Furnace atmospheres 3

Nitriding and Nitrocarburizing

by Torsten Holm, Lars Sproge
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Introduction

The composition, function and control of the furnace atmosphere are of crucial importance for the result of all hardening and thermochemical operations. The purpose of this booklet is to provide a brief introduction to the properties and function of the atmosphere in nitriding and nitrocarburizing. The special characteristics of nitrogen-based atmospheres are also described here.

The booklet comprises a part of a planned series that will deal with:

- Gas carburizing and carbonitriding
- Neutral hardening and neutral annealing
- Nitriding processes
- Sintering
- Brazing.
Why nitriding and nitrocarburizing

The purpose of nitriding and nitrocarburizing is to improve wear, corrosion and fatigue resistance of constructional parts. These improvements can be understood when looking at the surface microstructure and hardness after treatment, figure 1. The outermost layer of a nitrided or nitrocarburized steel is 2–30 µm thick and consists of ε-phase or γ'-phase, or a mixture thereof depending on atmosphere and steel grade. This layer is called the “compound layer” or sometimes also the “white layer”. Corrosion resistance and tribological properties (friction and wear) are mainly determined by the compound layer. Under the compound layer there is a “diffusion zone”, which goes deeper into the steel, typically 0.1–0.5 mm. Load bearing capacity, static and fatigue strength are largely determined by the hardness and depth of the diffusion zone.

Nitriding and nitrocarburizing are often alternatives to carburizing or carbonitriding. A very important advantage is that nitriding and nitrocarburizing are “low temperature methods” whereas carburizing and carbonitriding are “high temperature methods”. By low temperature here is meant a temperature below the one where phase transformation to austenite starts, and high temperature is above the said temperature. The valuable consequence is much less distortion of treated parts, which eliminates grinding and therefore shortens the production cycle.

Nitriding and nitrocarburizing give unique improvements in corrosion resistance and adhesive wear, which cannot be obtained by carburizing or carbonitriding. Further corrosion resistance improvements are obtained by a postoxidation treatment.

Terminology and processes

In a way it is unfortunate that there are two process names; nitriding and nitrocarburizing, as there is little difference in principle between the two and sometimes the two names are used for the same process, which creates confusion. Also there is often a confusion between nitrocarburizing and carbonitriding. One important borderline is that nitriding and nitrocarburizing are terms used for treatments at temperatures below the one where austenite starts to form...
Nitriding is the term used for classical gas nitriding in ammonia. As the name indicates, it is a process where nitrogen is transferred to and taken up by the steel. Also in nitrocarburizing the main element transferred to the steel is nitrogen but in addition also carbon. Both processes give the principal surface microstructure and hardness as shown in figure 1. Classical gas nitriding was developed for the purpose of increasing fatigue strength and load bearing capacity without getting significant distortion of treated components as in carburizing (or carbonitriding). To obtain sufficient case depths very long nitriding times, from ten to hundreds of hours, have been and are used. Nitrocarburizing started to grow remarkably with the development of the salt bath process Tenifer (Tufftride) and the gaseous process Nitemper developed in the sixties. As compared to classical nitriding, nitrocarburizing is a short time process, typically 30 minutes to 4 hours, performed at higher temperature, about 570°C compared to 500–510 °C for gas nitriding.

The compound layer may consist of either $\gamma'$-phase with the almost stoechiometric formulae Fe$_4$N or $\epsilon$-phase with variable composition of carbon and nitrogen depending on steel grade and atmosphere type. Normally both phases coexist but $\gamma'$ is dominating after nitriding and $\epsilon$ after nitrocarburizing. The $\gamma'$-phase causes brittle compound layers whereas $\epsilon$ has a higher ductility. The outermost part of the compound layer normally has some porosity.

A number of different names of variants of nitriding and nitrocarburizing exist on the market, figure 2. These names are company trade marks like Nitemper and Tenifer already mentioned. AGA Nitroflex is the AGA designation of nitrocarburizing or nitriding furnace atmospheres.

