Furnace Atmospheres
No. 3
Gas Nitriding and Nitrocarburising.
Preface

This booklet is part of a series on heat treatment, brazing and soldering process application technology and expertise available from Linde Gas. The booklet focuses on the use of furnace atmospheres; however, a brief introduction to each process is also provided. In addition to this work on nitriding and nitrocarburising, the series includes:

- Furnace Atmospheres No. 1 – Gas Carburising and Carbonitriding
- Furnace Atmospheres No. 2 – Neutral Hardening and Annealing
- Furnace Atmospheres No. 3 – Nitriding and Nitrocarburising
- Furnace Atmospheres No. 4 – Brazing of Metals
- Furnace Atmospheres No. 5 – Sub-zero treatment of steels
- Furnace Atmospheres No. 6 – Low pressure carburising and high pressure gas quenching
- Furnace Atmospheres No. 7 – Tube Annealing

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Nitriding and nitrocarburising of steel parts give unique improvements in wear and corrosion resistance that cannot be obtained by carburising or carbonitriding. Increased fatigue strength is also obtained. These improvements can be understood when examining the surface microstructure and hardness after treatment illustrated in Figure 1. The outermost compound layer of a nitrided or nitrocarburised steel is 2–30 μm thick and consists of the iron/nitrogen/carbon $\varepsilon$-phase with variable compositions of carbon and nitrogen and the $\gamma'$-phase with the virtually stoichiometric chemical formula Fe$_3$N. 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, and static and fatigue strength are largely determined by the hardness and depth of the diffusion zone.

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 carbonitried, 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. An elegant demonstration of the benefits of nitrocarburising was given in a paper by Dawes and Tranter [1] in which the application of a screen wiper linkage was described. The strength increase associated with nitrocarburising resulted in a weight decrease of 62%. The very good tribological properties made it possible to eliminate the bronze bearings previously used. 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. High alloy steels used for forging and extrusion tools are other examples that benefit from being nitrided or nitrocarburised.

Atmosphere composition and control are of crucial importance for the nitriding/nitrocarburising result with respect to final properties such as wear and fatigue resistance. This is exemplified in Figure 46, showing four very different compound layer morphologies, merely as the result of the use of different gas compositions during the process (See section V.E.2, page 27, for explanation).

Nitriding and nitrocarburising are thermochemical processes, as are carburising and carbonitriding, see Table 1. 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.

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 that where 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.

Austenitic nitrocarburising is a process that has characteristics in between the high temperature methods of carburising and carbonitriding and the low temperature processes of nitrocarburising and nitriding.

A consequence of the low process temperature, the short process time and the elimination of productions steps is low energy consumption. 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</th>
<th>Temperature °C (°F)</th>
<th>Typical process time</th>
<th>Element transferred</th>
<th>Case depth mm</th>
<th>Surface hardness HV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carburising</td>
<td>850-950 (1562-1742)</td>
<td>4-10h</td>
<td>C</td>
<td>0.2-1.5</td>
<td>750-850</td>
</tr>
<tr>
<td>Carbonitriding</td>
<td>750-900 (1382-1652)</td>
<td>2-5h</td>
<td>C+N</td>
<td>0.1-0.8</td>
<td>750-850</td>
</tr>
<tr>
<td>Austenitic nitrocarburising</td>
<td>600-700 (1112-1292)</td>
<td>2-4h</td>
<td>N+C</td>
<td>0.1-0.5</td>
<td>750-850</td>
</tr>
<tr>
<td>Nitrocarburising</td>
<td>560-580 (1040-1076)</td>
<td>2-4h</td>
<td>N+C</td>
<td>0.05-0.2</td>
<td>450-1200</td>
</tr>
<tr>
<td>Nitriding</td>
<td>500-510 (932-950)</td>
<td>5-100h</td>
<td>N</td>
<td>0.05-0.8</td>
<td>450-1200</td>
</tr>
</tbody>
</table>

Classical 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 drastically with the development of the salt bath process Tenifer (Tufftride) and the gaseous process

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

<table>
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<tr>
<th>Process step</th>
<th>Energy requirement, KWh</th>
<th></th>
</tr>
</thead>
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<tr>
<td>Harden, temper and nickel plate</td>
<td>265</td>
<td>163</td>
</tr>
<tr>
<td>Heat to processing temperature</td>
<td>27</td>
<td>66</td>
</tr>
<tr>
<td>Hold at processing temperature</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>Quench</td>
<td>94</td>
<td></td>
</tr>
<tr>
<td>Heat to tempering temperature</td>
<td>44</td>
<td></td>
</tr>
<tr>
<td>Hold at tempering temperature</td>
<td>20</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>
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</table>
Nitrocarburising Nitriding in the sixties. Compared to classical nitriding, nitrocarburising is a short-time process, typically lasting 30 minutes to 4 hours, and is performed at a higher temperature, about 570 °C (1058 °F) compared to 500-510 °C (932-950 °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.

There are numerous names on the market to describe nitriding and nitrocarburising. Some of them are given in Table 3. NITROFLEX® is Linde’s trademark for nitriding and nitrocarburising processes.

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. 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.

<table>
<thead>
<tr>
<th>Temperature °C (°F)</th>
<th>Time h</th>
<th>Name or trade name</th>
<th>Media</th>
</tr>
</thead>
<tbody>
<tr>
<td>500-510 (932-950)</td>
<td>5-100</td>
<td>Gas nitriding</td>
<td>NH₃/N₂/H₂</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Oxy-nitriding</td>
<td>NH₃/Air</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>NH₃/H₂O</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>NH₃/N₂O</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Plasma nitriding</td>
<td>N₂/H₂</td>
</tr>
<tr>
<td></td>
<td></td>
<td>High pressure nitriding</td>
<td>N₂, NH₃</td>
</tr>
<tr>
<td>560-580 (1040-1076)</td>
<td>0.5-5</td>
<td>NITROFLEX®</td>
<td>NH₃/N₂/CO₂/ (H₂/CO/C₃H₈)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Nitemper</td>
<td>NH₃/Endogas</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Nitrotec</td>
<td>NH₃/Endogas/air</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Nitroc</td>
<td>NH₃/Exogas</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Tenifer/Tufftride</td>
<td>Salt</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Plasma nitrocarburising</td>
<td>N₂/H₂/CH₄</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Post oxidation</td>
<td>Ar, H₂O, N₂O</td>
</tr>
</tbody>
</table>
II. 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 2.

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 17 and 19). 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 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 (See Table 2). Capital costs are highest for vacuum and plasma equipment, but the variable cost for utilities (electricity and gas) is much lower than for conventional atmospheric furnaces.

