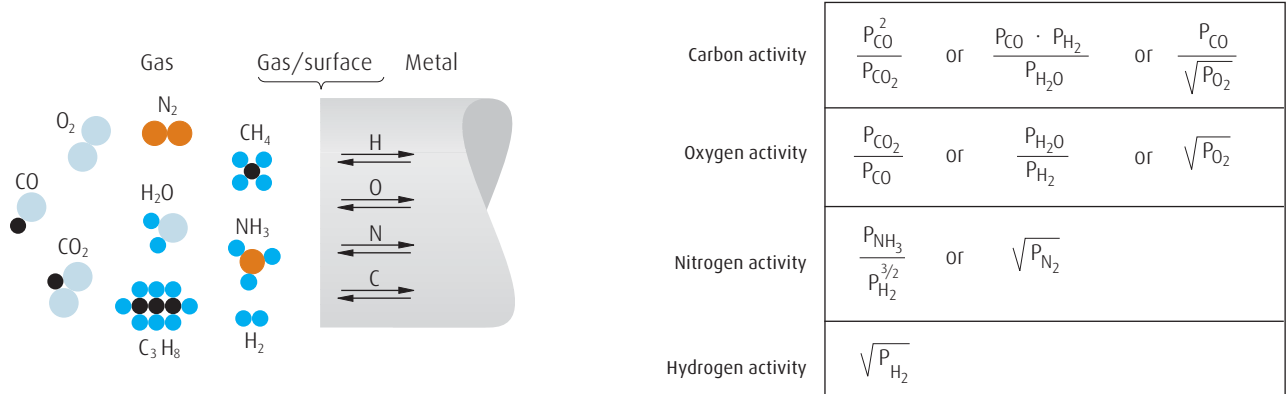


Figure 28: a.) Schematic illustration of atmosphere/metal interaction and b.) Expressions for oxygen, carbon, nitrogen and hydrogen activities in the atmosphere.

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 a number of possible reactions between the gas species in the furnace atmosphere and the metal surface. It is possible to reduce the problem of atmosphere control to the control of the elements oxygen and carbon present in the atmosphere. As indicated in Figure 28, the control is based on the atmosphere composition 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. The furnace atmosphere also serves as the thermal transfer medium for heating and cooling, especially in vacuum hardening processes.

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 annealed or hardened alloy. Neutrality implies that no net reactions occur between the metal/alloy and the atmosphere elements oxygen (O) and carbon (C). Reactions with nitrogen (N) and hydrogen (H) must be considered in certain cases. Figure 28 shows that these four elements may be present in

the furnace atmosphere as the gas molecules oxygen (O₂), hydrogen (H₂) and nitrogen (N₂) but preferentially as elements in multi-atom gaseous molecules such as carbon monoxide (CO), carbon dioxide (CO₂), and water vapour (H₂O). 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 (H₂) 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 6, the reducing effect of hydrogen (H₂) 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 6. Atmosphere constituents and their action

Active gases				Neutral or inert gases
Reducing	Oxidising	Carburising	Decarburising	
H ₂	H ₂ O	CO	H ₂ O	N ₂
CO	CO ₂	C _n H _m	CO ₂	Ar
	O ₂		O ₂	He

Truly inert atmospheres are made up only of the noble gases argon and helium. Nitrogen can be regarded as inert to most used 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 nitrated, 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
- maintain reducing conditions with respect to the metal oxides that may form during heat treatment
- maintain a neutral carbon activity (for steels) to avoid decarburising or carburising
- react with vapours, for instance from vaporised lubricants, and eliminate their detrimental effect on the annealing result

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

Reducing atmospheres not only prevent the formation of surface oxides during heat treatment but can also reduce and eliminate residual surface oxides which were present before heat treatment or formed during the heating process. A bright surface is not necessarily proof of neutrality with respect, for instance, to carbon. Under a bright surface there could be a decarburised layer.

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

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 N₂/C_nH_m (C_nH_m being a hydrocarbon such as methane, CH₄, or propane, C₃H₈) 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.

5.2 Oxidation control

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



with the equilibrium constant

$$K_A = 1/P_{\text{O}_2,1/2}$$

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

The oxygen partial pressure value, P_{O₂}, 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 29 displays the equilibrium oxygen partial pressure as a function of temperature for the metal oxides of copper, iron and chromium calculated using the Thermocalc program [6].

Figure 29 shows that 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 → steel → stainless steel. Consequently, the atmosphere oxygen partial pressure must be adjusted in relation to the heat-treated metal to yield a bright surface.

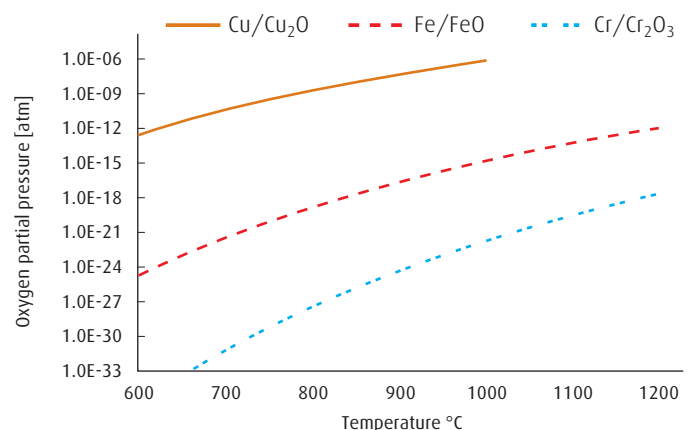


Figure 29: Relation between oxygen partial pressure (atm) and temperature for metal/metal oxide equilibrium for copper (Cu), iron (Fe) and chromium (Cr) [6].

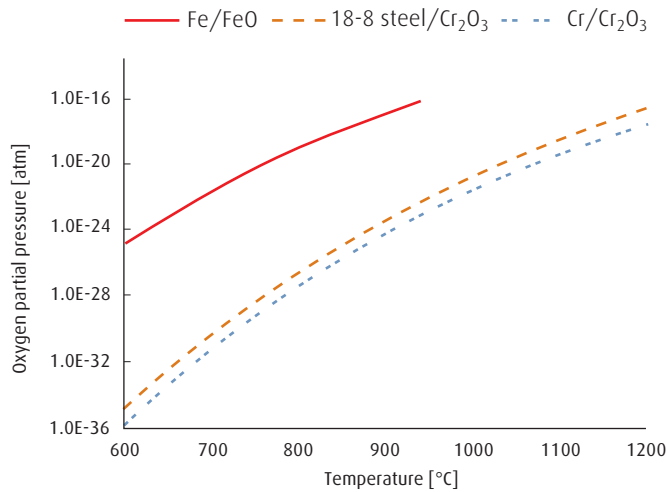


Figure 30: The equilibrium oxygen partial pressure for oxide formation over a standard 18/8 stainless steel. Oxidation of pure iron (Fe) and chromium (Cr) shown for reference [6].

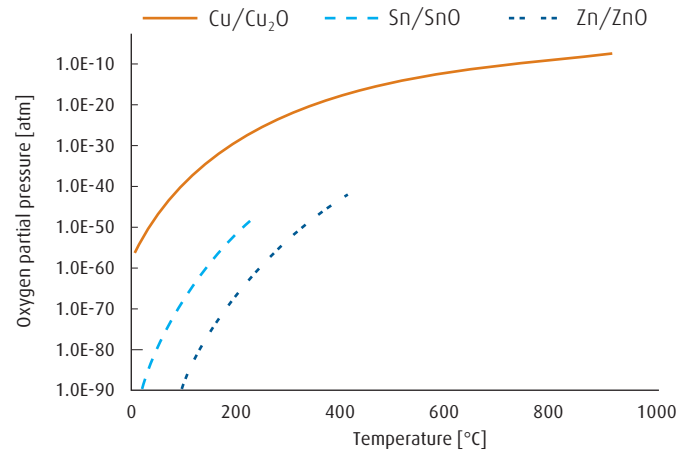


Figure 31: The equilibrium oxygen partial pressure for oxide formation over copper, tin and zinc. (The curves for Sn and Zn are calculated up to the melting temperature) [6].

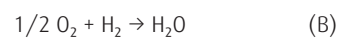
The partial pressures of oxygen needed to oxidise these metals are extremely low, ranging from approximately 10^{-6} atm for copper to 10^{-30} atm for chromium at typical annealing and hardening temperatures. (Expressed as volume concentrations, these numbers correspond to 1 ppm and 10^{-24} ppm of oxygen.) These very low values are unrealistic, in the sense that there are no free oxygen molecules to be measured at a partial pressure of the order of 10^{-30} atm. (The oxygen content of the heat treatment atmosphere, even using cryogenic-purity nitrogen as the source, may exceed the acceptable level of oxygen to avoid oxidising the surface.) Although there are no free oxygen molecules present, there are substantial and measurable amounts of oxygen bonded in the molecules CO , CO_2 and H_2O . By measuring and balancing the atmosphere ratios of CO_2/CO or $\text{H}_2\text{O}/\text{H}_2$, it is therefore possible to control the atmosphere oxygen level.

The atmosphere requirements for avoiding oxidation of commercial stainless steels, with oxidation of iron and pure chromium as references, are illustrated in Figure 30. The equilibrium oxygen partial pressure over iron oxide, which determines the oxidation of steels, is high compared to the equilibrium oxygen pressure for chromium oxide formation, which determines the oxidation of stainless steels. From the figure, it is clear that the equilibrium oxygen partial pressure value over the oxide is about the same for a common standard stainless steel as it is for pure chromium. Avoiding the formation of chromium oxide will require oxygen partial pressure that is several orders of magnitude lower than avoiding the formation of iron oxide. Therefore, hydrogen atmospheres or vacuum processes will be required.

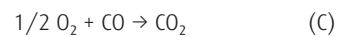
The oxidation diagram in Figure 31 shows the oxidation of the solid metals Cu (copper), Sn (tin) and Zn (zinc). The diagram illustrates that Sn and especially Zn oxidise much more easily than copper. For bright annealing of alloys such as brasses and bronzes, strongly

reducing atmospheres with high hydrogen concentrations in the range 25–100 vol% must be therefore used.

It is normally required to add a reducing gas, for example hydrogen, to lower the oxygen concentration to the required level. Oxygen enters the furnace atmosphere to a certain extent as an impurity in the supplied nitrogen, but mainly from external sources such as oxygen leaks into the furnace through doors and openings, and oxygen brought into the furnace by the parts (e.g. oxide layers, air inclusions). By reaction with a reducing gas, the oxygen concentration is lowered. Examples of reducing reactions are:



with $K_B = P_{\text{H}_2\text{O}} / (P_{\text{H}_2} \cdot \sqrt{P_{\text{O}_2}})$ and



with $K_C = P_{\text{CO}_2} / (P_{\text{CO}} P_{\text{O}_2}^{1/2})$

K is the chemical equilibrium constant and P denotes the partial pressure, which at atmospheric pressure is equal to the quantity vol%/100. From equilibrium A, B and C it follows that the atmosphere oxygen control can alternatively be realised by using:

- Direct measurement of the oxygen pressure
- Analysis of CO and CO_2
- Analysis of H_2 and H_2O

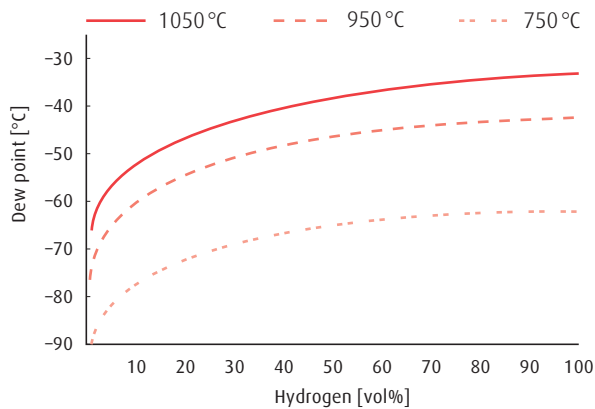
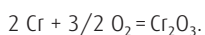


Figure 32: Theoretically calculated dew point as a function of hydrogen concentration for annealing of stainless steel without formation of chromium oxide.

These gas reactions have temperature-dependent equilibrium constants. The equilibrium data given in Appendix 1 can be used in several ways for a practical application. As an example, let us calculate the oxygen equilibrium pressure required for bright annealing of a stainless steel at 1050 °C (1922 °F) and the required corresponding dew point in a hydrogen atmosphere:

- From Appendix 1, we calculate the required oxygen partial pressure based for simplicity's sake only on the oxidation of pure chromium,



At 1050 °C (1922 °F) we get $P_{\text{O}_2} = 1.2 \cdot 10^{-21}$ atm

- Putting this oxygen partial pressure into the expression for the equilibrium constant for the reaction, $1/2 \text{O}_2 + \text{H}_2 = \text{H}_2\text{O}$, (see Appendix 1), we can calculate the ratio between water vapour and hydrogen concentrations. We get $\log P_{\text{H}_2\text{O}}/P_{\text{H}_2} = -3.59$. $P_{\text{H}_2\text{O}}$ can then be calculated for different P_{H_2} values. The water vapour concentration can be expressed as the dew point with the formula in Appendix 3. A presentation of such a calculation is shown in Figure 32.

Elements like Mn, Si and Cr have a higher affinity to oxygen than pure iron. When present as alloying elements, these elements therefore may form oxides by so-called selective oxidation. This does not result in a complete oxide layer but in the formation of internal oxides along grain boundaries and/or in internal oxide globules within the crystal grains. Brass and bronzes containing the oxidation-prone alloying elements Zn and Sn require highly reducing atmospheres according to Figure 31. Aluminium oxidises at such an extremely low oxygen partial pressure that such low oxygen pressures are impossible to realise in practice. The use of atmosphere for protecting aluminium from oxidation is not dependent on chemical equilibrium but on slowing down the oxidation

rate by minimising the amount of free oxygen. Titanium also oxidises extremely easily and a very low oxygen partial pressure is required to avoid oxidation. Vacuum is a preferred alternative for this purpose.

Figures 30–31 show that the oxygen equilibrium partial pressure over metal oxides decreases with decreasing temperature. From a chemical equilibrium point of view, the strongest purity requirements on the atmosphere are therefore set during heating and cooling. Figure 33 is an illustration of this fact. In this figure, the curves for SiO_2 , Cr_2O_3 , etc. are the theoretically calculated equilibrium curves for the formation of different oxides. The atmosphere oxidises to the right and reduces to the left of each curve. The curve A-B-C-D-E shows the registration of the atmosphere dew point during a bell furnace annealing cycle. At point A, the heating cycle is started. The atmosphere consists of 100% hydrogen. The atmosphere dew point is lowered upon heating from point A to point B. From point B to point C there is a slight increase in the dew point. This is mainly related to lubricant vaporising. Further heating from C to D is accompanied by a continued dew point reduction. From D to annealing temperature, E, there is a slight increase in the dew point as the result of oxide reduction with hydrogen with concurrent water formation. From the figure it is clear that the atmosphere oxidises upon heating with respect to Mn, Cr and Si oxides but not with respect to Fe oxides, up to a temperature of about 700 °C (1292 °F). At annealing temperature, the atmosphere becomes reducing with respect to Mn and Cr but not with respect to Si-oxide. For this specific alloy, the dew point should be below approximately -70 °C (-94 °F) in order to also be reducing with respect to Si at annealing temperature. For the best result in brightness, it is important that the dew point provides reducing conditions upon heating at the lowest temperature possible. To avoid oxidation upon cooling, it is likewise important that the atmosphere becomes oxidising at the lowest possible temperature and that cooling is fast.

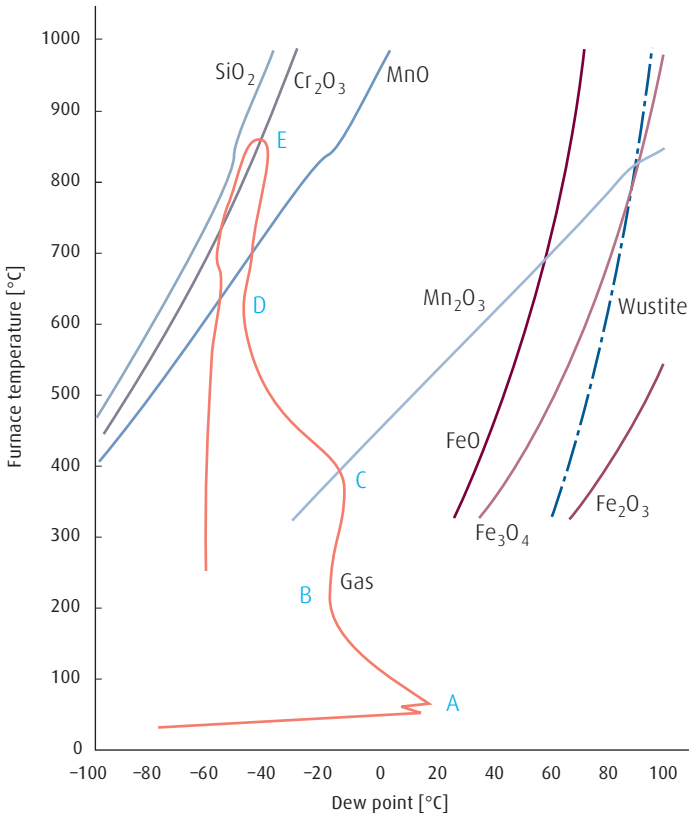


Figure 33: The dew point variation during a batch annealing cycle of strip coils related to the theoretical oxidation borderlines for treated steel (see text for explanation of letters A, B, C, D and E) [7].

A similar reasoning can be applied to a continuous furnace, where for certain points in the heating and cooling sections, corresponding to certain temperatures, the atmosphere may change from reducing to oxidising because of the temperature effect.

An example of how equilibrium calculation can be applied is to calculate what percentage of oxygen can be tolerated in the stream of nitrogen supplied to a furnace, without leading to oxidation of the metal, when the oxygen reacts with different hydrogen concentrations. The result of such a theoretical calculation using the Thermo-Calc software is shown in Figure 34.

Question: What maximum oxygen concentration in the inlet nitrogen gas stream can be tolerated at 850°C (1562°F) without oxidising copper and chromium for a hydrogen concentration of 1 and 10 vol% respectively?

Answer: Draw vertical lines from the points 1 and 10 vol% H₂ on the x-axis. Draw horizontal lines from the intersections of these (two) lines with the curves for Cu₂O and Cr₂O₃ respectively. Read the concentration on the intersection of these four horizontal lines with the O₂ concentration on the y-axis. The result is shown in Table 7.