**Figure 2. Nitriding and nitrocarburizing features and process names**

| Nitriding | Gas nitriding  
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NH$_3$ gas</td>
</tr>
<tr>
<td>AGA Nitroflex</td>
<td>NH$_3$/N$_2$/H$_2$ gas</td>
</tr>
</tbody>
</table>
| Plasma nitriding | Temperature: 450–580 °C  
|                 | Time: 10 min – 30 h  
|                 | Nitrogen plasma |

| Nitrocarburizing | AGA Nitroflex AH/AC  
|                 | NH$_3$/N$_2$/CO$_2$/H$_2$  |
|                 | AGA Nitroflex ACO  
|                 | Nitroflex + air or N$_2$O  |
|                 | Nitemper  
|                 | endogas/ammonia  |
|                 | Nitrotec  
|                 | Nitemper + air  |
|                 | Nitroc  
|                 | exogas/ammonia  |
|                 | Deganit  
|                 | exogas/endogas/ammonia  |
|                 | Tenifer  
|                 | salt  |
The names can be organized in three groups related to the process medium, which may be salt, gas or plasma. The salt bath processes are loosing market to the gas processes due to the environmental problems with salts, containing cyanide. Plasma processes are still used in a limited number of cases but the use increases because of specific advantages such as the possibility to use very low process temperature and to nitride e.g. stainless steel, which is difficult by other methods.

Properties and applications

The compound layer hardness is about 700 HV for low alloy steels and the hardness increases with increasing alloy content in the steel as shown in figure 3. The measured hardness falls as the degree of porosity in the outermost compound layer surface increases. Generally porosity is greater for low alloy steels as compared to high alloyed steels.

Alloy content is most important also for the diffusion zone hardness. There are two mechanisms which determine the diffusion zone hardness. First solid solution hardening is a mechanism which 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 kept in solid solution. Slow cooling rate means that there is enogh time for precipitation of iron or alloying element nitrides and this reduces the hardening effect from solid solution hardening. This is why low alloy steels are normally quenched in water or oil after nitrocarburizing.

The second hardening effect in the diffusion zone is precipitation hardening. For alloyed steels this hardening mechanism is dominant.
A dramatic consequence of this mechanism is that as wide a hardness range as 300–1300 Vickers is obtained depending on which steel has been nitrided or nitrocarburized, figure 4.

The hardness of the compound layer will determine the wear resistance. Increased hardness in the compound layer normally gives increased wear resistance. This is definitely valid for abrasive wear resistance, thus a situation where abrasive particles, e.g. sand, wears a surface. One important observation is that hardnesses after nitriding or nitrocarburizing may give wear situations on the "low level". This means that the surface hardness is higher than the hardness of the abrasive particles. However, the limited depth of the compound layer is a drawback and therefore nitriding or nitrocarburizing is applied successfully only in mild abrasive situations.

Adhesive wear resistance of steel is dramatically improved after nitriding or nitrocarburizing, figure 5, and more than could be expected from the hardness alone. The compound layer gives low friction and low tendency to "weld" opposing steel surfaces. A porous outer zone serves as lubricant reservoir. All these properties act together to give excellent adhesive wear resistance.

Compared to other thermal or thermochemical surface hardening methods on steels nitriding and nitrocarburizing are unique in that corrosion resistance is improved. New developments of the process have even more improved corrosion resistance at the added benefit of a deep black aesthetically pleasant surface appearance. This is obtained by a slight oxidation after the normal nitrocarburizing process.

The hardness and depth of the diffusion zone will determine fatigue strength. In addition to case depth and hardness also the obtained compressive residual stress state in the case is of major importance.
When translated to process parameters this means that temperature and time and notably cooling rate are important parameters.

Examples of applications are gears, crankshafts, camshafts, parts like cylinders and pistons where good tribological properties are needed, a great number of wear and fatigued parts earlier carburized or carbonitrided to small case depths. Further on, nitriding and specially nitrocarburizing can replace chromizing or other surface treatments for corrosion resistance and for aesthetically good looking surfaces (e.g. replacement of black oxidizing). Benefits of the processes, especially nitrocarburizing, are low cost, shortened production cycle as compared to carburizing and very small distortion of treated parts.

How it is done

Nitriding

Nitriding is normally performed at 500–520 °C in ammonia atmosphere in convection furnaces. The ammonia may be diluted with nitrogen or hydrogen. The parts to be nitrided are loaded on fixtures or in "baskets". Then the load is transferred to and put into the furnace. Cover or door is closed. The tightness of nitriding furnaces is most essential both for safety and because of the odour of ammonia gas. Purging of the furnace with nitrogen must be done before ammonia can be let into the furnace. This is to eliminate risk of explosion as ammonia and oxygen form an explosive mixture within a certain concentration range. It is for this reason advantageous also to perform heating to nitriding temperature in nitrogen. When nitriding temperature is reached, ammonia is let into the furnace. In the beginning a high flow rate is used to build up the nitrogen concentration in the steel surface as fast as possible.

