Furnace atmospheres no. 3.

Gas nitriding and nitrocarburising.
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.

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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## Contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Preface</td>
<td>2</td>
</tr>
<tr>
<td>Passion for innovation</td>
<td>3</td>
</tr>
<tr>
<td>1. Introduction</td>
<td>6</td>
</tr>
<tr>
<td>2. Process</td>
<td>7</td>
</tr>
<tr>
<td>2.2. Prior heat treatment condition</td>
<td>9</td>
</tr>
<tr>
<td>2.3. Cleaning</td>
<td>9</td>
</tr>
<tr>
<td>2.4. Preheating and pre-oxidation</td>
<td>10</td>
</tr>
<tr>
<td>2.5. Post oxidation</td>
<td>11</td>
</tr>
<tr>
<td>2.6. Austenitic nitrocarburising</td>
<td>11</td>
</tr>
<tr>
<td>2.7. Cooling/quenching</td>
<td>11</td>
</tr>
<tr>
<td>2.8. Process selection</td>
<td>12</td>
</tr>
<tr>
<td>2.9. Properties of nitrided and nitrocarburised steels</td>
<td>13</td>
</tr>
<tr>
<td>2.9.1. Hardness and wear resistance</td>
<td>13</td>
</tr>
<tr>
<td>2.9.2. Static and fatigue strength</td>
<td>14</td>
</tr>
<tr>
<td>2.9.3. Selection of nitriding/nitrocarburising</td>
<td>15</td>
</tr>
<tr>
<td>2.9.4. Corrosion resistance and surface appearance</td>
<td>15</td>
</tr>
<tr>
<td>2.9.5. Dimensional changes</td>
<td>16</td>
</tr>
<tr>
<td>2.9.6. Properties of nitrided/nitrocarburised stainless steel</td>
<td>16</td>
</tr>
<tr>
<td>3. Furnace and equipment</td>
<td>18</td>
</tr>
<tr>
<td>3.1. Nitriding</td>
<td>19</td>
</tr>
<tr>
<td>3.2. Nitrocarburising</td>
<td>19</td>
</tr>
<tr>
<td>3.2.1. Furnace interior influence</td>
<td>20</td>
</tr>
<tr>
<td>3.3. Vacuum, high pressure, and plasma nitriding</td>
<td>21</td>
</tr>
<tr>
<td>3.4. Nitriding + PVD or CVD</td>
<td>22</td>
</tr>
<tr>
<td>3.5. High-speed gas injection replaces ventilator</td>
<td>23</td>
</tr>
<tr>
<td>4. Atmosphere generation, gas supply</td>
<td>24</td>
</tr>
<tr>
<td>4.1. Nitrogen supply</td>
<td>25</td>
</tr>
<tr>
<td>4.2 Hydrogen supply</td>
<td>26</td>
</tr>
<tr>
<td>4.4. Nitriding gas supply set up</td>
<td>26</td>
</tr>
<tr>
<td>4.5. Nitrocarburising gas supply set up</td>
<td>27</td>
</tr>
</tbody>
</table>
5. Atmosphere control

5.2. The atmosphere nitriding potential 31
5.3. The atmosphere carbon potential 31
5.4. Atmosphere analysis 33
5.4.1. Ammonia and hydrogen analysis 33
5.4.2. Oxygen probe analysis 34
5.4.3. FTIR gas analysis of nitrocarburising atmospheres 35
5.5. Layer growth determination 35
5.6. Guidelines for regulating the atmosphere 36
5.6.1. Nitriding 36
5.6.2. Nitrocarburising 36
5.6.3. Post oxidation control 38
5.7. Compound layer and diffusion zone formation 39
5.7.1. Nitriding 39
5.7.2. Nitrocarburising 40
5.7.3. Furnace interior influence 42
5.7.4. Influence of amount of active gas 42
5.7.5. Steel alloy content effect 43
5.8. Pore formation 43
5.9. The NITROFLEX® solution 44
5.9.1. Nitrocarburising case studies 44
Case Study 1: Conveyor roller in a metal spraying shop 44
Case Study 2: Forging die manufactured from AISI L6 material 44
Case Study 3: Extrusion dies made of AISI H13 material 45
Case Study 4: Tag washers in SAE 1020 45
Case Study 5: Clutch plates in mild steel 45
Case Study 6: Mild steel slides 45
Case Study 7: Moulds in 1020 46
Case Study 8: Crankshafts 46

6. Safety

6.1 Safety awareness 48
6.2 Gases used in the process 48
6.3 Potential safety hazards and their sources 48
6.3.1 Explosions/flammability/fire 49
6.3.2 Toxicity and asphyxiation 50
6.3.3 Cold burn hazards 50
6.3.4 Pressurised piping and the gas expansion hazard 50
6.4 Control of safety hazards 51
6.4.1 General safety regulations and guidelines 51
6.4.2 Explosions/flammability/fire 51
6.5 Safe use of gases along the value chain 51

References 52
1. Introduction.

In order to achieve specific properties and the desired surface quality after heat treatment of a steel workpiece, numerous process parameters need to be controlled. A most critical parameter is the composition, function and control of the furnace atmosphere. In nitriding and nitrocarburising processes, the major function of the atmosphere is to supply the necessary amount and provide the right content of nitrogen and carbon to establish the right nitriding depth and surface layer properties. 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 workpieces.

The purpose of this expert edition is to deliver a comprehensive overview on nitriding and nitrocarburising 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.

Each of the expert editions displays a similar content structure. The first part focuses on the process, speaking about the basic principles of different nitriding and nitrocarburising 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 is 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 nitriding and nitrocarburising processes, safety issues need to be addressed in the last section; this is an important concern of Linde Gas.
Nitriding and nitrocarburising are thermochemical processes, as are carburising and carbonitriding. In these processes, nitrogen and/or carbon are transferred from the process medium, normally gas, to the surface of the treated steel. An elevated temperature is required in order to ensure fast transfer of carbon/nitrogen from the gas to the steel surface and also to allow carbon/nitrogen to diffuse into the steel at an appreciable rate.

Conventional gas nitriding was developed for the purpose of increasing fatigue strength and load-bearing capacity without involving significant distortion of treated components. Specially alloyed nitriding steels are used in order to achieve a high hardness. Very long nitriding times, from ten to hundreds of hours, have been and are used to obtain sufficient case depths.

Nitrocarburising began to grow at a considerable rate with the development of the salt bath process Tenifer® (Tufftride) and the gaseous process Nitemper® in the 1960s. Compared to conventional nitriding, nitrocarburising is a short-time process, typically lasting 30 minutes to four hours, and it is performed at a somewhat higher temperature, about 570 °C (1058 °F) compared to 500–520 °C (932–970 °F) for gas nitriding. It is typically applied to low-alloy steels but also to unalloyed steels and cast irons as well as to tool steels.

Nitriding and nitrocarburising give unique improvements in wear and corrosion resistance that cannot be obtained by carburising or carbonitriding. Increased fatigue strength is also obtained. These improvements are related to the surface microstructure and hardness after treatment illustrated in Figure 1. The outermost layer of a nitrided or nitrocarburised steel is 2–30 μm thick and consists of the ε-phase with variable compositions of carbon and nitrogen and the γ’-phase with the virtually stoichiometric chemical formula Fe₄N. This layer is called the compound layer, sometimes also referred to as the white layer or the ceramic layer. Corrosion resistance and tribological properties (friction and wear) are mainly determined by the compound layer’s properties, which differ notably from those of the base material.

Under the compound layer there is a “diffusion zone”, which goes deeper into the steel, typically 0.1–0.5 mm. Load-bearing capacity plus static and fatigue strength are largely determined by the hardness and depth of the diffusion zone.

An important feature of nitriding and nitrocarburising is that they are “low temperature methods” whereas carburising and carbonitriding are “high temperature methods”. Here low temperature refers to a temperature below which phase transformation to austenite starts (A₁), and high temperature is above said temperature. A valuable consequence is notably reduced distortion of treated parts. This can often save time and costs by eliminating the need for post-grinding to meet dimensional tolerance requirements. The production cycle of a part therefore becomes faster and cheaper. A limitation caused by the lower temperature is that the diffusion rate for nitrogen and carbon is modest, which sets limits on the case depths that can be obtained.

Carburising and carbonitriding give a surface hardness in the range of 750–850 HV that is largely independent of the steel type, whereas nitriding and nitrocarburising give a wide possible range of surface hardness determined by the steel selection.
2.1. The process steps in nitriding and nitrocarburising

A nitriding/nitrocarburising cycle has three major steps: 1) heating to temperature, 2) holding at temperature for a sufficient time to reach the required nitriding depth and 3) cooling. This is illustrated in Figure 2, which also shows the optional additional steps of preheating/pre-oxidation and post-oxidation used in nitrocarburising.

Table 2. An example of energy requirements for two process routes, one being nitrocarburising [1]

<table>
<thead>
<tr>
<th>Process step</th>
<th>Energy requirement, KWh</th>
<th>Nitrocarburising</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat to processing temperature</td>
<td>265</td>
<td>163</td>
</tr>
<tr>
<td>Hold at processing temperature</td>
<td>27</td>
<td>66</td>
</tr>
<tr>
<td>Quench</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>Heat to tempering temperature</td>
<td>94</td>
<td></td>
</tr>
<tr>
<td>Hold at tempering temperature</td>
<td>44</td>
<td></td>
</tr>
<tr>
<td>Electroplating</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>455</td>
<td>229</td>
</tr>
</tbody>
</table>

Because of the benefits of a shortened production cycle, limited distortion, elimination of post-grinding and attractive aesthetic surface appearance, a great number of parts subjected to wear and fatigue are nitrocarburised today instead of being carburised or carbonitrided, as was previously the case. Examples of applications for the nitriding and nitrocarburising of low-alloy steels are gears, crankshafts, camshafts and parts in sliding contact such as cylinders and pistons, where good tribological properties are needed. High-alloy steels used for forming and extrusion tools are other examples that benefit from being nitrided or nitrocarburised.

Low energy consumption for the nitrocarburising process is a consequence of the low process temperature, the short process time and the elimination of production steps such as grinding. Table 2 shows an example in which the energy saving was about 50% when the process route was changed to nitrocarburising.

Table 1. Characteristics of thermochemical processes involving nitrogen and/or carbon

<table>
<thead>
<tr>
<th>Process Type</th>
<th>Temperature [°C (°F)]</th>
<th>Typical process time [h]</th>
<th>Element transferred</th>
<th>Case depth [mm]</th>
<th>Surface hardness [HV]</th>
<th>Distortion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carburising</td>
<td>850-950 (1562-1742)</td>
<td>4-10</td>
<td>C</td>
<td>0.2-1.5</td>
<td>750-850</td>
<td>Increased</td>
</tr>
<tr>
<td>Carbonitriding</td>
<td>750-900 (1382-1652)</td>
<td>2-5</td>
<td>C+N</td>
<td>0.1-0.8</td>
<td>750-850</td>
<td></td>
</tr>
<tr>
<td>Austenitic nitrocarburising</td>
<td>600-700 (1112-1292)</td>
<td>2-4</td>
<td>N+C</td>
<td>0.1-0.5</td>
<td>450-1200</td>
<td></td>
</tr>
<tr>
<td>Nitrocarburising</td>
<td>560-580 (1040-1076)</td>
<td>2-4</td>
<td>N+C</td>
<td>0.05-0.2</td>
<td>450-1200</td>
<td></td>
</tr>
<tr>
<td>Nitriding</td>
<td>500-520 (932-968)</td>
<td>5-100</td>
<td>N</td>
<td>0.05-0.8</td>
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Figure 3 shows the gases that are used in the different nitriding steps. Nitrogen purging of the furnace is conducted to remove air before ammonia is let into the furnace. This purge is carried out to eliminate the risk of explosion, as ammonia and oxygen form an explosive mixture within a certain concentration range. For this reason, it is also advantageous to perform heating to nitriding temperature in nitrogen. When the nitriding temperature is reached, ammonia is let into the furnace. In the beginning, a high flow rate is used to increase the efficiency of nitrogen transfer to the steel surface.

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<td>750-850</td>
<td></td>
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As soon as a compound layer is formed, the nitriding rate is controlled by diffusion from the layer into the steel. The ammonia flow rate may then be lowered just to give a nitrogen transfer rate from gas to surface which keeps up with the diffusion rate [2]. Nitriding is continued until the desired nitriding depth is reached.

After finishing the nitriding step, the furnace interior is purged with nitrogen to remove the ammonia gas in order to ensure safety.

Cooling should continue in nitrogen to avoid discoloration by oxidation. In pit furnaces, the retort is normally lifted out of the furnace and put into a cooling station. In furnaces without a retort, cooling takes place in the furnace.