The table shows that the oxygen concentration has to be extremely low to avoid Cr₂O₃ formation. Even very small amounts of oxygen entering the furnace from openings or as impurities in the nitrogen will cause oxidation when heat treating stainless steels. This is also valid for alloys

that contain elements like Si, Mn, and Ti, which easily form oxides. Copper, on the other hand, tolerates a fairly high impurity concentration of oxygen if balanced by hydrogen addition.

Table 7. Maximum oxygen concentration permitted in the nitrogen supplied for heat treatment when mixed with two different hydrogen concentrations, 1 and 10 vol% respectively, to avoid the formation of copper and chromium oxide at 850°C (1562 °F).

Oxide	Hydrogen concentration	
	1% H ₂	10% H ₂
Cu ₂ O	~0.3% O ₂	~6% O ₂
Cr ₂ O ₃	0.16 ppm O ₂	1.6 ppm O ₂

This has a consequence as regards the suitable sources of nitrogen supply. Impure and low-cost membrane nitrogen can be used in cases where metals are not easily oxidised, assuming that there is enough reducing gas such as hydrogen or carbon monoxide present. High-purity nitrogen must be used when heat treating stainless steels and other alloys that are easily oxidised.

Theoretical equilibrium calculations such as those presented give conservative limits for maximum oxygen levels with regard to oxidation. In practice, somewhat higher levels may be accepted because the rate of oxidation is limited both in gas/surface reactions and diffusion.

Kinetics is the term that describes the rate of chemical reactions. At a low temperature, the oxidation rate is low and even negligible below a certain temperature. It means that although oxidation is predicted from an equilibrium point of view, it will not occur below this critical temperature because the reaction rate is too slow. This critical temperature is of the order 150°C (302°F) for steels and about 50°C (122°F) for copper alloys. Although the oxygen impurity concentration in nitrogen is oxidising from a theoretical point of view it is of orders of magnitude lower than the oxygen concentration in air. A very simple estimate made from basic oxidation kinetics indicates that the oxide scale growth rate, on a metal in a nitrogen atmosphere with an oxygen concentration of 100 ppm, is about 1% of the oxide growth rate in air. If an oxide scale with a thickness of 0.1 mm was formed in air changing by atmosphere from air to nitrogen, the thickness would be reduced to 0.001 mm or just 1 µm.

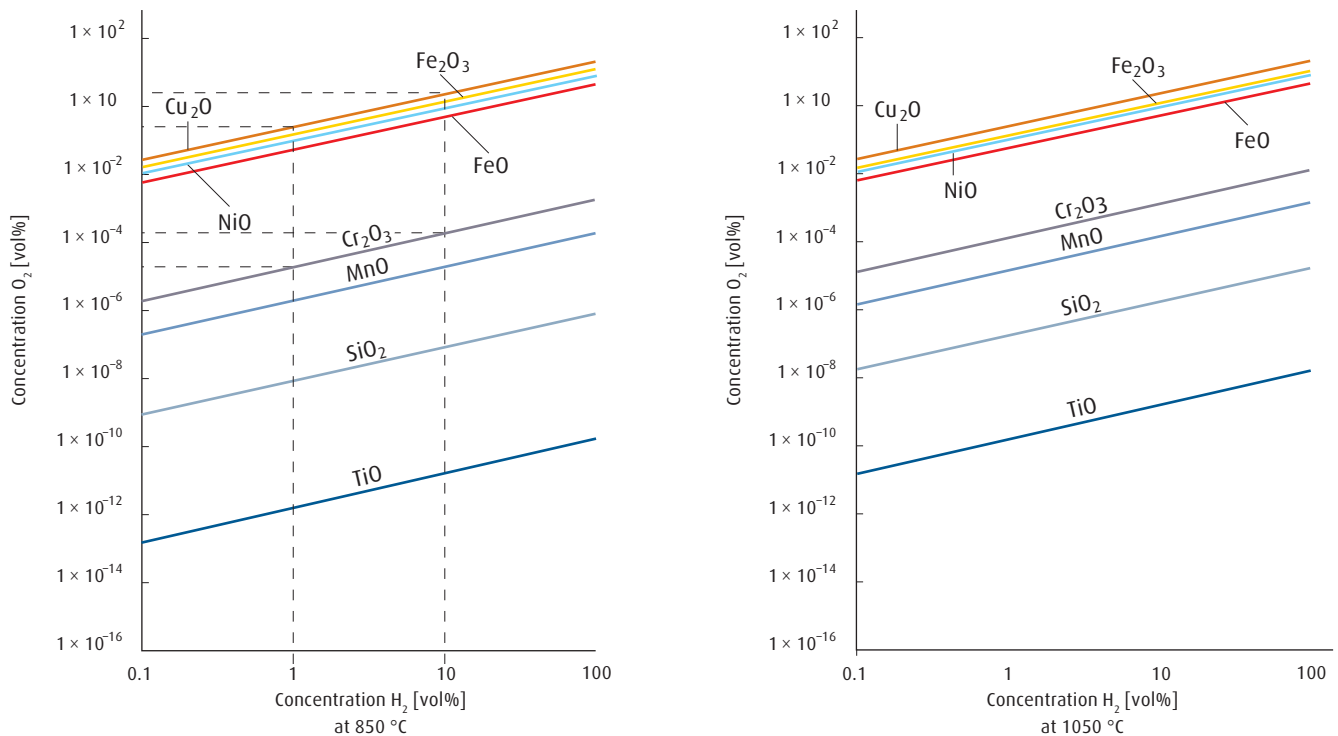


Figure 34: Theoretically calculated maximum impurity of oxygen in the inlet nitrogen gas at two temperatures, 850 °C (1562 °F) (left) and 1050 °C (1922 °F) (right) and at different hydrogen/nitrogen ratios with no oxidation of the metal as limitation. Note that logarithmic scales are used [6]. (Dotted lines in figure are explained in the text.)

5.3 Carbon control

For neutral conditions, thus neither decarburising nor carburising, the atmosphere carbon activity must be controlled to yield the nominal carbon concentration in the surface of the heat treated steel. As was indicated in Figure 28, it is possible to calculate the atmosphere carbon activity from the atmosphere concentrations of the species $\text{CO} + \text{CO}_2$, $\text{CO} + \text{H}_2 + \text{H}_2\text{O}$ or $\text{CO} + \text{O}_2$, which corresponds to well-known atmosphere control systems using CO_2 , dew point or oxygen probe analysis. Using chemical equilibrium formulas, we can express the carbon activity in the following alternative ways:

$$a_c = K_1 \cdot (P_{2\text{CO}}/P_{\text{CO}_2})$$

$$a_c = K_2 \cdot (P_{\text{CO}} \cdot P_{\text{H}_2}/P_{\text{H}_2\text{O}})$$

$$a_c = K_3 \cdot (P_{\text{CO}}/P_{1/2\text{O}_2})$$

Expressions for the equilibrium constants K_1 , K_2 and K_3 are found in Appendix 1. These expressions are the basis for atmosphere carbon control when assuming thermochemical equilibrium.

Industrial heat treaters seldom use the concept carbon activity but prefer to use the "carbon potential" to signify the atmosphere carbon concentration. The atmosphere carbon potential is defined as the carbon concentration expressed in weight % that a pure iron foil will have after

being equilibrated with the atmosphere. Expressions for the relation between carbon activity and carbon potential are given in Appendix 3. By using the expressions for the equilibrium constants in Appendix 1 combined with the expressions in Appendix 3, it is possible to generate the carbon potential from any CO/H_2 atmosphere with knowledge of the temperature and the analysis of CO , H_2 and CO_2 , dew point or millivolt value from an oxygen probe.

The atmosphere carbon potential is not thermochemically equal to the carbon concentration of the steel except for just a binary iron-carbon alloy. The carbon activity, however, is the same for the atmosphere and the steel at equilibrium. Therefore, the correct procedure, when choosing a neutral atmosphere, is to first calculate the carbon activity of the steel. The atmosphere carbon activity should then be controlled to the same value. The carbon activity of the atmosphere is easily calculated utilising the equations for K_1 , K_2 and K_3 . The corresponding atmosphere carbon potential may be taken from a graph or calculated with the equations given in Appendix 3.

Table 8. Calculated atmosphere carbon activity and carbon potential for neutral hardening or annealing of various steels (in austenitic condition).

Steel designation	Temperature	Alloy composition, wt%										Carbon activity, a_c	Carbon pot, %C		
		EN or DIN	ASTM/AISI	°C	°F	C	Si	Mn	Cr	Mo	Ni			V	W
Fe-C (Pure iron)				850	1560	0.42	-	-	-	-	-	-	-	0.35	0.42
C15R	1016			885*	1625	0.15	0.4	0.45						0.10	0.16
16MnCr5	5117			925*	1695	0.16	0.4	1.15	1.05					0.08	0.15
20MnCr5	5120/5120H			925*	1695	0.20	0.4	1.25	1.15					0.10	0.19
20NiCrMoS2-2	8620			925*	1695	0.20	0.4	0.80	0.50	0.20	0.55			0.11	0.21
16NiCr4	4320/4320H			925*	1695	0.15	0.27	0.9	1.0	0.15	1.0			0.08	0.15
42 CrMo4	4140			850**	1560	0.42	0.27	0.75	1.05	0.22				0.28	0.38
100Cr6	52100			850**	1560	1.0	0.25	0.35	1.5					0.72	0.81
WNR1.2201	D2			1000**	1830	1.5	0.3	0.45	12	0.8		0.9		0.12	0.29
WNR 1.0904	9255			850**	1560	0.56	0.75	0.75	0.15					0.66	0.76
HS 6-5-2	M2			750*	1380	0.85	0.30	0.30	4.00	5.00		2.0	6.3	0.05	0.05

*Annealing or normalising temperature; ** Hardening temperature

For low-alloy steels, simplified formulas can be used to calculate the neutral atmosphere carbon potential (see Appendix 3), but for high-alloy steels such as tool and high-speed steels, a more rigorous equilibrium calculation must be done. In Table 8, this is illustrated with calculations for some steels. From the table it is clear that the carbon concentration for low-alloy steels in equilibrium with the atmosphere is almost the same as the atmosphere carbon potential. However, for high-alloy steels, the difference between the atmosphere carbon potential and the equilibrium carbon concentration in the steel may be considerable. Consider for instance the steel WNR1.2201. The carbon concentration of that steel is 1.5% C, but the equilibrium atmosphere carbon potential at 1000 °C (1830 °F) is only 0.29% C. The reason for this is that the steel WNR1.2201 has a high chromium content and chromium attracts carbon and lowers the carbon activity in the steel to the same level as for a 0.29% C binary iron-carbon alloy.

In some cases, it is possible to use a principle for carbon control based on kinetics instead of on equilibrium. By keeping the amounts of carburising and decarburising species so low that the carburising and decarburising rate is negligible, it is possible to maintain carbon neutral conditions. This principle is utilised for instance for annealing steel in pure hydrogen with an extremely low dew point. Another example of a neutral atmosphere is a nitrogen/hydrocarbon (/hydrogen) atmosphere with low concentration of hydrocarbons (natural gas or propane) and a low atmosphere dew point.

Copper does not react with carbon. This means that atmospheres containing carbon in the form of CO or CO₂ etc. such as exogas, endogas, nitrogen/methanol and so on can be used if they have the correct oxygen potential. The risk of soot deposits has to be considered and taken into account.

Carbon is a “poison” for most stainless steels as carbon easily reacts with chromium to form chromium carbide. If this occurs, it leads to lowered corrosion resistance. This is because the chromium will be bonded in the chromium carbides. The chromium concentration in solid solution, which is what determines corrosion resistance, will consequently be lowered. Therefore, atmospheres for annealing of stainless steels must be free of any carbon source. The same is valid for titanium.

5.4 Relation between carbon and oxygen control

Consider, as an example, the atmosphere requirement for avoiding oxidation of pure iron. The required atmosphere oxygen partial pressure and the corresponding atmosphere concentrations of CO₂/CO and H₂O/H₂ are given in Table 9 for the temperatures 800 °C (1470 °F) and 900 °C (1650 °F). If the atmosphere should also be neutral with respect to carbon for steels with different carbon concentrations, then the required oxygen partial pressure is lowered as seen in the table. At 800 °C (1470 °F), for instance, the requirement to avoid oxidation of iron is a partial pressure of oxygen of maximum 1 x 10⁻¹⁹ atm, whereas for avoiding decarburisation of a 0.5% C steel, the corresponding oxygen partial pressure is 7 x 10⁻²³ atm. The corresponding required atmosphere concentrations of CO₂ and H₂O can be calculated from the table. A maximum CO₂ concentration of 2.5 vol% is enough to avoid iron oxide formation, but a maximum 0.003 vol% is permitted for carbon neutral heat treatment of the 0.5% C steel. Corresponding H₂O concentrations are 4.3 vol% (dew point +27 °C) and 0.11 vol% (dew point -19 °C). The example shows that there is a significant difference in atmosphere requirements for bright annealing compared to the requirements for carbon neutral annealing of steels.

Table 9. Atmosphere equilibrium oxygen partial pressure, P_{O_2} (eq), and corresponding CO_2/CO and H_2O/H_2 volume concentration ratios to yield a bright surface and no decarburisation of pure iron and iron alloyed with carbon. The concentration ratios are given for an atmosphere having 5 volume % CO and 10 vol% H_2

Anneal. temp., °C (°F) in steel	wt% C in steel	P_{O_2} (eq) atm,	CO_2/CO	H_2O/H_2
800 (1472)	0	1×10^{-19}	0.52	0.43
	0.1	3×10^{-21}	0.090	0.075
	0.3	2×10^{-22}	0.023	0.019
	0.5	7×10^{-23}	0.014	0.011
900 (1652)	0	2×10^{-17}	0.50	0.58
	0.1	5×10^{-20}	0.13	0.029
	0.3	5×10^{-21}	0.008	0.0092
	0.5	1×10^{-21}	0.004	0.0041

5.5 Nitrogen pick-up

When heat treating 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.

In the nitriding reaction



a nitrogen molecule, N_2 , splits into two nitrogen atoms, $2 N$, which dissolve in the metal. This reaction can be neglected in most cases, but not for stainless steels, where chromium attracts nitrogen and considerable amounts of nitrogen may dissolve in the steel as shown in Figure 35. The surface nitrogen concentration is approximately proportional to the square root of the atmosphere nitrogen concentration as long as nitrogen is entering into solid solution in austenite. This corresponds to the curve marked γ in the left part of the diagram. At a certain nitrogen activity, there is a break point in the diagram at about $\sqrt{PN_2} = 0.3$ and $\sqrt{PN_2} = 0.8$ respectively. Above this nitrogen activity, there is a steeper slope of the theoretical curve caused by the formation of ϵ -nitride. In practice, the obtained nitrogen surface concentrations may be somewhat lower than theoretically predicted, because the residence time is too short for equilibrium to be established.

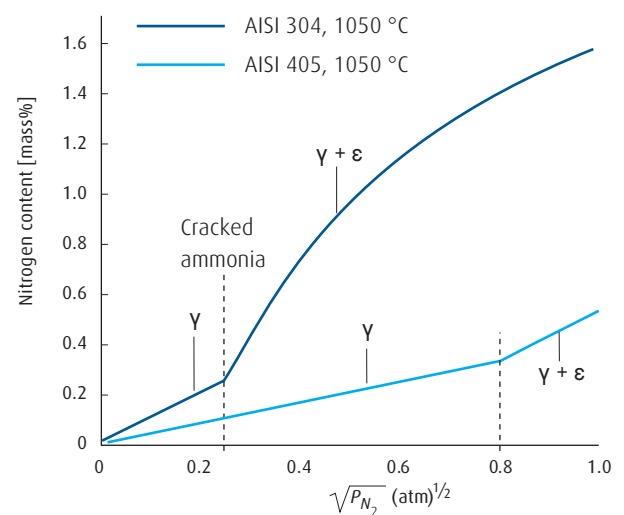


Figure 35: Theoretically calculated equilibrium surface nitrogen concentrations as a function of atmosphere nitrogen activity after annealing of two stainless steels at 1050°C (1920°F) of an austenitic 18% Cr/8% Ni stainless steel type AISI 304 and a ferritic 13% Cr steel type AISI 405 (calculated by Thermo-Calc) [6].

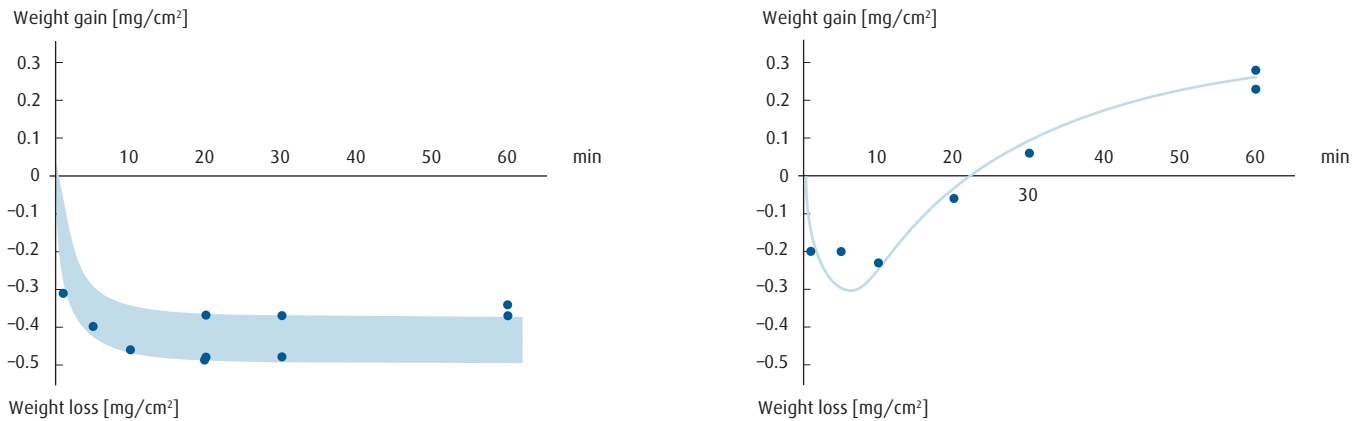


Figure 36: Weight loss and weight change for oxidised stainless steel specimens when annealed in a reducing a) 100% hydrogen and b) 50% hydrogen/50% nitrogen atmosphere at 1050 °C (1922 °F).

Figure 36 shows the results of experiments conducted with the intention of reducing oxide scales on an austenitic 18/8-type stainless steel by annealing in hydrogen at high temperature in a reducing atmosphere. The left figure shows the weight loss due to oxide reduction when a 100% hydrogen atmosphere was used. The weight loss curve for that case stabilises after approximately 10 minutes annealing time. After that time, all oxide has been reduced. When the same experiment is conducted in a 50/50 nitrogen/hydrogen mixture, there is initially a weight loss, but after 5–10 minutes the curve changes from weight loss to weight gain. The weight increase is caused by nitrogen pick-up. The explanation is that as long as there is an oxide scale, the nitrogen pick-up is retarded or even stopped, but when the surface becomes “naked” then nitrogen pick-up occurs at a fast rate.

