

# **Properties of Nitrided Components – a result of the material and the Nitriding process**

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## PROPERTIES OF NITRIDED COMPONENTS – A RESULT OF THE MATERIAL AND THE NITRIDING PROCESS

Ovako has an extensive R&D since many years, an area that now is in an even higher intensity. Some of the R&D work is published in our technical reports.

Due to that Ovako of today has had a number of different company names and used various trade marks we have until now chosen to not have these reports publicly available. However, many of these technical reports contain valid data about material and steel grades that we still promote, but with other names etc.

The following Technical Report from 1999 is about both the Nitriding process in general and a specific Ovako grade very suitable for Nitriding, Ovako 225.

Data and processes in this report represent state of art at time of publishing, that still in many cases are used.

Ovako 225 is a grade is part of our current offer. In the Ovako Steel Navigator this material is described under the version names Ovako 225A and Ovako 225C.

In this Technical Report there is used the following Company names and trade marks that no longer is used by Ovako AB.

Ovako Steel; This company name is no longer used. The organization is now part of Ovako AB.

## **Technical Report 1/1999**

# **Properties of Nitrided Components – A Result of the Material and the Nitriding Process**

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## **OVAKO STEEL**

Ovako Steel is the world's leading manufacturer of bearing steel and a major producer of other special engineering steels. We are a fully owned subsidiary in the SKF group.

Our main strength is in the field of long special engineering steel products – seamless tube, bar, and surface removed wire. Rolled rings are also a specialty. A large part of the production is further processed by machining. This share is increasing and illustrates our intention to progress towards further processing and higher specialization.

The most important customer segments are the rolling bearing industry, the automotive industry together with their subcontractors as well as the rock drilling and general engineering industries.

We have manufacturing units in Sweden, France, the U.K and the United States. Steel production is confined to Hofors, in Sweden. The production capacity is approx. 500,000 tonnes of special engineering steel per year.

### **Research & Development**

Our R&D mission is to pursue an efficient product and process development, adapted to existing and new technology, and within our product areas be recognized as the world leader in metallurgy, materials technology, machinability and metal cutting technology as well as heat treatment. The ultimate target is to offer our customers the best total economy in their production.

## **Bodycote Metal Technology**

In January 1997 Brukens became a member of the Bodycote Group. Bodycote is a British holding company with subsidiaries carrying on business in the fields of materials technology and metal processing. The name Bodycote Metal Technology represents high quality service in Heat Treatments, Metallurgical Coatings, Materials Testing and manufacture of special steel and metal products using the Hot Isostatic Pressing technology. Bodycote currently provide a range of metallurgical processing services from 195 Service Centres in 20 countries.

## Abstract

The report shows briefly how the nitridability of steel is influenced by different material and heat-treatment factors. The effects on nitriding rate, mechanical properties, tribological properties and corrosion properties are addressed.

The different nitriding and nitrocarburizing processes are reviewed. The advantages and disadvantages of different processes are described, as well as how component properties can be controlled with the process parameters.

An Ovako Steel nitriding steel, Ovako 225A, is presented. The steel's behaviour during hardening and tempering, machining, nitriding etc. is covered and the possibilities and advantages of using Ovako 225A as an alternative to different steel grades and heat treatments are discussed.

## 1. Introduction

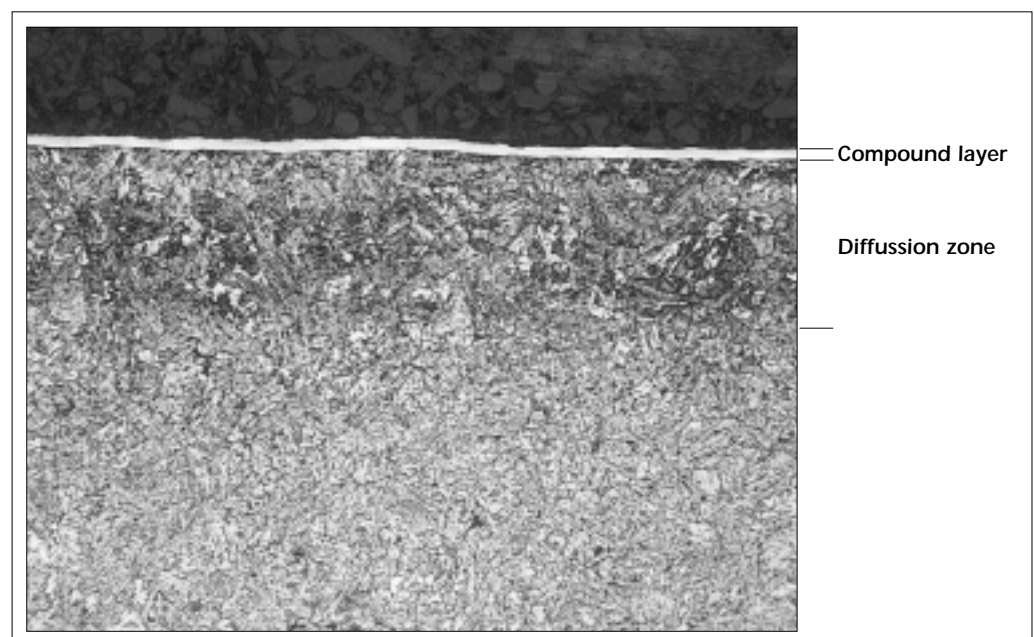
The surface zone is very often the most stressed part of a component. The stresses are highest in the surface zone during bending and twisting and it is the surface that is exposed to tribological and chemical attack. It is therefore natural that a number of methods to improve the surface properties have been developed.