The process cycle diagram shown in Figure 4 is similar to that shown in Figure 3 with the main difference that CO₂ (carbon dioxide) is also an added gas. There is sometimes a post-oxidation step after finalised nitrocarburising. Final cooling is carried out in gas or oil. The fast cooling in oil reduces the process time compared to when slow gas cooling is used. It also results in better properties as regards the hardness and residual stress pattern of the nitrocarburised steel. Milder cooling has the benefit of minimising distortion. One cost benefit of gas cooling is that it can be conducted in a one-chamber furnace, which is less costly than a multi-purpose furnace with an integrated oil quench.

2.2. Prior heat treatment condition

For parts subjected to high stress, the normal state of the steel prior to nitriding or nitrocarburising is hardened and tempered at a tempering temperature of at least 20–30 °C (68–86 °F) higher than the nitriding/nitrocarburising temperature in order to prevent loss of hardness during nitriding/nitrocarburising. If nitriding/nitrocarburising is conducted primarily to increase resistance to wear and scuffing, steels in annealed or normalised conditions can be used. Cast irons may be nitrided or nitrocarburised in the annealed state.

For parts that have been subject to turning, drilling or any other machining or cold forming operation, it is necessary to release internal stresses by stress-relieving annealing. After stress relieving, the part dimensions are adjusted by fine machining or grinding to meet the tolerance requirements before nitriding/nitrocarburising. The temperature for stress relieving should preferably be 20–30 °C (68–86 °F) above the nitriding/nitrocarburising temperature in order to avoid stress relieving and concurrent distortion during nitriding/nitrocarburising.

2.3. Cleaning

Cleaning is an important process step before nitriding/nitrocarburising as surface contaminants disturb nitride layer formation. In manufacturing steps before heat treatment, contamination sources are lubricants, coolants and cutting oils used in machining and grinding. There may also be pollution from manufacturing machinery in the form of hydraulic fluids, tool wear debris, chips, turnings, blasting agents and abrasives, and, if machines are used for different metals such as aluminium, even residues from non-ferrous metals. Anti-corrosives used to protect parts from rust in storage and transport may be a further source. Contamination may be in the form of surface films or layers, or particles.

Haase [3] studied the effect of different additives in cutting oils on nitriding results with results shown in Figure 5. An increased amount of additive reduced hardness and gave uneven and locally zero compound layer thickness. In another study, Persson and Troell [4] found that the specific chemicals sulfur and phosphorous added to the cutting oil as well as sodium, boron and calcium in cutting fluids all had a negative
2.4. Preheating and pre-oxidation

Preheating in air at a temperature in the range of 350–450 °C (662–842 °F) for 30–60 minutes is a standard procedure before nitrocarburising for a number of reasons:

- The process time in the nitrocarburising furnace, which is costlier than the preheat furnace, is reduced.
- Heating in air leads to surface oxidation that is found to accelerate compound layer nucleation and growth during nitrocarburising (see Figure 6).
- Residues on the part surfaces are oxidized and vaporised, resulting in cleaner parts and improved nitriding ability.
- Safety is ensured for salt bath nitriding/nitrocarburising by removing any water that has adhered to the parts.

One possible reason for the positive effect of pre-oxidation is that oxide formation results in a notable increase in the surface area, which facilitates nitrogen uptake and the nucleation and growth of the nitride compound layer [6]. Other possible explanations are that nucleation and growth of ε-carbonitride is facilitated and/or that the reverse process of nitriding, i.e. desorption of nitrogen, is retarded by oxidation [7].
2.5. Post-oxidation

A remarkable improvement in corrosion resistance is obtained if nitrocarburising is followed by a short oxidation in the temperature range 450–550 °C (842–1022 °F). The aim is to create a Fe₃O₄ oxide layer with a thickness of about 1 µm formed on top of the compound layer, as shown in Figure 7. Fe₂O₃ must not be formed because it deteriorates both the aesthetic surface appearance and corrosion resistance. If done properly, the oxidation treatment gives the processed parts an aesthetically attractive black colour with high surface corrosion resistance.

The first gaseous post-oxidation process was developed by Lucas, England, and is called Nitrotec® [8]. It is based on the Nitemper process with an added oxidation step in air. Other oxidation methods using water vapour [9] or nitrous oxide (N₂O) [10] have later been successfully developed and found to yield good properties.

2.6. Austenitic nitrocarburising

Austenitic nitrocarburising is developed in order to create thicker cases that can sustain greater surface loads or bending stresses. It is performed at a temperature above the temperature for the partial transformation of the steel to austenite. At the process temperature, austenite enriched with carbon and nitrogen is formed beneath the compound layer. Upon cooling after finalised nitrocarburising, some of this austenite will remain as retained austenite and some will transform into bainite, pearlite or martensite. A sub-zero treatment will transform the retained austenite further into martensite with a hardness in the range of 750 to 900 HV. Alternatively, a tempering operation can be carried out to transform the retained austenite into bainite/martensite. This will also raise the hardness both in the diffusion zone and in the compound layer as shown in Figure 8.

2.7. Cooling/quenching

Cooling after nitriding is usually performed in nitrogen gas with no or moderate convection, whereas the cooling step after nitrocarburising can be accelerated by quenching in oil or by forced gas cooling (water quenching is an alternative after salt bath processes). If the cooling rate is low, it will lead to the precipitation of needle-like iron nitrides in the diffusion zone when unalloyed steels are treated as shown in Figure 9. With increased cooling intensity, the amount of nitrogen, kept in solid solution in ferrite, is increased. This increases the hardness in the diffusion zone. This effect is pronounced only in unalloyed or low-alloy steels. For steels containing high concentrations of nitride-forming alloying elements such as chromium and aluminium, the precipitation hardening effect of nitrides dominates the hardness contribution and the solution hardening effect is negligible.

An increased cooling rate increases the compressive residual stress in the case. Both hardness and compressive residual stresses contribute to fatigue hardness, which means that the best fatigue hardness is obtained with high cooling rates. Increasing part dimension leads to a decreased cooling rate for a given cooling setup. This leads to lowered hardness as seen in Figure 10.
The interdependence between required functional properties, the selected steel and nitriding/nitrocarburising specifications is illustrated in Table 3.

The steel alloy and carbon content and the type of prior heat treatment determine the core strength of the part and will also influence the development of the compound layer structure, case depth and hardness (see Figures 12 and 14). Surface fatigue strength and wear resistance are therefore to a great extent dependent on the steel specified and will improve with increased alloy content.

The functional part properties that essentially depend on the compound layer are wear resistance, tribological properties, corrosion resistance and general surface appearance. Both abrasive and adhesive wear resistance increase with hardness and with minimised porosity of the compound layer. Porosity can be positive in lubricated machinery parts.

Table 3: Relation between part properties, steel selection and nitriding/nitrocarburising parameters

<table>
<thead>
<tr>
<th>Part properties</th>
<th>Static and fatigue strength</th>
<th>Contact load fatigue</th>
<th>Abrasive wear resistance</th>
<th>Adhesive wear resistance</th>
<th>Corrosion resistance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steel</td>
<td>High-alloy and nitriding steels</td>
<td>Moderate</td>
<td>High- and low-alloy steels</td>
<td>High- and low-alloy steels, cast irons, sintered steels</td>
<td>High hardness, high ε-content</td>
</tr>
<tr>
<td>Compound layer</td>
<td>Minor influence</td>
<td>High hardness and depth</td>
<td>High hardness and depth</td>
<td>Minor influence</td>
<td>Dense, post-oxide</td>
</tr>
<tr>
<td>Diffusion layer</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Process</td>
<td>Gas nitriding</td>
<td></td>
<td></td>
<td></td>
<td>Nitrocarburising and post-oxidation</td>
</tr>
</tbody>
</table>

If high fatigue strength or surface contact load-bearing capacity is required, a fast cooling should be applied. If wear and/or corrosion resistance is the main objective, the properties of the compound layer are decisive. Compound layer properties are to a lesser extent dependent on the cooling rate. Therefore, the cooling rate is unimportant in such cases. The process time is of course decreased with increased cooling rate.

2.8. Process selection

The functional properties of a part, such as fatigue and static strength, or wear and corrosion resistance, are the basis for specifying the proper process and steel as illustrated in Figure 11.
as the pores act as lubricant reservoirs. The compound layer depth has to be deep enough not to be worn away. The diffusion layer (depth, hardness and residual stress) determines surface fatigue resistance and resistance to surface contact loads.

Cost is a factor that limits the number of options. Variable costs increase proportionally to increased time for nitriding/nitrocarburising. Increased treatment temperature will also increase running costs due to higher energy losses and wear of equipment. Capital costs are highest for vacuum and plasma equipment, but the variable cost for utilities (electricity and gas) is lower than for conventional atmospheric furnaces.

2.9. Properties of nitrided and nitrocarburised steels

A very elegant demonstration of the benefits of nitrocarburising was conducted in a paper by Dawes [8], a pioneer in advancing nitrocarburising. Using the example of a windscreen wiper assembly, he showed that by using nitrocarburising it was possible to achieve a 62% weight reduction, eliminate special bronze bearings and eliminate separate surface corrosion protection coating procedures. The corrosion resistance was very good and corresponded to a neutral salt corrosion resistance of 250 hours. Finally, the parts were made aesthetically attractive with a black surface produced by a post-oxidation treatment.

2.9.1. Hardness and wear resistance

The case on nitrided/nitrocarburised steel is divided into the compound zone, typically 5–20 μm thick, and the diffusion zone, with a thickness typically of several tenths of a millimetre. The hardness of the compound zone is about constant through its thickness with the exception of the outer porous zone, where hardness is reduced due to porosity. It is higher than the diffusion zone hardness, which continuously decreases from the surface into the steel interior.

Compound layer hardness after nitrocarburising is about 700 HV for low-alloy steels and hardness increases with increasing alloy content in the steel as shown in Figure 12. The measured hardness falls as the degree of porosity in the outermost compound layer surface increases.

There are two mechanisms which determine diffusion zone hardness. First, solid solution hardening is a mechanism that is of high importance for low-alloy steels. The process temperature determines the degree of solid solution of nitrogen, carbon and alloying elements. Quench rate from the process temperature determines how much can be maintained in solid solution. A slow cooling rate allows sufficient time for the precipitation of iron or alloying element nitrides, which reduces the hardening effect from solid solution hardening (see Figure 13). This is why low-alloy steels are normally quenched in water or oil after nitrocarburising.

The second hardening effect is precipitation hardening. This hardening process is predominant with alloyed steels. A dramatic consequence of this mechanism is that a hardness range as wide as 300–1300 Vickers is obtained depending on which steel has been nitrided or nitrocarburised (see Figure 14).

The hardness of the compound layer will determine wear resistance. Increased hardness in the compound layer gives increased resistance to abrasive wear, in which abrasive particles such as sand wear a surface. An important point is that compound zone hardness after nitriding or nitrocarburising can give rise to “low level” abrasive wear situations. This means a very low wear rate when the surface hardness is higher than the hardness of the abrasive particles. The limited depth of the compound layer is a drawback and thus nitriding or nitrocarburising can only be used successfully in mild abrasive wear situations.
Figure 15 shows that both the dry and lubricated adhesive wear resistance of nitrocarburised steels is superior to that of carburised steels, and is higher than could be expected from hardness alone. The compound layer, which is a ceramic, gives low friction and a low tendency to “weld” opposing steel surfaces. The oil retention properties of the porous outer zone of the compound layer offer self-lubrication properties similar to those of sintered non-ferrous bearing materials. These properties act together to give excellent adhesive wear resistance. Adhesive wear resistance improves with an increased ratio $\varepsilon/\gamma'$ in the compound layer [15] and is highest for 100% $\varepsilon$-phase layers [16]. The initial lubricated wear rate of nitrocarburised parts is higher than the steady state wear rate, probably due to porosity. In certain situations, this can be an advantage as running-in wear will smoothen the contact surfaces, which leads to a low steady state wear rate.

Abrasive wear resistance is proportional to hardness, and for nitrocarburised or nitrided steels is therefore dependent on the type of steel used (see figures 12 and 14). For alloyed steels, hardness and thus abrasive wear resistance is superior to that of carburised steels. However, abrasive wear will increase drastically when the thin case of a nitrocarburised steel part is worn off.

Nitriding or nitrocarburising improves the service life of hot and cold work tools. The adhesive wear resistance of the compound layer contributes to this effect, as does the fact that the hardness of the diffusion zone of hot work tool steels is maintained at temperature levels of the order of 500 °C (932 °F). Aluminium extrusion dies that are nitrided and nitrocarburised exhibit improved wear resistance and endurance [18].

2.9.2. Static and fatigue strength
Static strength increases with increased surface layer hardness and relative case depth (=case depth divided by part thickness). Related to nitriding process parameters, this means that static strength increases with increased nitriding/nitrocarburising time and also with increased cooling rate after nitrocarburising. In order to achieve the best effect from solution and precipitation hardening, it is essential that cooling starts from the nitrocarburising temperature before the temperature drops. A drop in temperature from 550 °C (1022 °F) to 450 °C (842 °F) can reduce static strength by more than 20% [9].
The improvement in fatigue strength is greatest for specimens with notches as stress raisers (see Table 4). This is because the hard case will withstand high stress much better than the core material.