The possible consequences of unwanted nitrogen pick-up are illustrated by the following example. Neutral hardened 13% chromium martensitic stainless steel parts were made in a conveyor furnace with 100% nitrogen as an atmosphere. The parts showed a clean and almost bright surface, which was accepted as regards surface quality. After some time, it was observed that ready hardened parts showed cracks apparently formed in storage. Nitrogen analysis and hardness tests revealed that the hardened parts had picked up nitrogen to very high levels, which caused a strong hardness increase as shown in Figure 37.

Further examinations clearly showed a relation between the nitrogen pick-up level and the atmosphere nitrogen content as foreseen by theory. An interesting observation in Figure 38 is that nitrogen pick-up does not occur in air although the nitrogen activity in air is high (=79 vol%). This is because an oxide forms, which is a barrier to nitriding (compare with Figure 36b). After replacing nitrogen with argon, the nitrogen pick-up problem was eliminated. A further proposal was to run the furnace with pure hydrogen, which should have the advantages of both improved surface finish and increased productivity. Safety

regulations, however, in this case made argon the final solution. If the nitrogen concentration is above the solubility limit, meaning that nitrides are precipitated, then a negative effect on corrosion resistance will be obtained. This is because the solid solution of chromium is lowered when chromium is concentrated in the nitrides in the same way as when chromium carbides are formed. Deteriorated corrosion resistance and brittleness are potential risks for stainless steels.

The use of argon, hydrogen or mixtures thereof is recommended in such cases. Titanium and zirconium may become brittle if annealed in atmospheres containing nitrogen.

Positive effects from active nitriding of austenitic stainless steels are obtained in cases when nitrogen is not precipitated as nitrides but only enters into solid solution in the austenite. An increase in the nitrogen solid solution concentration improves corrosion resistance. Mechanical properties can also improve, as an increase of nitrogen in solution will increase yield stress.

5.6 Hydrogen embrittlement

When annealing oxygen-bearing copper (not deoxidised), hydrogen gas can react with the oxygen to form water vapour. Due to the high pressure of water vapour formed and enclosed in the copper, embrittlement may be a detrimental result.

Certain high-strength steels with an ultimate tensile strength above 1050 MPa [8] can be sensitive to what is generally referred to as hydrogen embrittlement. 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

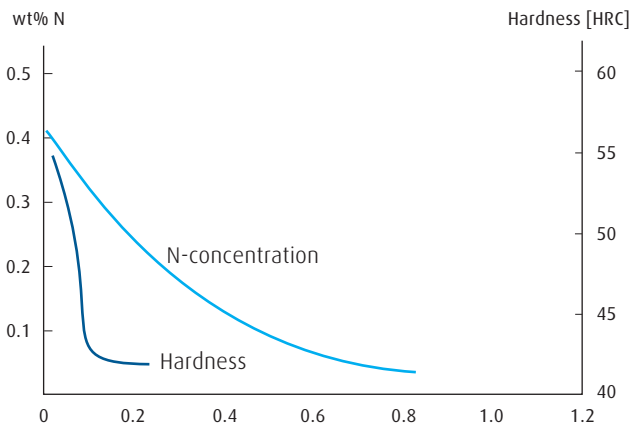


Figure 37: Relation between hardness and nitrogen pick-up after hardening in 100% N_2 at 1050°C (1922°F) of a 13% Cr steel.

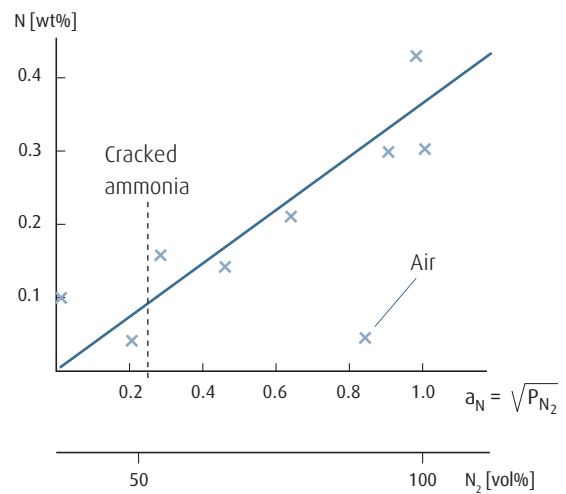


Figure 38: Experimentally analysed nitrogen pick-up in a 13% Cr steel as a function of atmosphere nitrogen content.

low as 2–2.5 ppm can drastically reduce steel ductility. Embrittlement is caused by atomic hydrogen in highly supersaturated solution.

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

5.7 Lubricant removal

Lubricants, used in cold forming operations before annealing, remain on the metal part surfaces. When the parts are heated to high enough temperatures, these lubricants will vaporise, thermally decompose, or react to form new compounds. It is important that the gaseous lubricant products are effectively removed from the furnace. If not, there is a risk that discolouration is obtained on the surfaces after annealing. This is particularly important in strip coil batch furnace annealing of both steels and nonferrous metals, but also when annealing is carried out in continuous furnaces.

A general guideline for batch furnaces is that a high gas flow rate should be used in the temperature range where the lubricant starts to vaporise. This temperature range varies depending on lubricant, but is typically in the range of 250–500 °C (482–932 °F). By using a high gas flow rate in this temperature range, it is possible to transport away the gaseous lubricant reaction products to ensure a bright surface. As the purging procedure takes some time, it is useful to stop the heating in this vaporising region until all vapour is purged away. The vaporising sequence can be tracked by gas analysis during heating as shown in Figure 39, which shows CO and CH_4 gas analysis in a bell furnace during heating of strip coils. By purging away the vaporised lubricant, it is possible to eliminate carbon deposits, which result from reactions at higher temperatures.

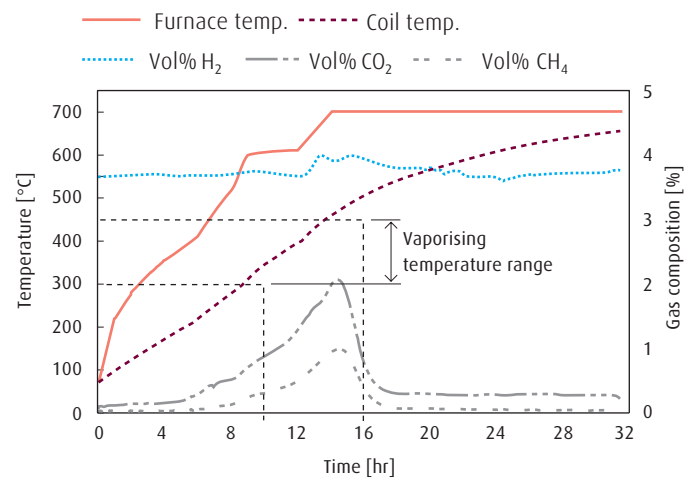


Figure 39: Gas analysis during heating of strip coils in a bell furnace.

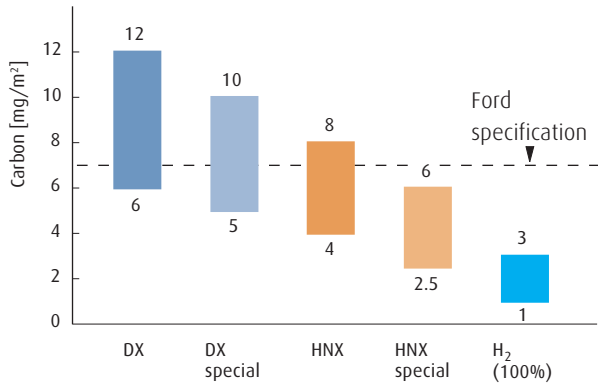


Figure 40: Carbon deposits for steel coupons annealed in different atmospheres. DX=exogas, HNX=monogas [9].

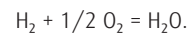
The use of 100% hydrogen atmospheres in strip coil bell furnace annealing has the benefit that very clean surfaces are attained. This is for two reasons. First, the high reducing power assures an oxide-free and bright surface. Selective oxidation of alloying elements is minimised or avoided. Secondly, hydrogen helps to vaporise and remove the adhering lubricant upon heating. The lubricants are hydrogenated, which lowers their boiling point and accordingly makes evaporation easier. The hydrogen molecule is small and can penetrate between the strip coil turns, which improves the transport of lubricant vapour out of the furnace. As a result, surface carbon residue concentrations are markedly reduced when annealing is conducted in 100% hydrogen, as seen in Figure 40.

Not only 100% hydrogen atmospheres provide this advantage but also in nitrogen/hydrogen atmospheres any additional hydrogen percentage will improve surface cleanliness. As an example, the amount of carbon deposits in one case was reduced by 35% when increasing the hydrogen concentration in the atmosphere from 3.5 to 6.5 vol%. Improved cleanliness has beneficial consequences for the quality of post surface treatments such as phosphatising with respect to adherence and coating thickness.

In continuous furnaces, the lubricant vapours can be removed by having a gas flow direction that purges the vapours from the furnace. As seen in Figure 41, it can be visually checked whether the lubricant vapour is exiting the furnace.

5.8 Buffering capacity

Buffering means the ability of the atmosphere to level out the disturbing influence of oxygen due to leakage and drag-in. High amounts of reducing gas species, mainly carbon monoxide (CO) and hydrogen (H₂), result in a high buffering capacity and also a high quality atmosphere with good controllability. Reduction of oxygen with hydrogen takes place by formation of water vapour according to the reaction



If, as an example, there is ingress of 1 vol% O₂ into the furnace atmosphere, we thus need a minimum of 2 vol% H₂ in the furnace atmosphere to reduce the oxygen by water formation. If the amount of oxygen ingress increases above 1 vol%, there will not be any hydrogen left for further reduction. The result will be a certain amount of free oxygen in the furnace atmosphere, leading to an oxidising atmosphere against metals. If on the other hand the furnace atmosphere consists of 99% hydrogen, there will still be 97 vol% H₂ left after reducing the 1% oxygen. The remaining hydrogen gives the atmosphere a high buffering capacity. The buffering effect may be quantified by the ratio vol% H₂O/vol% H₂ as a function of the atmosphere hydrogen concentration. The ratio H₂O/H₂ is a direct measure of the oxidising effect of the atmosphere. The higher the ratio, the more oxidising is the atmosphere. The calculation gives the results shown in table 10.

It can be seen that the H₂O/H₂ ratio is very high at low hydrogen concentrations but low at high hydrogen concentrations. In other words, high hydrogen concentration atmospheres have a high buffering capacity that can level out the disturbing influence of air ingress. In addition to improved quality of processed metals, a high buffering capacity also gives a potential to reduce gas flow rates and costs.

Table 10. The ratio H₂O/H₂ as a function of furnace atmosphere hydrogen concentration when there is a disturbing ingress of 1 vol% O₂ into the atmosphere (the oxygen is assumed to react completely with hydrogen to form water vapour).

Vol% H ₂ in the inlet atmosphere	2.1	2.5	4	10	50	75	100
Vol% O ₂ in the inlet atmosphere	1	1	1	1	1	1	1
Vol% H ₂ O after reduction	2	2	2	2	2	2	2
Vol% H ₂ remaining after reduction	0.1	0.5	2	8	48	73	98
Ratio H ₂ O/H ₂	20	4	1	0.25	0.04	0.03	0.02



Figure 41: Oil vapours exiting the tube ends at the inlet of a furnace.

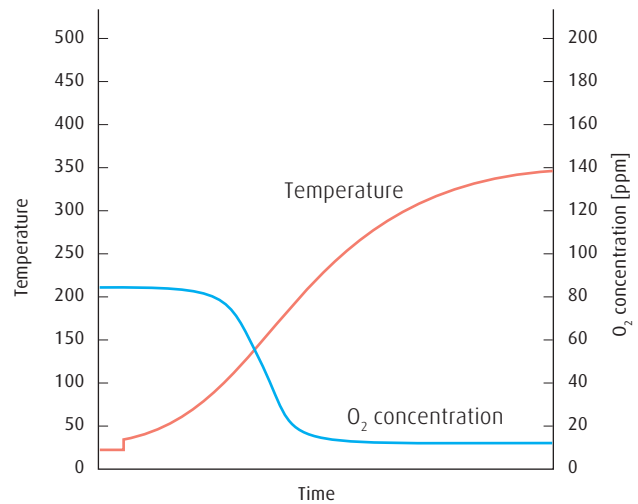


Figure 42: Measured oxygen concentration as a function of temperature when reacting 100 ppm oxygen in nitrogen with 1% hydrogen in a furnace with a copper wire coil as load.

5.9 Non-equilibrium

A homogenous reduction of oxygen by reaction with hydrogen will first occur at a noticeable rate above approximately 600 °C. In the presence of catalysing surfaces, this temperature is lowered. Figure 42 shows measurements from an experiment in a furnace filled with copper material. The analysis was made with respect to oxygen instead of the dew point. In this experiment, oxygen already starts to react and form water at a temperature of about 100 °C (212 °F), documented by a decreasing oxygen concentration. At a temperature of about 200 °C (392 °F), all the oxygen seems to have reacted to form water. This illustrates the effect of catalysing surfaces on gaseous reactions. Two important conclusions can be drawn from the experiment. The first is that hydrogen additions will be useful and provide reducing conditions only above a certain temperature. The second is that oxygen in the atmosphere, coming from leakages or from impure gas, cannot be compensated by the addition of reducing gas below a minimum temperature. Clean gases therefore are required at low temperatures for high quality results because oxygen impurities cannot be reduced by hydrogen or carbon monoxide.

Some gaseous reactions are sluggish also at high temperatures. Slow reacting gas species include the hydrocarbons, methane, propane or propylene. The equilibrium concept for carbon and oxygen control cannot be applied when these gases are used. Empirical control provides good results in situations with air-tight furnaces and low disturbances from air ingress. Annealing and hardening in N₂/CH₄ or N₂/CH₄/H₂ mixtures are therefore used with good results in such cases.

5.10 Gas flow rate and flow pattern

To minimise gas cost and to improve productivity, it is essential to adapt the gas flow rate to actual conditions. General guidelines are:

- Use high flow rate in the beginning of a cycle and when changing the atmosphere composition to condition the atmosphere as fast as possible. Later in the cycle, low flow rates can be used to maintain stable conditions. Figure 43 shows the purging curve for a furnace originally filled with air. By using a high nitrogen flow rate during start-up, up to the point corresponding to 3–5 furnace volumes, it is possible to shorten the time to reach atmosphere conditions good enough for starting the annealing or hardening cycle.
- The total gas flow into the furnace has to be increased by means of increased furnace inlet and exit cross section areas in contact with ambient air. Furnace suppliers recommend a flow corresponding to 3–4 m³/h of gas per dm² area open to air. The consequence in tube annealing is that the flow should increase with increased tube diameter.
- More gas is needed in a furnace room subjected to air drafts from open doors for example.
- Adapt the flow rate to the degree of disturbance from lubricant vaporising.
- The flow rate can be lowered if the atmosphere buffering capacity is increased. This means that the flow rate can be lower for a 100% hydrogen atmosphere than for a 100% nitrogen atmosphere.

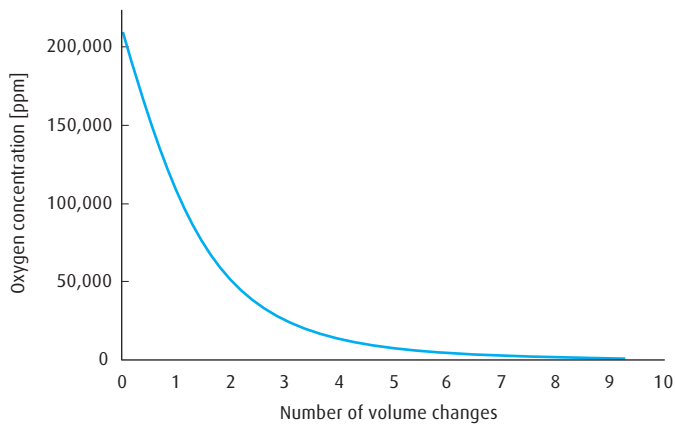


Figure 43: Purging curve showing the number of furnace volumes of nitrogen required to come down to a certain oxygen concentration in a furnace room originally filled with air (perfect mixing assumed).

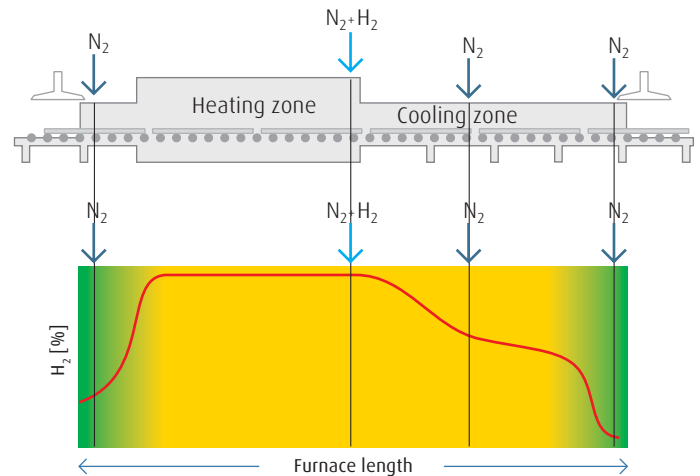


Figure 44: Hydrogen concentration over the length of a continuous furnace

It is difficult to give general guidelines for flow rates, but here are a few rough rules of thumb:

- 0.5–5 furnace volumes per hour in tight batch furnaces.
- 0.5–1.5 furnace volumes per hour in continuous furnaces with air-tight loading and unloading openings.
- 2–10 furnace volumes per hour in continuous furnaces with open loading and unloading openings.

The atmosphere flow in a continuous furnace should be directed towards the furnace inlet, thereby purging air, moisture and residual lubricant vapours out of the furnace. A typical distribution is 2/3 towards the furnace inlet and 1/3 towards the outlet.

Different gases and methanol may be introduced in different relative amounts and at different locations of the furnace in order to yield specific properties and functions of the atmosphere. Correct choice leads to lower gas consumption, improved quality, higher productivity, and to a safer process. Active gases, such as hydrogen, endogas, and dissociated methanol are introduced at a location where their reactive and reducing properties are useful. This is normally a high temperature location. Nitrogen inlets are chosen to give the required composition at different locations. Gas inlets and flow rates are located and chosen to ensure safety, that is to give non-flammable compositions at furnace inlets and outlets.