Table 4. 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>
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<td>Steel</td>
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<td>Low alloy steels, cast irons, sintered steels</td>
<td>High and low alloy steels</td>
<td>High and low alloy steels, cast irons, sintered steels</td>
<td></td>
</tr>
<tr>
<td>Compound layer</td>
<td>Minor influence</td>
<td>High hardness, high e-content</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diffusion layer</td>
<td>High hardness and depth</td>
<td>Moderate hardness and depth</td>
<td>High hardness and depth</td>
<td>Minor influence</td>
<td></td>
</tr>
<tr>
<td>Process</td>
<td>Gas nitriding</td>
<td>Nitrocarburising</td>
<td>Gas nitriding and nitrocarburising</td>
<td>Nitrocarburising + postoxidation</td>
<td></td>
</tr>
</tbody>
</table>
Part geometry and dimensions may limit the number of possible alternatives. Very long objects such as shafts or axles cannot be treated in standard box or sealed quench furnaces, for instance, but tend to be treated in cylindrical pit furnaces. Requirements for 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.

Nitriding and nitrocarburising have significant cost benefits that include:

1. **Cycle times**: Short cycle times lead to reductions in energy and atmosphere costs. In addition, the furnace capacity and the furnace equipment life will increase. This will also increase the production capacity of the manufacturing facility.

2. **Materials**: Many engineering components are made from expensive highly alloyed steels, not because the properties they offer are required throughout the material, but because they are required at or near the surface. The use of lower cost materials combined with nitriding/nitrocarburising can reduce costs.

3. **Energy costs**: There are a number of possibilities to decrease energy costs. These include decreasing cycle times, as described above, and decreasing process temperature. Nitriding/nitrocarburising processes operate at lower temperatures than conventional methods, resulting in energy savings.

4. **Dimensional scraps**: The low temperature nitriding/nitrocarburising processes reduce distortion, compared to high temperature processes.

5. **Elimination of post grinding**: It is possible in certain situations to predict the dimensional change after treatment. The limited distortion makes it possible to eliminate tolerance adjustment operations such as post grinding.

6. **Additional processes**: With gaseous treatments there is no need to remove salt residues from the surface after treatment, thus eliminating post cleaning operations. Nitrocarburising treatments produce a compound layer which is scuff and corrosion resistant. This layer does not need to be ground after treatment, and is more flexible than the white layer that is produced by traditional nitriding treatments. Processes also produce an excellent surface finish that requires no post operation and that can be used directly on the assembly.
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 3, which also shows the optional additional steps of preheating/pre-oxidation and post-oxidation used in nitrocarburising.

III. The Process Steps in Nitriding and Nitrocarburising

A. 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 at least 20-30 °C 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 normalized 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 above the nitriding/nitrocarburising temperature in order to avoid stress relieving and concurrent distortion during nitriding/nitrocarburising.

B. 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 cuttings 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. Contaminations 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 4. 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 sulphur and phosphorous added to the cutting oil as well as sodium, boron, and calcium in cutting fluids all had a negative impact on compound layer formation. They also found a negative influence if fluids were allowed to dry on the surface before nitriding/nitrocarburising.

Figure 4. Uneven nitriding results due to the effect of surface passivation. Micrographs showing compound layer after a) grinding and b) milling. c) Surface hardness of steel after machining with mineral oil containing different additives. Steel 42CrMo4 [3].
Cleaning agent residues can lead to passive surface layers if not removed by thorough rinsing. Their negative effect on surface hardness after nitriding depends on their volatility; inorganic salts such as silicates and phosphates have high melting points and do not vaporize at nitriding temperature. Furthermore, they form glassy films, which may completely prevent diffusion or nitrogen uptake. However, if a cleaning installation provides rinsing stages, they can be removed completely.

Water-based cleaning solutions have to a large extent replaced chlorinated hydrocarbons that are no longer permitted for environmental reasons. In addition to water (> 80%), the washing liquid consists of active cleaning agents such as surfactants, inorganic builders, and complex agents and anti-corrosives. The surfactants remove oil films whereas particles are removed by the inorganic builders.

The amount of the metal ions calcium and magnesium defines the water hardness. Both these ions are detrimental if left on the surface before nitrocarburising as this may lead to spots with thin or no compound layer [5]. The washing agents dissolved in the water should react with and bind the Ca and Mg ions into chemical complexes, thereby eliminating the deposits of free ions and the risk of weak spots. If the water hardness is high, then the amount of washing agent and complex building capacity may not be sufficient to bind all Ca and Mg ions into complexes to avoid spot defects. Low water hardness is therefore preferred to guarantee good and even nitrocarburising results.

Plastic deformation in the surface region prior to nitrocarburising will also reduce compound layer growth. A 25 µm plastic deformation zone has been found to reduce the layer thickness by 30% [4].

C. 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 more costly 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 5.
- Residues on the part surfaces are oxidized and vaporized, 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].

D. Nitriding

Gas nitriding is typically performed in convection furnaces, either of pit type as in Figure 6 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 with enough good furnace temperature uniformity, typically ± 5 °C (9 °F).

Figure 5. Nitrogen concentration profiles after short-time nitriding of the cold work steel X155CrVMo12-1 with and without pre-oxidation [3].

Figure 6. Example of a nitriding furnace installation [courtesy of Nitrex Metal Inc].
A nitriding cycle consists of the steps illustrated in Figure 7. 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.

![Figure 7. Nitriding steps and connected gas consumption.](image)

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 [8]. 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.

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

### E. 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 is usually fast. Brick-lined sealed quench furnaces with an oil quenching capability of the same type as for carburising are therefore used (see Figure 8a). Other common solutions are box-type atmosphere furnaces, often with fibre lining, and batch furnaces with a vacuum pumping option for quick atmosphere conditioning and with integrated gas cooling (Figure 8b), as well as metallic retort furnaces of the type shown in Figure 6. Table 5 gives specific advantages and disadvantages of each type of furnace.

![Figure 8. Furnaces for gaseous nitrocarburising: a) Sealed quench furnace with integrated oil quench bath. b) Side view of one chamber vacuum/atmosphere furnace with integrated gas cooling also showing the gas system and c) Cross section of the same furnace as in b) [Courtesy of Ipsen International GmbH].](image)

<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>Slow change in atmosphere</td>
</tr>
<tr>
<td></td>
<td>Modular construction</td>
<td></td>
</tr>
<tr>
<td>Metallic retort furnace</td>
<td>Fast change in atmosphere</td>
<td>Fast ammonia dissociation</td>
</tr>
<tr>
<td></td>
<td>Low nitriding potential</td>
<td>Lifetime of retort</td>
</tr>
<tr>
<td></td>
<td>without hydrogen addition</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Evacuation possible</td>
<td></td>
</tr>
</tbody>
</table>

After the parts have been cleaned, they are loaded into baskets or fixtures and transferred to the furnace for heating (preceded by pre-heating) 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 (9°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.