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 must then be lowered just to give a nitrogen transfer rate from gas to surface, which keeps up with the diffusion rate. Nitriding is continued until the desired nitriding depth is reached. By purging with nitrogen again the ammonia gas is removed. Cooling should continue in nitrogen to avoid discolouration by oxidation. In pit furnaces normally the retort is lifted out of the furnace and put into a cooling station. In furnaces without retort cooling proceeds in the furnace.

Nitrocarburizing

Nitrocarburizing was first done in salt baths which still is a common method. Pit salt bath furnaces are used. Before loading the parts are normally preheated to about 400 °C in a separate atmosphere furnace. This is to ensure that the parts are not bringing moisture into the salt as this can cause explosion. Also the treating time in salt is reduced.

Nitrocarburizing in gas is, however, growing at the expense of the salt bath processes. The major reason is the improved enviroment. Also nitrocarburizing in gas is often preceeded by preheating in a separate furnace. As, in addition to nitrogen, carbon is to be trans-
ferred to the steel surface, the atmosphere should contain not only ammonia but also carbon monoxide and hydrogen. Principally the same type of furnaces as in gas nitriding could be used for such atmospheres but one special feature with nitrocarburizing is that the final cooling is (often) fast. Most commonly sealed quench furnaces of the same type as for carburizing are used. Thus, after loading and heating to process temperature there is a nitrocarburizing time corresponding to the desired compound layer or diffusion depth.

It has been the practice to maintain a constant gas composition and gas flow rate during the nitrocarburizing process. This practice is slowly changing very much due to the benefits and possibilities connected with the use of nitrogen based synthetic atmospheres. The AGA Nitroflex concept gives the possibility to optimize the atmosphere composition.

Type of final cooling media is determined from several requirements. As mentioned earlier cooling rate has an influence on properties like hardness and residual stresses in the diffusion zone. Thus, when 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 object the properties of the compound layer are decisive. Compound layer properties are not or to a small extent depending on cooling rate. Therefore cooling rate is unimportant in such cases. Of course increased cooling rate increases the risk of distortion and from this point of view as mild a cooling rate as possible should be applied.

**Plasma nitriding**

In a plasma nitriding furnace an electrical voltage is applied between workload, the cathode, and the furnace vessel, the anode. A vacuum of the order of a few torr is held 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 nitrogen ions bombard the load which results in nitriding of the steel. Hydrogen may be added to get proper reducing conditions.

One advantage with the plasma nitriding process is that the surface is highly activated, which means that e.g. stainless steels may be nitrided, which is not possible with other methods because of surface passivation. Another advantage is that the treatment temperature can be lower, down to 400–450 °C, than for other methods. Lower distortion is the result.

**Interaction between atmosphere and steel**

**Function of the atmosphere and steel**

The primary function of the atmosphere is to transfer nitrogen (and carbon) to the steel surface. The atmosphere composition must fulfill this function and also the requirement to give the right nitrogen (and carbon) surface concentration(s). Therefore the possibility to control the atmosphere composition which exists with the AGA Nitroflex system is advantageous.
In order to obtain an even result on all treated parts the gas composition should be the same throughout the furnace chamber. Forced gas circulation by fans is therefore required (although nitriding furnaces without forced gas circulation exist). At the fairly low treatment temperature 500–580 °C heat transfer is mainly controlled by convection, which is another reason to maintain good gas circulation.

Nitriding (nitrocarburizing) temperature is near or even below the ignition temperature for the gas mixture used. Therefore the gas system must ensure that explosive conditions cannot arise.

In summary the furnace atmosphere has the following functions:

- Maintain nitrogen (carbon) transfer
- Give correct nitrogen (carbon) surface concentration
- Transfer heat
- Maintain safety.

**Transfer of carbon and nitrogen**

Transfer of nitrogen from gas to the steel surface is given by ammonia, which decomposes at the surface enabling nitrogen atoms to be adsorbed and dissolved in the steel surface, figure 6.

Contrary to high temperature carburizing atmospheres nitriding atmospheres are in "non equilibrium". In fact ammonia concentrations used correspond at equilibrium to a nitrogen gas pressure of more than 1000 kbar. Thus, at the steel surface a high "nitrogen activity" is given from the ammonia. This nitrogen activity may be calculated from the equilibrium, \( \text{NH}_3 \rightarrow N + 3/2 \text{H}_2 \) with

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

where \( P_{\text{H}_2} \) and \( P_{\text{NH}_3} \) are the partial pressures of hydrogen and ammonia, which at atmospheric furnace pressure are the same as the volume-%-values divided by 100. \( N \) means nitrogen dissolved in the steel and \( a_N \) is the nitrogen activity. The equilibrium constant \( K \) is...
a function of temperature:

$$\log K = 6.196 - \frac{2943}{T}$$

where $T$ is to be given in kelvin.