Figure 44 shows a concentration profile that can be achieved by the injection of proper amounts of nitrogen and hydrogen respectively at the proper locations in a continuous annealing furnace. A high reducing power is created in the hot part of the furnace, where it is needed, by injecting all the hydrogen there. At the furnace inlets and outlets,

a non-flammable atmosphere is obtained by dilution with nitrogen at these points.

5.11 The atmosphere control system

Based on the principles described previously, an atmosphere control system 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 vary in different zones of the furnace. In a batch furnace, the atmosphere composition set points can change with process time.

An example of an atmosphere control system is shown in Figure 45. Samples of the furnace atmosphere from different zones are taken with the help of a gas sample pump and a scanning system that gradually changes the location in the furnace from where the sample is taken. The sample is analysed in the control cabinet. The flow control valves in the flow train are in a closed loop connected with the atmosphere analysis. A control system often includes a PC enabling the visualisation of the process, alarm handling, data logging, recipe handling and so on.

Carbon potential control of the atmosphere, required for neutral annealing and hardening of steels, is conducted by the use of an "enriching gas", usually propane or natural gas. The enriching gas is usually fed into the furnace via an on/off solenoid valve, which is controlled by the difference between carbon potential set point and actual carbon potential. The solenoid valve opens when the actual atmosphere carbon potential falls below the set point and closes above the set point. The amount of enriching gas, sometimes called carrier gas, is very small compared to the amount of main gas supplied.

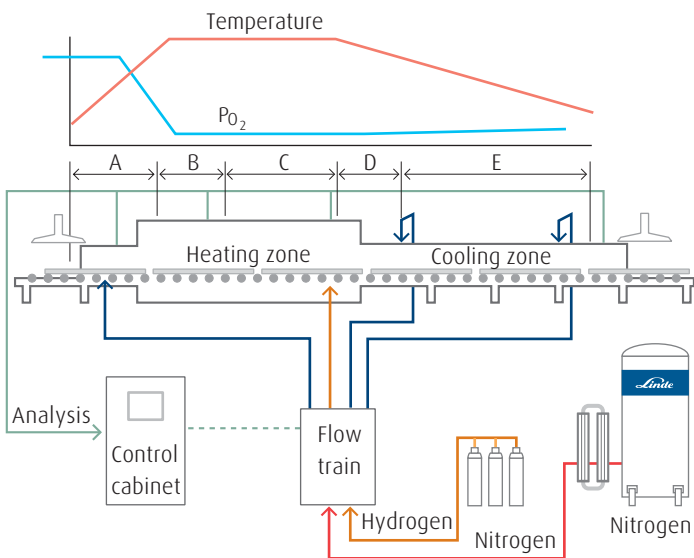


Figure 45: Principal atmosphere controlling zones in a continuous annealing furnace.



Figure 46: Example of a control cabinet for a nitrogen/endogas system

The letter notations A, B, C, etc. in the upper part of Figure 45 refer to the following atmosphere requirements in the different zones:

- A: The atmosphere should help to eliminate vaporised surface contaminants such as adhering lubricants in order to avoid the formation of soot deposits.
- B: When the temperature exceeds approximately 500°C (930°F), the oxidation rate is considerable. The atmosphere must accordingly be reduced 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 Figures 30–34). The atmosphere must therefore be highly reducing in this zone.
- E: Although the oxygen equilibrium pressure decreases with lowered temperature, the rate of oxidation will be low at temperatures below about 150 °C (300 °F) for steels. In this section it is therefore sufficient to have a neutral and oxygen-free atmosphere.

Atmosphere analysis and control for the system shown in Figure 45 is based on dew point analysis in the hot zone and oxygen control in the cooling zone. An example of a control cabinet for a nitrogen/endogas system is shown in the left part of Figure 46. The cabinet is equipped with a PC as the man/machine interface, a PLC for process control, a gas sampling system, a gas analyser, a modem for remote supervision and control, and a UPS (uninterrupted power supply) unit. 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. The gas flows for nitrogen, endogas and enriching gases are controlled in the flow train seen on the right. The flows of the flammable gases, endogas, natural gas and air are automatically switched off and the furnace purged with nitrogen in the event of safety-related alarms or a power failure.

With a closed loop control system, the annealing quality is ensured through proper composition control of the atmosphere in the different furnace zones. In the hot zone, this is achieved either by changing the total flow of nitrogen and 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. This will lead to quality assurance and gas savings as illustrated in Figure 47.

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 atmosphere conditions are stable and constant. Gas flow rate and mixing for such a system are adjusted to yield the correct atmosphere analysis and required heat treatment quality.

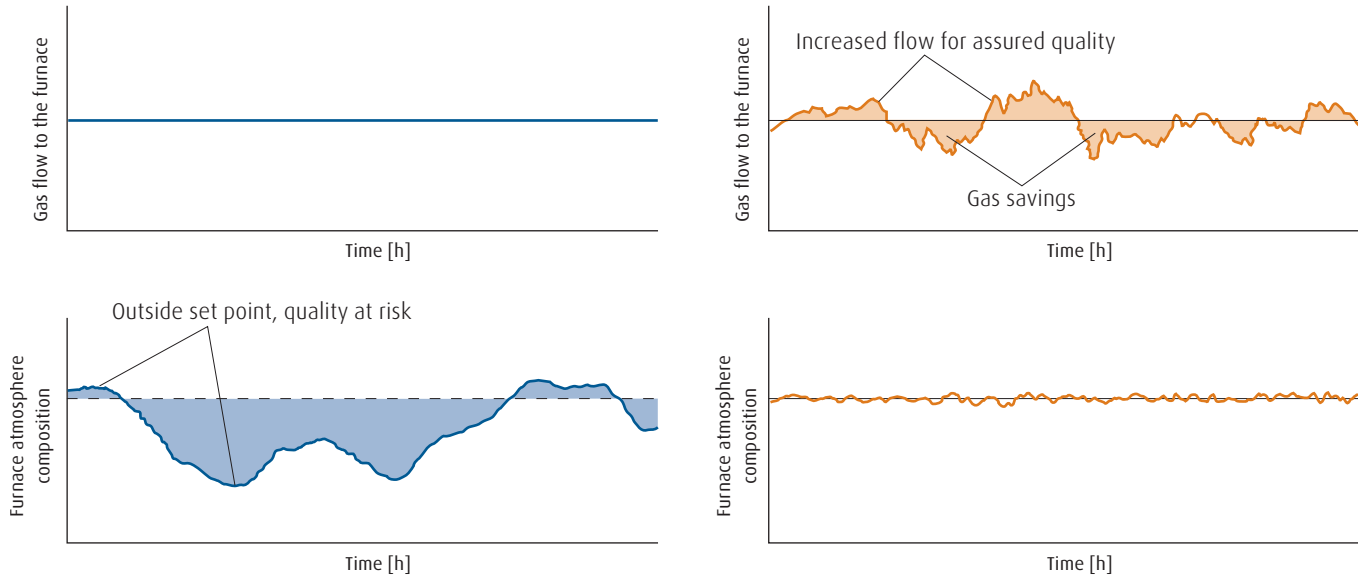


Figure 47: Illustration of quality assurance and potential gas savings by using a closed loop atmosphere control system for a) fixed gas flow and b) closed loop variable gas flow.

5.12 Examples of applications

Just pure nitrogen is used for purging upon start-up or shutdown. It is also used during idling when production is stopped, for instance in continuous furnaces. In this way good conditions are created for short atmosphere conditioning when starting production again. Nitrogen or carbon dioxide is also used for fire extinguishing.

In very tight furnaces, the amount of oxygen brought into the furnace with the nitrogen can be completely consumed, resulting in a complete stop of any oxidation process. Reducing vapours for instance from vaporised lubricants may help to reduce the oxygen level. Therefore, nitrogen atmospheres can under certain circumstances produce completely bright or slightly oxidised surfaces, often with a light grey surface appearance on steels.

5.12.1 Stress relieving and tempering of steels

Stress relieving and tempering is performed at low temperature, typically below 600 °C (1112 °F). At this low temperature, hydrogen or other reducing gases will not react fast enough to reduce the oxygen that enters the furnace. Pure nitrogen atmospheres therefore are the primary choice in these cases. High-purity nitrogen is recommended in order to limit the risk of oxidising the alloy. It is not enough to have a high purity of the nitrogen source. It is even more important to maintain the purity inside the furnace. Typically, the oxygen concentration level should be below 100–200 ppm to avoid discolouration from oxidation. This can be realised by analysing the oxygen concentration inside the furnace and by regulating the nitrogen flow into the furnace. The flow should be high enough to assure that the oxygen concentration is below a required set point. A similar system to the one described in the next section, “Annealing of aluminium strip coils”, can be used to fulfil these requirements.

5.12.2 Annealing of aluminium strip coils

It is practically impossible to create an atmosphere which is reducing against aluminium oxide. Nevertheless, pure nitrogen atmospheres are used with positive results. The reason is that even if a thin oxide is formed, the use of nitrogen retards its growth.

A specific and important beneficial effect of the use of nitrogen atmospheres with controlled oxygen concentration and dew point can be seen in the annealing of cold rolled strip coils. Adhering lubricant tends to create discoloured areas and staining, when annealing is done in air or in an oxidising atmosphere. By using nitrogen with low oxygen content it is possible to eliminate the discolouring. Figure 48 is an illustration of how the discolouring occurs within an area of the strip coil, where the atmosphere oxygen concentration lies within a certain range. Above and below this concentration range the strip surface is bright.

The discolouring problem is severe especially for Mg-alloyed qualities. According to recommendations by furnace suppliers this problem can be avoided by using an atmosphere with less than 0.1 vol% oxygen. It has been demonstrated that the surface finish also improves when lowering the oxygen level below 0.1 vol%.

Figure 49a shows the atmosphere dew point and oxygen analysis made during heating of strip coils in a batch furnace. After heating for approximately 1.5 hours corresponding to a temperature of approximately 200 °C (390 °F) there are peaks registered both for the dew point and for the oxygen concentration in a restricted temperature range. The peaks originate from reaction products from vaporised lubricants. Experience has shown that the discolouring is correlated to the height of these gas concentration peaks. High peaks correspond to heavy discolouration and vice versa.

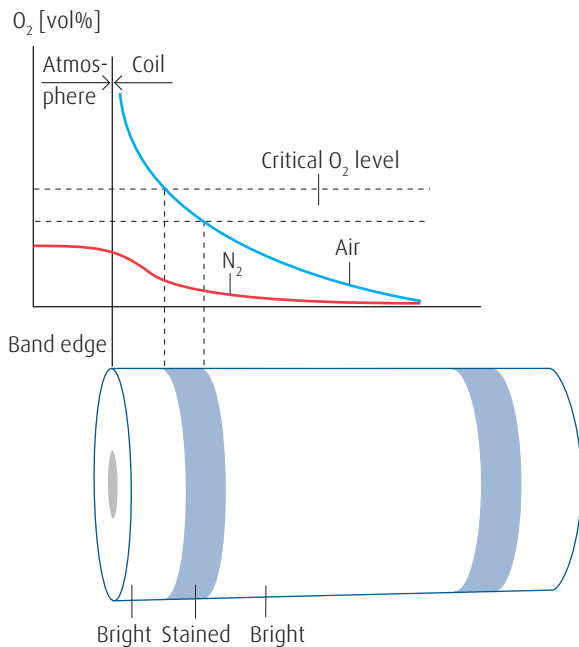


Figure 48: Illustration of the relation between discolouring and atmosphere oxygen concentration for aluminium strip coils.

By using a high flow rate of nitrogen of liquid purity during heating through the critical temperature regime for lubricant vaporising, it is possible to minimise the above mentioned gas concentration peaks and therefore also discolouration. In this way, the lubricant vapours are purged out of the furnace before their concentration reaches the level that can cause discolouring reactions. A closed loop flow control system based on atmosphere concentration analysis ensures proper quality. Figure 49b shows how a closed atmosphere flow rate control system can suppress the dew point and oxygen peaks, thereby assuring a high quality strip surface appearance.

5.12.3 Copper wire coil annealing

A system originally developed for a nitrogen/hydrogen atmosphere system turned out to give bright and good surface quality with only nitrogen when annealing copper wire coils in a batch furnace. As shown in Table 11, a condition for obtaining a bright surface was low enough oxygen impurity level (< 20 ppm in the test).

Table 11. Surface appearance of copper wire after annealing in nitrogen with different oxygen impurity levels

Test No.	H ₂ vol%	Oxygen level in gas exhaust, ppm	Comments
1	0	< 20	Bright
2	0	500	Oxidised
3	0	100	Oxidised
4	3	very low	Bright

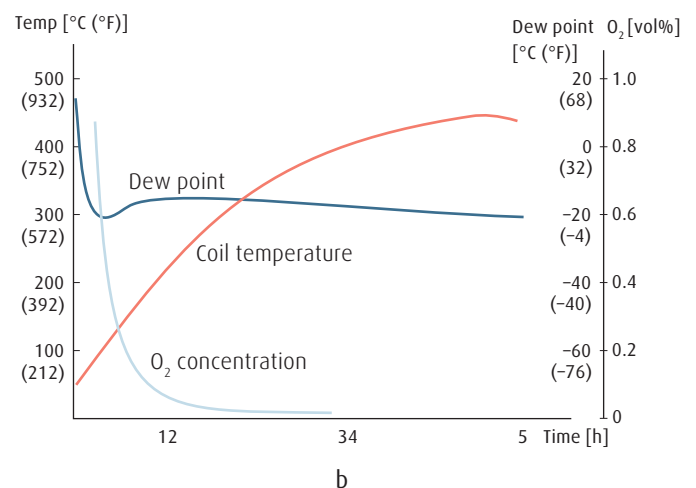
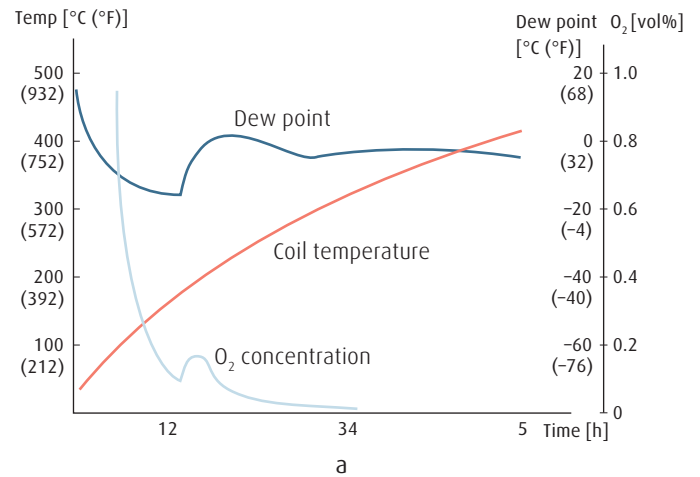


Figure 49: Atmosphere concentration measurements as a function of temperature for a) fixed nitrogen flow rate controlled over time and b) controlled nitrogen flow rate by analysis.

From this result and additional experiments, a nitrogen flow control system based on oxygen analysis was developed. The total flow is continuously controlled by the O₂ analysis. If the actual O₂ concentration is higher than the set point, the total gas flow rate is increased. If the actual O₂ concentration is lower than the set point, the total gas flow rate is decreased. This results in minimised gas consumption and quality assurance. In the manual mode, the system maintains a constant flow rate of nitrogen into the furnace and the O₂ concentration is monitored.

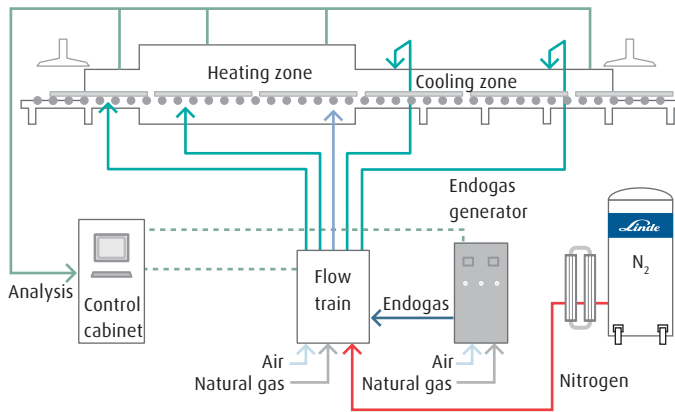


Figure 50: The CARBOFLEX atmosphere control system incorporating an external endogas generator.

5.12.4 CARBOFLEX atmospheres

The predominant class of atmospheres capable of high quality carbon potential control has nitrogen (N_2), carbon monoxide (CO) and hydrogen (H_2) as major constituents. The CO and H_2 parts originate either from endogas or from cracked methanol.

In a rotary retort furnace, the parts processed are continuously moved and accordingly all surfaces are evenly exposed to the atmosphere. In a fluidised bed, the gas also comes into close and even contact with the parts. For such furnaces, it is often a good solution, with respect to carbon neutrality, to use a non-equilibrium N_2 /natural gas atmosphere.

5.12.5 Steel tube annealing

Steel tube elements are more and more used in cars for critical parts. The automotive industry thus requires tubes which meet strict decarburisation specifications. These demands are impossible to meet if exogas is used.

Figure 50 shows the features of a CARBOFLEX atmosphere control system based on the combination of nitrogen and an external endogas generator.

The gas flow train, shown in Figure 50 and as installed in Figure 46, contains flow meters, regulating valves and pressure sensors for nitrogen, endogas, natural gas and air. The gas flows for nitrogen and endogas into the different zones of the furnace are regulated from the flow train. Gas samples are taken from different positions in the furnace and the gas sample is pumped to the control cabinet, seen on the far left in Figure 46. There the sample is analysed with respect to different species by the analysers mounted in the control cabinet. A sample gas scanning system makes it possible to conduct step-by-step gas analysis from different positions in the furnace. The actual gas analysis is compared with set points for different parts of the furnace and the

deviation between actual reading and set point is the input signal for automatic adjustment. The adjustment signal is sent from the control cabinet to the flow train, which automatically adjusts flows and mixtures in order to attain the set point gas analysis inside the furnace. There is on-line carbon potential control of the atmosphere in the hot zone of the furnace. In other parts of the furnace, other regulating algorithms are used, for instance to eliminate the risk of soot deposits from vaporised or cracked lubricants and to assure a bright end result.

The CARBOFLEX control cabinet contains a PLC for control and a PC with a touch screen as the man/machine interface, seen on the left in Figure 46. Settings of the atmosphere parameters, recipe handling, alarm setting, start up and stop, calibration of analysers, and viewing of actual furnace atmosphere data are carried out from the PC touch screen on the control unit.

The system enables historical logged data to be stored, viewed and evaluated for statistical process control and it can be connected to a central computer supervision system and made remotely accessible via modem or Internet.

A major benefit of the installed systems is carbon control, which has enabled decarburisation-free annealing to be carried out to meet strict quality requirements. Active controlled carburising is also possible. This may be done on tubes that have to withstand mechanical loads or wear. Even controlled decarburising is possible; this can for instance improve the bending properties of the tubes.