The process cycle diagram shown in Figure 9 is similar to that shown in Figure 6 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 sealed quench furnace with an integrated oil quench.

F. Vacuum, High Pressure and Plasma Nitriding and Nitrocarburising

A low pressure 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. It is necessary to use a higher relative amount of ammonia than for atmospheric pressure nitriding. 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 [9]. 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 disadvantage is very high equipment costs, which has been a barrier to its use outside research laboratories.

The fourth state of matter, plasma, is characterized by the fact that it consists of free charged particles, ions and electrons. In a DC plasma nitriding furnace (see Figure 10a) 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 arching. The availability of pulse plasma technology with multiple heating and cooling options minimize these drawbacks explicitly (see Figure 14). An ongoing development that also 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, Figure 10b.

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 6), 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.

Table 6. Comparison of effluent emission data for gaseous and plasma nitrocarburising [10].

<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 (32)</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>

The combination of plasma nitriding with atmosphere nitrocarburising has been shown to give excellent surface appearance, wear and corrosion resistance. An example is the Corr-I Dur process, see Figure 11.

Figure 11. Micrograph cross section of a steel specimen treated in the CORR-I-DUR® process [11].

G. 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 12. 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 [1]. It is based on the Nittemper process with an added oxidation step in air. Other oxidation methods using water vapour [12] or nitrous oxide (N₂O) [13] have later been successfully developed and found to yield good properties.

H. 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 subzero 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 13.

Figure 12. Compound layer with oxide layer at top.

Figure 13. The influence of tempering at 350 °C (662 °F) for 2 hours on the hardness profile across an austenitic nitrocarburised case produced at 700 °C (1292 °F) in a mixture of 14 % ammonia and 86% endogas [14].
I. Combined Processes

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 14 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.

Figure 14. 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].

J. Cooling/Quenching and Post Treatment

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 15. 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 16.

Figure 15. Microstructure showing precipitates of needle-like nitrides in the diffusion zone.

Figure 16. Hardness of bars with two diameters after gaseous nitrocarburising followed by oil quenching. Steel approx. corresponding to 16MnCr5. [15].

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. Productivity is of course increased with increased cooling rate.

The number of available cooling options depends on the type of furnace used as illustrated in Table 7. 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 sealed quench 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 increasing and varying the gas pressure and velocity.

Table 7. Cooling options for different types of nitriding/nitrocarburising furnaces.

<table>
<thead>
<tr>
<th>Furnace type</th>
<th>Possible cooling options</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Atmosphere furnaces</strong></td>
<td></td>
</tr>
<tr>
<td>Sealed quench furnace with integrated oil quench</td>
<td>Oil</td>
</tr>
<tr>
<td></td>
<td>Gas, slow convection</td>
</tr>
<tr>
<td>Box furnace</td>
<td>Gas, slow convection</td>
</tr>
<tr>
<td>Box furnace with integrated high speed gas circulation</td>
<td>Gas, high convection</td>
</tr>
<tr>
<td>Pit retort furnace</td>
<td>Gas, slow convection</td>
</tr>
<tr>
<td>Furnace line with integrated high pressure gas cooling</td>
<td>Gas, high pressure and high convection</td>
</tr>
<tr>
<td><strong>Vacuum furnaces (including plasma furnaces)</strong></td>
<td></td>
</tr>
<tr>
<td>Single chamber</td>
<td>Gas, slow convection</td>
</tr>
<tr>
<td>Single chamber/high pressure</td>
<td>High pressure, high convection</td>
</tr>
<tr>
<td>Furnace line with integrated high pressure gas cooling</td>
<td>High pressure, high convection</td>
</tr>
</tbody>
</table>
IV. Properties of Nitrided and Nitrocarburised Steels

Nitriding and nitrocarburising of parts is carried out to improve wear resistance and strength, in particular fatigue strength, and corrosion resistance. Sometimes improved aesthetic surface appearance is also a desired property.

A. 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 17. The measured hardness falls as the degree of porosity in the outermost compound layer surface increases. Generally porosity is greater for low alloy steels than for high alloy steels.

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 (Figure 15), which reduces the hardening effect from solid solution hardening, see Figure 18. 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 19.

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.

Abrasive wear resistance is proportional to hardness and for nitrocarburised or nitrided steels is therefore dependent on the type of steel used (See Figure 19). 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. The thicker case of a carburised part will result in longer resistance to wear.

Figure 20 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 [18] and is highest for 100% $\varepsilon$-phase layers [19]. 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.

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 is an application in which nitriding and nitrocarburising have proven to yield improved wear resistance and endurance [21].

Figure 19. Typical hardness after nitriding and nitrocarburising. Please note the logarithmic length scale in the right hand figure [13].

Figure 20. Adhesive wear resistance measured by a pin/disc test: a. With lubrication. b) Dry (without lubrication). [20]
B. 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 (1022) to 450°C (842°F) can reduce static strength by more than 20% [1].

The improvement in fatigue strength is greatest for specimens with notches that act as stress raisers, see Table 8. This is because the hard case will withstand high stress much better than the core material.

Table 8.
Bending fatigue strength improvement after nitriding [22].

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

The fatigue strength is improved by a state of compressive residual stresses in the surface layer after nitriding/nitrocarburising. This is also the case for the diffusion zone as illustrated in Figure 21. 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 [23]. 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 quench rate that gives 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 (see section VI, page 30). In rare cases the white layer is removed after nitriding to obtain the best fatigue properties.

C. 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 9.

Table 9.
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 &amp; bending fatigue</td>
<td>Diffusion zone hardness and residual stress state</td>
<td>Enough to incorporate maximum point of stress</td>
</tr>
</tbody>
</table>

D. Corrosion Resistance and Surface Appearance

Compared to 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 10, nitrocarburising can replace chromium plating or other surface treatments for salt spray corrosion resistance. By additional

Table 10. Corrosion data [1, 2, 25].

<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 gives the surface a light grey surface appearance. By post-oxidizing, possibly combined with oiling or waxing, a dark black, shiny surface appearance can be obtained, see Figure 22.

Nitriding or nitrocarburising of stainless steels will deteriorate corrosion resistance because the passive chromium oxide layer that provides the corrosion protection of stainless steels will be destroyed. (Certain plasma nitriding techniques explained in IV.F are exceptions to this).