Now what are $P_{NH_3}$ and $P_{H_2}$ in a real case?

If 100% $NH_3$ (ammonia) is added to the furnace, which is fairly normal in gas nitriding, some ammonia dissociates into nitrogen and hydrogen gas when the ammonia hits the hot furnace interior. This is expressed by the following reaction:

$$2NH_3 \rightarrow N_2 + 3H_2$$

The part of the ammonia which does not dissociate is called residual ammonia. In the expression for $a_\alpha$ above, $P_{NH_3}$ is thus the residual ammonia partial pressure (concentration) and $P_{H_2}$ is the partial pressure of hydrogen, formed by dissociation and if relevant in addition separately added hydrogen. Figure 7 shows experimental results on the relation between residual ammonia and added ammonia. For reference the figure also shows the line of no ammonia decomposition.

In nitrocarburizing carbon is transferred simultaneously with nitrogen. Carbon is provided to the steel surface by the reaction between carbon monoxide and hydrogen:

$$CO + H_2 \rightarrow C + H_2O$$
Carbon activity is expressed principally in the same way as nitrogen activity:

\[
a_c = K_2 \cdot \frac{P_{CO} \cdot P_{H_2}}{P_{H_2O}}
\]

with

\[
\log K_2 = -1.613 + \frac{1731}{T}
\]

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

\[
\frac{dm_N}{dt} = k_1 \left[ c_{N(gas)} - c_{N(surf)} \right]
\]

\[
\frac{dm_C}{dt} = k_2 \left[ c_{C(gas)} - c_{C(surf)} \right]
\]

Here \( m \) denotes mass, \( t \) time, \( c \) concentration per volume unit and \( k_1 \) and \( k_2 \) are reaction rate coefficients. (For convenience concentrations, \( c_N \) and \( c_C \), are used instead of activities, \( a_N \) and \( a_C \), as above.

From the expressions for mass transfer it is evident that there are principally two ways to influence the nitriding and carburizing rates. First the rate depends on concentrations of nitrogen and carbon in the gas. The higher the concentration the higher the transfer rate. This principle may be used to “boost” the process in the same way as in boost carburizing. There are upper limits on concentrations depending on risk for porosity and the requirement of right surface concentrations and compound layer microstructure. The second rate controlling parameter is the mass transfer coefficient. One may say that this coefficient contains the influence from a great number of parameters which are not known in detail. Atmosphere composition and surface conditions are major influences.

Transfer of nitrogen and carbon 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:

\[
\frac{dm}{dt}_{(comp \ layer)} = -D \frac{dc}{dx}
\]

\[
\frac{dm}{dt}_{(diff \ zone)} = -D \frac{dc}{dx}
\]

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

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

The slowest of these three steps will in each moment control nitrogen (carbon) transfer rate.
Growth of compound layer and diffusion zone

Gas nitriding

In gas nitriding the atmosphere is normally ammonia, possibly diluted by hydrogen or nitrogen. The compound layer formed consists predominantly of $\gamma'$-phase. The atmosphere composition expressed by the ratio $P_{NH_3}/P_{H_2}^{3/2}$ has influence on thickness of both compound layer and diffusion zone as indicated in figure 8. It should be emphasized that this figure refers to results in a furnace not equipped with a fan. With forced convection there is not such a notable effect on compound layer thickness from atmosphere composition.

![Figure 8. Changes in diffusion zone hardness gradient and compound layer thickness after nitriding of an Al-alloyed steel at 510 °C/24 h. The NH$_3$ content is varied between the different tests.](image)

![Figure 9. Relation between nitriding depth and treatment time for different steels. (Ref: Lightfoot, B.J., Jack D.H., Heat treatment 73. Metals Society, London.)](image)

Alloy content in the steel has an influence on compound layer thickness, which gets thinner with increased alloy content of the steel.

As $\gamma'$-phase is an almost stoichiometric compound, Fe$_2$N, with limited concentration variation, it follows that the driving force for diffusion, equal to the concentration difference [nitrogen at surface] minus [nitrogen at interface nitride/diffusion zone], is small. Growth rate of the compound layer is therefore relatively low.