Compared to exogas, the nitrogen/endogas atmosphere has a much better buffering capability (the ratio $(CO + H_2)/(CO_2 + H_2O)$), which eliminates the disturbing effects of air entering the furnace. Less gas is consequently required to maintain the atmosphere quality.

Optimised recipes with different flows are available to adapt flow to tube dimension and tube qualities. Special idling programs are used to minimise gas consumption when there is no production.

5.12.6 Hardening of steel parts

There are hundreds of CARBOFLEX nitrogen methanol systems installed in sealed quench furnaces used both for hardening and for carburising. Neutral hardening requires a lower methanol fraction compared to carburising. This is because there is no need for the atmosphere to actively transfer carbon to the steel. Typically, an 80% N_2 /20% methanol atmosphere is used. It is important to adjust the settings for CO_2 , oxygen probe or dew point for the carbon potential control to the applied nitrogen/methanol mixture (see Appendix of furnace atmospheres 1: Gas carburising and carbonitriding).

Methanol can usually be injected into the furnace ventilator area. This has the advantage that the liquid methanol is dispersed by the ventilator and is therefore correctly vaporised and dissociated into carbon monoxide (CO) and hydrogen (H_2).

A conveyor furnace typically has a low height and a restricted cross section. It is a poor solution to inject methanol as liquid into the interior of such a furnace. The reason is the risk of creating a cold spot at the

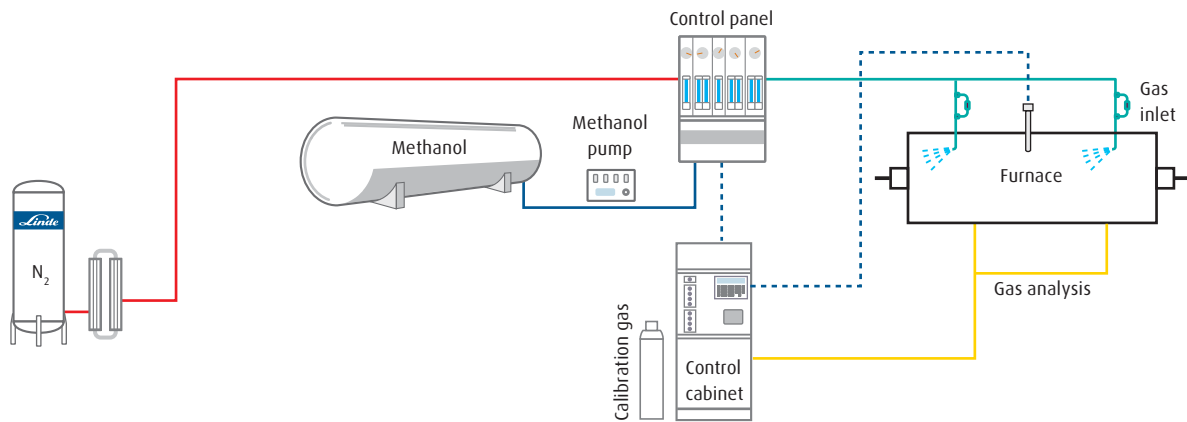


Figure 51: A nitrogen/methanol CARBOFLEX system with nitrogen supply from a membrane unit.

point of injection, because methanol dissociation requires energy, which is taken from the limited surrounding volume. This results in a locally decreased temperature. Negative consequences can be deposits of soot at the point of injection. A better solution is to use a vaporiser for methanol, in which methanol is vaporised before entering the furnace. Upon vaporising, there is a volume increase of approximately a factor of 600. When entering the furnace, the vapour is spread into a wide space. The energy required for heating to furnace temperature and for dissociation of methanol is also taken from this wide space, resulting in a negligible temperature drop. Figure 26 shows an example of how such a methanol vaporiser is positioned at the rear furnace wall, just over the quench chute in a conveyor furnace.

The use of membrane nitrogen, containing up to 1 vol% oxygen is, when applicable, usually a cost advantage compared to the use of high-purity liquid nitrogen, provided that the temperature is high enough and that there are enough of the reducing components CO and H₂ that can react with oxygen to form CO₂ and H₂O respectively. A diagram of a CARBOFLEX membrane nitrogen/methanol system for hardening of parts is shown in Figure 51. The membrane unit produces nitrogen with a typical purity of 99.5%. For peak flows and for back up purposes, a liquid nitrogen tank is also installed. Carbon potential control is performed with an oxygen probe and with propane as an enriching gas. All methanol is injected at the location of one of the furnace ventilators in the hot zone. Nitrogen inlets are located towards the inlets and outlets.

The same principal atmosphere system as shown in Figure 50 has been applied in continuous furnaces for hardening of bearing components. Air-cooled endogas generators with analysis control of the endogas composition are used. In case of generator failure, there is a stand-by generator that can be put into production while the failed generator is maintained. Additionally, there is a backup storage of gas cylinders which, in the worst case of double generator failure, can supply the required furnace atmosphere. The system was set up to include remote supervision, managed from a Linde Gas control centre. The control centre

is responsible for taking appropriate measures if there is an alarm. With this system, the customer can fully concentrate on producing parts without having to bother about maintenance of the atmosphere system including the generators.

5.12.7 Stainless steel tube annealing

A HYDROFLEX nitrogen/hydrogen atmosphere control system with dew point control for bright annealing of stainless steels is shown in Figure 52.

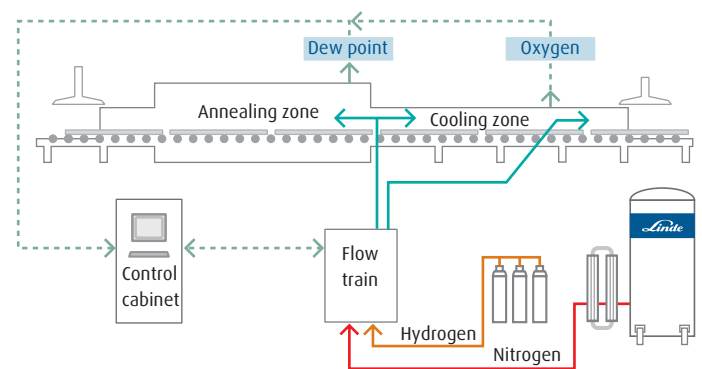


Figure 52: HYDROFLEX nitrogen/hydrogen system for bright annealing

The result of the dew point analysis is registered in the control cabinet and compared with a set point value. The difference between the actual value and the set point is the control parameter for the flow control in the gas mixing panel.

There are three different lines for nitrogen in the gas mixing panel in Figure 52, one for flow control into the hot furnace, one for safety nitrogen purging and one to the cooling zone.

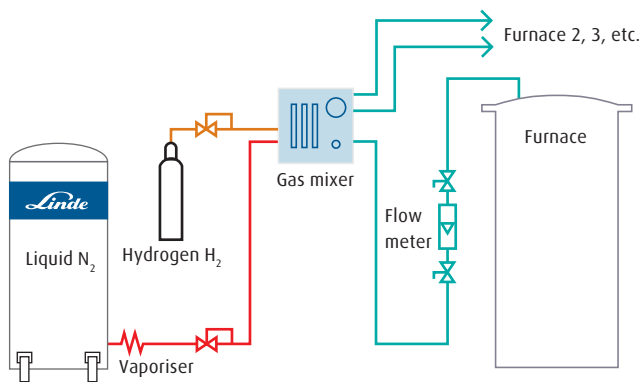


Figure 53: A HYDROFLEX system for copper annealing in a pit furnace.

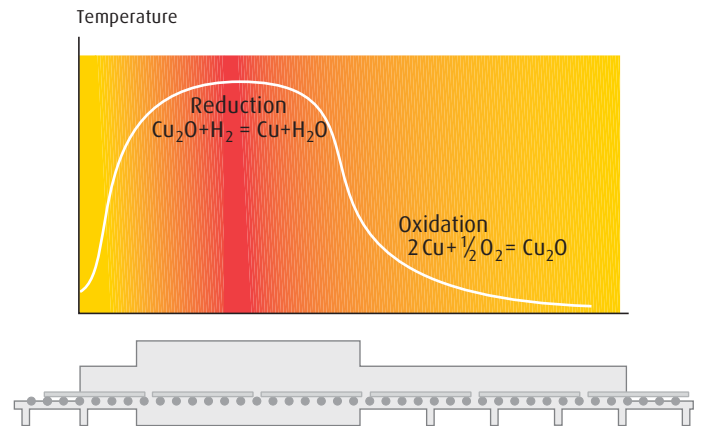


Figure 54: Temperature profile for reducing and oxidising reactions in a copper tube annealing furnace.

5.12.8 Steel strip and wire coil annealing

The important advantages of using 100% hydrogen with respect to productivity and cleanliness have resulted in a replacement of N_2/H_2 or HNX atmospheres. The higher gas cost is compensated by increased productivity and improved surface quality. Annealing in bell furnaces with pure hydrogen atmospheres has the same advantage for copper strip coils as for steel strip coils. In fact, 100% hydrogen bell furnaces were first developed for annealing brass strip coils and the furnace technology was later further developed for steel.

5.12.9 Continuous stainless steel wire annealing

In one case, a cracked ammonia system was replaced by a nitrogen/hydrogen system. The lowest possible hydrogen concentration to yield a bright annealing result was found to be 25 vol%. However, the degree of nitrogen pick-up, caused by the 75% nitrogen in the atmosphere, was unacceptably high. Therefore, nitrogen was replaced with argon, maintaining the hydrogen concentration level at 25%. The cooling rate was then too low, which meant that the wire exited the furnace at too high a temperature, resulting in oxidation and discolouring. A 100% hydrogen atmosphere was therefore chosen as the final solution. There were fears that gas costs would run too high. However, it was found that the huge buffering capacity of this atmosphere meant a possible gas flow reduction of 60%. Furthermore, the productivity was increased due to faster heating and cooling by approximately 25%. In conclusion, the hydrogen system paid off and resulted in improved product quality.

5.12.10 Annealing of copper and brass strip coils

A customer wanted to replace an exogas generator system for annealing of copper strip coils in pit furnaces. There were two major reasons; first a desire to get rid of the generator, which had high maintenance and repair costs, and secondly, a need to improve surface quality of annealed coils.

After testing pure nitrogen and different nitrogen/hydrogen mixtures, it was found that a HYDROFLEX nitrogen/1% hydrogen mixture provided a proper product quality. The nitrogen/hydrogen system provided a lower cost than for exogas. This was because the gas flow rate could be drastically reduced, from $30 \text{ m}^3/\text{h}$ with exogas to $7 \text{ m}^3/\text{h}$ for the nitrogen/hydrogen system. Additional gas savings were obtained with flow reductions during idling and non-productive hours. The gas system, shown in Figure 53, consists of a central gas mixer for nitrogen/hydrogen and separate flow meters for each furnace.

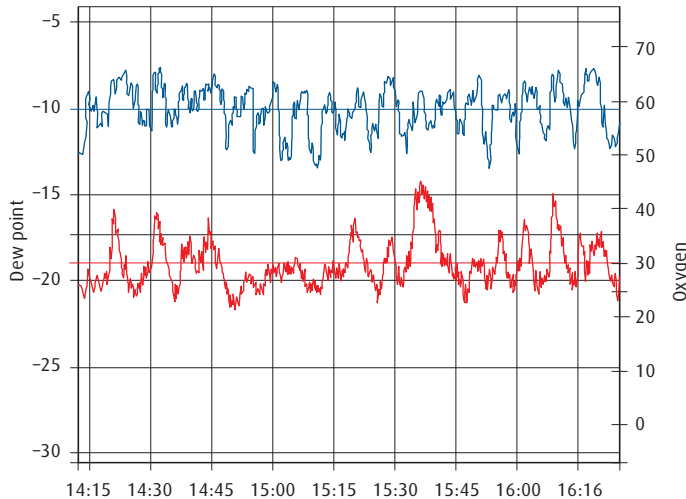
In the case of brass strip coil annealing in a high convection bell furnace, it was found that an atmosphere of pure nitrogen gave bright surfaces. However, when 25% hydrogen was added, the annealing treatment cycle was reduced by about two hours due to faster heating and cooling. An additional benefit was that the furnace fan requires less electric power due to the lower density of the N_2/H_2 mixture compared with pure N_2 .

5.12.11 Copper tube annealing

The use of exogas is common for copper annealing. The buffering capacity and the oxygen potential of the exogas at annealing temperature are sufficiently high. However, there are frequent problems with discolouration of parts due to oxidation in the cooling zone of the annealing furnace. With an exogas generator, it is not possible to have an on-line closed loop atmosphere control that reacts to a registration of an excessive free oxygen concentration in the cooling zone. This is because of the inflexibility of an exogas generator with respect to changes in flow rate or in atmosphere composition. A nitrogen/hydrogen system can however be made to react to and level out such disturbances.

Figure 54 illustrates that the risk of oxidation in copper tube annealing is highest in the cooling zone. One requirement is therefore to assure that the level of free oxygen in the cooling zone is below a critical value. In

HYDROFLEX controller graphics



HYDROFLEX flow graphics

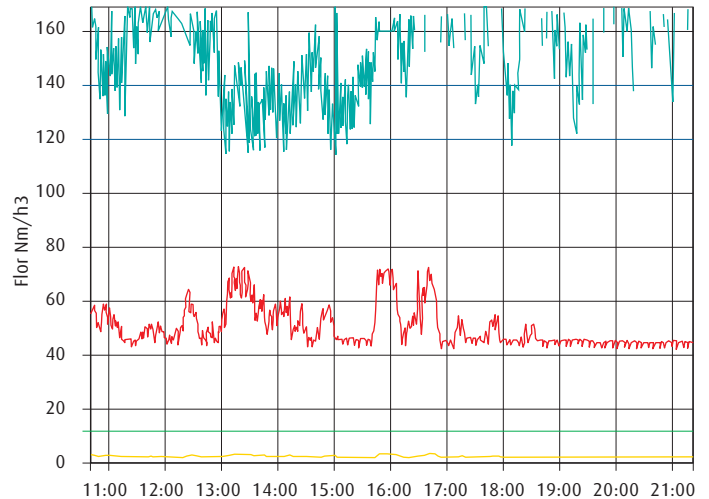


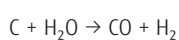
Figure 55: The HYDROFLEX atmosphere control system displaying: a) The variation of the actual analysis values for dew point (upper curve) and oxygen (lower curve) and b) The variation of the flow rates to the hot zone (lower curve) and cooling.

the hot zone, soot deposits must be eliminated by removing lubricant vapours. This is realised by keeping the atmosphere dew point as high as possible without oxidising the copper. The lubricants are removed by an atmosphere flow that is directed towards the furnace inlet. In the hot zone, there is a possibility to reduce copper oxides, which may remain from earlier processing.

A HYDROFLEX nitrogen/hydrogen atmosphere control system for copper annealing has the same principal layout as the one shown in Figure 52. The level of hydrogen in the gas mixture is, however, kept at 1–2 vol%. It may be advantageous to have a central gas mixing station shared by several furnaces, but to have a separate atmosphere control system for each furnace. Pictures of the HMI (Human Machine Interface) part of the control cabinet and the flow train of such an atmosphere control system are shown in Figure 55.

5.12.12 Decarburisation annealing

Decarburisation of steel is performed mainly for the reason of improved magnetic properties. Sample products include silicon iron sheets for transformer laminations, motor cores, and so on. Decarburisation is most efficiently done in nitrogen/hydrogen/water vapour atmospheres as the fastest decarburising reaction is:



Decarburisation rate increases with increased water vapour concentration. The upper limit of water vapour concentration is set by the limit where iron is oxidised. This limit can be expressed as an $\text{H}_2\text{O}/\text{H}_2$ ratio (see section 5.2). A water vapour concentration increase can be compensated by increased hydrogen concentration to achieve the fastest possible decarburisation, while still not oxidising the iron.

This application does not require the highest nitrogen purity and therefore PSA or membrane nitrogen may be a good nitrogen supply alternative if the flow rate is above $10\text{m}^3/\text{h}$.

Figure 56 shows a diagram of a decarburising furnace with gas supply and process requirements. Decarburising is carried out in the hot part of the furnace at about $800\text{ }^\circ\text{C}$ ($1472\text{ }^\circ\text{F}$) with the help of water injected in that zone together with nitrogen and hydrogen. There is usually a second oxidising step, marked blueing in the figure, in which a thin blue oxide is formed. The oxide acts as a dielectric on the decarburised parts.



Figure 56: Atmosphere system for decarburising.

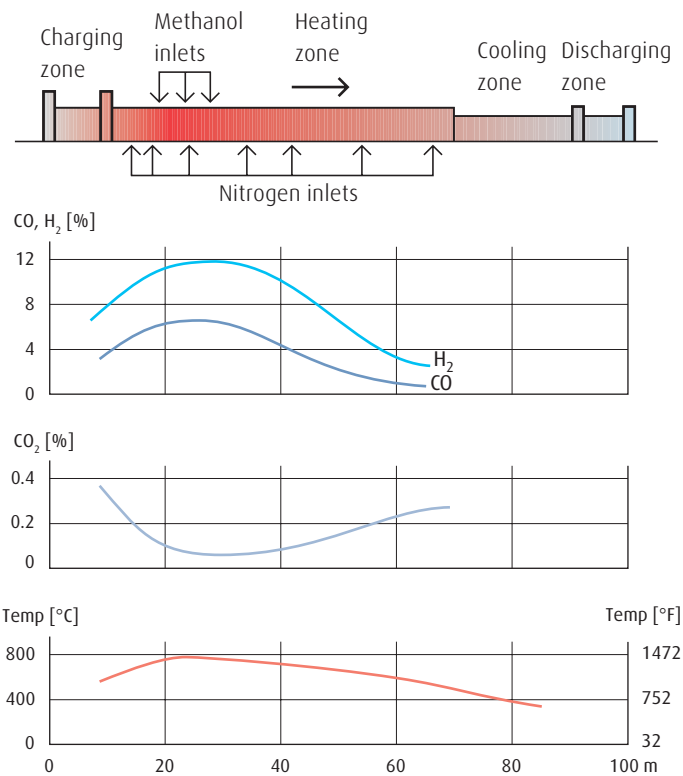


Figure 57: Atmosphere composition variation in a long continuous furnace.

5.12.13 Steel strip coil annealing

Figure 57 shows the setup of a nitrogen/methanol CARBOFLEX system in a roller hearth furnace for strip coil annealing. Methanol inlets are located in the hot zones of the furnace to ensure proper dissociation and to produce an active, reducing and carbon neutral atmosphere. Nitrogen inlets are located along the furnace some distance away from the methanol inlets. In this way a proper atmosphere composition gradient is obtained, with a high concentration of active and reducing gas in the hot zone and a non-flammable composition at inlets and outlets, as illustrated in Figure 57.