E. Dimensional Changes

Compound layer growth results in dimensional growth. A solid bar will therefore grow in diameter during nitriding/nitrocarburising. Figure 23 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 > 25mm) hollow 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.

Figure 23. Growth of the compound layer and of the diameter of cylindrical parts made from 16MnCr5 and C45 steel, depending on the nitrocarburising time [26].

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 24-25. For a real part with a complex shape the dimensional change is more difficult to predict, especially for a non-uniform part.

Figure 24. Diameter change as a function of the wall thickness of hollow cylinders (70 mm diameter) nitrided for 72 hours [27].

Figure 25. Diameter change after nitrocarburising (2h) followed by oil quenching for cylinders with varying wall thickness [15].

Figure 26 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.

Figure 26. 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 [15].
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 27. Corrosion resistance is maintained, as shown in Figure 28. The highly supersaturated S-phase is not thermochemically stable but will decompose at temperatures above approximately 700°C (1292°F).

Somers [28] 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 29.

![Figure 27](image1.png)

**Figure 27.** Hardness profiles of low temperature plasma nitrided 18/8 type stainless steel [10].

![Figure 28](image2.png)

**Figure 28.** Corrosion resistance of stainless steel AISI 316 plasma nitrided at 450 (842), 500 (932) and 550°C (1022°F) compared to untreated steel. Dipping test in 50%HCl+25%HNO₃+25%H₂O [10].

![Figure 29](image3.png)

**Figure 29.** Surface microstructure and hardness gradients obtained after gas nitriding at two nitriding potentials of stainless steel, type AISI 316 [26].

Examples of S-phase nitriding and carburising processes that have been developed are given in Table 11.
### Table 11. Different processes for S-phase nitriding and carburising of stainless steel [10].

<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, UK</td>
<td>LTPN</td>
<td>N</td>
<td>&lt;450 (842)</td>
<td>Plasma</td>
</tr>
<tr>
<td>University, UK</td>
<td>LTPC</td>
<td>C</td>
<td>&lt;550 (1022)</td>
<td>Plasma</td>
</tr>
<tr>
<td>Nitruvid, France</td>
<td>Nivox2</td>
<td>N</td>
<td>&lt;400 (752)</td>
<td>Plasma</td>
</tr>
<tr>
<td></td>
<td>Nivox4 &amp; NivoxLH</td>
<td>C</td>
<td>&lt;460 (860)</td>
<td>Plasma</td>
</tr>
<tr>
<td>Nihon Parkerizing, Japan</td>
<td>Palsmite</td>
<td>N+C</td>
<td>450-490 (842-914)</td>
<td>Cyanide salt bath</td>
</tr>
<tr>
<td>Airwater Ltd, Japan</td>
<td>NV Super Nitriding</td>
<td>N</td>
<td>300-400 (572-752)</td>
<td>Gas + Fluorine</td>
</tr>
<tr>
<td></td>
<td>NV Pionite Process</td>
<td>C</td>
<td>&lt;500 (932)</td>
<td>Gas + Fluorine</td>
</tr>
<tr>
<td>Bodycote, UK</td>
<td>Kolsterising</td>
<td>C</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>DTU, Denmark</td>
<td>Gas nitriding</td>
<td>N</td>
<td>&lt;450 (842)</td>
<td>Gas</td>
</tr>
</tbody>
</table>
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 30a. In nitrocarburising it is additionally necessary to have a carbonaceous gas transferring carbon to the steel surface. This is illustrated in Figure 30b 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 stages of nitrogen/carbon transfer:

1. From the gas to the steel surface
2. Diffusion through the compound layer
3. Diffusion into the diffusion zone

(Additional stages 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 31.

**Figure 30. Schematic illustration of the nitriding and carburising processes.**

**Figure 31. Concentrations and concentration gradients of nitrogen and carbon.**
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:

\[
\frac{dm_N}{dt}_{(\text{surface})} = k_1 \left[ c_N(\text{gas}) - c_N(\text{surf}) \right]
\]
\[
\frac{dm_C}{dt}_{(\text{surface})} = k_2 \left[ c_C(\text{gas}) - c_C(\text{surf}) \right]
\]

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 stages controls the nitrogen and carbon transfer rates. For a compound layer consisting of alternating \( \varepsilon '-\varepsilon \) layers, the rate will be determined by the phase with the slowest diffusion properties.

### A. The Atmosphere Nitriding Potential

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

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

with the chemical equilibrium constant

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

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

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

where \( a_N \) is proportional to the concentration, \( c_N \). The ratio

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

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 according to reaction 4.1. In the expression for the nitrogen potential,

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

is \( P_{\text{NH}_3} \) 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,

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

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

\[
(1 - \alpha) + 3/2 \alpha + 1/2 \alpha = 1 + \alpha
\]

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

\[
P_{\text{NH}_3} = (1 - \alpha) / (1 + \alpha)
\]
\[
P_{\text{H}_2} = 3/2 \alpha / (1 + \alpha)
\]
\[
P_{\text{N}_2} = 1/2 \alpha / (1 + \alpha)
\]

and the nitriding potential as

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

(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

\[
\gamma_N = 8/\sqrt{3} \cdot P_{\text{NH}_3} / (1 - P_{\text{NH}_3})^{3/2}
\]
\[
\gamma_N = (1 - 4/3 P_{\text{H}_2}) / P_{\text{H}_2}^{3/2}
\]

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 [29, 30].
B. 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

\[ K = a_C \cdot P_{\text{H}_2\text{O}} / (P_{\text{CO}} \cdot P_{\text{H}_2}) \]

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

\[ r_{C1} = P_{\text{CO}} \cdot P_{\text{H}_2} / P_{\text{H}_2\text{O}} \]
\[ r_{C2} = P_{\text{CO}}^2 / P_{\text{CO}_2} \]

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 alternative developed with NITROFLEX® technology is to use carbon dioxide, \( \text{CO}_2 \), which by reacting with the hydrogen inside the furnace produces CO according to the reaction,

\[ \text{H}_2 + \text{CO}_2 = \text{CO} + \text{H}_2\text{O} \]

The hydrogen needed for this reaction originates from dissociated ammonia or from a separate addition of hydrogen. Figure 32 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/\( \text{CO}_2 \) has much lower carbon activity, see Table 12.

C. 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 (\( \text{NH}_3 \), \( \text{H}_2 \), \( \text{CO} \), \( \text{CO}_2 \) and \( \text{H}_2\text{O} \)) 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.