Diffusion zone thickness increases parabolically with time. For a certain time and temperature the depth is lower for high alloy steels, figure 9. This can be understood from the fact that alloying elements...
like chromium trap nitrogen when forming nitrides. More nitrogen atoms thus have to diffuse into the steel to reach a certain depth as compared to the case when no alloy elements trap nitrogen.

**Nitrocarburizing**

A major difference between nitrocarburizing and nitriding is that the \( \varepsilon \)-phase forms to a great extent in the former case. There is a wide concentration range for nitrogen as well as for carbon in the \( \varepsilon \)-phase. From this follows that the driving force for diffusion, [concentration at surface] minus [concentration at interface compound layer/diffusion zone], may be high. Also the effect of the higher temperature at nitrocarburizing must be taken into consideration as the diffusion coefficients for nitrogen as well as for carbon are increased. The thermodynamical stability of the \( \varepsilon \)-phase will at the higher temperature also increase. Therefore also the compound layer growth rate may be high. It is then important to note that the concentration at the surface is given by the atmosphere nitrogen and carbon concentrations. These concentrations vary greatly between atmospheres. This is part of the reason why the same treatment time and temperature can result in very different compound layer thickness, porosity and microstructure.

Increasing alloy content of the steel means decreased compound layer thickness, figure 10, as for gas nitriding. Also decreased carbon content of the steel will decrease the compound layer thickness.

![Figure 10. The thickness of the compound layer decreases with increasing alloying content of the treated steel for a given treatment time.](image)

The outer part of the compound layer is somewhat porous. Pores are formed at discontinuities (grain boundaries, slag inclusions) because of the denitriding step:

\[
2\, N \rightarrow N_2
\]

As equilibrium nitrogen gas pressures are very high, the pressure is high enough to create porosity (see Section "Transfer of carbon and nitrogen", page 10).

The depth of the diffusion zone follows the same rules as in nitriding.
Postoxidation

A remarkable improvement in corrosion resistance is obtained if nitrocarburizing is followed by a short oxidation at about 450 °C. A 1–2 µm thick Fe₃O₄ layer is formed on top of the compound layer. Properly done the oxidation treatment gives the processed parts an aesthetically attractive black colour. The first gaseous process was developed by Lucas, England, and is called Nitrotec. It is based on the Nitemper process to which is added an oxidation treatment in air. Other oxidation methods using for example water vapour or nitrous oxide (N₂O) have later on been used.

Control of atmosphere composition

In comparison with high temperature process atmospheres, e.g. for carburizing, the degree of atmosphere control in practice is low. Normally just the ingoing gas flow rates and mixtures are measured. There are three major reasons to this: The first is that proper gas analyzing methods and instruments are lacking. The second reason has been the uncertainty what control parameters should be used. A third reason is that used atmosphere systems have not given a possibility to change composition. The AGA Nitroflex system, however, gives this possibility.

Gas nitriding

As shown under "Transfer of carbon and nitrogen", the atmosphere nitrogen activity is proportional to the ammonia (residual) content and is inversely proportional to the hydrogen content to the power 3/2. Based on this there exist two control methods. The first is to measure and control the residual ammonia content. This can either be done by direct analysis of NH₃ or indirectly by H₂-analysis. This is the basis of the so called Floe process, in which the residual ammonia content is controlled by changing the ammonia inlet flow rate. At a high flow rate most ammonia remains undissociated but at low flow rates it dissociates into nitrogen and hydrogen because the residence time in the furnace is long enough. A nitriding process starts with high flow rate (= high residual ammonia = high nitrogen activity) 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-%. The degree of dissociation is however very much depending on the total area of catalyzing surfaces in the furnace. Area and thus size of load is important as are furnace retort or fixture surfaces.

A more advanced method to control the nitrogen activity is by hydrogen addition, as in the AGA Nitroflex ACH system. In such a case the atmosphere nitrogen activity can be varied over much wider range than is possible by just changing the ammonia flow rate. To maintain accurate controllability it is then required to combine hydrogen and ammonia gas analysis.

It is also possible to dilute ammonia with nitrogen, the AGA Nitroflex A system. The effect on nitriding potential is then limited, but from the viewpoints of safety and economy it may be advantageous.

As shown in figure 11, the nitriding potential, P_{NH₃}/P_{H₂}³/², determines which phase that will form in the compound layer, γ' or ε.

Figure 11. Nitriding potential, P_{NH₃}/P_{H₂}³/², determines type of phase formed, ε or γ'.
compound layer is formed. Thus, it is possible to nitride without "white layer". Compare with figure 8.