Table 4. Bending fatigue strength improvement after nitriding [19]

<table>
<thead>
<tr>
<th>Type of steel</th>
<th>Bending fatigue strength increase, nitrided/not nitrided, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitriding steels</td>
<td>Smooth test bars</td>
</tr>
<tr>
<td>Cr-Mo-Al</td>
<td>28-41</td>
</tr>
<tr>
<td>Cr-V</td>
<td>64-130</td>
</tr>
<tr>
<td>Cr-Mo-V</td>
<td>Notched test bars</td>
</tr>
<tr>
<td>Oil hardening steels</td>
<td></td>
</tr>
<tr>
<td>Cr-Mo-Mn</td>
<td>43-55</td>
</tr>
<tr>
<td>C-steel</td>
<td>7-96</td>
</tr>
<tr>
<td>Cr-Mo</td>
<td></td>
</tr>
</tbody>
</table>

The fatigue strength is improved by a state of compressive residual stresses in the surface layer after nitriding/nitrocarburising as illustrated in Figure 16. There is also a state of compressive stress in the compound zone if it consists of a γ’-layer, whereas tensile surface stress has been predicted but not clearly confirmed for ε-layers [20]. The highest compressive stresses are obtained when nitrocarburising is completed with a fast quench in water or oil. As distortion will increase with increased quench severity, it is necessary to find the best quench rate balance for the best combination of strength and minimised distortion.

Fatigue crack initiation in the compound zone has been observed, especially after gas nitriding. Therefore, there is sometimes a need to perform gas nitriding without the formation of the compound layer (often called white layer after nitriding). This is possible by proper adjustment of the nitriding potential of the nitriding atmosphere. In rare cases, the white layer is removed after nitriding to obtain the best fatigued properties.

2.9.3. Selection of nitriding/nitrocarburising case depth

The case depth is determined by process time and temperature and by the type of steel nitrided. After nitriding/nitrocarburising, there are two depths that are of interest: 1) the compound zone thickness and 2) the diffusion zone depth. Which depth is important depends on the application involved, as outlined in Table 5.

2.9.4. Corrosion resistance and surface appearance

Compared with other thermal or thermochemical surface hardening methods on steels, nitriding and nitrocarburising are unique in that corrosion resistance is improved because of the superior electrochemical properties of the “ceramic surface layer” consisting of ε or ε/γ’ carbonitride. Nitrocarburised parts have excellent humidity corrosion resistance that is better than that of mild steel. Although better than that of steels, salt water corrosion resistance is modest. Corrosion resistance is greatly improved by a post-oxidation step that creates a thin oxide layer on top of the compound layer. As shown in Table 6, nitrocarburising can replace chrome plating or other surface treatments for salt spray corrosion resistance. By additional oiling, waxing or painting, it is possible to increase the corrosion resistance of nitrocarburised parts even more [1, 8 and 22].

Table 5. Selection of surface properties after nitriding/nitrocarburising

<table>
<thead>
<tr>
<th>Type of application</th>
<th>Primary objective</th>
<th>Depth</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abrasive wear</td>
<td>Compound zone hardness</td>
<td>Enough for wear life</td>
</tr>
<tr>
<td>Adhesive wear</td>
<td>Compound zone hardness, porosity and phase constituency</td>
<td>Enough for wear life</td>
</tr>
<tr>
<td>Corrosive protection</td>
<td>Compound layer porosity and phase constituency</td>
<td>Enough to ascertain a dense layer</td>
</tr>
<tr>
<td>Contact and bending fatigue</td>
<td>Diffusion zone hardness and residual stress state</td>
<td>Enough to incorporate maximum point of stress</td>
</tr>
</tbody>
</table>

Table 6. Corrosion data [1, 8, and 22]

<table>
<thead>
<tr>
<th>Type of finish</th>
<th>Salt spray corrosion resistance (ASTM B117), hours to failure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phosphate/oiled</td>
<td>64</td>
</tr>
<tr>
<td>Passivated zinc plating</td>
<td>64</td>
</tr>
<tr>
<td>Electroless nickel plating</td>
<td>64</td>
</tr>
<tr>
<td>Passivated cadmium plating (10/12 µm)</td>
<td>348</td>
</tr>
<tr>
<td>Passivated cadmium plating (25/35 µm)</td>
<td>3800</td>
</tr>
<tr>
<td>Nitrocarburised</td>
<td>17</td>
</tr>
<tr>
<td>Nitrocarburising + post-oxidation (10/20 µm)</td>
<td>645</td>
</tr>
<tr>
<td>Nitrocarburising + post-oxidation (25/35 µm)</td>
<td>3800</td>
</tr>
<tr>
<td>Hard chrome plating</td>
<td>120</td>
</tr>
</tbody>
</table>

Nitriding and nitrocarburising give the surface a light grey surface appearance. By post-oxidising, possibly combined with oiling or waxing, a dark black, shiny surface appearance can be obtained (see Figure 17). Nitriding or nitrocarburising of stainless steels using standard processes will deteriorate corrosion resistance because the passive chromium oxide layer that provides the corrosion protection of stainless steels will be destroyed. See section 2.9.6 regarding special processes for stainless steels.
2.9.5. Dimensional changes

Compound layer growth results in dimensional growth. A solid bar will therefore grow in diameter during nitriding/nitrocarburising. Figure 18 shows that dimensional growth is proportional to compound layer thickness. A guideline is that diameter growth is 30–50% of the compound layer thickness. Thick-walled (wall thickness > 25 mm) cylindrical parts will decrease on the inner and increase on the outer diameter by about the same factor as the growth of a solid bar.

The dimensional change is determined not only by compound layer growth but also and primarily by the thermal stress history during nitriding/nitrocarburising. The inner diameter of cylinders will shrink for large wall thicknesses but will grow for thin thicknesses as shown in Figures 19–20. For a real part with a complex shape, the dimensional change is more difficult to predict, especially for a non-uniform part.

Figure 21 shows that both the inner and outer diameter changes are positive in the range from 30 to 100 μm for thin-walled long cylinders. The figure also shows that the least diameter change is obtained after salt bath treatment (Tenifer) with water quench, but that the scatter of measured diameter changes is highest for that treatment.

2.9.6. Properties of nitrided/nitrocarburised stainless steel

It is not possible to carry out standard gas nitriding or nitrocarburising of stainless steels in a reproducible way without deteriorating corrosion resistance. The first reason is that the thin chromium oxide covering the surface of stainless steels that gives them such good corrosion resistance acts as a barrier to nitriding. A second reason is that the nitrogen that actually enters into the steel will form chromium nitrides and thereby deplete the chromium concentration in the matrix. Although high hardness can be achieved, the nitriding will result in reduced corrosion resistance.

It is possible to partly eliminate these drawbacks with plasma nitriding. The plasma activates the surface, enabling nitrogen to be transferred and diffused into the steel. It has additionally been shown to be possible to avoid chromium nitride formation by performing nitriding at a low temperature. The nitriding will then result in a surface layer consisting of austenite with a highly supersaturated concentration of nitrogen, called the S-phase. The hardness of the supersaturated S-phase is very high, as shown in Figure 22. Corrosion resistance is maintained, as shown in Figure 23. The highly supersaturated S-phase is not thermochemically stable but will decompose at temperatures above approximately 700 °C (1292 °F).
Gas nitriding and nitrocarburising

Figure 21: Measured diameter changes after nitrocarburising of 300-mm-long cylinders with outer diameter 108 mm and wall thickness 4 mm. Nitrocarburising was conducted by Tenifer with water quench and Nitemper with both oil and atmosphere cooling [12].

Figure 22: Hardness profiles of low temperature plasma nitrided 18/8 type stainless steel [10].

Figure 23: Corrosion resistance of stainless steel AISI 316 plasma nitrided at 450 °C (842 °F), 500 °C (932 °F) and 550 °C (1022 °F) compared to untreated steel. Dipping test in 50%HCl+25%HNO₃+25%H₂O [25].

Somers [26] has developed a method to perform gaseous nitriding of stainless steel without plasma. The problem of nitriding inhibition due to the chromium oxide surface is overcome by using a special coating applied to the steel surface before nitriding. Examples of results achieved with this process are given in Figure 24.

Table 7. Different processes for S-phase nitriding and carburising of stainless steel [25]

<table>
<thead>
<tr>
<th>Company</th>
<th>Process</th>
<th>Element</th>
<th>Temperature, °C (°F)</th>
<th>Medium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Birmingham University, UK</td>
<td>LTPN/LTPC</td>
<td>N</td>
<td>&lt;450 (842)</td>
<td>Plasma</td>
</tr>
<tr>
<td>Nitruvid, France</td>
<td>Nivox2</td>
<td>C</td>
<td>&lt;550 (1022)</td>
<td>Plasma</td>
</tr>
<tr>
<td>Nihon Parkerizing, Japan</td>
<td>Palsonite</td>
<td>N+C</td>
<td>&lt;400 (752)</td>
<td>Plasma</td>
</tr>
<tr>
<td>Airwater Ltd, Japan</td>
<td>NV Super Nitriding</td>
<td>N</td>
<td>&lt;460 (860)</td>
<td>Plasma</td>
</tr>
<tr>
<td>Bodycote, UK</td>
<td>NV Pionite Process</td>
<td>C</td>
<td>450–490 (842–914)</td>
<td>Cyanide salt bath</td>
</tr>
<tr>
<td>DTU, Denmark</td>
<td>Kolsterising®</td>
<td>N+C</td>
<td>300–400 (572–752)</td>
<td>Gas + Fluorine</td>
</tr>
<tr>
<td></td>
<td>Gas nitriding</td>
<td>N</td>
<td>&lt;500 (932)</td>
<td>Confidential</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>&lt;450 (842)</td>
<td>Gas</td>
</tr>
</tbody>
</table>
3. Furnace and equipment.

Table 8. Cooling options for different types of nitriding/nitrocarburising furnaces

<table>
<thead>
<tr>
<th>Atmosphere furnaces</th>
<th>Furnace type</th>
<th>Possible cooling options</th>
</tr>
</thead>
<tbody>
<tr>
<td>Multipurpose furnace with integrated</td>
<td>Oil, gas, slow convection</td>
<td></td>
</tr>
<tr>
<td>oil quench</td>
<td></td>
<td>Gas, slow convection</td>
</tr>
<tr>
<td>Box furnace</td>
<td>Gas, high convection</td>
<td></td>
</tr>
<tr>
<td>Box furnace with integrated high-speed</td>
<td>Gas, slow convection</td>
<td></td>
</tr>
<tr>
<td>gas circulation</td>
<td>Gas, high pressure and high convection</td>
<td></td>
</tr>
<tr>
<td>Pit retort furnace</td>
<td>Gas, slow convection</td>
<td></td>
</tr>
<tr>
<td>Furnace line with integrated</td>
<td>High pressure, high convection</td>
<td></td>
</tr>
<tr>
<td>high-pressure gas cooling</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Single chamber</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Single chamber/high pressure</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Furnace line with integrated</td>
<td></td>
<td></td>
</tr>
<tr>
<td>high-pressure gas cooling</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| Vacuum furnaces (including plasma      | Furnace type                                      | Possible cooling options                      |
| furnaces)                             |                                                  |                                                 |
| Multipurpose furnace with integrated  | Oil, gas, slow convection                         |
| oil quench                             |                                                  | Gas, slow convection                           |
| Box furnace                            | Gas, high convection                              |
| Box furnace with integrated            | Gas, slow convection                              |
| high-speed gas circulation             | Gas, high pressure and high convection            |
| Pit retort furnace                     | Gas, slow convection                              |
| Furnace line with integrated           | High pressure, high convection                    |
| high-pressure gas cooling              |                                                  |                                                 |
| Single chamber                         |                                                  |                                                 |
| Single chamber/high pressure           |                                                  |                                                 |
| Furnace line with integrated           |                                                  |                                                 |
| high-pressure gas cooling              |                                                  |                                                 |

The process medium can be salt, gas or plasma. The salt bath processes are losing market to atmospheric gas pressure processes due to the environmental problems with salts, which contain cyanide. Therefore, salt bath equipment is omitted in the following description. The use of plasma processes has steadily increased in recent decades although the number of installations is still limited in comparison with atmospheric pressure processes.

Part geometry and dimensions may limit the number of possible furnace alternatives. Very long workpieces such as shafts or axles cannot be treated in standard box or multi-purpose furnaces, and tend for example to be treated in cylindrical pit furnaces. Requirements on dimensional tolerances may also limit the number of alternatives with respect to treatment temperature as increased treatment temperature leads to increased dimensional changes. Cooling options are also limited as increased cooling severity will increase distortion.