1. Ammonia and Hydrogen Analysis

The simplest method of determining the nitriding potential is ammonia analysis with the ammonia burette technique shown in Figure 33. The analysing principle is based upon 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

---

**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>( \text{N}_2 )</td>
<td>( \text{H}_2 )</td>
</tr>
<tr>
<td>50% Endogas</td>
<td>24.1</td>
<td>25.9</td>
</tr>
<tr>
<td>40% Endogas</td>
<td>29.2</td>
<td>24.3</td>
</tr>
<tr>
<td>50% ( \text{NH}_3 )</td>
<td>58.8</td>
<td>15.5</td>
</tr>
<tr>
<td>35% ( \text{NH}_3 )</td>
<td>54.4</td>
<td>15.9</td>
</tr>
<tr>
<td>35% ( \text{NH}_3 )</td>
<td>45.4</td>
<td>26.6</td>
</tr>
<tr>
<td>20% ( \text{H}_2 )</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 (\( \text{FeO} \)), for nitrogen, carbon and oxygen respectively.

---

Figure 32. Relation between the added amount of \( \text{CO}_2 \) and produced amount of CO.

Figure 33. Ammonia analyser
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 34. 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 analyzed 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 utilizes a Wheatstone bridge in which a resistor is in contact with the gas to be analyzed. 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 35 shows the principle of analysis.

Hydrogen can also be analyzed with a sensor with a similar appearance to an oxygen probe as shown in Figure 36. It uses a measuring tube material with the ability to sensor 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 the hydrogen concentration after the complete dissociation of ammonia, \( P'_{H_2} \). From these two measurements the nitriding potential is expressed by

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

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

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 (see equation 4.3) and the nitriding potential from equation 4.4. 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 [32]

$$D = \frac{A}{B} = \frac{1}{\alpha}$$

One development of the oxygen probe to determine the nitriding potential is the type of sensor shown in Figure 37. 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 DU is a measure of the difference in oxygen potentials between 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 [32, 33].

$$DU = 0.0992 T \log \alpha$$

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

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

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

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 38 and is connected to a furnace as in Figure 39, which also includes a hydrogen analyser.

![Figure 38. Basic components of a computerized FTIR spectrometer system.](image)

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 40. It is used for calibrating individual furnaces.

![Figure 40. Example of FTIR analysis result.](image)

D. 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 41.
the ammonia flow rate. A control system incorporating a hydrogen sensor and using the combination of ammonia and hydrogen is shown in Figure 42. Hydrogen could alternatively be supplied from cracked ammonia.

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.

E. Guidelines for Regulating the Atmosphere

1. Nitriding

Controlled nitriding is realized 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-percent [8].

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 42. Hydrogen could alternatively be supplied from cracked ammonia.

2. Nitrocarburising

The atmosphere for nitrocarburising consists of 20-50% ammonia, 2-20% carbon dioxide and the balance nitrogen, the specific composition 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 often sufficient (see Figure 32).

Figure 43 gives examples of analysis results for residual NH₃ in a nitrocarburising process where 50% NH₃ + 50% endogas were introduced into a sealed quench ceramic lined furnace. The figure shows a

Figure 43. Examples of residual ammonia concentration variations during nitrocarburising cycles at 570°C (1058°F) in a sealed quench furnace.

The "b" cycle was the same as the "a" cycle with the exception that the furnace was preconditioned with an active atmosphere in the "b" cycle.
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 diffusion zone correlated positively with residual ammonia analysis results.

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 44-45 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.

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 46. For high nitrogen activities entailing a high ratio for $P_{NH_3}/P_{H_2}^{1/2}$, 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, see the lower right photograph.

In order to lower the nitrogen activity during the later 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.

![Figure 44. Theoretically calculated carbon and nitrogen activities at 580°C (1076 °F) for different ammonia additions to an atmosphere based on N₂+5%CO₂.](image1)

![Figure 45. Theoretically calculated carbon and nitrogen activities at 580°C (1076 °F) for different carbon dioxide additions to an atmosphere based on N₂+35%NH₃.](image2)

![Figure 46. Four examples of compound layer depth and morphology as the result of different gas recipes. Treatment temperature and time were the same in all four cases. Unalloyed 0.1% C steel. Gas atmospheres: a) 35% NH₃, 5% CO₂, balance N₂, a_C = 0.93, a_N = 2390, b) 33% NH₃, 5% CO₂, 5% CO, balance N₂, a_C = 2.95, a_N = 2320, c) 28% NH₃, 4% CO₂, balance N₂, a_C = 1.54, a_N = 1300, d) 60% NH₃, balance endogas, a_C = 23.5, a_N = 1690 [16, 36].](image3)
with the propane addition. Other hydrocarbons such as ethylene and propylene are also commonly used to provide carbon [37].

### 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). The post oxidation temperature should therefore be below that for formation of FeO, although FeO formation is very slow up to 700°C (1292°F) [38].

Figure 47 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 10⁻³¹ to 10⁻³⁰ 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:

\[
2.4 \times 10^{-26} < P_{O_2} < 3.7 \times 10^{-25} \quad \text{or} \quad 0.30 < \frac{P_{H_2O}}{P_{H_2}} < 1.18 \quad \text{or} \quad 0.69 < \frac{P_{CO_2}}{P_{CO}} < 2.71
\]

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.

If H₂O is used as an oxidant, it is necessary to purge effectively with nitrogen to bring down the H₂ concentration before H₂O addition, in order to achieve sufficient oxidizing power (\(P_{H_2O} / P_{H_2}\)). Alternatively a larger amount of water may be added.

Corrosion test results indicate that a thin oxide with a thickness of approx. 1 µm is the best for yielding good corrosion results. The oxidation time must therefore be short. In order to achieve sufficient oxidation to yield a black surface within this short time, there must be enough oxidizing gas inside the furnace. Typically 10 vol% of the input gas (the remainder being nitrogen) is used when N₂O is the oxidant and the oxidation time is of the order of 10-15 minutes. Results with respect to corrosion resistance are shown in Figure 48.

Pitting corrosion resistance tests of test specimens post oxidised with water vapour have given almost double resistance for post oxidised variants compared to purely nitrocarburised specimens. The best results were obtained after post oxidation at 450°C (842°F) [13].

---

**Table 14. Equilibrium oxygen partial pressures over iron oxides at 580°C (1076°F).**

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Equilibrium partial pressure, atm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(P_{O_2})</td>
</tr>
<tr>
<td>FeO</td>
<td>(3.4 \times 10^{-27})</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>(2.4 \times 10^{-26})</td>
</tr>
<tr>
<td>Fe₃O₄</td>
<td>(3.7 \times 10^{-25})</td>
</tr>
</tbody>
</table>

---

**Figure 48.** Corrosion after one week 5% NaCl test. Specimens were post oxidised at different temperatures and in different gas atmospheres as indicated by the test 1-10 description.