During annealing of strip or wire coils in a bell furnace, the temperature rises fairly slowly from ambient to treatment temperature.

Annealing temperature normally is in the range 700–800 °C (1292–1472 °F). The slow heating rate and the low process temperature make nitrogen/methanol a rarely used atmosphere choice. In some cases, it is, however, a proper choice, but methanol must not be introduced until the temperature exceeds approximately 700 °C (1292°F). Methanol injection must normally be carried out from the furnace bottom and flow upwards. A methanol vaporiser is used for proper introduction. This procedure is described in section 4.

5.13 Vacuum as atmosphere

Vacuum acts like an inert gas in the sense that there are no gas species that can cause detrimental oxidation or other reactions. Vacuum is even active in removing detrimental surface residues on parts to be heat-treated by vaporising the residues and pumping them out of the furnace. At high enough temperature and low enough pressure, oxide removal by dissociation is possible.

In vacuum heat treatment, the occurrence of gaseous molecules is so rare that there are no net reactions such as oxidation or carburising with the metal surface. If the vapour 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 heat treatment cycle therefore are mostly cleaner than upon entering.

5.13.1 Classification of vacuum systems

In order to create a vacuum within a closed container, or vessel, the molecules of air and other gases that reside inside must be removed by means of a pumping system. The vacuum system includes the pumps and furnace, together with the associated piping, valves, vacuum gauges/instrumentation and other components of the system. Vacuum systems can be classified by the pressure range achieved, as shown in Table 12. Vacuum is, as evident from the table, a relative status.

Table 12. Classification of vacuum systems

Quality of vacuum	Pressure range		Number of oxygen molecules per m ³
	Pa	mbar	
Atmospheric pressure			5.6×10^{24}
Rough	10^2 – 10^5	1 – 10^3	5.6×10^{21}
Fine	10^{-1} – 10^2	10^{-3} – 1	5.6×10^{18}
High	10^{-5} – 10^{-1}	10^{-7} – 10^{-3}	5.6×10^{14}
Ultra-high	$<10^{-5}$	10^{-7}	

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

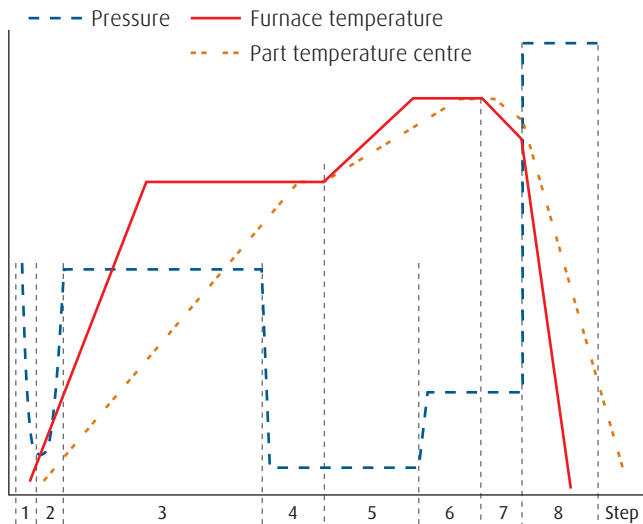


Figure 58: Temperature and pressure cycles in vacuum heat treatment. (The steps, 1–8, are explained in the text.)

the initial pump-down from atmospheric pressure to approximately 3 Pa (3×10^{-2} 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 (1.3×10^{-2} mbar) to 0.1 Pa (1×10^{-3} mbar). In this intermediate pressure range, the roughing pump loses efficiency while the diffusion (vapour) pump just begins to gain efficiency. 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 (3×10^{-2} mbar) and discharge pressures not exceeding 65 Pa (6.5×10^{-1} Torr). 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.

5.13.2 The role of gas in vacuum heat treatment

Although vacuum in simple terms means freedom from gas, for vacuum heat treatment there is a need for substantial amounts of gases; mainly nitrogen but also argon, and sometimes hydrogen and helium. The gases are used primarily for cooling, but also for initial purging, and as back-fill gas during heating and holding. This is explained by Figure 58, which shows that a vacuum annealing or hardening cycle is made up of steps of varying pressures. Vacuum is used during the “hot” part of the cycle. High pressure is used during cooling and increased pressure may also be used on heating. Instead of a continuous supply of industrial gases as is required for atmosphere pressure furnaces, the vacuum heat treatment furnace requires a discontinuous supply of protective gas provided almost instantaneously at elevated pressures and at significant flow rates.

Referring to Figure 58, the heat treatment cycle follows these steps:

- 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. Nitrogen can be used for backfilling after the initial vacuum pump-down. After backfilling, the furnace is again evacuated. Backfilling and subsequent pumping can be repeated and result in an appreciable lowering of oxygen and humidity concentrations.
- 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. (Modern vacuum furnaces are equipped with a fan for convective heating. Nitrogen is mostly used for convective heating. Argon, hydrogen or helium could also be used.) If there is no fan, the pressure is maintained at a low value. Heating in that case is slower as it 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 final annealing or hardening temperature to assure that the whole load uniformly reaches the temperature before going to Step 5.
- Step 4: At the end of the holding time, vacuum pumping is activated. This is to lower the atmosphere oxygen partial pressure and to efficiently remove all volatile species and dirt on the parts.
- Step 5: The temperature is increased to the annealing or hardening temperature.

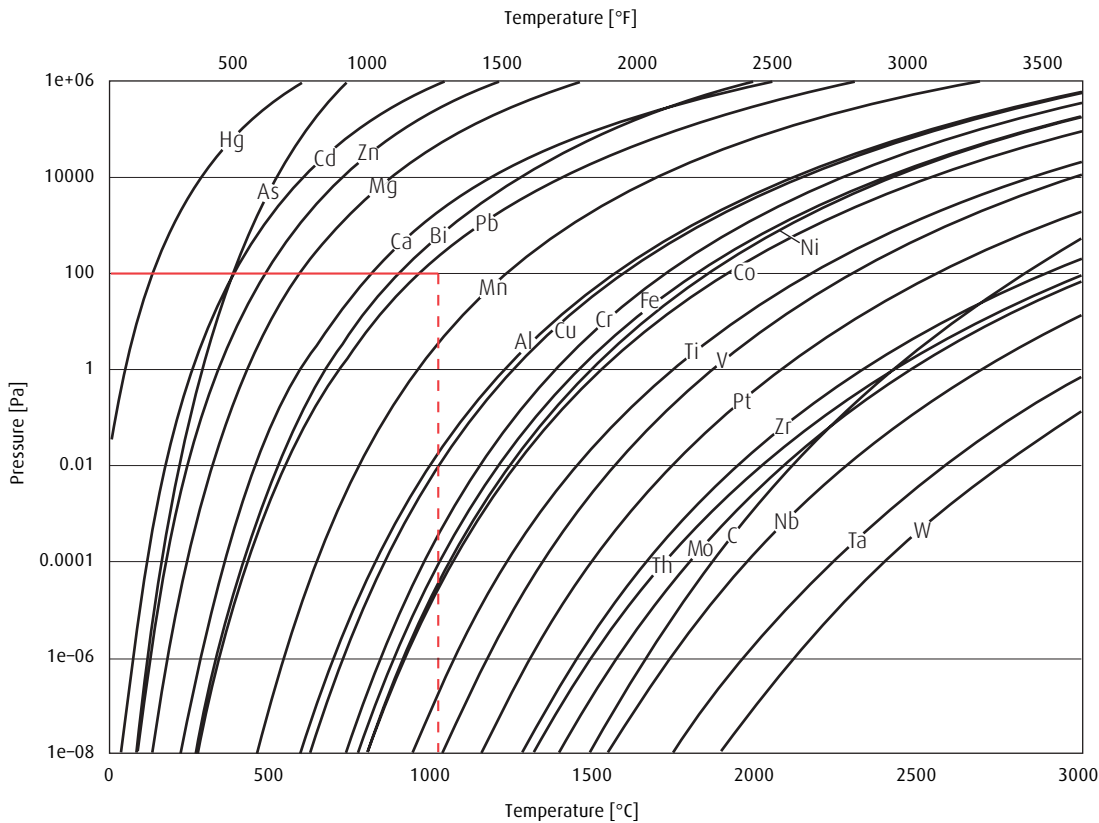


Figure 59: Vapour pressure curves for metals as a function of temperature calculated by Thermo-Calc [6]. If the pressure in the vacuum furnace is below the vapour pressure curve for a certain element, that element will vaporise. Example for the vacuum/temperature combination 100 Pa/1000 °C (1832 °F) indicated in the diagram: Mn, Al, Cu, etc. are stable but Pb, Bi, Ca, etc. will vaporise.

- Step 6: Alloys containing metals that easily vaporise may require the process to run not at high vacuum but at a certain elevated pressure. The backfill gas, mostly nitrogen, is then added to maintain the pressure at the desired level.
- Step 7: By introducing inert gas into the furnace up to a certain elevated pressure, a fast cooling to room temperature is achieved. Nitrogen from 1 to 6 bar (up to 90 psig) pressure is common. Furnaces for 10 bar and higher are used for even higher cooling capacities.

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 alloy.

5.13.3 Vapour pressure

The vapour pressure of an element is the pressure where the solid and vapour are in equilibrium with each other. The vapour pressure of metals varies with temperature, as seen in Figure 59. Cadmium, zinc, magnesium, bismuth, manganese, and also chromium are elements with high vapour pressures as seen from that diagram. Such elements vaporise more easily during vacuum heat treatment. Vaporising leads to negative effects both because of loss of material from the alloy and because vapours 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 not suited for vacuum heat treatment because the zinc would vaporise. The only way to avoid vaporising is to use a pressure above the vaporising pressure, although this is counteractive with respect to keeping the best vacuum for a good result.

5.13.4 Dissociation and reduction of oxides

The metal oxides will decompose into their constituent elements when heated to sufficiently high temperatures at a low enough vacuum level. The dissociation pressure is the same as the oxygen equilibrium partial pressures over the metal oxide as was shown in Figure 29. Figure 60 shows the dissociation pressures for some additional alloying elements. 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.

At an ultra-high vacuum of the order 10^{-5} Pa (10^{-7} mbar) there are still about 10^{15} 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 the molecules are oxygen as in air, the oxygen partial pressure, PO_2 , will be about 10–11 atm. From a theoretical equilibrium point of view, this is an oxidising atmosphere for many metals at normal annealing and hardening temperatures according to Figure 61. If the furnace is purged with nitrogen before the vacuum pumping, the resulting oxygen partial pressure is reduced to about 10^{-16} atm. This is still oxidising towards metals like chromium. Repeated nitrogen purging and vacuum pumping could reduce this further. That is, however, not the case in practice. How could vacuum heat treatment result in completely bright parts? The major reason is that the oxygen concentration is in reality lower than predicted on the foregoing simplified assumptions because the available oxygen is consumed. The graphite used for heating elements, charging bricks and the furnace chamber may consume oxygen both by adhesion of oxygen molecules to the graphite and by CO formation. Another reason why oxidation does not occur is slow kinetics. Although chemical equilibrium considerations indicate oxidising conditions, the rate of oxidation is very slow in vacuum.

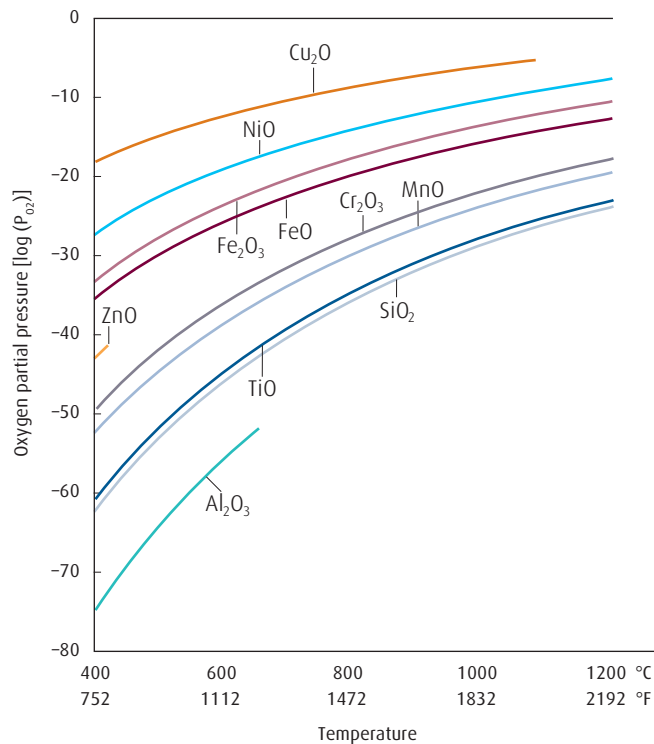


Figure 60: Dissociation pressures (oxygen equilibrium partial pressures) for some metal oxides [6].

Hydrogen has positive effects on reducing power for oxides and on the cooling rate when used as a cooling gas. A negative effect is that hydrogen may react with the graphite used in heating elements and for other parts inside the furnace.

5.13.5 Contaminants and leak testing

Oxygen, water and hydrocarbons are the most common contaminants in vacuum atmospheres. Oxygen can be introduced with air through vacuum leaks or contaminated backfill 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 locating these leaks nearly impossible before they begin causing considerable problems. Occasionally, water is introduced with the parts either from incomplete drying after cleaning or attached hygroscopically to the part surface or the furnace interior. Discolouration of vacuum heat-treated 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. Vacuum furnaces should have all doors closed and be kept under vacuum to minimise moisture and air infiltration when not in use.

Leak testing should be done when required because of discoloration of treated 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 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.

Carbon flux	Heat flux
$dm/dt = \beta \times (C_{\text{gas}} - C_{\text{surf}})$	$Q = h \times (T_{\text{gas}} - T_{\text{surf}})$
β prop. $\text{CO} \times \text{H}_2$	h prop. $(\text{Pressure})^n \times (\text{Velocity})^m$
$dm/dt = D \times dc/dx$	$Q = D^T \times dT/dx$

Figure 61: Analogy between mass transfer and diffusion and heat transfer and diffusivity.

5.14 Heat transfer

5.14.1 Convective heating and cooling

Heat transfer occurs by two major mechanisms: radiation and convection. (Direct contact heat transfer occurs in cases like wire annealing in strand tubular furnaces.) At high temperatures, radiation is the dominating mechanism and at low temperature convection predominates. In the radiation regime, which corresponds to temperatures above approximately 700 °C (1292 °F), the influence from the atmosphere on heat transfer is negligible. At low temperatures the heat transfer rate by radiation is low.

Today vacuum furnaces are commonly equipped with a convection fan and made to work at a certain elevated pressure during heating up. In this way the heating time can be shortened as compared to heating in vacuum. The elevated pressure is maintained up to a temperature where the risk of oxidation becomes apparent and the radiation heat transfer reaches a substantial rate.

The principles for heat transfer by convection are analogous to those for mass transfer and diffusion as illustrated in Figure 61.

Heat transfer from the metal surface to the atmosphere follows the equation

$$Q = h (T_{\text{gas}} - T_{\text{surface}})$$

where T is temperature and Q is energy flow per area and time unit, and h is the heat transfer coefficient. The heat flux from surface to atmosphere must be the same as the flux from the inside of the metal part to the surface.

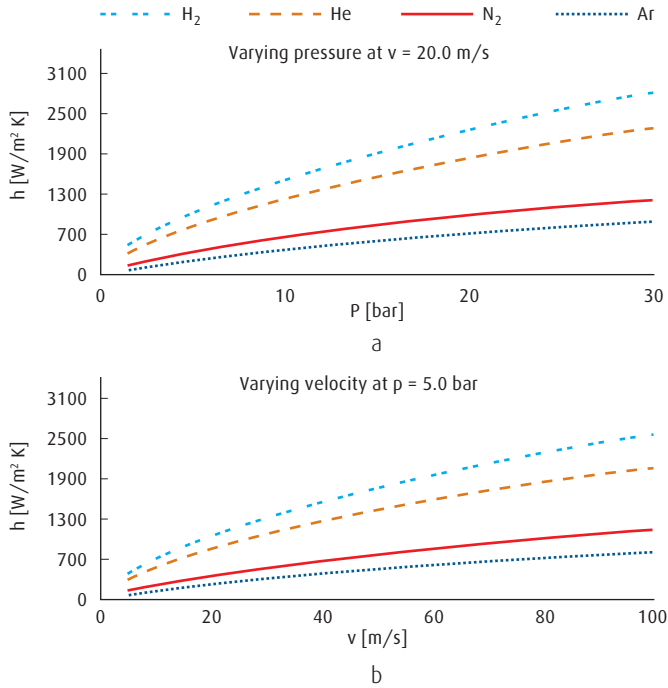


Figure 62: Theoretically calculated heat transfer coefficient for different gases in cross flow forced convection as a function of gas a) pressure and b) velocity.

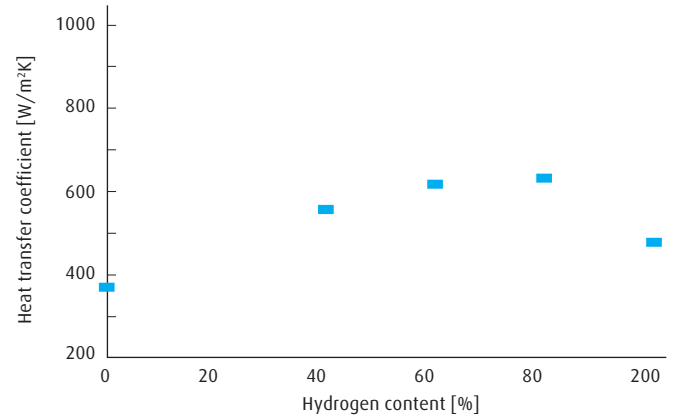


Figure 63: Average experimentally evaluated heat transfer coefficients for different hydrogen/nitrogen blends at 10 bar [10].

The heat flux going into or out of the solid metal is described by the equation

$$Q = D_T \, dT/dx$$

where D_T is the diffusivity and dt/dx is the temperature gradient.