The number of available cooling options depends on the type of furnace used, as illustrated in Table 8. Water, the fastest type of quench medium (not included in the table), is used only in connection with salt bath nitriding/nitrocarburising. Oil quenching, the second fastest, is common as it is the standard quench method in multi-purpose furnaces for which gaseous nitrocarburising was primarily developed, such as in the Ipsen Nitemper process. Gas quenching is growing in importance for several reasons. Gas quenching is the only method that can be integrated into single-chamber furnaces of both vacuum and atmosphere types. Gas quenching has environmental advantages compared to oil quenching, both for the external and work environment. Gas quenching also has the advantage that post-cleaning can be eliminated. It is possible to increase and vary the cooling rate by type of gas, and by increasing and varying the gas pressure and velocity.

Linde engineers will support customers in setting up the necessary procedures including furnace requirements, safety arrangements, process specifications, gas installation and furnace control. This may involve retrofitting an existing furnace or starting up a new one. In retrofitting, the first step is to conduct a survey to find out the required furnace modifications. There are a number of important requirements that must be fulfilled to ascertain safety and treatment quality. Necessary points to be considered are as follows.

a. Pit and bell type furnaces must be equipped with a sealable retort that must be checked for any defects.

b. A circulating fan must be present within the retort of the pit or bell type furnace. CARBOJET® is an alternative that eliminates the ventilator (see section 3.5).

c. Provisions must be made for exhaust gases to be burnt off outside the furnace.

d. The furnace must have a temperature uniformity capability typically of ±5 °C (±41 °F)

e. The furnace should preferably be capable of ramped cooling.
3.1. Nitriding

Gas nitriding is typically performed in convection furnaces, either of pit type or a box furnace, at a temperature in the range of 500–520 °C (932–968 °F) and in an ammonia atmosphere. The ammonia may be diluted with nitrogen or hydrogen. The parts to be nitrided are placed on fixtures or in “baskets”, which are transferred to and loaded into the furnace. The furnace cover or door is then closed. To ensure precision with regard to compound layer and diffusion zone thickness, it is important to have good enough furnace temperature uniformity, typically ±5 °C (±41 °F).

Nitriding furnaces have to be tight for safety reasons and also because of the odour resulting from possible leakage of ammonia gas.

3.2. Nitrocarburising

In principle, the same type of furnaces can be used in nitrocarburising as in gas nitriding; however, one special feature of nitrocarburising is that the final cooling often is fast. Brick-lined multi-purpose furnaces with an oil quenching capability of the same type as for carburising are therefore commonly used (see Figure 25a). Common solutions are box-type atmosphere furnaces, with fibre lining, and batch furnaces with a vacuum pumping option for quick atmosphere conditioning and with integrated gas cooling (Figure 25b), as well as metallic retort furnaces of the type shown in Figure 25b+c. Table 9 gives the specific advantages and disadvantages of each type of furnace.

After the parts have been cleaned, they are loaded into baskets or fixtures and transferred to the furnace for heating (preceded by preheating) to process temperature, 570–580 °C (1058–1076 °F), and kept at that temperature for a time that yields the desired compound layer and diffusion depth. As in the case of nitriding, close temperature uniformity, typically ±5 °C (±41 °F), is required. In addition to containing ammonia, the furnace atmosphere should also contain carbon monoxide and hydrogen in order to transfer both carbon and nitrogen to the steel surface.

<table>
<thead>
<tr>
<th>Furnace type</th>
<th>Advantage</th>
<th>Disadvantage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brick-lined atmosphere furnace</td>
<td>Slow ammonia dissociation</td>
<td>Fast change in atmosphere</td>
</tr>
<tr>
<td></td>
<td>Modular construction</td>
<td>Low nitriding potential without hydrogen addition</td>
</tr>
<tr>
<td>Metallic retort furnace</td>
<td>Fast change in atmosphere</td>
<td>Low nitriding potential without hydrogen addition</td>
</tr>
</tbody>
</table>

Table 9. Specific features of each furnace type

After the parts have been cleaned, they are loaded into baskets or fixtures and transferred to the furnace for heating (preceded by preheating) to process temperature, 570–580 °C (1058–1076 °F), and kept at that temperature for a time that yields the desired compound layer and diffusion depth. As in the case of nitriding, close temperature uniformity, typically ±5 °C (±41 °F), is required. In addition to containing ammonia, the furnace atmosphere should also contain carbon monoxide and hydrogen in order to transfer both carbon and nitrogen to the steel surface.
3.2.1. Furnace interior influence

Gas reaction rates depend on the catalysing effect from available surfaces inside the furnace and will therefore vary between furnaces, depending on whether the type of furnace interior materials are metals or ceramics. Figure 26 shows experimental results regarding the relation between residual ammonia and added ammonia for two types of furnaces: 1) a multi-purpose furnace (Ipsen RTQ-1) with a ceramic interior and 2) a pit furnace with a steel retort (UTAB). For reference, the figure shows the line of no ammonia decomposition. The figure illustrates both the effect of gas residence time and of the catalysing effect of the furnace interior material. A high flow rate, in this case 4m³/h (1.41 • 100ft³/h), corresponds to a low gas residence time, which results in higher residual ammonia concentrations (lower dissociation of the inlet ammonia). Residual ammonia concentrations are lower for the metallic retort furnace because the metallic retort catalyses ammonia dissociation to a higher degree than the ceramic interior of the multi-purpose furnace.

The ammonia dissociation is also catalysed by the surface of the steel parts loaded into the furnace. An increase in surface area increases the degree of dissociation. An example from a laboratory test is shown in Figure 28.

In a study where identical nitrocarburising atmosphere recipes were applied (constant gas mixture and flow rate settings), the compound layer thicknesses obtained on steel samples varied from 11 to 26 μm. To interpret the differing results, the FTIR gas analysis results from these trials are plotted as a function of nitriding potential ($P_{NH_3}/P_{H_2}^{3/2}$) and carbon potential ($P_{CO^2}/P_{CO_2}$) in Figure 29. The direction of the arrows in the figure indicates analysing results with progressing process time.

The figure shows large differences between furnaces both with respect to absolute values of the potentials as to the direction of change in these potentials during the nitrocarburising process. The two fibre-insulated furnaces showed a greater variation in atmosphere activities during the process compared to the brick-walled furnaces. This may be connected to the fact that the water content was initially very high in the fibre lining furnaces. The steel retort furnace is the extreme and exhibits the lowest nitrogen activities close to the borderline γ'/ε in the phase diagram, but also the highest carbon activities. This is explained by the catalysing effect of the steel retort on ammonia dissociation and on the reaction between hydrogen and CO₂ to form CO respectively. Logically, the lowest compound layer thickness was measured for the steel retort furnace. The ammonia dissociation rate will decrease when the steel retort has been exposed for a long time to the nitriding atmosphere and is becoming saturated with nitrogen.

The carbon activities calculated from FTIR gas analysis could not be related to compound layer thickness results. Carbon activities determined from CO, H₂, and H₂O were found to be an order of magnitude lower than those calculated from CO and CO₂, which shows that the atmosphere is far from the state of equilibrium.
3.3. Vacuum, high-pressure and plasma nitriding

A low-pressure (vacuum) nitriding process starts with the evacuation of the furnace chamber followed by refilling it with nitrogen to atmospheric pressure to enable fast heating by convection. When the process temperature is reached, vacuum pumping to a pressure of 150–400 mbar is performed. Ammonia and hydrogen are added as nitriding media. The major benefits of the vacuum nitriding process are low consumption of gases, almost no effluents, a pure atmosphere, clean surfaces and fast change of nitriding parameters [28]. The disadvantages are relatively high equipment costs and problems with uniformity in the nitriding result for parts with deep narrow bores.

High-pressure nitriding is a very different process. It is carried out in nitrogen, which at normal ambient pressure is neutral with respect to nitriding ability, but which at very high pressure up to 1000 bar has a nitriding effect. Its benefits are the use of environmentally friendly nitrogen gas and the possibility to treat steels that are difficult to nitride. The major disadvantages are relatively high equipment costs and problems with uniformity in the nitriding result for parts with deep narrow bores.

High-pressure nitriding is a very different process. It is carried out in nitrogen, which at normal ambient pressure is neutral with respect to nitriding ability, but which at very high pressure up to 1000 bar has a nitriding effect. Its benefits are the use of environmentally friendly nitrogen gas and the possibility to treat steels that are difficult to nitride. The major disadvantage is very high equipment costs, which has been a barrier to its use outside research laboratories.

The fourth state of matter, plasma, is characterised by the fact that it consists of free charged particles, ions and electrons. In a DC plasma nitriding furnace (see Figure 28a), an electrical voltage is applied between workload (the cathode) and the furnace vessel (the anode). A vacuum of the order of a few mbar is maintained in the vessel, which contains nitrogen gas. In the near vicinity of the load, the electrical potential drops and a plasma with nitrogen ions is obtained. The positively charged nitrogen ions are accelerated by the electrical voltage towards the load. The nitrogen ion bombardment results in the nitriding of the steel as well as the heating of the part. Hydrogen is added to obtain reducing conditions and to control the nitriding potential. Argon is sometimes used as a cleaning agent before actual nitriding. The argon ions are heavy and therefore efficient in cleaning the surface by so-called sputtering, which is the removal of surface layer atoms by ion bombardment.

The DC plasma technology has weaknesses with respect to temperature uniformity and the risk of damage from arcing. A development that eliminates these drawbacks is active screen plasma. In this case, the plasma is created in a separate chamber, and a metal screen surrounding the load is used as the cathode (see Figure 28b).

The plasma technique offers similar benefits to those of vacuum nitriding, including very low consumption of gases, the environmental advantage of almost no effluents (see Table 10), the possibility to tailor the phase constituency in the compound layer to be pure γ' or pure ε, and the possibility to nitride to only yield a diffusion zone without the compound layer. Plasma nitriding can be used at very low process temperatures, down to 400–450 °C (752–842 °F), which means that hardened and tempered steels can maintain their hardness. Lower distortion is a connected benefit. Because of the ion bombardment, surfaces are activated to make it also possible to nitride stainless steels and even the nonferrous metals aluminium and titanium.
3.4. Nitriding + PVD or CVD

PVD (Physical Vapour Deposition) and CVD (Chemical Vapour Deposition) are processes that produce coatings such as TiN or CrN with very high hardness. These coatings are thin and their load-bearing capacity is limited, which makes the coating susceptible to failure because of cracking or flaking. Performing nitriding or nitrocarburising as a preceding operation before the PVD or CVD coating improves bearing capacity. Combined processes have therefore been developed. Figure 30 shows a cross section of equipment capable of performing both plasma nitriding and PVD coating. An example of the resulting hardness profile after nitriding + PVD/TiN coating is also shown in the figure.

Table 10. Comparison of effluent emission data for gaseous and plasma nitrocarburising [25]

<table>
<thead>
<tr>
<th></th>
<th>Plasma</th>
<th>Gaseous</th>
<th>Reduction in %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amount of gas used m³/h (100ft³/h)</td>
<td>0.6 (0.21)</td>
<td>6.0 (2.12)</td>
<td>90</td>
</tr>
<tr>
<td>Total carbon emission via CO/CO₂, mg/m³</td>
<td>504</td>
<td>137253</td>
<td>99.63</td>
</tr>
<tr>
<td>Total amount of NOX gas, mg/m³</td>
<td>1.2</td>
<td>664</td>
<td>99.82</td>
</tr>
<tr>
<td>Output of residual carbon-bearing gas, mg/h</td>
<td>302</td>
<td>823518</td>
<td>99.96</td>
</tr>
<tr>
<td>Output of residual NOX gas</td>
<td>0.72</td>
<td>3984</td>
<td>99.98</td>
</tr>
</tbody>
</table>

Figure 29: Micrograph cross section of a steel specimen treated in the Corr-i-Dur® process [29]

Figure 30: a) Cross section of a unit for both plasma nitriding and PVD coating. b) Result of plasma nitriding followed by PVD-TiN coating. Note logarithmic distance scale [Courtesy of Sulzer Metaplas GmbH]
3.5. High-speed gas injection replaces ventilator

CARBOJET high-speed gas injection is a patented technology by 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 position 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 NITROFLEX® 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 but also in pit furnaces for different heat treatment processes including nitriding/nitrocarburising and carburising where significant savings on maintenance costs have been achieved [30]. CARBOJET is able to steer the atmosphere circulation with uniform velocity from the top of the pit furnace to the bottom of the furnace.

The lances are practically maintenance-free; furnaces where ventilators have been replaced by the CARBOJET high-speed injection system can therefore be operated longer without shutdowns. Shutdowns caused by broken ventilators and disturbances of vibrating ventilators are 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 due to improved gas homogeneity and mixing
- No ventilators are needed, maintenance-free technology
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, as is evident from Table 11, which describes a restricted selection of the numerous nitriding and nitrocarburising trade names existing on the market. NITROFLEX is Linde’s trademark for nitriding and nitrocarburising processes.