---

**Table 13. Wear test results for crankshafts in steel C45 nitrocarburised at 570°C (1058°F) [18].**

<table>
<thead>
<tr>
<th>Process gas mixture,</th>
<th>Compound layer,</th>
<th>Nitriding depth,</th>
<th>Relation</th>
<th>Wear rate</th>
<th>Ductility</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>µm</td>
<td>mm</td>
<td>(\gamma'?:\delta)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>55N₂/43NH₃/3CO₂</td>
<td>20</td>
<td>0.95</td>
<td>1.4</td>
<td>High</td>
<td>Worst</td>
</tr>
<tr>
<td>92NH₃/5CO₂/3C₃H₈</td>
<td>18</td>
<td>1.0</td>
<td>1.11</td>
<td>Low</td>
<td>Best</td>
</tr>
</tbody>
</table>

---

**Figure 47.** Iron oxide equilibrium as a function of temperature.
VI. Compound Layer and Diffusion Zone Formation

A. Nitriding

From the Fe-N phase diagram in Figure 49, 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 by point A in the diagram. Later $\epsilon$ is expected to form on top of $\gamma'$ (point B) when the surface nitrogen concentration exceeds the solubility limit in $\gamma'$ (point B), then a monophase $\gamma'$-layer will be the end result. 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 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 $\epsilon$ to be formed.

The $\gamma'$-phase is an almost stoichiometric compound, Fe$_4$N, with limited concentration variation. The growth rate of the $\gamma'$-compound layer is therefore relatively low since the difference $c_n$(surface) - $c_n$(nitride/$\alpha$) is low (see Figure 31). On the other hand $\epsilon$-nitride has a high solubility range for nitrogen, which leads to higher growth rate. This is illustrated in Figure 50, which shows that the compound layer thickness increases markedly when the nitriding potential is very much higher than the lower solubility limit for $\epsilon$ to form, expressed by the ratio $P_{\text{NH}_3}/P_{\text{H}_2}^{3/2}$ (test no. 1 in the figure).

Figure 49. The Fe-N phase diagram plotted as a function of temperature and of the nitriding potential, $P_{\text{NH}_3}/P_{\text{H}_2}^{3/2}$ [39].

The diffusion zone thickness increases with increased nitrogen potential, Figure 50, and with time in a parabolic manner, Figure 51. As seen in Figure 51, 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.

Figure 50. Changes in diffusion zone hardness gradient and compound layer thickness after nitriding of an Al-alloyed steel at 510°C (950°F) over 24 h. The $\text{NH}_3$ content of the ingoing gas mixture as indicated by the number at each curve was achieved by addition of hydrogen [40].

Figure 51. Relation between nitriding depth and treatment time for different steels. [41].
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 as shown in Table 15. The table also shows that oxygen addition favours the formation of ε-phase.

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 52.

The nitrogen take-up and thus also the layer growth rate increases with increased surface area (surface roughness) as shown in Figure 53.

### 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 [41].

<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, γ: 47</td>
</tr>
<tr>
<td>No oxygen but pre-oxidised</td>
<td>2.9-3.5</td>
<td>ε: 67, γ: 25</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 52.

### Figure 52. Effect of oxygen and water vapour on weight gain during nitriding in a thermo-balance at 550°C (1022°F) of Fe20Cr powder. The ratio NH₃/H₂ is indicated at each graph [42].

### Figure 53. Dependence of the thickness of the compound layer on the mean surface roughness Rz. 0.45%C carbon steel, nitriding temperature 570°C (1058°F), nitriding time 3 hours [43].

### B. 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 [44, 45]. 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 additionally evidence that cementite formation at moderate atmosphere carbon activity is favoured by the presence of ammonia in the atmosphere. [46]. 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 54.

The nitrogen surface concentration increases with increased process time and increased nitriding potential (Figure 55), whereas the carbon surface concentration decreases (Figure 54). 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 54 with a depletion of carbon in the intermediate γ'-layer, an accumulation of carbon in the ε phase adjacent to the core ferrite/cementite matrix and a positive carbon concentration gradient in the outer ε 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 ε phase, (see the lower part of Figure 54).

The contact between the ε- and the α-phases observed at the interface compound layer/matrix is consistent with the phase diagram evaluated by Du [39] and shown in Figure 56. (It does not, however, correspond to the phase diagram from Naumann and Langenscheid [48] that is often referred to.)

Figure 54. Nitrogen and carbon concentration profiles after nitrocarburising at 575°C (1067°F) [45].

Figure 55. Surface and ε/γ interface nitrogen concentration plotted as a function of nitriding potential for gaseous nitriding of pure iron at 500°C (932°F) [47].

Figure 56. Isothermal section at 580°C (1076°F) of the ternary Fe-N-C phase diagram [39].

Figure 57 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 46. In a study by Bell and Wells [49] the atmosphere carbon activity was shown to affect the phase constituency of the compound as follows:

- At low carbon activities there is a $\gamma'$-layer positioned in between the $\varepsilon$-layer and the core ferrite/cementite structure;
- At intermediate carbon activities a $\gamma'$-layer forms as a band inside the $\varepsilon$-layer.
- At high carbon activity no $\gamma'$ at all was observed but the compound layer was $\varepsilon$-monophase.
- At very high carbon activity a duplex thin layer was formed consisting of $\varepsilon$ + 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 $\varepsilon$-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 must not be so long that the porosity and thickness of the compound layer reach excessively high values. Poor adherence and low hardness will be the result. In view of this, practice has shown that a treatment time of 1.5 to 3 hours is optimum.

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 58 shows experimental results regarding the relation between residual ammonia and added ammonia for two types of furnaces: 1) a sealed quench 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 4m$^3$/h (1.41 100ft$^3$/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 higher degree than the ceramic interior of the sealed quench 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 59.
In a study tests were made in different types of furnaces 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 \( \left( \frac{P_{\text{NH}_3}}{P_{\text{H}_2}} \right) \) and carbon potential \( \left( \frac{P_{\text{CO}}}{P_{\text{CO}_2}} \right) \) in Figure 60. 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 walling in the furnaces was initially very high in the fibre lining furnaces. The steel retort furnace is the extreme and exhibits the lowest nitrogen content was initially very high in the fibre lining furnaces. The other furnaces with 40 vol% and 20 vol% of active gas respectively. Figure 62 from Figure 57 are shown for reference [50].

2. 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 (\( \text{NH}_3, \text{H}_2, \text{CO}, \text{CO}_2 \)) [51] 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 62 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.
The depth of the diffusion zone also decreases with increased alloy content principally in the same way as in nitriding (See Figure 51).