Upon cooling, heat is transferred away from the hot metal surface by the gas molecules. By increasing the number of gas molecules that hit the metal surface, either by increasing the gas pressure or the gas velocity, it will be possible to increase the heat transfer coefficient. Increased turbulence in the gas flow pattern also increases the heat transfer rate. The quantitative value of the heat transfer coefficient therefore depends not only on physical gas properties like density, viscosity and heat capacity, but also on geometrical dimensions like part diameter and part distances, the type of flow direction being perpendicular or parallel to the parts and, as mentioned, on the degree of turbulence. An expression for h is:

$$h = C \cdot V_\alpha \cdot \rho_\beta \cdot v_\delta \cdot (c_p)_\mu \cdot k_\varphi / d_\lambda$$

where

V = upstream flow velocity (m/s)

ρ = density of the gas (kg/m³)

v = kinematic viscosity of the gas (Ns/m²)

c_p = specific heat capacity of the gas (kJ/kg/K)

k = thermal conductivity of the gas (W/m/K)

d = geometrical unit (m), equal to the diameter in the case of a cylinder

and $C, \alpha, \beta, \delta, \mu, \varphi$ and γ are all constants

Hydrogen and helium have low density, high specific heat capacity, and high thermal conductivity as compared to nitrogen and argon, see Table 13. This gives helium and hydrogen much better heat transfer properties than nitrogen and argon, as shown in Figure 62, which also shows the effect of velocity and pressure.

Table 13. Physical properties of gases (15 °C, 1 bar)

Properties:	Argon	Nitrogen	Helium	Hydrogen
Density (kg/m ³)	1.669	1.170	0.167	0.084
Specific heat capacity (J/kg×K)	523	1040	5190	14300
Thermal conductivity (W/m×K)	0.0173	0.0255	0.1536	0.1750
Dynamic viscosity (Ns/m ²)	23×10 ⁻⁶	18×10 ⁻⁶	20×10 ⁻⁶	9×10 ⁻⁶

When mixing a light gas such as hydrogen with a heavy gas such as nitrogen, theory predicts a maximum heat transfer coefficient for a certain mixture of about 80% hydrogen/20% nitrogen. This is confirmed by experiments as shown in Figure 63. The position of the maximum depends on the flow conditions. Increased turbulence shifts the maximum towards lower hydrogen concentrations.

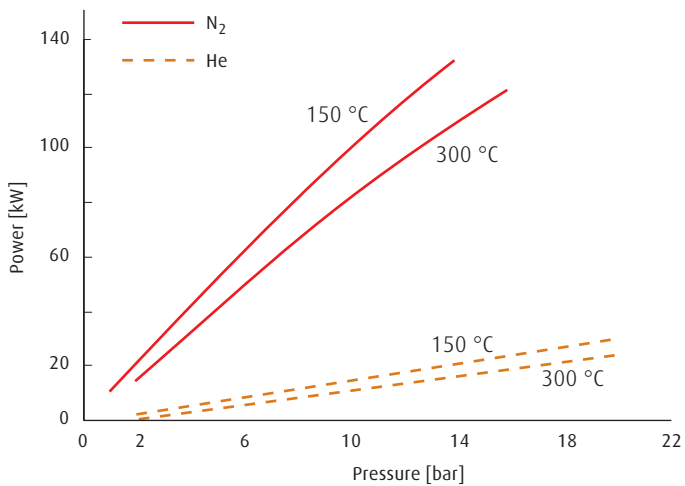


Figure 64: Power demand of the fan motor in a vacuum furnace as a function of cooling gas and gas pressure, at two gas temperatures [11].

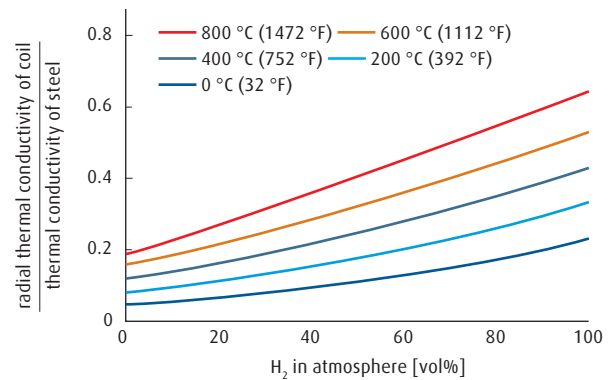


Figure 65: The relation between radial heat transfer and atmosphere hydrogen concentration in a strip coil annealing case [13].

The use of low-density gases (hydrogen or helium) has the additional benefit that furnace ventilator or fan power is reduced, as illustrated in Figure 64. For a certain fan power, it means that the use of helium and hydrogen will result in higher gas velocities as compared to the use of nitrogen or argon. Also in atmosphere furnaces this is beneficial when changing from an atmosphere with nitrogen to 100% hydrogen. Bell furnace annealing in 100% hydrogen is an example.

For single-chamber vacuum furnaces, it is important that the chamber is quickly filled with gas up to the required pressure after the completed heating cycle in order to allow cooling to start as fast as possible. The filling time is dependent on the type of gas. As shown in Table 14, the filling time is reduced from approximately 13 seconds to only 4 seconds when changing the gas composition from 60% nitrogen/40% hydrogen to 100% hydrogen for a specific installation.

Table 14. Filling time for various nitrogen/hydrogen mixtures from a buffer vessel at a pressure of 135 bar [9].

Gas composition	Filling time [sec]
60% N ₂ , 40% H ₂	12.8
40% N ₂ , 60% H ₂	10.0
20% N ₂ , 80% H ₂	9.3
100% H ₂	4.0

The improvement of gas quenching efficiency in vacuum furnaces is a development that has increased the use of vacuum furnaces to include hardening of low-alloy steels. This has mainly been achieved with nitrogen as cooling gas by increasing the pressure and improving the gas flow pattern. Helium and especially hydrogen still has the potential to improve the cooling rates further, making vacuum hardening even more widespread.

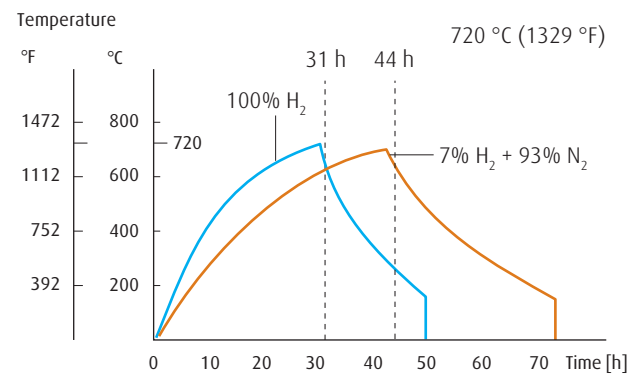


Figure 66: Example of time reduction during strip coil bell annealing when using hydrogen atmosphere instead of nitrogen with 7% hydrogen [12].

The use of 100% hydrogen in bell furnace strip coil annealing reduces both heating and cooling time as seen in Figure 66. In addition to the generally good heat transfer in hydrogen, an additional benefit is that the small hydrogen molecules can penetrate between the strip wraps, thereby radically improving the radial heat transfer, as seen in Figure 66. Wire coil annealing in 100% hydrogen results in annealing time reductions, although not as great as for strip coils.

The heating and especially the cooling time are also reduced when using hydrogen in continuous annealing furnaces. By replacing a cracked ammonia atmosphere with 100% hydrogen, it is possible to increase the throughput in continuous strip and wire annealing typically by 10–20%.

An alternative to using a homogenous gas flow for gas quenching is to use the CARBOJET Cooling technique suitable for installation in continuous furnaces described in section 3.4.2. An example of the improved cooling rate achieved is shown in Figure 67.

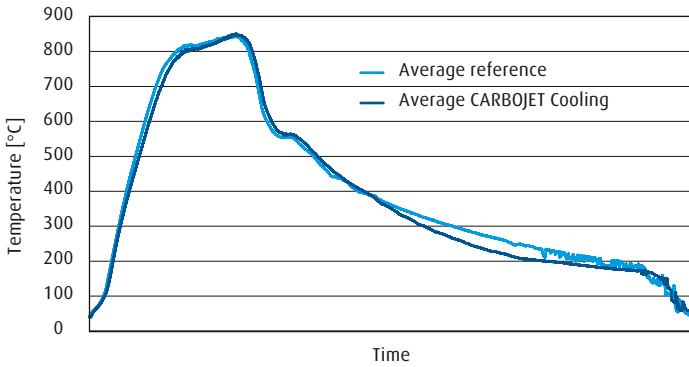


Figure 67: Temperature registrations in the cooling section of a roller hearth furnace show a time saving of about 16% when using the CARBOJET Cooling equipment.

5.14.2 Comparison with oil quenching

In oil quenching, there are three phases of cooling: vapour film cooling at high temperature, boiling in an intermediate temperature range, and convection at low temperature. The cooling rate is highest during boiling, which occurs in the temperature regime of 600–700 °C (1112–1292 °F). In gas quenching, heat transfer occurs only by convection. Therefore, the heat transfer coefficient varies greatly during oil quenching but is fairly constant during gas quenching. The result is that the cooling rate varies more during oil quenching as illustrated in Figure 68.

The average heat transfer coefficient for high-pressure gas quenching with hydrogen or helium can be as high as for oil quenchants. However, the fast cooling rates obtained in the boiling phase make oil quenching advantageous for hardening of low hardenability steels, because the cooling rate in the critical temperature regime is higher than for gas quenching. This is illustrated in Figure 69. However, the non-uniform cooling rate in oils is negative with respect to distortions.

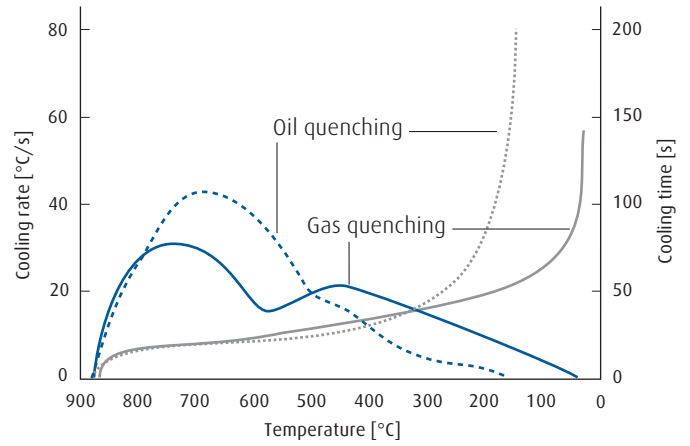


Figure 68: Two ways to present the difference in cooling behaviour in gas and oil. The first is cooling rate as a function of temperature (blue curves). The second is temperature as a function of time (grey curves). Quench oil temperature was 130 °C (266 °F). Gas quenching was conducted at 20 bar in helium [15].

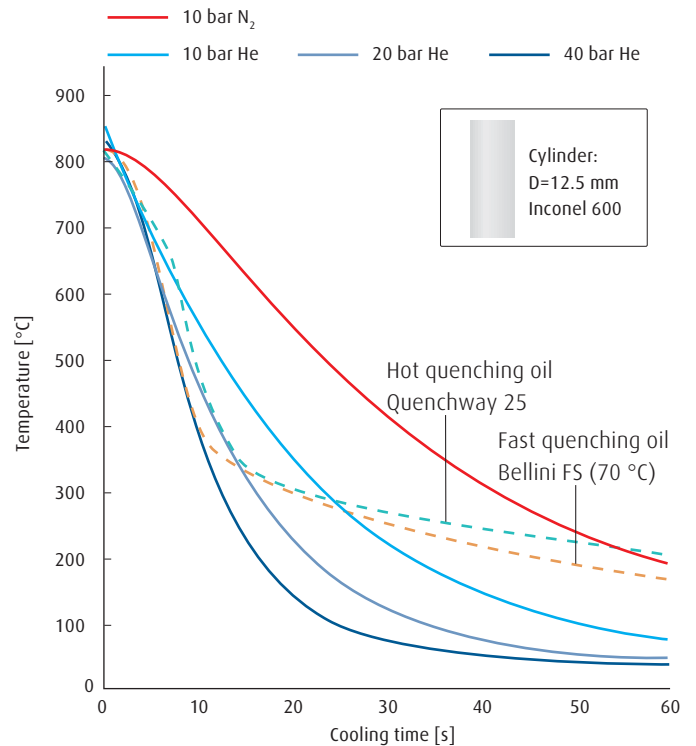


Figure 69: Cooling curves for a cylindrical specimen cooled in oil and high-pressure gas [14].

Table 15. Atmosphere requirements related to alloy at typical annealing temperatures

Alloy	Atmosphere requirements Oxygen activity, PO_2 , atm			Carbon activity			Nitrogen activity* Zero	Hydrogen activity* Zero
	$<10^{-22}$	$10^{-22} - 10^{-12}$	$>10^{-12}$	0	0–0.5	>0.5		
Steels		x		x	x	x		(x)
Tool steels	x	x			x	x		(x)
Stainless steels	x			x				(x)
Copper			x					
Brass or bronze	x	x						
Aluminium			x					
Nickel		x						
Chromium	x			x				x
Titanium	x			x				x (x)
Noble metals		x						

* Note: Brackets indicate requirement in specific cases.

Table 16. Atmosphere properties

Composition	Oxygen activity, PO_2 , atm			Carbon activity			Nitrogen activity Zero	Hydrogen activity Zero
	$<10^{-22}$	$10^{-22} - 10^{-12}$	$>10^{-12}$	0	0–0.5	>0.5		
N_2			x	x				x
N_2/H_2	x	x		x				
N_2/C_nH_m	x	x			x			
$N_2/CO/H_2$		x	x		x	x		
Ar			x				x	x
Ar/H_2	x	x					x	
H_2	x							
He		x	x		x	x		

5.15 Selection of atmosphere

A scheme for choosing an atmosphere system is illustrated by the Furnace-Alloy-Process triangle, shown in Figure 70. The choice may be made in steps, numbered in Figure 70, as follows:

1. Determine the required chemical properties of the atmosphere such as oxygen activity and carbon potential with respect to alloy and process.
2. List available atmospheres from Table 4 with matching chemical properties.
3. Consider restrictions with regard to process temperature and heat transfer requirements.
4. Consider restrictions with regard to furnace type.
5. Consider restrictions with regard to quality.
6. Make final choice.

5.15.1 The alloy requirements of the atmosphere – step 1

For both ferrous and nonferrous alloys, the most important requirement is that oxidation must not occur. This requirement puts a certain limit on the oxygen potential of the atmosphere. This limit is different for metals and alloys, as explained in the foregoing text. For steels, there is the additional requirement that decarburisation or carburisation must not occur. A certain value of the carbon potential of the atmosphere is thus required (see Table 8). Sometimes nitrogen and hydrogen activity must also be taken into account. These criteria are shown schematically in Table 15. The background to the values given for the oxygen partial pressure and carbon activity is given in sections 5.2–5.3.

5.15.2 Review of chemical properties of atmospheres – step 2

The atmospheres from Table 8 may now be characterised in the same way as the requirements of the alloy in Table 15. This is done in Table 16.

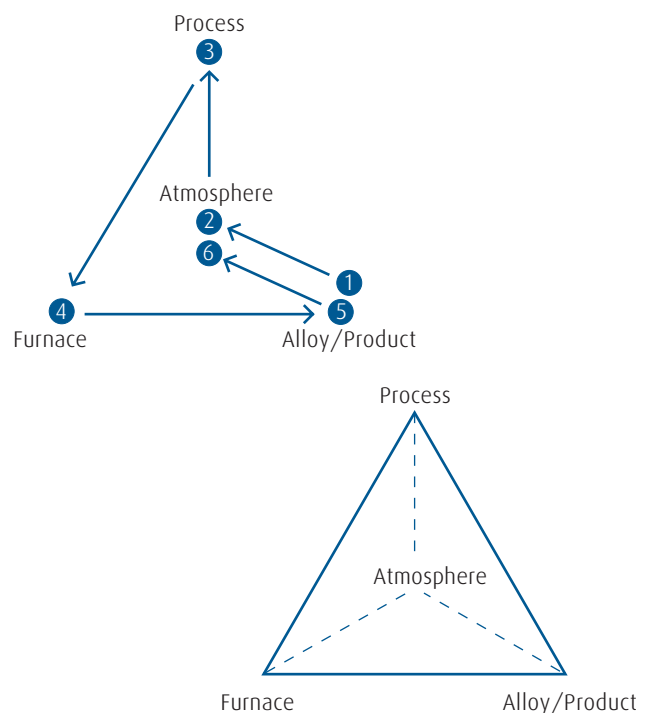


Figure 70: The Furnace-Alloy-Process triangle.

The most reducing atmosphere (= lowest oxygen activity) is obtained in pure hydrogen (H₂). N₂/H₂ and Ar/H₂ mixtures with a high share of H₂ (possibly combined with C_nH_m) also yield very reducing atmospheres. There is no reason to choose a more reducing atmosphere than is needed. Nitrogen/hydrogen atmospheres with 1–10 vol% hydrogen can produce excellent brightness on steels and copper. Pure nitrogen atmospheres will not yield bright surfaces but may be used if there is a need to provide protection from excessive oxidation and to slow down the decarburisation rate.

Carbon activity (or carbon potential) control precision is best for N₂/CO/H₂ atmospheres, thus nitrogen/methanol or nitrogen/endogas atmospheres.

Natural gas as a carbon source has the advantage of simplicity and low installation cost. The amount of natural gas must be kept below approximately 5 vol% in order to avoid the risk of soot deposits. This type of atmosphere has a low capacity to buffer disturbances from air because of the low concentration level of active and reducing gas. The low buffering capacity must be compensated for with a high gas flow rate, typically 20–50% higher than with a CARBOFLEX nitrogen/endogas or nitrogen/methanol system. These atmospheres are sensitive to disturbances from reactions with oxygen and the degree of carbon control is therefore very limited. To avoid the risk of sooting, the hydrocarbon should not be introduced until the temperature exceeds typically 400–500 °C (752–1292 °F). The reactivity of the hydrocarbon increases in the order: natural gas (methane), propane and propylene. Nitrogen/natural gas systems can replace exogas systems with equal or better quality as the result. Adding hydrogen to a nitrogen/hydrocarbon system increases the atmosphere buffering capacity. The gas flow rate can be decreased to pay off the extra cost for hydrogen.

Decarburisation-free annealing may be conducted in very dry and oxygen-free nitrogen or nitrogen/hydrogen atmospheres.

Where nitrogen pick-up is detrimental, Ar/H₂ or H₂ atmospheres are alternatives. Pure Ar or pure He atmospheres are alternatives to nitrogen in vacuum furnaces.

By combining Tables 8, 15 and 16, it is now possible to briefly list possible atmosphere systems for different processes and alloys as shown in Table 17.