In nitriding, straight ammonia may be used, but nitrogen has to be added for safety purging upon start-up and at the end of the process. In nitrocarburising, a carbonaceous gas must be added to the ammonia to enable both nitrogen and carbon transfer to the steel surface.

In-situ methods can create widely varying atmosphere compositions and the flow can 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.

### Table 11. Nitriding and nitrocarburising features and process names

<table>
<thead>
<tr>
<th>Nitriding</th>
<th>Temperature, °C (°F)</th>
<th>Time, h</th>
<th>Name or trade name</th>
<th>Media</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>500–520 (932–968)</td>
<td>5–100</td>
<td>Gas nitriding</td>
<td>NH₃/N₂/H₂</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Oxynitriding</td>
<td>NH₃/Air</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Plasma nitriding</td>
<td>NH₃/H₂</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>High-pressure nitriding</td>
<td>NH₃/N₂/O₂/ (H₂/CO/C₃H₈)</td>
</tr>
<tr>
<td>Nitrocarburising</td>
<td>560–580 (1040–1076)</td>
<td>0.5–5</td>
<td>NITROFLEX</td>
<td>NH₃/Endogas</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Nitemper</td>
<td>NH₃/Endogas/air</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Nitrotec</td>
<td>NH₃/Exogas</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Nitroc®</td>
<td>Salt</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Tenifer/Tufftride</td>
<td>N₂/H₂/CH₄</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Plasma nitrocarburising</td>
<td>Air, H₂O, N₂O</td>
</tr>
</tbody>
</table>

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.
4.1. Nitrogen supply

There are five major supply forms for nitrogen (see Figure 32):

**Gaseous nitrogen in cylinders or bundles**
For cost reasons, this option is relevant only for limited gas consumption.

**Liquid nitrogen**
Liquid nitrogen is supplied by truck to a vacuum-insulated container (see Figure 32a) at the customer site. This is the most common supply method that is cost-efficient for a flow from 10 up to about 200 m$^3$/h. Nitrogen supplied in the liquid form has a high purity, with typical contamination levels of O$_2$ + H$_2$O 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 32b, yields high purity, typically 5 ppm oxygen and moisture content. It is relevant for flow rates from 250 to 2000 m$^3$/h.

**Nitrogen from adsorption (PSA) units installed on-site**
Nitrogen produced on-site using the PSA (Pressure Swing Adsorption) technique, Figure 32c, has a purity of 99 to 99.99%. Flow rates from 10 up to 2000 m$^3$/h can be accommodated. ECOVAR® is a family of PSA on-site production units supplied by Linde Gas.

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

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

Figure 32: Nitrogen supply methods. a) Storage tank and vaporiser for liquid nitrogen. b) Cryogenic nitrogen production with CRYOSS. c) PSA (Pressure Swing Adsorption); ADSOSS
4.2 Hydrogen supply

Hydrogen is alternatively supplied by:

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

Examples of different supply methods for hydrogen are shown in Figure 33.

4.3. Ammonia, carbon dioxide and nitrous oxide

Ammonia is delivered as a liquid in large containers for high consumption, in semi-containers for moderate consumption or in cylinders for moderate consumption.

Carbon dioxide is also delivered as a liquid for large-scale customers and as gas in cylinders for small to medium-sized customers.

Nitrous oxide for post-oxidation is delivered in cylinders.

4.4. Nitriding gas supply setup

Figure 34 shows the schematic setup of a cylinder ammonia installation suitable for moderate consumption. When cylinders are used, it is an advantage to have two separate cylinders or cylinder bundles. One cylinder is used and the other is on standby to be automatically connected when the pressure from the first falls below the required supply pressure. This ensures continuous and safe gas supply. For liquid bulk ammonia supply, it is necessary to have a vaporiser connected. When a cylinder supply is used, it is necessary either to ensure that the temperature of the cylinders is sufficiently high for vaporisation or to have a vaporiser installed.

Nitrogen required for purging at heating, upon cooling and for dilution during nitriding is supplied in cylinders for moderate consumption and in a liquid tank for higher amounts. If nitriding is only one of several heat treatment operations in a heat treatment plant, the gas supply is dimensioned to cover the whole installation, which normally means that liquid nitrogen supply is best.

Hydrogen used for nitrogen potential control is commonly supplied in cylinders.
4.5. Nitrocarburising gas supply setup

Nitrocarburising gas supply has the special feature that carbon dioxide is added in addition to the nitrogen/ammonia/hydrogen supply used in nitriding. Figure 35 shows the schematic setup of a gas supply system with a liquid nitrogen tank and gas cylinders for ammonia and carbon dioxide respectively. Figure 36 shows a gas storage installation also incorporating propane and methanol for carburising. From storage, gases are led via pipes to the mixing panel. Here the flow rates are controlled. Figure 37a shows a flow mixing panel. In advanced setups, the flow rate and temperature control can be built into a closed loop control system as shown in Figure 37b.
If carbon dioxide is mixed with ammonia, there will be reactions leading to ammonium carbonate formation, which deposits in the pipeline, leading to clogging and flow disturbances. Ammonia gas and nitrogen, or carbon dioxide gas and nitrogen, can be mixed before feeding to the furnace. Therefore, there are two alternatives:

1. Nitrogen + ammonia in one mixer and from one inlet, carbon dioxide from another pipe and inlet

2. Nitrogen + carbon dioxide in one mixer and from one inlet, ammonia from another pipe and inlet

Figure 38 shows the alternative with ammonia mixed with nitrogen and a separate line for carbon dioxide. Gases enter the furnace through a specially designed injector formed by two concentric tubes. The nitrogen/ammonia mixture passes through the outer wider tube. Carbon dioxide flows through the inner tube, which extends into the furnace. All three gases do not mix until they reach the hot furnace interior, which is essential in order to avoid the risk of ammonium carbonate deposits.

As in the case of nitriding, gas cylinders are adequate supply forms for hydrogen used in nitrogen potential control.
Gas nitriding and nitrocarburising

Figure 37b: Closed loop control system.

Figure 38: Gas inlet design for nitrocarburising.
During nitriding, ammonia (NH₃) in the furnace atmosphere decomposes into hydrogen and nitrogen at the surface, enabling nitrogen atoms to be adsorbed at the steel surface and to diffuse further into the steel as illustrated in Figure 39a. In nitrocarburising, it is additionally necessary to have a carbonaceous gas transferring carbon to the steel surface. This is illustrated in Figure 39b by the carbon depositing surface reaction with carbon monoxide, CO. A compound layer consisting of ε and γ' nitride is formed when a sufficiently high surface nitrogen (and carbon) concentration forms on the steel surface.

There are three major steps in nitrogen/carbon transfer:
1. From the gas to the steel surface
2. Diffusion through the compound layer
3. Diffusion into the diffusion zone

(Additional steps not considered here are transport within the gas boundary layer and carbon diffusion from the steel matrix into the compound zone.) The concentration gradients driving the transport of nitrogen and carbon are shown in Figure 40.

The flux of nitrogen and carbon from the gas to the steel surface is proportional to the concentration differences between the gas and the surface:

\[
\frac{dm_N}{dt_{\text{(surface)}}} = k_1 [c_{N\text{gas}} - c_{N\text{surf}}]
\]

\[
\frac{dm_C}{dt_{\text{(surface)}}} = k_2 [c_{C\text{gas}} - c_{C\text{surf}}]
\]

Here m denotes mass, t time, c concentration per volume unit and \(k_1\) and \(k_2\) are reaction rate coefficients.
The transfer of nitrogen and carbon from the surface further into the steel is controlled by diffusion. Diffusion rates follow Fick’s first law, which for the compound layer and diffusion zone are respectively:

\[
\frac{dm}{dt}_{\text{comp layer}} = -D_{\text{comp}} \frac{dc}{dx}
\]

\[
\frac{dm}{dt}_{\text{diff zone}} = -D_{\text{diff}} \frac{dc}{dx}
\]

Balance of mass requires that all three mass transfer rates are equal:

\[
\frac{dm}{dt}_{\text{surface}} = \frac{dm}{dt}_{\text{comp layer}} = \frac{dm}{dt}_{\text{diff zone}}
\]

The slowest of the three steps controls the nitrogen and carbon transfer rates. For a compound layer consisting of alternating ε-γ'-ε layers, the rate will be determined by the phase with the slowest diffusion properties.

### 5.2. The atmosphere nitriding potential

The nitrogen activity in the gas is determined by the equilibrium,

\[ \text{NH}_3 = N + \frac{3}{2} \text{H}_2 \]

with the chemical equilibrium constant

\[ K = a_n \frac{P_{\text{H}_2}^{3/2}}{P_{\text{NH}_3}} \]

where \( P_{\text{H}_2} \) and \( P_{\text{NH}_3} \) are the partial pressures of hydrogen and ammonia respectively. Accordingly, the nitrogen activity, \( a_n \), can be expressed as

\[ a_n = K \frac{P_{\text{NH}_3}}{P_{\text{H}_2}^{3/2}} \]

where \( a_n \) is proportional to the concentration, \( c_n \). The ratio

\[ r_n = \frac{P_{\text{NH}_3}}{P_{\text{H}_2}^{3/2}} \]

is commonly called the nitriding potential.

If 100% \( \text{NH}_3 \) (ammonia) is added to the furnace, which is fairly commonplace in gas nitriding, some ammonia dissociates into nitrogen and hydrogen gas when the ammonia hits the hot furnace interior. The part of the ammonia which does not dissociate is called residual ammonia, and is what causes nitriding. In the expression for the nitrogen potential, \( r_n = \frac{P_{\text{NH}_3}}{P_{\text{H}_2}^{3/2}} \), \( P_{\text{NH}_3} \) is the residual ammonia partial pressure and \( P_{\text{H}_2} \) is the partial pressure of hydrogen, formed by the ammonia dissociation (in addition possibly with separately added hydrogen).

The ammonia dissociation may be described by the reaction,

\[ \text{NH}_3 \rightarrow (1 - \alpha)\text{NH}_3\text{(residual)} + \frac{3}{2} \alpha\text{H}_2 + \frac{1}{2} \alpha\text{N}_2 \]

where \( \alpha \) is the degree of dissociated ammonia. The total number of moles after dissociation is

\[ (1 - \alpha) + \frac{3}{2} \alpha + \frac{1}{2} \alpha = 1 + \alpha \]

For a nitriding atmosphere produced from 100% ammonia, the partial pressures can therefore be expressed as

\[ P_{\text{NH}_3} = \frac{(1 - \alpha)}{(1 + \alpha)} \]

\[ P_{\text{H}_2} = \frac{3\alpha}{2(1 + \alpha)} \]

\[ P_{\text{N}_2} = \frac{1}{2\alpha(1 + \alpha)} \]

and the nitriding potential as

\[ r_n = \frac{(1 - \alpha)(1 + \alpha)^{1/2}}{(3/2\alpha)^{3/2}} \]

(This method of calculating the nitriding potential is only fully accurate if the amount of ammonia consumed in the nitriding reaction \( 2\text{NH}_3 \rightarrow 2\text{N} + 3\text{H}_2 \) can be neglected in comparison to the available amount of ammonia.)

The nitriding potential can alternatively be expressed as a function of the residual ammonia or the hydrogen partial pressure according to the equations

\[ r_n = 4^*2^{1/2}P_{\text{NH}_3}/[3/2(1-P_{\text{NH}_3})^{3/2}] = 8/\sqrt{3} x P_{\text{NH}_3}/(1-P_{\text{NH}_3})^{3/2} \]

\[ r_n = (1 - 4/3P_{\text{H}_2})/P_{\text{H}_2}^{3/2} \]

As each dissociated ammonia molecule produces two gaseous molecules \( (1/2\text{N}_2+3/2\text{H}_2) \), the furnace pressure will increase as a result of the volume expansion. A measure of the furnace pressure is therefore an indication of the degree of ammonia dissociation and accordingly also of the nitriding potential [31, 32].

### 5.3. The atmosphere carbon potential

Similar to nitriding, the carburising reaction

\[ \text{CO} + \text{H}_2 \rightarrow \text{C} + \text{H}_2\text{O} \]

has an equilibrium constant expressed by

\[ K_j = a_c P_{\text{H}_2}/P_{\text{CO}} \]

where \( P \) stands for the partial pressure, and the carbon activity, \( a_c \), is proportional to the carbon concentration,

\[ a_c = \text{const} \times c_c \]
The atmosphere carbon potential can alternatively be expressed by the ratios

\[ r_{C1} = \frac{P_{CO}}{P_{H_2O}} \]

\[ r_{C2} = \frac{P_{CO}}{P_{CO_2}} \]

Endogas or exogas, which both contain carbon monoxide, have been and are used as CO sources. Pure CO is an alternative carbon source but the high cost is a barrier to its use. The carbon source for the NITROFLEX system is carbon dioxide, CO₂, which by reacting with hydrogen inside the furnace produces CO according to the reaction,

\[ H_2 + CO_2 = CO + H_2O \]

The hydrogen needed for this reaction originates from dissociated ammonia or from a separate addition of hydrogen. Figure 41 shows that CO forms according to this reaction. Furnace walls, retort and load catalyse the reaction, which means that the reaction rate shown will be different for different furnaces.