**Pore Formation**

The depth of porosity in the outer part of the compound layer on un- and low-alloy steels is of the order 30-40% of the total compound layer depth, as illustrated in Figure 64a. 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 64b, 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.

**Steel Alloy Content Effect**

As in the case of nitriding, increasing the alloy content of the steel leads to decreased compound layer thickness, Figure 63.

The thickness of the compound layer decreases with increasing alloying content of treated steels for a given treatment time [16].

Figure 62. Compound layer thickness as a function of the amount of active gas (\(\text{NH}_3+\text{H}_2+\text{CO}+\text{CO}_2\)) and carbon activity. Low alloy steel. [51].

Figure 63. The thickness of the compound layer decreases with increasing alloying content of treated steels for a given treatment time [16].

Figure 64. Depth measurements of compound (blue text) and porous (red text) layer on a) carbon steel (St50-2) and b) alloy steel (34NiCrMo5). Nitrocarburising process recipes were identical for both steels [51].
VII. The NITROFLEX® Solution

When Linde and BOC merged in 2006, a substantial concentration of expertise on 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 (the content of this booklet) and specifications of the complete details of process cycles and of safety instructions.

The NITROFLEX® atmosphere system has the inherent advantages of flow rate and mixing (composition) flexibility typical of synthetic in situ generated atmospheres. It provides an opportunity to optimise the gas composition in relation to the type of furnace, steel and to the different stages in the process with the objective of obtaining the required final part properties of wear resistance, fatigue resistance or corrosion resistance. If used efficiently, these advantages lead to minimized costs and high quality. Safety and the potential for increased productivity are additional benefits.

One feature of NITROFLEX® atmospheres is a carbon activity that is much lower than that in systems using endogas together with a higher oxygen activity (see Table 11). 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 65. 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 22) with markedly improved corrosion resistance (Table 10).

A. Gas Supply

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

There are five major supply forms for nitrogen:

a. Gaseous nitrogen in cylinders
b. Liquid nitrogen supplied by truck to the customer container
c. Nitrogen produced on-site with cryogenic technology (CRYOSS®)
d. Nitrogen from adsorption (PSA) units installed on-site at the facility (ADSOSS®)
e. Nitrogen from on-site membrane units installed on-site at the facility (MEMOSS®)

Nitrogen supplied in liquid form has high purity, with typical contamination levels of O₂ + H₂O of 5 ppm. Liquid supply is common for a flow from 10 to 100-200 m³/h. The liquid nitrogen is supplied by truck to a liquid nitrogen storage tank at the manufacturing plant, as illustrated in Figure 66. The liquid nitrogen supply form has the advantage that

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Figure 65. Compound layer thickness for different atmospheres showing faster growth for the NITROFLEX® system [13].

Figure 66. Filling of a storage tank for liquid nitrogen.
the amount of nitrogen supplied to the furnaces can be varied within wide limits. The customer only takes the amount needed at any time.

ECOVAR® is a family of on-site production units supplied by Linde Gas. Nitrogen produced using the PSA (Pressure Swing Adsorption) technique, Figure 67a, has a purity of 99 to 99.99%. Flow rates from 10 to 1500-2000 m³/h can be accommodated. Nitrogen produced at the customer site using the membrane technique, Figure 67b, has a purity of 90-99%. Flow rates from 5 to 1000 m³/h can be accommodated. The purity requirement of membrane nitrogen is normally not sufficiently high for nitriding and nitrocarburising.

Cryogenic on-site production, Figure 68, yields high purity, typically 5 ppm oxygen and moisture content. It is relevant for flow rates from 250 to 1500-2000 m³/h.

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

Figure 67. a) PSA (Pressure Swing Adsorption), ADSOSS®, and b) Membrane, MEMOSS®, unit for nitrogen production on site.

Figure 68. Cryogenic nitrogen production with CRYOSS®
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 69.

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 moderate or smaller customer.

Laughing gas for post oxidation is delivered in cylinders.
1. Nitriding

Figure 70 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 required supply pressure. This ensures continuous and safe gas supply. For liquid bulk ammonia supply, it is necessary to have a vaporiser connected. When 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.

2. Nitrocarburising

Nitrocarburising gas supply has the special feature that carbon dioxide is added in addition to the nitrogen/ammonia/hydrogen supply used in nitriding. Figure 71 shows the schematic setup of a gas supply system with a liquid nitrogen tank and gas cylinders for ammonia and carbon dioxide respectively. Figure 72 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 73a shows a flow mixing panel assembled from cassettes for each gas and flow rate range. In advanced setups, the flow rate and temperature control can be built into a closed loop control system as shown in Figure 73b.
If carbon dioxide is mixed with ammonia before entering the hot furnace there will be reactions leading to ammonium carbonate formation, which deposits in the line, 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 work and inlet
2. Nitrogen + carbon dioxide in one mixer and from one inlet, ammonia from another pipe work and inlet.

Figure 74 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.

### C. Case Studies

#### 1. Nitrocarburising

The cases described here are taken from reference [52].

**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 75a. Because no form of classical heat treatment could solve both the wear and corrosion attack problems on its own, the NITROFLEX® nitrocarburising treatment adapted to a sealed quench furnace was tried. Figure 75b 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 75. a. Conveyor rollers in use in a paint shop. b. Conveyor rollers](image)

**Case Study 2: Forging die manufactured from 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 sealed quench 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 76 shows the component produced. The surface finish of the forgings was improved when the NITROFLEX® treated die was used.

![Figure 76. Forging produced by the NITROFLEX® treated forge die.](image)
Case Study 3: Extrusion dies made of H13 material.
The time between re-polishing was significantly improved by a NITROFLEX® nitrocarburising treatment, performed in a sealed quench furnace with a process recipe adapted to the steel. A very high surface hardness of the order of 1200HV was achieved. The appearance of treated dies is shown in Figure 77.

Figure 77. 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 rusted after 100 cycles in these working conditions. The NITROFLEX® nitrocarburising treated clamps attained 300 cycles without rust.

Case Study 6: 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 sealed quench 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 79.

Figure 79. Clutch plate in mild steel treated by the austenitic nitrocarburising process

Case Study 7: 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, performed in a sealed quench 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 80.

Figure 80. Mild steel mail handling tracks

Case Study 8: Moulds in 1020
Most moulds or forming tools are manufactured from H13 material. H13 material is expensive and typically requires vacuum hardening and tempering. These moulds are now manufactured from mild steel, a low-cost material, and treated with extended austenitic nitrocarburising performed in a sealed quench 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. Two examples of these moulds are shown in Figure 81. In addition to cost savings, surface quality has also been improved because the compound layer eliminates pickup.