Table 17. Possible atmosphere choices for different processes

Process	Alloy	Linde designation
Hardening	Medium carbon steels	CARBOFLEX
	High carbon steels	CARBOFLEX
	Tool steels	CARBOFLEX
	Stainless steels	Hydrogen, HYDROFLEX
Annealing	Low carbon steels	Nitrogen, Hydrogen, CARBOFLEX, HYDROFLEX
	Med. carbon steels	CARBOFLEX
	High carbon steels	CARBOFLEX
	Tool steels	CARBOFLEX
	Stainless steels	Hydrogen, HYDROFLEX
	Copper	Nitrogen, HYDROFLEX, CARBOFLEX
	Brass/bronze	Hydrogen, HYDROFLEX
	Aluminium	Nitrogen
	Nickel	HYDROFLEX
	Chromium	Hydrogen, HYDROFLEX
	Titanium	Hydrogen, HYDROFLEX
	Noble metals	HYDROFLEX
	Vacuum heat treatment	Steels
Titanium		Argon, Helium
Ni-Cr alloys		Argon, Helium, Hydrogen

5.15.3 Restrictions with respect to temperature and heat transfer – step 3

Flammable atmosphere constituents like methanol, hydrogen and hydrocarbons must not be introduced if there is a possibility to form a flammable mixture with oxygen (air) below flammability temperature. Therefore, either the temperature must be above the ignition temperatures or the oxygen concentration must be below the flammability range. To ensure safety when using flammable gases, the temperature must be above the safety temperature of 750 °C (1382 °F), or the flammable gas must be below 25% of the flammability range, or the oxygen concentration must be below 0.5%. See section 6 on Safety.

For quality reasons, hydrocarbons should not be introduced below a certain temperature because of the risk of sooting. Methanol should not be introduced below approximately 800 °C (1472 °F) for the same reason.

When fast convective heat transfer is a requirement, hydrogen (or helium) is preferable to nitrogen or argon, see Table 13.

5.15.4 Restrictions with regard to furnace – step 4

The type of furnace (and related process) also puts restrictions on the choice of atmosphere. The main criteria are:

1. existence of exhaust gas ignition,
2. batch or continuous furnace,
3. loading into hot or cold furnace.

Depending on whether the atmosphere is ignited and burnt off or not when exiting the furnace, flammable or non-flammable compositions should be selected. For a continuous furnace, this requirement applies at the furnace exit and entrance. By using the zoning concept, it is possible to have a non-flammable mixture at these locations, although a flammable mixture is used in the high temperature zones of the furnace. Continuous furnaces may operate with doors and batch type loading, for instance in the case of roller hearth annealing furnaces for wire or strip coils. Disturbance should be minimised by adequate gas flow arrangements at the doors.

The furnace atmosphere in a batch furnace is disturbed at each loading or unloading when the furnace is exposed to air. High gas flow rate at these occasions will condition the atmosphere. The primary difference between loading into hot or cold furnaces is the aspect of safety. A flammable gas can be used when loading is done into a furnace operating above safety temperature, set to 750 °C (1382 °F). A cold furnace must not be supplied with flammable gas unless it is first purged with nitrogen down to an oxygen concentration below the safety limit.

Of great importance is the degree of air leaking into the furnace. If, for instance, the leakage rate is at zero, it may be possible to make carbon neutral annealing with a low buffering atmosphere like nitrogen/natural gas. On the other hand, a high buffering atmosphere with high CO and H₂ concentrations will be required if there is a high air leakage rate.

5.15.5 Restrictions with regard to quality – step 5

The quality requirements of the atmosphere increase as annealing or hardening is conducted closer and closer to the final state for the product. Annealing after hot rolling or forging may therefore require a lower-quality atmosphere than annealing after cold rolling.

Reducing power is important to give bright and clean surfaces as well as to minimise selective oxidation. High hydrogen concentrations are favourable in this respect. Where there are very strong requirements for reducing power such as for stainless steels and some tool steels, N₂/CO/H₂ atmospheres cannot be used; pure hydrogen or N₂/H₂ atmospheres must be used instead.

Quality requirements for freedom from decarburisation and oxidation do not always coincide. Pure nitrogen atmospheres will sometimes give less decarburisation than a slightly reducing HYDROFLEX atmosphere containing hydrogen, even though the HYDROFLEX atmosphere may have lower oxygen potential. There are two reasons for this. The first reason is that the pure nitrogen atmosphere will produce a thin oxide on the steel, which acts as a barrier for decarburisation. The second reason is that water vapour is much more active in decarburisation and the water vapour content in the pure nitrogen atmosphere is lower than in the low-hydrogen HYDROFLEX atmosphere. The risk of decarburisation is also related to the carbon content of the steel. High carbon content means a higher risk than low carbon content.

5.15.6 Make final choice – step 6

In the final choice, the technical features have to be analysed from an economic point of view. When making a cost calculation, it is not wise just to compare gas prices cubic metre by cubic metre. Instead, the investment and running costs should be related to overall cost savings in terms of quality, potential indirect savings in downstream operations, labour costs, costs for rework and scrap, throughput, energy costs, improved environment protection, and so on. These savings should be balanced against the total gas cost, for instance for a year. A price comparison of gas cubic metre by cubic metre will not take these effects into account and can lead to a wrong decision. Consider for instance the example of copper strip coil annealing in section 5.12.11 The exogas cost was less than the nitrogen cost per cubic metre. But the gas savings were dramatic using nitrogen, almost 75%, which more than outweighs the cubic metre price difference.

The selection of atmosphere and related control has an influence on further processing such as blasting, pickling, grinding or turning. The elimination of a blasting or a pickling step is clearly a cost saving. Freedom from oxides and proper surface hardness also affects the wear of tools and the efficiency of grinding or turning operations. Reduced distortion after hardening and related reduced grinding costs are related to atmosphere control, particularly when gas quenching is used. Fewer rejects of products with improper quality with respect to surface finish or decarburisation can also be quantified in economic terms.



Figure 71: Vacuum furnace with related argon high pressure surge tank, seen on the right (Courtesy of Seco Warwick Corporation).

Different atmospheres can result in different throughput. The most outstanding example is the dramatic cycle reduction obtained when using hydrogen in high-convection bell furnaces. The use of hydrogen also results in increased throughput in a number of annealing processes and furnaces because of the good thermal transfer properties of hydrogen. Efficient flow rate and mixing control can minimise availability and performance losses through for example shorter conditioning times at start-ups, after weekend idling periods or when changing the atmosphere composition.

Atmospheres enabling good carbon control have either endogas or methanol as the carbon source. The endogas alternative has the following advantages. Natural gas needed for endogas production is often available. Existing piping from an old system can partly be used. Methanol as a carbon source has the advantage that the endogas generator is eliminated, as is related supervision and maintenance work. The disadvantages are environmental concerns and safety restrictions

The value of a clean, bright surface, freedom from decarburisation, freedom from nitrogen pick-up, accurate surface carbon concentration, and so on can justify a higher price for the annealed or hardened product.

By using atmosphere control systems for on-line closed-loop atmosphere control and for supervision and process data logging, the required labour time can be reduced. The amount of labour needed for supervision and maintenance is closely related to the technical complexity of the atmosphere system. HNX generators have the highest degree of complexity and therefore also require the highest amount of labour hours for maintenance and supervision. Next in complexity are exogas generators and the least complex are endogas generators. The systems for direct supply into the furnace of the atmosphere constituents, examples being nitrogen, methanol and natural gas, are the least labour-intensive with regard to maintenance and supervision.

5.16 Atmosphere systems for vacuum heat treatment

For hardening in vacuum furnaces, an important requirement for the gas system is ability to fill the quench module up to the required pressure in as short a time as possible. Figure 71 shows how this is fulfilled by a buffer vessel installed as close as possible to the furnace in order to minimise the filling time.

The filling time is reduced with increased buffer vessel pressure and volume and with increased pipe diameter for the supply line to the furnace. Shorter filling times are obtained with hydrogen or helium as compared to nitrogen as was shown in Table 14.

Nitrogen is the predominantly used purge, backfill and cooling gas. Small additions of hydrogen, up to about 5 vol%, are used to increase cooling capacity and reduce power. Argon is used for materials that are sensitive to nitrogen pick-up, like titanium and stainless steels.

Hydrogen has outstanding cooling properties and is also a reducing gas. However, 100% hydrogen is rarely used because of safety concerns. There are only a few installations where safety arrangements are assured. The following list of requirements set up by the regulating authority had to be fulfilled in one installation [10]:

- redundant installation of relevant safety valves
- gas warning system in the workshop (hydrogen sensor)
- sufficient air circulation in the workshop
- fan wheel made of non-spark-creating material
- fan motor must not be located in the circulating gas flow
- fan must be able to work at two different speeds
- lightning conductor
- electrical grounding of all devices used in the workshop
- error-free signal amplifier
- emergency cooling water circulation in the event of electricity failure
- corrosion inhibitor in cooling water
- double sealing on the furnace door to indicate leakage
- only authority-approved flanges, welding seams and thread joints
- registration of the load changes in the furnace logbook
- no hydrogen usage if system error detected
- automatic leakage test before filling with hydrogen
- purging of the exhaust tube with nitrogen before using it for hydrogen
- hydrogen release out of the chamber only if temperature < 80 °C
- compliance with all appropriate authority regulations

Although the list of requirements is very demanding, it is believed that the future will prove investing to fulfil the requirements to be worthwhile. As already mentioned, the reasons are faster cooling and reducing environment. As a result of the better cooling, vacuum hardening with high-pressure hydrogen cooling would open up possibilities to vacuum harden many more parts and steels including low-alloy steels.

Helium has almost as good heat transfer properties as hydrogen and has the advantage of being a safe gas. A major disadvantage is the low availability and the fact that helium is a finite resource, which leads to high prices and price volatility. Recycling has to be considered to lower the cost.

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 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, its 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 of 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 taken into account 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

The gases and methanol used in the carburising and carbonitriding processes cover both atmospheric pressure carburising and carbonitriding, as well as the low pressure processes. In this expert edition, the description is limited to the atmospheric pressure processes and therefore the gases C_2H_2 (acetylene), H_2 (hydrogen),

and He (helium), which are used in the low pressure processes, are not covered here. For further information on these processes, the reader is referred to reference [2].

Gas and methanol usage in atmospheric pressure processes is divided into:

- 1) usage as carrier gas that includes N_2 (nitrogen) and CH_3OH (methanol) and
- 2) usage as enriching gas that includes hydrocarbons

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

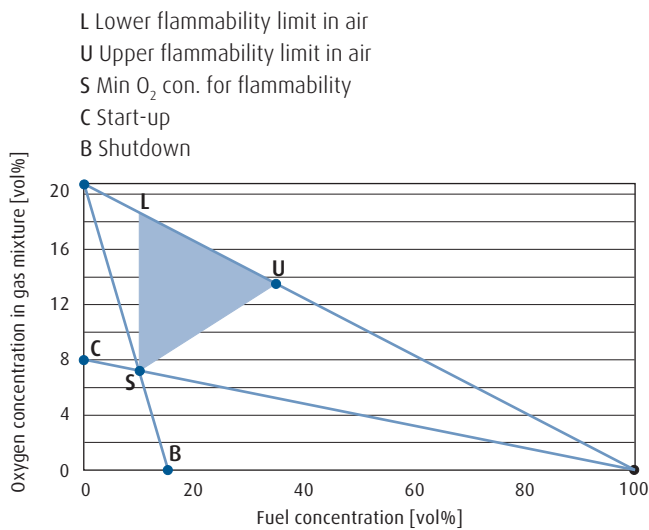


Figure 72: The flammability triangle.

treatment, carburising 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
- 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.

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 72. 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 [16] gives a more definite description of the flammability range:

“As a general rule, any gas mixture containing more than 5 volume percent combustibles H₂+CO+CH₄ 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 (NH₃) 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 72. 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 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% to 10%, 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.

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 cryo-treatment 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 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 [17], 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 [16, 18] as well as other national standards will for some time still serve as guidelines.

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 [16], the safety temperature is defined at 750 °C (1382 °F). The process temperature for carburising and carbonitriding 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 heat treatment furnaces below the safety temperature, which is relevant at the inlet and outlet of continuous carburising 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 meet the industrial codes of the company where it will be installed. A number of emergency safety functions should be integrated into the furnace and they should in an emergency situation 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.

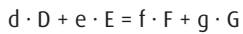
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18. NFPA 86C, Standard for Industrial Furnaces Using a Special Processing Atmosphere. This standard is incorporated in and replaced by the 2003 edition of NFPA 86.

Appendix 1. Equilibrium constants.

A chemical reaction between D, E, F and G may be written as



This reaction has a chemical equilibrium constant, K;

$$K = \frac{a_F^f \cdot a_G^g}{a_D^d \cdot a_E^e} \quad (a = \text{activity})$$

or for gaseous reactions

$$K = \frac{p_F^f \cdot p_G^g}{p_D^d \cdot p_E^e}$$

P = partial pressure, atm.

If the atmospheric total pressure = 1 atm, $P = \text{vol}\% / 100$.

For oxidation reactions of pure metals, the following is valid:

$$\log K = -\log P_0$$

The temperature dependence is tabulated below according to the relation

$$\log K = A + B/T \quad (T = \text{temp, kelvin})$$

Free energy data is related to K accordingly:

$$-RT \ln K = \Delta G^\circ$$

	Reaction	A	B	Standard state
Gaseous	$\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$	-1.613	1731	
	$\text{H}_2 + 1/2 \text{O}_2 \rightarrow \text{H}_2\text{O}$	-2.860	12874	
	$2 \text{NH}_3 \rightarrow \text{N}_2 + 3 \text{H}_2$	12.392	-5886	
	$\text{CO}_2 \rightarrow \text{CO} + 1/2 \text{O}_2$	4.501	-14720	
Carburising	$\text{CH}_4 \rightarrow \text{C} + 2\text{H}_2$	5.764	-4761	Graphite
	$2 \text{CO} \rightarrow \text{C} + \text{CO}_2$	-9.107	8861	Graphite
	$\text{CO} + \text{H}_2 \rightarrow \text{C} + \text{H}_2\text{O}$	-7.494	7130	Graphite
Nitriding	$\text{CO} \rightarrow \text{C} + 1/2 \text{O}_2$	-4.606	-5859	Graphite
	$\text{NH}_3 \rightarrow \text{N} + 3/2 \text{H}_2$	6.196	-2943	N_2 (g. atm)
	$1/2 \text{N}_2 \rightarrow \text{N}$	0	0	N_2 (g. atm)
Oxidation	$4/3 \text{Al} + \text{O}_2 \rightarrow 2/3 \text{Al}_2\text{O}_3$	-11.46	58853	
	$4 \text{Cu} + \text{O}_2 \rightarrow 2 \text{Cu}_2\text{O}$	-7.33	17704	
	$2 \text{Fe} + \text{O}_2 \rightarrow 2 \text{FeO}$	-6.78	27570	
	$3/2 \text{Fe} + \text{O}_2 \rightarrow 1/2 \text{Fe}_3\text{O}_4$	-7.61	28166	
	$4/3 \text{Fe} + \text{O}_2 \rightarrow 2/3 \text{Fe}_2\text{O}_3$	-8.62	28121	
	$4/3 \text{Cr} + \text{O}_2 \rightarrow 2/3 \text{Cr}_2\text{O}_3$	-8.75	39260	
	$2\text{Ni} + \text{O}_2 \rightarrow 2 \text{NiO}$	-8.82	24530	
	$2\text{Zn} + \text{O}_2 \rightarrow 2 \text{ZnO}$	-10.44	36580	
	$2\text{Sn} + \text{O}_2 \rightarrow 2 \text{SnO}$	-9.99	29307	

Appendix 2. Physical data for gases.

N_2	H_2	He	Ar	
$\lambda_{25^\circ C}$	0.02550	0.17495	0.15363	0.01785
R	297	4124	2079	208
$\rho_{25^\circ C, 100 \text{ kPa}}$	1.13	0.0814	0.1614	1.603
$\eta \cdot 10^6$	17.2	8.6	19.7	22.9
$u \cdot 10^6$	15.2	105.7	122.1	14.3
c_p	$1.04 \cdot 10^3$	$14.26 \cdot 10^3$	$5.19 \cdot 10^3$	$0.52 \cdot 10^3$
$a \cdot 10^6$	21.7	150.7	183.4	21.06
Pr	0.701	0.701	0.666	0.679

$25^\circ C = 77^\circ F$

Thermal conductivity, W/m K

λ

Gas constant, J/kg K

$$R = \frac{8314}{M}$$

Density

$$\rho = \frac{P}{RT}$$

Dynamic viscosity, Ns/m²

η

Kinematic viscosity, m²/s

$$u = \frac{\eta}{\rho}$$

Thermal capacity ("specific heat"), J/kg K

c_p

Thermal diffusivity, m²/s

$$a = \frac{\lambda}{c_p \rho}$$

Prandtl's number

$$Pr = \frac{u}{a}$$

Reynold's number

$$Re = \frac{c \cdot d_h}{u}$$

Nusselt's number

$$Nu = \frac{\alpha \cdot d_h}{\lambda}$$

Thermal transmittance, W/m² K

α

Characteristic dimension, m

d_h

Gas velocity, m/s

C

Appendix 3. Useful equations.

1. Relation between oxygen partial pressure and mV:

T = temp K, E = mV reading, P_{O_2} = partial oxygen pressure.

$$\log P_{O_2} = -0.678 - E / 0.0496 \cdot T$$

2. Relation between dew point and water vapour partial pressure:

D_p = Dew point °C

P_{H_2O} = water vapour partial pressure.

$$\log P_{H_2O} = -2310 / (273 + D_p) + 6.243 \text{ for } T > 0^\circ\text{C}$$

$$\log P_{H_2O} = -2675 / (273 + D_p) + 7.576 \text{ for } T \leq 0^\circ\text{C}$$

3. Relation between carbon concentration (= carbon potential) and carbon activity

$$a_c = \gamma x_c / (1 - 2x_c)$$

where

$$\gamma = \exp \{ [5115.9 + 8339.9 x_c / (1 - x_c)] / T - 1.9096 \}.$$

T is the temperature in kelvin.

The conversion between the carbon potential C_p , which is equal to the carbon content by weight percent in a binary Fe-C system, and the molar fraction x_c , is carried out according to the formula below:

$$x_c = \frac{C_p / 12.01}{C_p / 12.01 + (100 - C_p) / 55.85}$$

4. The Gunnarsson formula

A simple expression calculating the relationship between carbon content in low-alloy steels, C, and carbon potential, C_p , is:

$$\log \frac{C_p}{C} = 0.055 \cdot (\% \text{ Si}) - 0.013 \cdot (\% \text{ Mn}) - 0.040 \cdot (\% \text{ Cr}) + 0.014 \cdot (\% \text{ Ni}) - 0.013 \cdot (\% \text{ Mo})$$

The formula is valid only for low-alloy case hardening steels.

Appendix 4. Pressure unit conversions.

	Pa (=1N/m ²)	Bar	Torr	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 = 10³;

m = millionth = 10⁻⁶;

M = million = 10⁶;

Example: 1 kPa = 1 000 Pa

Example: 1 mbar = 0.000001 bar

Example: 1 Mbar = 1 000 000 bar

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