Nitriding and nitrocarburizing are thermo-chemical case hardening processes. Both processes are used for improving mechanical properties, tribological properties and corrosion properties. These improvements are obtained due to structural changes in the surface zone that a nitrided/nitrocarburized component is subject to.

A nitrided/nitrocarburized surface consists normally of two layers, a thin  $<30\text{ }\mu\text{m}$ , "white" nitride/carbo-nitride layer called a compound layer and beneath, the diffusion zone which can vary in depth up to about 0.6 mm (*Figure 1*).

The compound layer determines the tribological properties and the corrosion properties. The diffusion zone determines mechanical properties through its hardness and depth.

Nitriding and nitrocarburizing are often favourable alternatives to heat-treatment processes such as carburizing, induction hardening, hardening and tempering etc. The major advantages with nitriding/nitrocarburizing are the minimal dimensional changes and distortions of the treated component due to the low process temperature and the fact that the core of the component does not undergo structural changes.



*Figure1. Nitrocarburized surface zone. Micrograph 200 times magnification.*

## 2. Nitridability of Steel

### 2.1 Nitriding Rate

The main factors governing the depth and structure of the compound layer and the diffusion zone are nitrogen/carbon activity, treatment temperature, treatment time, and the process utilised, but steel composition also has a significant effect on the nitriding rate.

Nitriding is, like carburizing, basically a diffusion controlled process and the nitriding depth is thus controlled by the temperature and time. A certain time advantage exists however for plasma nitriding due to faster nitrogen saturation of the surface, which gives a somewhat higher nitriding rate at the start of the nitriding process. For longer nitriding times, and in comparison with the importance of the temperature, the effect on the nitriding time is however marginal.

The deepest nitrogen-inflicted cases are attained when the steel has low carbon and alloy contents. *Figure 2* shows the nitrogen diffusion coefficient as a function of the carbon content.

*Figure 3* shows the nitriding depth as a function of the nitriding time for some steel grades with different alloy contents. The more alloyed steel grades have more shallow hardness profiles.

The advantage of having a low alloy content for improving the nitriding rate is in conflict with the need to have a high alloy content for getting a high surface hardness, high hardenability, etc.

*Figure 4* shows the depth of the compound layer as a function of the temperature.

The compound-layer thickness increases with an increasing temperature and reaches a maximum at about 580°C. At low temperatures the layer is thinner because of a low diffusion rate. At high temperatures the thickness is smaller due to a decreasing partial pressure value ( $P_{NH_3}/P_{H_2}^{3/2}$ ) which decreases the nitrogen activity in steel in equilibrium with the gas atmosphere.

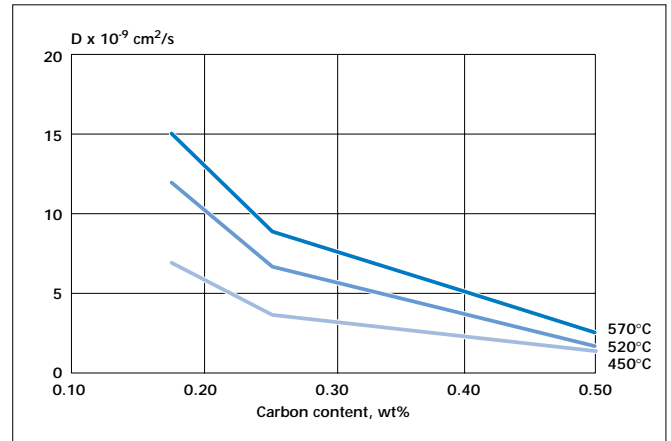


Figure 2. Nitrogen diffusion coefficient as a function of the carbon content at various temperatures. Ref. 1.