Although atmosphere nitrogen activity is the major control parameter there are some other composition parameters that influence the compound layer thickness and microstructure. However, they do not influence diffusion zone depth as this is controlled by the interface (compound layer/diffusion zone) concentrations and these are not influenced by the atmosphere. Small additions of oxidants like air, CO₂ or N₂O, have shown to increase the compound layer thickness.

**Nitrocarburizing**

The same principles as for nitriding control are valid. In addition there is a desire to control the atmosphere carbon activity. This will be covered more in detail in the following chapter “AGA’s concept”. At this point we may just note that both nitrogen and carbon activities vary very much between different commercially applied atmospheres.

Nitrocarburizing atmospheres exhibit a more complex composition containing NH₃, H₂, CO, CO₂ and H₂O. Gas analysis of a such atmosphere is difficult depending on precipitation of ammonium carbonate clogging the sample gas pipes. Heating the gas sample lines is one way to overcome this problem.

![Figure 12. Examples on residual ammonia concentration variations during nitrocarburizing cycles in a sealed quench furnace. The "b"-cycle was the same as the "a"-cycle with the exception that the furnace was preconditioned with active atmosphere in the "b"-cycle.](image)
Figure 12 gives some examples on analysis of residual NH$_3$ in a process where 50 % NH$_3$ + 50 % endogas was introduced into the furnace. From the figure the fairly large variation in residual ammonia content should be noted although the same gas flow ratios and mixing ratios were used. It should also be noted that obtained depths on compound layer and diffusion zone correlate positively with residual ammonia analysis results.

**AGA Nitroflex system for nitrocarburizing**

**Basic approach**

AGA did take a fundamental approach in the development of a nitrocarburizing atmosphere. By consulting the ternary Fe-C-N phase diagram guidelines are obtained for the relation between atmosphere nitrogen and carbon activities and compound layer structure. From such a phase diagram it is for instance found that carbon activities of commercial atmospheres, in particular the Nitemper atmosphere, are much too high, compare the figures 13 and 14. From practice it is known that sooting may be a problem in furnaces running with such atmospheres for a long time. Such a phase diagram also tells us that it is impossible to get a compound layer of ε-phase on pure iron or low carbon steels if the atmosphere does not contain carbon (compare processes based on N$_2$/NH$_3$/N$_2$O-mixture).

These basic facts led AGA to compose the atmosphere from a mixture between nitrogen, ammonia and carbon dioxide. Ammonia answers as usual for the nitriding action. CO$_2$ constitutes the carbon source in the atmosphere. It should be noticed from figure 14 that

<table>
<thead>
<tr>
<th>Added gas mixture</th>
<th>Quasi equilibrium composition (vol-%)</th>
<th>Activities $^1$</th>
<th>Activities $^1$</th>
<th>Activities $^1$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>N$_2$</td>
<td>H$_2$</td>
<td>CO</td>
<td>H$_2$O</td>
</tr>
<tr>
<td>50 % Endogas 50% NH$_3$</td>
<td>24.1</td>
<td>25.9</td>
<td>9.0</td>
<td>0.76</td>
</tr>
<tr>
<td>40% Endogas 10% Air 50 % NH$_3$</td>
<td>29.2</td>
<td>24.3</td>
<td>6.7</td>
<td>2.46</td>
</tr>
<tr>
<td>5 % CO$_2$ 60 % N$_2$ 35 % NH$_3$</td>
<td>58.8</td>
<td>15.5</td>
<td>2.9</td>
<td>2.98</td>
</tr>
<tr>
<td>5 % CO$_2$ 5 % CO 55 % N$_2$ 35 % NH$_3$</td>
<td>54.4</td>
<td>15.9</td>
<td>6.4</td>
<td>2.22</td>
</tr>
<tr>
<td>5 % CO$_2$ 20 % H$_2$ 45 % N$_2$ 30 % NH$_3$</td>
<td>45.4</td>
<td>26.6</td>
<td>3.4</td>
<td>3.50</td>
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</tbody>
</table>

$^1$ The reference stated for the activity values are nitrogen gas at 1 atm, graphite and wüstite, FeO, for nitrogen, carbon and oxygen respectively.
such an atmosphere has much lower carbon activity than i.e. the 50% endogas/50% NH₃ atmosphere.