The atmosphere carbon activities of atmospheres based on blends between ammonia/endogas and ammonia/exogas are excessively high and practice has shown that soot deposits may be a problem in furnaces running with these atmospheres for a long time. An atmosphere based on a blend between ammonia/CO₂ has much lower carbon activity (see Table 12).

### Table 12. Calculated quasi equilibrium compositions of various nitrocarburising atmospheres at 580 °C (1076 °F)

<table>
<thead>
<tr>
<th>Added gas mixture</th>
<th>Quasi equilibrium composition (vol%)</th>
<th>Activities(^{*})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>N₂</td>
<td>H₂</td>
</tr>
<tr>
<td>50% Endogas, 50% NH₃</td>
<td>24.1</td>
<td>25.9</td>
</tr>
<tr>
<td>40% Endogas, 10% Air</td>
<td>29.2</td>
<td>24.3</td>
</tr>
<tr>
<td>50% NH₃, 5% CO₂, 60% N₂</td>
<td>58.8</td>
<td>15.5</td>
</tr>
<tr>
<td>35% NH₃, 5% CO₂, 5% CO, 55% N₂</td>
<td>54.4</td>
<td>15.9</td>
</tr>
<tr>
<td>35% NH₃, 5% CO₂, 20% H₂, 45% N₂</td>
<td>45.4</td>
<td>26.6</td>
</tr>
</tbody>
</table>

\(^{*}\) The reference state for the activity values are nitrogen gas at 1 atm, graphite and wustite (FeO), for nitrogen, carbon and oxygen respectively.
5.4. Atmosphere analysis

The nitriding potential is determined by gas analysis. In nitrocarburising, the gas analysis aims to determine both the nitriding and the carbon potentials. The analysis of nitrocarburising atmospheres is difficult due to the complex gas composition (NH₃, H₂, CO, CO₂, and H₂O) with fairly high water vapour content, which may result in the precipitation of ammonium carbonate, which clogs the analyser and analysing sample gas pipes. The use of a heated sample gas system is one way to inhibit condensation.

5.4.1. Ammonia and hydrogen analysis

The simplest method of determining the nitriding potential is ammonia analysis with the ammonia burette technique shown in Figure 42. The analysing principle is based upon the fact that ammonia gas dissolves in water. The valves at the top and bottom of the graduated container in the figure are first placed in purging position. Closing the upper valve leads to a gas sample being locked into the container. During analysis, the bottom valve is opened to allow water from the left-hand container into the measuring container. The un-dissociated ammonia will thereby dissolve in the water, causing the water to rise in the graduated container. The more un-dissociated ammonia there is, the higher the water level will rise.

On-line analysis can be performed with infrared analysis of ammonia or hydrogen analysis with a thermal conductivity analyser or a combination of both. The principle of IR analysis is based on the ability of multi-atomic gas molecules to absorb an IR wavelength that is specific to each gas molecule. The principle is illustrated in Figure 43. A beam of infrared light is split into two separate beams, one of which passes through a cell containing the sample gas, the other through a reference cell, which in the figure is filled with nitrogen. A rapidly alternating splitter (on the left of the figure) separates the radiation reaching the detector on the right of the figure. A measure of the amount of ammonia is obtained by comparing the detector signals for the two beams.

Hydrogen gas, being a one-atom gas, cannot be analysed by IR analysis. However, due to the very high thermal conductivity of hydrogen gas, analysis based on thermal conductivity can be used. A classic thermal conductivity detector design utilises a Wheatstone bridge in which a resistor is in contact with the gas to be analysed. Changes in the hydrogen concentration will result in a temperature change in the resistor and thus a resistance change, which can be measured as a signal. Figure 44 shows the principle and the appearance of an analysing unit. Cross sensitivity on analysis from ammonia has to be taken into account.
Hydrogen can also be analysed with a sensor with a similar appearance to an oxygen probe as shown in Figure 45. It uses a measuring tube material with the ability to determine the difference in the hydrogen partial pressure between a reference gas inside and the actual furnace atmosphere outside the tube. The analysis signal is a direct value of the hydrogen concentration in the furnace atmosphere.

In cases where nitriding is performed with a variable unknown ammonia/nitrogen mixture, two hydrogen analysers can be used to accurately establish the nitriding potential. The analysers are positioned so that one analyses hydrogen in the furnace atmosphere, \( P_{H_2} \), and the second analyses the hydrogen concentration after the complete dissociation of ammonia, \( P'_{H_2} \). From these two measurements, the nitriding potential is expressed by

\[
r_N = \frac{(P'_{H_2} - P_{H_2})}{(3/2 - P'_{H_2}) P_{H_2}}
\]

An alternative atmosphere analysis is hydrogen analysis combined with oxygen probe readings.

### 5.4.2 Oxygen probe analysis

Oxygen probe analysis can be used to gain a measure of the nitriding potential even though oxygen is not active in the nitriding process. The atmosphere oxygen partial pressure is proportional to the water/hydrogen ratio and thus the oxygen probe signal \( A \) can be expressed by the following equation:

\[
A = \frac{P_{H_2O}}{P_{H_2}}
\]

The principle of the oxygen probe method is based on the fact that the inlet gas composition is known, as is its water content, which means that \( P_{H_2O} \) is also known. The hydrogen concentration, \( P_{H_2} \), can be expressed as a function of the degree of ammonia dissociation and the nitriding potential (see equations in section 5.2). \( A \) is accordingly an indirect measure of the nitriding potential.

With two separate oxygen probes, the nitriding potential can be determined without any knowledge of the ingoing gas composition. The first probe measures the oxygen potential \( A \) in the actual furnace atmosphere, whereas the second measures the oxygen potential after passing the atmosphere through an ammonia cracker, which completely dissociates all ammonia (\( \alpha = 1 \)). The second oxygen probe measures the signal:

\[
B = \frac{P_{H_2O,\text{Diss}}}{P_{H_2,\text{Diss}}}
\]

where the superscript “Diss” refers to the atmosphere composition after the ammonia cracker. If the nitriding atmosphere consists only of ammonia, it can be shown that the ratio between the two oxygen probe signals is a measure of the degree of ammonia dissociation inside the furnace according to the equation [34]

\[
D = A/B = 1/\alpha
\]

One development of the oxygen probe to determine the nitriding potential is the type of sensor shown in Figure 46. The outer electrode is in direct contact with the furnace atmosphere. The furnace atmosphere is also led into the inner side of the ceramic tube, but passes through a catalyst that promotes complete dissociation of all residual ammonia before it comes into contact with the inner electrode. The resulting voltage \( \Delta U \) is a measure of the difference in oxygen potentials between

---

Figure 45: a) Principle and b) appearance of the hydrogen sensor [33] [Courtesy of Ipsen International GmbH]

Figure 46: Oxygen probe as a nitrogen sensor [36]

Figure 47: Basic components of a computerised FTIR spectrometer system
the actual furnace atmosphere and the atmosphere of completely dissociated ammonia. This voltage is a direct indication of the degree of ammonia dissociation, $\alpha$, in the furnace atmosphere expressed by \[34–35\].

$$\Delta U = 0.0992 \, T \log \alpha$$

An oxygen probe signal will also be a measure of the atmosphere carbon activity, $a_c$, according to the relations

$$a_c = K_1 \frac{P_{CO}}{(P_{O_2})^{1/2}} = K_2 \frac{P_{CO}^2}{P_{CO_2}} = K_3 \frac{P_{CO} P_{H_2}}{P_{H_2O}}$$

where $K_1$, $K_2$, $K_3$ are constants.

5.4.3. FTIR gas analysis of nitrocarburising atmospheres

FTIR (Fourier Transform Infrared) analysis gives as a result a wavelength-dependent interference pattern called an interferogram that makes it possible to quantitatively determine the concentrations of all multi-atomic gas species in a gas sample, in contrast to detecting absorption at one specific IR wavelength as in conventional IR spectroscopy. The principle setup of such a system is shown in Figure 47 and Figure 48.

This method also suffers from the clogging and corrosion problems caused by condensation, but for short time analysis it is a method of obtaining a complete gas analysis “footprint” not only from NH$_3$ and H$_2$ but also from CO, CO$_2$, H$_2$O, N$_2$O etc., as indicated in Figure 51. It is used for calibrating individual furnaces.

5.5. Layer growth determination

In addition to analysing the atmosphere, it is possible to register the compound layer thickness and its growth with a sensor that utilises electromagnetic principles. It is inserted into the furnace as shown in Figure 50.
5.6. Guidelines for regulating the atmosphere

5.6.1. Nitriding
Controlled nitriding is realised by a control system that determines the actual nitriding potential and adjusts the atmosphere composition to the chosen set point value. This can be achieved either by manual analysis and flow adjustments or by automatic closed loop control.

At a high flow rate, most ammonia supplied for nitriding to a furnace remains un-dissociated, but at low flow rates it dissociates more easily into nitrogen and hydrogen as the residence time in the furnace is sufficiently long. One way to perform controlled nitriding is therefore to start the process with a high ammonia flow rate (= high residual ammonia = high nitriding potential) in order to build up the compound layer as fast as possible. Later on, the ammonia flow rate is decreased to typically give a residual ammonia concentration of about 60 vol% [2].

An alternative method of controlling the nitrogen activity is by hydrogen addition. In such cases, the atmosphere nitrogen activity can be varied over a much wider range than is possible by simply changing the ammonia flow rate. A control system incorporating a hydrogen sensor and using the combination of ammonia and hydrogen is shown in Figure 51.

It is also possible to dilute ammonia with nitrogen, thereby affecting the nitriding potential. The controllability range, however, is then limited, but from the viewpoints of safety and economy it may be advantageous.

5.6.2. Nitrocarburising
The atmosphere for nitrocarburising consists of 20–50% ammonia, 2–20% carbon dioxide and the balance nitrogen, depending on which furnace equipment is used and which properties are desired. Experiments have shown that an addition of about 5 vol-percent CO₂ is sufficient (see Figure 41).

Figure 52 gives examples of analysis results for residual ammonia in a nitrocarburising process where 50% NH₃ + 50% endogas were introduced into a multi-purpose furnace with ceramic lining. The figure shows a large variation in residual ammonia content both during one process cycle and between two different cycles. The same gas flow ratios and mixing ratios were used. Obtained depths on the compound layer and in the diffusion zone correlated positively with residual ammonia analysis results.
In order to lower the nitrogen activity during the latter part of the treatment, the addition of carbon dioxide could be lowered or completely shut off. It is also possible to lower the ammonia addition in order to lower the nitrogen activity; however, the carbon activity will drastically decrease as well.

The shortest possible cycle for a certain compound layer thickness is achieved if the atmosphere composition is changed during the cycle, with high nitrogen activity and a carbon activity promoting ε-nucleation and growth in the first part of the process.

For medium- and high-carbon steels, carbon is donated to the compound layer by the steel. The atmosphere carbon activity is then less important, which explains why carbon-free atmospheres work in such cases even though such atmospheres are “pure nitriding” and not “nitrocarburising” atmospheres. With low-carbon steels, on the other hand, it is necessary that the atmosphere has a balanced carbon activity to ensure a good compound structure with mainly ε-phase.

Figures 53–54 show how adjusting the atmosphere concentrations of CO₂ and NH₃ can change the atmosphere carbon and nitrogen activities. This possibility is of great value when optimising compound layer properties for different steels, especially ones with different carbon contents.

With the NITROFLEX system, it is possible to use a “boost” technique with high nitrogen activity in the first stage of the process and a lower activity in a second stage. There is an upper limit for the nitrogen activity corresponding to excessive porosity formation. In this way, it is possible to control the degree of porosity and compound layer thickness.

Examples of the influence of atmosphere composition on compound layer microstructure are shown in Figure 55. For high nitrogen activities entailing a high ratio for $P_{NH_3}/P_{H_2}^{3/2}$, the compound layer is thick and has extensive porosity, as illustrated in the photographs on the left, whereas a lower nitrogen activity gives a dense layer, as illustrated in the photographs on the right. By increasing the atmosphere carbon activity, the porosity decreases and the amount of ε-phase in the compound layer increases, as seen in the lower right photograph.

In order to lower the nitrogen activity during the latter part of the treatment, the addition of carbon dioxide could be lowered or completely shut off. It is also possible to lower the ammonia addition in order to lower the nitrogen activity; however, the carbon activity will drastically decrease as well.
In order to attain high carbon concentrations, one alternative is to add propane to the atmosphere. This has given positive results for the obtained hardness and wear resistance of treated parts. This is because the carbon provided by the propane addition favours nucleation and growth of the ε-phase. This is illustrated in Table 13, which also shows wear results. Care must be taken not to create soot with the propane addition. Other hydrocarbons such as ethylene and propylene are also commonly used to provide carbon [39].