Figure 81. austenitic nitrocarburised SAE 1020 tag washer
3. Nitriding

Case Study 9: 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 82 and a comparison between classical gas nitriding and the NITROFLEX® nitrocarburising treatment is shown in Table 16.

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 1326 GBP (cost level of the year 2001) per furnace cycle.

Table 16. Comparison of gas nitriding and NITROFLEX® nitrocarburising.

<table>
<thead>
<tr>
<th>Process</th>
<th>Classical 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 × 6 cylinder crank shafts</td>
<td>6 off × 6 cylinder crank shafts</td>
</tr>
<tr>
<td>Operating cost</td>
<td>2199 GBP (105 hrs floor-to-floor)</td>
<td>1100 GBP (55 hrs floor-to-floor)</td>
</tr>
<tr>
<td>Process cost</td>
<td>350 GBP/component</td>
<td>183 GBP/component</td>
</tr>
<tr>
<td>Post grinding cost</td>
<td>52 GBP/component (white layer)</td>
<td>No post-grinding (compound layer)</td>
</tr>
<tr>
<td>Total cost</td>
<td>404 GBP/component</td>
<td>183 GBP/component</td>
</tr>
<tr>
<td>Saving</td>
<td>221 GBP/component</td>
<td></td>
</tr>
</tbody>
</table>
The European Committee for Standardisation, CEN, has issued a series of heat treatment safety standards, listed in references [53-58]. The standard covering the use of atmospheres is CEN 746-3: Industrial thermoprocessing equipment – Part 3: Safety requirements for the generation and use of atmosphere gases [55]. In addition to the European Standards there are national standards and safety regulations that have to be taken into account. The National Fire Protection Association (NFPA) maintains the main safety standard for heat treatment in the USA, see reference [59]. In addition standards and regulations are issued by the U.S. Occupational Safety and Health Administration (OSHA), and by insurance underwriters. The Compressed Gas Association (CGA) maintains standards for gases. National electrical codes and local requirements of states and communities will also apply. An overview of safety hazards and required precautions in heat treatment is given in reference [60].

The main hazards related to the use of gases in heat treatment are explosions/flammability, toxicity, asphyxiation, and exposure to hot objects, surfaces and flames. Specific safety issues connected to nitriding/nitrocarburising are related to the toxicity and flammability of the gases used and to the fact that operation temperature is below the safety temperature.

A. 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.

Carbon dioxide, which is normally present in atmospheric air at the level of approximately 300 ppm, regulates breathing; an increase in concentration will increase the breathing rate. The workplace exposure limit is 5000 ppm (0.5 %), but changes in breathing rate may not be noticed until there is a concentration of 20,000 ppm (2 %), when the rate will increase to 50 % above normal. Exposure at this level for several hours may cause a headache and a loss of concentration. A concentration of 15 % soon causes unconsciousness, and may cause death after some hours’ exposure. Carbon dioxide is odourless, and thus gives no warning of its presence by any odour, except at very high concentrations when a slight acidic pungency may be detectable.

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.

B. Flammability

Both nitriding and nitrocarburising are performed at a temperature below the safety temperature (700 °C (1292 °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 occurs 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 NITROFLEX® system typically utilizes about 40 vol-% of ammonia and optionally up to 10vol-% of hydrogen, which are the only flammable gases in the going gas mixture. This can be compared to the
50 vol-% endogas + 50 vol-% ammonia process, which holds approximately 80 vol-% hazardous components (H\textsubscript{2}, CO, NH\textsubscript{3}) in total.

The Safety Triangle, Figure 83, shows how to operate safely. The flammability triangle is depicted in the area L-S-U and this area should always be avoided. This is done as follows. When starting up a 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. The level of required purging furnace volumes can be taken from theoretical purging curves. The CEN standard in reference [155] states: “The volume of inert purge gas needed to displace either air or a flammable gas from a furnace chamber/enclosure to achieve 1% (V/V) or less oxygen and/or a non-flammable atmosphere gas and/or 25 % of the lower flammability limit is typically equal to five times the volume of the thermoprocessing equipment chamber to be purged”. When point C in Figure 83 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 83 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 (see Figure 8b). The vacuum level that is seen to be required before introducing flammable gas is 45 mbar according to CEN 746-3 [55].

Sealed quench 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, as was illustrated in Figure 6.

For mixture in air at 200 °C (392 °F) and 1.0 bar (a)
(1) Lower flammability limit in air = 5.1 vol% mixture
(2) Upper flammability limit in air = 43.5 vol% mixture
(3) Min O\textsubscript{2} -conc. for flammability = 4.6 vol% (Fuel = 5.1 vol %)
(4) Start up = max 4.9 vol% oxygen
(5) Shut down = max 6.5 vol% mixture

For mixture in air at 580 °C (1076 °F) and 1.0 bar (a)
(1) Lower flammability limit in air = 0.2 vol% mixture
(2) Upper flammability limit in air = 49.8 vol% mixture
(3) Min O\textsubscript{2} -conc. for flammability = 0.2 vol% (Fuel = 0.2 vol %)
(4) Start up = max 0.2 vol% oxygen
(5) Shut down = max 0.2 vol% mixture

A safety factor is not included in the data given above!
IX. Concluding Remarks

Nitriding and nitrocarburising have the outstanding advantages of:

- Offering surfaces with extremely good tribological properties (low wear and friction).
- Improved corrosion resistance.
- Aesthetically attractive surface appearance.
- Good static and fatigue strength with levels that depend on the steel selection.
- Dramatically reduced distortion compared to carburising and carbonitriding. This gives cost savings due to the elimination of post grinding.
- A low temperature process that lowers energy consumption.

Compared to gas nitriding, nitrocarburising has the advantage of being a short time process that leads to cost savings.

The NITROFLEX® package offers solutions that include:

- The advantages of gas flow rate and mixing flexibility connected to the use of synthetic in situ generated atmospheres. Beneficial consequences are 1) safety, 2) improved process control that guarantees high quality, 3) a potential to increase productivity and 4) cost savings.
- Options for installations as retrofits on existing furnaces or as new installations.
- Manual, semi- or full-automatic control systems.
- Recipe options to meet demands on final properties and to suit different steels and furnaces.
- Access to the extensive expertise and the support of knowledgeable, experienced and skilled Linde engineers.
X. References

Author:
Torsten Holm

15. Holm T., unpublished.

Books
Getting ahead through innovation.

With its innovative concepts, Linde is playing a pioneering role in the global market. As a technology leader, it is our task to constantly raise the bar. Traditionally driven by entrepreneurship, we are working steadily on new high-quality products and innovative processes.

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Furnace Atmospheres publishings:
- Furnace Atmospheres No. 1 – Gas Carburising and Carbonitriding
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