In Section “Transfer of carbon and nitrogen” page 11, it was stated that the main carbon transfer reaction is:

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

Thus, carbon dioxide must be reacted at least partially to carbon monoxide. This is achieved by the reversed water gas reaction:

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

Hydrogen needed for this reaction originates from dissociated ammonia or by separate addition of hydrogen. Figure 15 shows that CO forms in this way. The reaction is catalyzed by furnace walls, retort and load. The atmosphere for nitrocarburizing consists of 20–50% ammonia, 2–20% carbon dioxide and the balance nitrogen, depending on what furnace equipment is used and what properties that are desired. From experiments has been found that an addition of about 5 vol-% CO₂ is in many cases proper. This should be changed and adapted to the actual case to give optimum results.

The N₂/NH₃/CO₂ system, AGA Nitroflex AC, gives in addition to nitrogen activity control also the possibility of carbon activity control, which is not possible with other existing methods. In the figures 16 and 17 is shown how this control is possible by adjusting the atmosphere concentrations of CO₂ and NH₃. This possibility is of great value when optimizing compound layer properties for different steels especially with different carbon contents.

The gas system may be further developed by hydrogen addition which gives improved nitrogen and carbon activity control. With the AGA 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. Degree of porosity and compound layer

![Figure 15. Relation between added amount of CO₂ which reacts to CO.](image-url)
thickness is possible to control in this way. Examples of the influence on compound layer microstructure from atmosphere composition are shown in figure 18. For high nitrogen activities meaning a high ratio for $P_{NH_3}/P_{H_2}^{2/3}$ the compound layer is thick and has extensive porosity. However, by reducing the treatment time the porosity is decreased. The thickness of the compound layer will then also be lesser.

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**Figure 16.** Theoretical carbon and nitrogen activity for different ammonia additions.

**Figure 17.** Theoretical carbon and nitrogen activity for different carbon dioxide additions.
By adjusting the nitrogen activity it is possible to achieve both high growth rate and a low degree of porosity. High carbon activity favors formation of ε-phase.

**Postoxidation**

By combining nitrocarburizing in an atmosphere just described with post oxidation in air or nitrous oxide, AGA Nitroflex ACO, the same order of improvement in corrosion resistance will be obtained as after the Nitrotec and QPQ processes, figure 19.

Treatment time in normal nitrocarburizing processes is limited on low alloy, low carbon steels by the fact that porosity and thickness of the compound layer reach too high values. Poor adherence and low hardness result. From these facts it is experienced that a treatment time of 1 1/2 to 3 hours is optimum. As shown by the micrographs in figure 18, however, it is in principle possible to control both porosity and compound layer thickness by adjustment of the furnace atmosphere composition.
Now, if shortest possible cycle for a certain compound layer thickness is the goal, these basic facts should be utilized. This is achieved if the atmosphere composition is changed during the cycle.

The principles given make it possible to adjust the atmosphere composition to give optimum properties for a certain steel. A few examples:

- During nitrocarburizing of medium or high carbon steels carbon is donated to the compound layer by the steel. The atmosphere carbon activity then is less important, which explains why carbon free atmospheres work in such cases (compare the NH$_3$/N$_2$O/N$_2$ system) although such atmospheres are pure "nitriding" and not "nitrocarburizing" atmospheres.

- On low carbon steels it is on the other hand a requirement that the atmosphere has a balanced carbon activity to give a good compound structure with mainly $\varepsilon$-phase.

There are several ways possible to adjust the nitrogen activity and the carbon potential of the atmosphere. 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. A more
sophisticated way to adjust the nitrogen activity is to add hydrogen to
the atmosphere. The AGA Nitroflex concept, hence, makes it possi-
ble to adjust the nitrocarburizing atmosphere composition to type of
furnace as well as to the stage of the process cycle.

System design

With reference to figure 20, the gas supply system has a gas storage
for liquid nitrogen and normally gas cylinders for ammonia and
carbon dioxide respectively. From the storage, gases are led via
pipes to the mixing panel. Here the flow rates are controlled. Ammo-
nia is here mixed into the nitrogen line but a separate line is needed
for carbon dioxide to the furnace. If carbon dioxide is mixed with the
ammonia there will be unwanted reactions leading to ammonium
 carbamate formation, which deposits in the line leading to clogging
and flow disturbances.

If flow rates are controlled with mass flowmeters there is opportunity
for flow rate and mixing control from a program in a process com-
puter. Thus, the potential advantage of flexibility in flow rate may be
utilized to control e.g. the level of oxygen, nitrogen and carbon
activities.