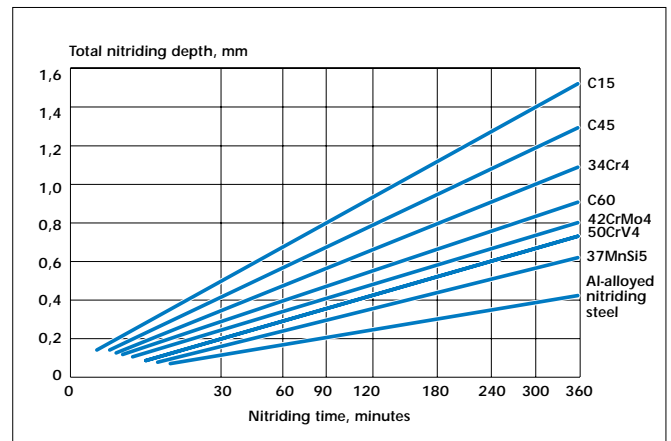


Figure 3. Nitriding depth as function of the nitriding time. Salt bath nitriding. Ref. 2.

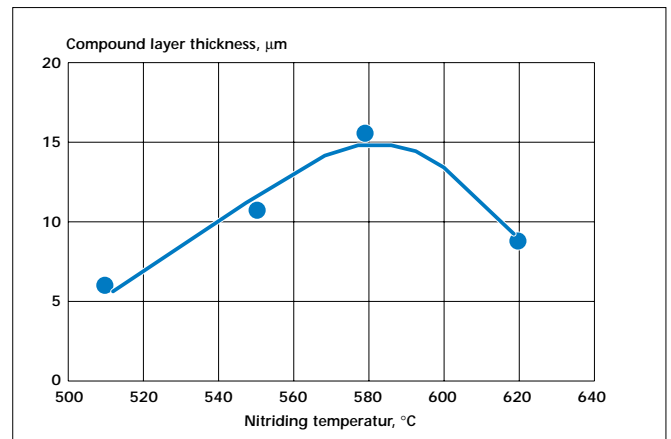


Figure 4. Compound-layer thickness as a function of the nitriding temperature. Ref.3.

## 2.2 Mechanical Properties

### 2.2.1 Hardness

The hardness decreases with an increase in carbon content and increases with an increase in the content of nitride forming elements as chromium, molybdenum, vanadium, aluminium and titanium.

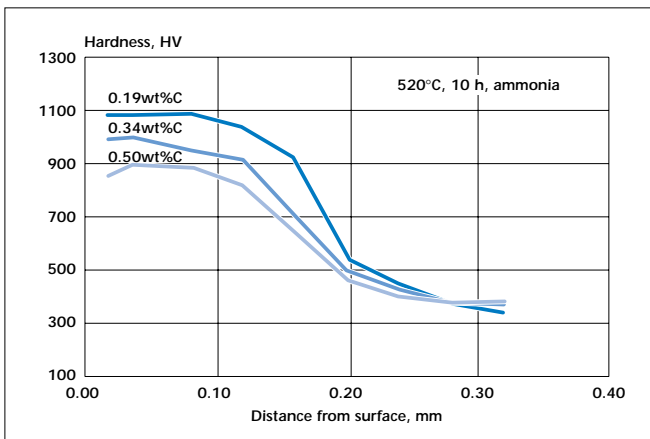
The hardness of the diffusion zone is determined by two hardening mechanisms: solid solution hardening and/or precipitation hardening.

Solid solution hardening is most important for low-alloyed steels and precipitation hardening is the predominant mechanism for alloyed steels.

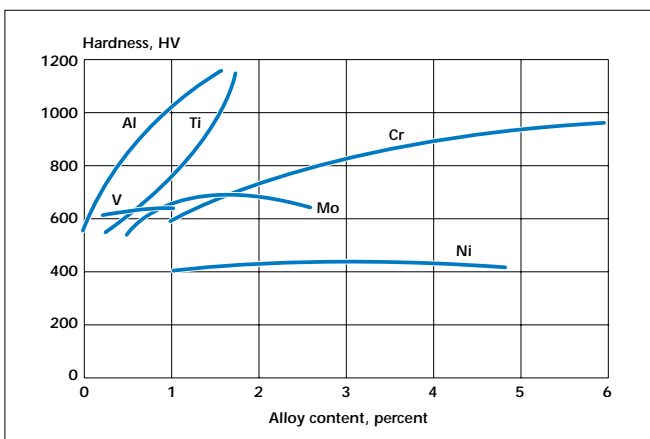
The effect of carbon content on the hardness profile is shown in *Figure 5*. The more carbon in the steel, the more chromium is tied up in the form of carbides and the less chromium is available to form chromium nitrides.

*Figure 6* shows the influence of nitride forming elements on hardness.