5.6.3. Post-oxidation control
To obtain a result with an adhering iron oxide that provides corrosion protection, it is necessary that only the Fe₃O₄ oxide is formed. If Fe₂O₃ forms, the result will be poor surface appearance with varying colour and flaking of the oxide.

In an atmosphere with oxygen partial pressure higher than that required for the formation of Fe₂O₃, the equilibrium conditions are expected to allow all three iron oxides to form. However, FeO will only form at temperatures above 570 °C (1058 °F). This requires a post-oxidation temperature below that for formation of FeO, although FeO formation is very slow up to 700 °C (1292 °F) [40].

Figure 56 shows the equilibrium oxygen pressures over Fe₂O₃ and Fe₃O₄ plotted versus inversed temperature (1/K) as straight lines. It can be seen that the equilibrium oxygen pressure stability range for Fe₃O₄ is approximately $10^{-26}$ to $10^{-27}$ atm at 450 °C (842 °F). Table 14 indicates that, in order to avoid Fe₂O₃ but to form Fe₃O₄ at 580 °C (1076 °F), the following condition must be fulfilled: $2.4 \times 10^{-26} < \frac{P_{O_2}}{P_{H_2}} < 7.1 \times 10^{-26}$ or $0.30 < \frac{P_{O_2}}{P_{N_2}} / \frac{P_{H_2}}{P_{N_2}} < 1.18$ or $0.69 < \frac{P_{CO_2}}{PCO} < 2.71$. It is possible to avoid Fe₂O₃ formation and thus only to form Fe₃O₄ by adjusting the oxygen partial pressure in accordance with the guidelines given in the table and figure.
5.7. Compound layer and diffusion zone formation

5.7.1. Nitriding

From the Fe-N phase diagram in Figure 60, it follows that as the nitriding potential, \( P_{\text{NH}_3}/P_{\text{H}_2}^{3/2} \), is increased, the compound layer is expected to start to form by \( \gamma' \) nucleation, illustrated at 510 °C (950 °F) by point A in the diagram. Later \( \varepsilon \) is expected to form on top of \( \gamma' \) when the surface nitrogen concentration exceeds the solubility limit in \( \gamma' \) (point B). If the nitrogen activity in the gas is kept below the maximum nitrogen solubility limit in \( \gamma' \) (point B), then a monophase \( \gamma' \)-layer will be the end result. If the nitrogen activity is kept below the maximum nitrogen solubility in \( \alpha \) (point A), then no compound layer is formed but nitrogen uptake is fully contained in \( \alpha \). In order for \( \gamma' \) to be formed at 500 °C (932 °F), the nitriding potential, \( P_{\text{NH}_3}/P_{\text{H}_2}^{3/2} \), has to be above approximately 0.25 and above approximately 3 for \( \varepsilon \) to be formed.

The \( \gamma' \)-phase is an almost stoichiometric compound, \( \text{Fe}_4\text{N} \), with limited concentration variation. The growth rate of the \( \gamma' \)-compound layer is therefore relatively low since the difference \( c_N(\text{surface})-c_N(\text{nitride/}\alpha) \) is low (see Figure 40). On the other hand, \( \varepsilon \)-nitride has a high solubility range for nitrogen, which leads to a higher growth rate. This is illustrated in Figure 59, which shows that the compound layer thickness increases markedly when the nitriding potential is very much higher than the lower solubility limit for \( \varepsilon \) to form, expressed by the ratio \( P_{\text{NH}_3}/P_{\text{H}_2}^{3/2} \) (test no. 1 in the figure).

The diffusion zone thickness increases with increased nitrogen potential (Figure 59) and with time in a parabolic manner (Figure 60). As seen in Figure 60, nitriding depth at a certain time and temperature is lower for high-alloy steels. This can be understood from the fact that alloying elements like chromium trap nitrogen when forming nitrides. More nitrogen atoms thus have to diffuse into the steel to reach a certain depth compared to when no alloy elements trap nitrogen.
The nitriding rate increases if small concentrations of oxygen are present in the nitriding atmosphere (see Table 15). The table also shows that oxygen addition favours the formation of ε-phase.

**Table 15. Influence of oxygen addition on compound layer thickness and phase composition in gas nitriding at 30 minutes at 550 °C (1022 °F). Steel DIN C10 [43]**

<table>
<thead>
<tr>
<th>Nitriding atmosphere</th>
<th>Compound layer, µm</th>
<th>Phase composition, vol%</th>
</tr>
</thead>
<tbody>
<tr>
<td>No oxygen</td>
<td>1.5-2.0</td>
<td>ε: 34</td>
</tr>
<tr>
<td>No oxygen but pre-oxidised</td>
<td>2.9-3.5</td>
<td>γ’: 47</td>
</tr>
<tr>
<td>Oxygen added during nitriding</td>
<td>2.5-3.5</td>
<td>ε: 67, γ’: 25</td>
</tr>
</tbody>
</table>

The addition of CO₂ and NO₂ has also been found to increase the nitriding rate. Small additions of water, however, seem to retard nitriding (see Figure 61).

The nitrogen take-up and thus also the layer growth rate increases with increased surface area (surface roughness) as shown in Figure 62.

### 5.7.2. Nitrocarburising

In nitrocarburising, the compound layer starts to form by nucleation of cementite even if the carbon activity of the gas is lower than that of cementite [46, 47]. A possible explanation is that the gas/surface reaction delivering carbon to the surface (the heterogeneous water gas reaction) is faster and kinetically favoured compared with the nitriding (ammonia decomposition) reaction during heating before reaching the nitrocarburising temperature. There is additional evidence that cementite formation at moderate atmosphere carbon activity is favoured by the presence of ammonia in the atmosphere [48]. Within the order of minutes after reaching the nitrocarburising temperature, ε phase is nucleated on the primary formed cementite. ε is favoured because its crystal structure is similar to that of cementite. The ε phase layer then grows at the expense of cementite, which is consumed by transformation to ε phase, leading to an almost homogeneous ε phase layer. Later γ’ forms at the interface between the substrate and the ε-layer. Redistribution of nitrogen and carbon at the γ’/substrate interface will eventually create a second ε phase layer between the γ’-layer and the substrate α-phase. The compound layer will therefore ultimately consist of three alternating layers of ε/γ’/ε. This is indirectly shown by the N and C concentration profiles shown in Figure 63.
The nitrogen surface concentration increases with increased process time and increased nitriding potential (see Figure 64), whereas the carbon surface concentration decreases (see Figure 63). The total amount of nitrogen in the compound layer increases, whereas the total amount of carbon is constant or decreases with increased treatment time. Carbon is redistributed as shown in Figure 63, with a depletion of carbon in the intermediate $\gamma'$-layer, an accumulation of carbon in the $\varepsilon$ phase adjacent to the core ferrite/cementite matrix and a positive carbon concentration gradient in the outer $\varepsilon$ phase compound layer. For nitrocarburising of medium- and high-carbon steels, carbon originating from the steel matrix is incorporated in the compound layer, resulting in carbon enrichment of the $\varepsilon$ phase (see the lower part of Figure 63).

The contact between the $\varepsilon$- and the $\alpha$-phases observed at the interface compound layer/matrix is consistent with the phase diagram evaluated by Du [41] and shown in Figure 65. (It does not, however, correspond to the phase diagram from Naumann and Langenscheid [49] that is often referred to.)
Gas nitriding and nitrocarburising

Figure 66 shows an interpretation of compound layer growth data: The growth rate is initially low (step I) when cementite growth is dominating. After cementite has transformed to ε-phase the growth rate is high (step II). This high growth rate is lowered in step III after γ' has formed as an interlayer between ε and the substrate.

The influence of atmosphere nitrogen and carbon activities on compound layer morphology, especially porosity and depth, was illustrated in Figure 55. In a study by Bell and Wells [50] the atmosphere carbon activity was shown to affect the phase constituency of the compound as follows:

→ At low carbon activities there is a γ'-layer positioned in between the ε-layer and the core ferrite/cementite structure;
→ At intermediate carbon activities a γ'-layer forms as a band inside the ε-layer.
→ At high carbon activity no γ' at all was observed but the compound layer was ε-monophase.
→ At very high carbon activity a duplex thin layer was formed consisting of ε + cementite.

The higher temperature for nitrocarburising compared to that for nitriding means that the diffusion coefficients for nitrogen and carbon are higher. Austenitic nitrocarburising utilises this to create thicker cases (diffusion + compound layer). The thermodynamic stability of the ε-phase is favoured by increased temperature. For these two reasons the compound layer growth rate is higher in nitrocarburising compared to nitriding.

The treatment time in normal nitrocarburising processes for low alloy, low carbon steels is limited by the fact that the porosity and thickness of the compound layer reach excessively high values. Poor adherence and low hardness result. In view of this, practice has shown that a treatment time of 1.5 to 3 hours is optimum.

5.7.3. Furnace interior influence

In the study described in section 3.2.1, it was found that furnaces that start the nitrocarburising process from room temperature have the poorest results with respect to compound layer thickness. (A possible explanation could be that formation of γ' during heating up slows down layer growth.) The highest thicknesses were obtained for cases when the start value of the atmosphere nitrogen activity was high. A low start value for the nitrogen potential was found not to be compensated by layer growth even if the activity value later increased to a high value.

In Figure 67, these results are compared with the results predicted by Hong Du (see Figure 66). An interpretation of this comparison is that the slow compound layer growth for the steel retort furnace corresponds to γ' growth rate control and the high compound layer growth to ε growth rate control.

5.7.4. Influence of amount of active gas

The fact that the surface nitrogen concentration increases with time is evidence of the fact that the gas/surface nitrogen transfer is a rate-limiting step. This was confirmed in a study of the influence of the amount of active gas species (NH₃, H₂, CO, CO₂) [52] on compound layer growth. A comparison of the nitrocarburising result was made between high and low active gas percentages, being atmospheres with 40 vol% and 20 vol% of active gas respectively. Figure 68 illustrates that compound layer thickness as well as total case depth showed a significant dependence on the amount of active gas for low-alloy steel. However, no significant effect was determined for a high-alloy steel. Increased nitriding potential led to an increase in the compound layer thickness, whereas no significant effect of the carbon potential was determined.
5.7.5. Steel alloy content effect

As in the case of nitriding, increasing the alloy content of the steel leads to decreased compound layer thickness (see Figure 69).

The depth of the diffusion zone also decreases with increased alloy content principally in the same way as in nitriding (see Figure 60).

5.8. Pore formation

The depth of porosity in the outer part of the compound layer on unalloyed and low-alloy steels is of the order of 30–40% of the total compound layer depth, as illustrated in Figure 70a. The degree of porosity increases with increased process time and increased nitrogen potential. For high-nitrogen activities, the porosity depth may exceed 50% of the total compound layer depth. High-alloy steels are somewhat less prone to porosity formation, as illustrated in Figure 70b, probably due to the lowering effect of alloying elements on nitrogen activity.

Pores are formed at discontinuities (grain boundaries, slag inclusions) because of the denitriding step:

\[ 2 \text{N} \rightarrow \text{N}_2 \]

The equilibrium nitrogen gas pressure is high enough to create pores in the compound layer. The probability of pore formation increases drastically above nitrogen activities over 650–750.

The pores will grow together, forming channels in which effusion of nitrogen out to the surface may take place. Carbonaceous gas can enter the channels and cause carbon uptake within the layer.
5.9. The NITROFLEX solution

When Linde and BOC merged in 2006, a substantial concentration of expertise in nitriding and nitrocarburising was created by adding together the Epsilon and the NITROFLEX packages of BOC and Linde respectively. This merged solution package has been maintained, further developed and marketed under the NITROFLEX trademark. The package covers the atmosphere supply solutions, flow control units, related know-how and specifications of the complete details of process cycles and of safety instructions.

One major feature is carbon activity, which is much lower than that in systems using endogas together with a higher oxygen activity (see Table 12). Due to this fact, practice has shown that a faster growth rate of the compound layer can be obtained. It has been demonstrated that alloyed steels such as hot work tool steels obtain a thicker and more even compound layer (see Figure 71). The balanced carbon activity means that the driving force for soot deposits in furnaces is low.

Post-oxidation with air, water or N₂O gives aesthetically attractive black surfaces (Figure 17) with markedly improved corrosion resistance (Table 6).

5.9.1. Nitrocarburising case studies

The cases described here and summarised in Table 16 are taken from reference [53].

Case Study 1: Conveyor roller in a metal spraying shop

Experience has shown that cast iron conveyor rollers operating in a metal spraying shop are subjected to very aggressive wear and corrosion in operation (see Figure 72a). Because no form of conventional heat treatment could solve both the wear and corrosion attack problems on its own, the NITROFLEX nitrocarburising treatment adapted to a multi-purpose furnace was tried. Figure 72b illustrates the condition of a conveyor roller treated using the process (left) compared to an untreated and worn roller (right). One of the rollers is worn flat whereas the treated one is intact.