Gases enter the furnace through a specially designed injector, figure
21, built up by two concentric tubes. In the outer wider tube the
nitrogen/ammonia mixture passes. Carbon dioxide flows through the
inner tube, which extends into the furnace. Thus, all three gases do
not "meet" each other until they reach the hot furnace interior and
this is essential in order to avoid the above mentioned formation of
ammonium carbamate.
Safety

The AGA Nitroflex system utilizes typically only about 40 vol-% of ammonia which is the only flammable gas component in the ingoing gas mixture. This can be compared to the 50 vol-% endogas + 50 vol-% ammonia process, Nitemper, which holds totally approximately 80 vol-% hazardous components (H₂, CO, NH₃).

To ensure safety it is, however, important to follow safety guidelines. The major safety aspect to be taken care of is that the process temperature is below or near the ignition temperature. Thus if air (oxygen) enters into a furnace the atmosphere is not ignited and will not burn as compared to high temperature processes like carburizing and carbonitriding. Therefore if not controlled it may happen that a great amount of a flammable ammonia + air mixture forms which could explode if ignited by a flame or spark.

The AGA Safety Triangle, figure 22, tells principally how to operate safely. The flammability triangle is depicted in the area L-S-U and

![Figure 22. AGA safety system, flammability triangle.](image)

For mixture in air at 200 °C and 1.0 bar (a)
(L) Lower flammability limit in air = 5.1 vol% mixture
(U) Upper flammability limit in air = 43.5 vol% mixture
(S) Min O₂ -conc. for flammability = 4.6 vol% (Fuel = 5.1 vol %)
(C) Start up = max 4.9 vol% oxygen
(B) Shut down = max 6.5 vol% mixture

For mixture in air at 580 °C and 1.0 bar (a)
(L) Lower flammability limit in air = 0.2 vol% mixture
(U) Upper flammability limit in air = 49.8 vol% mixture
(S) Min O₂ -conc. for flammability = 0.2 vol% (Fuel = 0.2 vol %)
(C) Start up = max 0.2 vol% oxygen
(B) Shut down = max 0.2 vol% mixture

A safety factor is not included in the data given above!
this area should always be avoided. This is done in the following way. When starting up a process where the furnace is partly or wholly filled with air one must not introduce ammonia until the oxygen concentration has been lowered to point C. This may be done by purging the furnace with nitrogen. Number of required purging furnace volumes may be taken from principal purging curves. Now, when point C is reached, ammonia can be safely introduced.

From these diagrams it can be seen that an oxygen content exceeding 5.8 % at 580 °C makes the atmosphere flammable. The air content in this gas volume should therefore not exceed 27 %. At 200 °C the maximum allowed oxygen content is around 8 % corresponding to an air content of 36 %. As the auto ignition point for this mixture is about 580 °C the risk for explosions must be considered to be located to all volumes in the furnace.

If nitrocarburizing is done, i.e. in a pit furnace, a reversed sequence is required before closing the process and opening the furnace. The ammonia concentration must now be lowered to point B before the furnace can be opened and exposed to the air.

Many furnaces which are built for nitrocarburizing have a flame curtain at the furnace door. In such cases there is not a requirement to purge with nitrogen before opening the doors. In all cases a pilot burner must be installed. This pilot burner has the function to burn the outgoing gas mixture to ensure that ammonia is not causing odour and safety problems. Also by burning the outlet gas, entrance of air backways into the furnace is avoided.

Results with the AGA Nitroflex system

The AGA Nitroflex nitrocarburizing system has the inherent advantages of synthetic in situ generated atmospheres. Flow rate and mixing (composition) flexibility are major advantages, which efficiently utilized lowers cost, improves quality, is a potential for increased productivity and ensures safety.

A carbon activity much lower than in systems using endogas together with a higher oxygen activity is a major feature. Due to this fact it is the experience that a faster growth rate of the compound layer is obtained. It is found that alloyed steels like hot work tool steels obtain a thicker and more even compound layer. Thus, the AGA Nitroflex process means increased productivity.

The balanced carbon activity means that the driving force to deposit soot in furnaces is low.

The AGA Nitroflex nitrocarburizing system gives an opportunity to optimize the gas composition both in relation to type of steel and to the different stages in the process with respect to the major concern: wear resistance, fatigue resistance or corrosion resistance.

Postoxidation with air or N₂O gives aesthetically attractive black surfaces with markedly improved corrosion resistance.

Figure 23. Compound layer thickness for different atmospheres showing faster growth for the AGA Nitroflex system.