![Figure 72: a. Conveyor rollers in use in a paint shop, b. Conveyor rollers](image)

Case Study 2: Forging die manufactured from AISI L6 material

Forging dies are generally subject to high indentation and aggressive wear. Therefore, high-alloy tool steel is used to increase life, but in order to save costs, an additional surface is required. However, the core hardness achieved after conventional hardening and tempering operations still needs to be preserved. A NITROFLEX nitrocarburising treatment, performed in a multi-purpose furnace with a process recipe adapted to alloy steel and to yield a low case depth, was used to increase surface hardness without affecting core hardness. The final service life was improved, and hence costs were effectively reduced. Figure 73 shows the component produced. The surface finish of the forgings was improved when the NITROFLEX-treated die was used.

![Figure 73](image)

### Table 16. Nitrocarburising case studies with NITROFLEX technology

<table>
<thead>
<tr>
<th>Part</th>
<th>Steel</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spray shop conveyor roller</td>
<td>Cast iron</td>
<td>Improved wear and corrosion resistance</td>
</tr>
<tr>
<td>Forging die</td>
<td>Tool steel</td>
<td>Improved wear resistance</td>
</tr>
<tr>
<td>Extrusion die</td>
<td>Tool steel</td>
<td>Increased time between re-polishing</td>
</tr>
<tr>
<td>Tag washers</td>
<td>SAE 1020</td>
<td>Improved process environment due to replaced salt bath carbonitriding</td>
</tr>
<tr>
<td>Clutch plates</td>
<td>Mild steel</td>
<td>Reduced distortion, elimination of costly post-treatments</td>
</tr>
<tr>
<td>Mail sorting slides</td>
<td>Mild steel</td>
<td>Replaced carbonitriding which gave lower scrap rate, improved properties and reduced cost</td>
</tr>
<tr>
<td>Moulds</td>
<td>SAE 1020</td>
<td>Nitrocarburised cheap steel replaced costly tool steel</td>
</tr>
<tr>
<td>Crankshafts</td>
<td></td>
<td>Short-time nitrocarburising replaced conventional long-time gas nitriding</td>
</tr>
</tbody>
</table>

![Figure 71: Compound layer thickness for different atmospheres showing faster growth for the NITROFLEX system](image)
Gas nitriding and nitrocarburising

Figure 73: Forging produced by the NITROFLEX treated forge die

Case Study 3: Extrusion dies made of AISI H13 material
The time between re-polishing was significantly improved by a NITROFLEX nitrocarburising treatment, performed in a multi-purpose furnace with a process recipe adapted to the steel. A very high surface hardness of the order of 1200 HV was achieved. The appearance of treated dies is shown in Figure 74.

Figure 74: NITROFLEX-treated H13 extrusion dies

In another case, nitrocarburising was performed on pipe welding clamps made of hardened and tempered H13 tool steel working in sea water under conditions of repetitive cooling. The untreated clamp on the left rusted after 100 cycles in these working conditions. The NITROFLEX nitrocarburising-treated clamps attained 300 cycles without rust.

Case Study 4: Tag washers in SAE 1020
Due to the unacceptable distortion in traditional carbonitriding, the NITROFLEX austenitic nitrocarburising treatment was performed in a multi-purpose furnace and with a process recipe adapted to mild steel to yield a low case depth. By producing a deeper diffusion zone to support the compound layer, this treatment successfully solved the problems. Figure 75 shows the appearance of the parts. Previously carbonitrided components were also processed in a salt bath, but the properties produced were not sufficient to prevent collapse of the surface in service.

Case Study 5: Clutch plates in mild steel
Automobile clutch plates were previously carbonitrided using conventional methods. The main problem was unacceptable distortion and even high scrap rates. Austenitic nitrocarburising, performed in a multi-purpose furnace with a process recipe adapted to mild steel, was used in an attempt to eliminate the distortion problem and to bring down costs. As a result, the scrap rate decreased by 30% and the need for phosphating after carbonitriding was eliminated. This decreased costs by an additional 36%. The components are shown in Figure 76.

Case Study 6: Mild steel slides
Mild steel slides used in mail sorting offices are subject to considerable wear. As a result, they must be replaced regularly. Several materials and processing options were tried during their manufacture. The slides are commonly made of mild steel and then carbonitrided, but this method results in an excessively high level of scrap. The use of the austenitic nitrocarburising process, performed in a multi-purpose furnace and with a process recipe adapted to mild steel to yield a moderate case depth, with its lower processing temperature, solved the scrap problem. It also increased service life by improving wear and corrosion resistance. The treated components are shown in Figure 77.

Figure 75: Austenitic nitrocarburised SAE 1020 tag washer

Figure 76: Clutch plate in mild steel treated by the austenitic nitrocarburising process

Figure 77: Mild steel mail handling tracks
Case Study 7: Moulds in 1020
Most moulds or forming tools are manufactured from H13 material. H13 material is expensive and typically requires vacuum hardening and tempering. Two examples of these moulds are shown in Figure 80. These moulds are now manufactured from mild steel, a low-cost material, and treated with extended austenitic nitrocarburising performed in a multi-purpose furnace and with a process recipe adapted to yield a high case depth to achieve the properties that are required for H13 material to be treated by vacuum processes. In addition to cost savings, surface quality has also been improved because the compound layer eliminates pickup.

Case Study 8: Crankshafts
Crankshafts were previously gas nitrided in a pit furnace for 105 hours to achieve the required properties. Post-grinding was carried out for finishing. The use of the NITROFLEX nitrocarburising treatment performed in a pit furnace and with a process recipe adapted to the alloy steel and to yield a modest case depth resulted in a shorter process cycle and the elimination of the post-grinding process. As a result, overall costs were reduced. The treated crankshafts are shown in Figure 79. Nitrocarburising treatment is shown in Table 17.

Table 17. Comparison of gas nitriding and NITROFLEX nitrocarburising.
Note: Cost originally given in EURO with cost level of the year 2001 [53]

<table>
<thead>
<tr>
<th>Process</th>
<th>Conventional gas nitriding</th>
<th>NITROFLEX nitrocarburising</th>
</tr>
</thead>
<tbody>
<tr>
<td>Furnace</td>
<td>Pit nitriding furnace</td>
<td>Pit nitriding furnace</td>
</tr>
<tr>
<td>Load size</td>
<td>6 off X 6-cylinder crank shafts</td>
<td>6 off X 6-cylinder crank shafts</td>
</tr>
<tr>
<td>Operating cost</td>
<td>2750 EURO (105 hrs floor-to-floor)</td>
<td>1275 EURO (55 hrs floor-to-floor)</td>
</tr>
<tr>
<td>Process cost</td>
<td>440 EURO/component</td>
<td>No post-grinding</td>
</tr>
<tr>
<td>Post grinding cost</td>
<td>65 EURO/component (white layer)</td>
<td>(compound layer)</td>
</tr>
<tr>
<td>Total cost</td>
<td>515 EURO/component</td>
<td>228 EURO/component (compound layer)</td>
</tr>
<tr>
<td>Saving</td>
<td>276 EURO/component</td>
<td>276 EURO/component (compound layer)</td>
</tr>
</tbody>
</table>

The shorter cycle utilised by the NITROFLEX process increased the production capability of the existing furnace equipment by 48% and gave a cost saving of 1660 EURO (cost level of the year 2001) per furnace cycle.
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, their sources and control options in heat treatment-related processes. Avoiding harm to people, society and the environment are important priorities for The Linde Group. This means that we expect all 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 used are mainly nitrogen and ammonia in the nitriding processes and additionally carbon dioxide in the nitrocarburising processes. Hydrogen and carbon monoxide or hydrocarbon gas are in certain cases used for nitrogen and carbon potential control respectively. Nitrous oxide is used for post-oxidation.

6.3 Potential safety hazards and their sources

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

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

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

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

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

- Pressure increase from heating (fire)
- Leakages

Detailed information on these hazards is found in safety standards and regional and national safety regulations. Only hazards related to heat treatment, 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
6.3.1 Explosions/flammability/fire

Both nitriding and nitrocarburising are performed at a temperature below the safety temperature (750 °C (1382 °F)) for igniting a flame of the combustible parts of the gas. This means that air (oxygen) can enter into a furnace and mix with the combustible gas (CO, H₂, NH₃, CH₄ etc.) without igniting a burning flame. (In high-temperature processes such as carburising and carbonitriding, a flame is ignited automatically in such cases.) Therefore, if not controlled, it may occur that a large amount of a flammable ammonia/hydrogen + air mixture forms. In the worst case, this mixture, if ignited by a flame or spark, would create a devastating explosion. This places strict requirements on the use of flame curtains and safety pilot burners at all doors and on safe start-up, shut-down and operation procedures.

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 either absorbed by the surroundings or 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.
- Catalysts 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, lighted cigarettes, or flame curtains.

The NITROFLEX system typically utilises about 40 vol% of ammonia and optionally up to 10 vol% of hydrogen, which are the only flammable gases in the ingoing gas mixture. This can be compared to the 50 vol% endogas + 50 vol% ammonia process, which holds approximately 80 vol% hazardous components (H₂, CO, NH₃) in total.

For ignition or explosion to occur, the following must be present: fuel, oxygen, ignition source. Flammability risk can be described in relation to the Safety Triangle shown in Figure 80. 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 the temperature decreases.

The flammable gases commonly found in these atmospheres are hydrogen, carbon monoxide, hydrocarbons, vapourised or dissociated methanol (dissociation produces hydrogen and carbon monoxide) and dissociated ammonia (forms hydrogen and nitrogen).

The European safety standard EN-746-3 [54] 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 (C₅H₁₁) 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 shut-down of furnaces may be illustrated in relation to Figure 80. 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 I–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.

When starting up a nitriding process where the furnace is partly or wholly filled with air, ammonia must not be introduced until the oxygen concentration has been lowered to point C. This may be done by purging the furnace with nitrogen. When point C in Figure 80 is reached, ammonia can be safely introduced.

If nitrocarburising is performed in a furnace that will be opened to air access after nitriding or nitrocarburising, i.e. in a pit furnace, a reversed sequence is required before closing the process and opening the furnace. By purging with nitrogen, the ammonia concentration must now be lowered to point B in Figure 80 before the furnace can be opened and exposed to air.

Vacuum pumping is an alternative to purging that is gaining in use by the development of suitably equipped furnaces. The vacuum level required before introducing flammable gas is 45 mbar according to CEN 746-3 [54].

Multi-purpose or chamber furnaces that are built for nitrocarburising have a flame curtain at the furnace door. A flame guard ensures that the flame curtain is ignited. In such cases, there is no requirement to purge with nitrogen before opening the door. In all cases, double pilot burners should be installed at doors for safety reasons. This pilot burner has the function of burning the outgoing gas mixture to ensure that ammonia does not cause odour and safety problems.

The outlet gas should be burnt and vented off. This is done in a separate exhaust gas neutraliser.

6.3.2 Toxicity and asphyxiation

Ammonia is a corrosive gas attacking moist skin, mucous membranes and eyes. Severe exposure is unlikely except in confined spaces, as its characteristic smell at 20 ppm or more usually provides adequate warning. Ammonia at 100 ppm causes irritation of the eyes and nose after a few minutes' exposure, and at 700 ppm causes severe eye and nose irritation but no permanent effects if the exposure is lower than half an hour. Concentrations above 1700 ppm cause serious coughing, bronchial spasm, acute pulmonary oedema and asphyxia, and at these levels death can occur within half an hour.

Carbon monoxide is not added but formed at a low concentration level of the order of a few volume percent within the furnace room when using the NITROFLEX system. Other systems based on endogas/ammonia have a CO concentration of the order of 10 volume percent. 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 when this is when repair or inspection is required in a furnace that has been filled with nitrogen. Personnel must not enter that space until the oxygen concentration has been determined to be safe.

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 uninsulated 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.
6.4 Control of safety hazards

6.4.1 General safety regulations and guidelines
The international standard ISO 13577-3 [55], on “Generation and use of protective and reactive atmosphere gases”, was published in 2017 but is still subject to possible revisions. The intention is that the new ISO standard will replace regional or national standards, but the existing European, American and Chinese standards [54, 56, 57] as well as other national standards will still be regionally valid.

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 atmospheres from the furnace by controlled combustion of the exit gas.
- Use good natural ventilation, especially when controlled combustion of the exit gas cannot be assured.
- 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 operating heat treatment furnaces below the safety temperature, which is relevant in nitriding and nitrocarburising furnaces, precautions must be taken to ensure that explosive mixtures are not created, as already specified in the foregoing text.

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 be 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 their 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 should 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.

An overview of safety hazards and required precautions in heat treatment is given in reference [58].
References.

Authors: Michael Graf, Torsten Holm

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