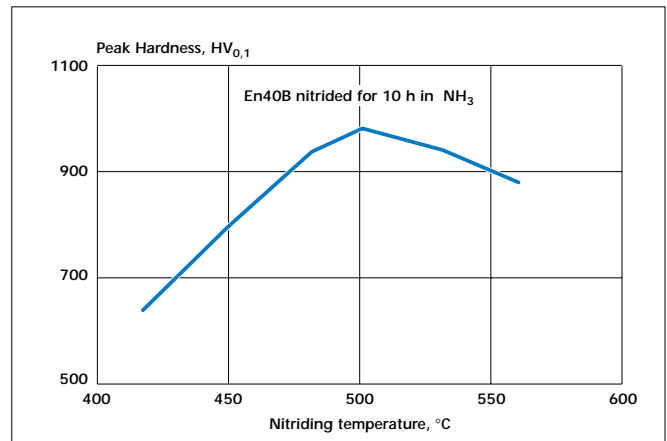
The strong nitride formers, aluminium and titanium have a pronounced effect on hardness even at small concentrations, but the case is shallow and brittle and may exfoliate in service.



*Figure 5. Effect of carbon content on the hardness profile. Plasma nitriding, chromium-alloyed steel. Ref.1.*



*Figure 6. Hardness as a function of the content of nitride-forming elements. Ref.4.*



*Figure 7. Hardness as a function of the nitriding temperature. Ref.1.*

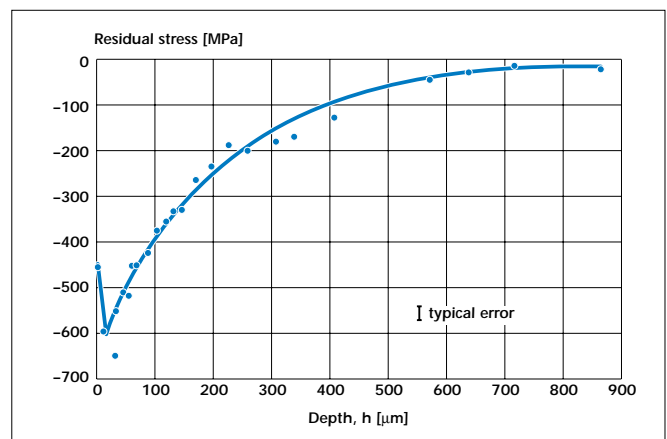
Surface hardness is also strongly influenced by the nitriding temperature (*Figure 7*). Maximum hardness is attained at approximately 500°C.

At the lowest temperature the nitrogen take up and precipitate density are low and therefore the hardness increase is low. At higher temperatures and/or longer treatment times both precipitate growth and tempering of the matrix become important.

### 2.2.2 Fatigue Properties

Nitriding improves fatigue properties considerably by increasing hardness and inducing compressive surface residual stresses. These residual stresses are created through the solution and precipitation hardening in the diffusion zone.

*Figures 8 and 9* show the residual stress depth profile respectively fatigue test results for a low alloyed quenched and tempered material with a ultimate tensile strength of 873 MPa. The fatigue test specimens were plasma nitrided at 480°C for 24 hours.



*Figure 8. Residual stresses as a function of the distance from surface. Ref. 5.*

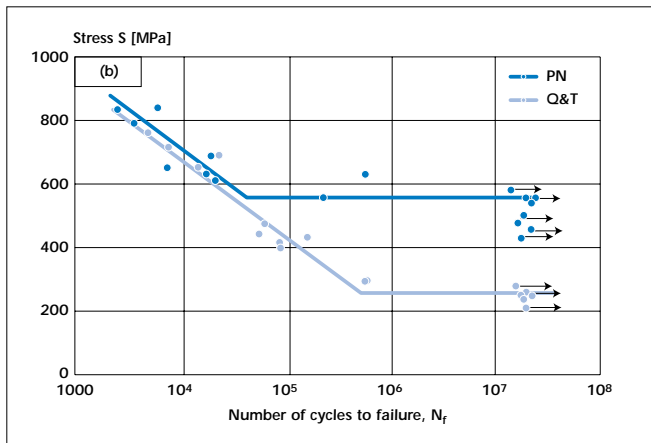


Figure 9. Fatigue test results, notched specimens. Quenched and tempered (Q+T) and plasma nitrided (PN). Ref.6.

The plasma nitriding improved the fatigue limit by 53% with respect to smooth specimens and by 115% with respect to notched specimens.

A thick porous and brittle compound layer can initiate fatigue cracks.

## 2.3 Tribological Properties

Figure 10 schematically shows the wear resistance of the different surface zones of a nitrided/nitro-carburized component.

The outer part of the compound layer usually contains pores and has in general a relatively low wear resistance due to bad mechanical properties.

The next zone, the porous-free part of the compound layer, has very good wear resistance due to the non-metallic character of the hard nitrides and carbonitrides.

The diffusion zone has a lower wear resistance which is reduced as a function of the depth below the surface.

The porous outer part of the compound layer may serve as a lubricant reservoir and can therefore

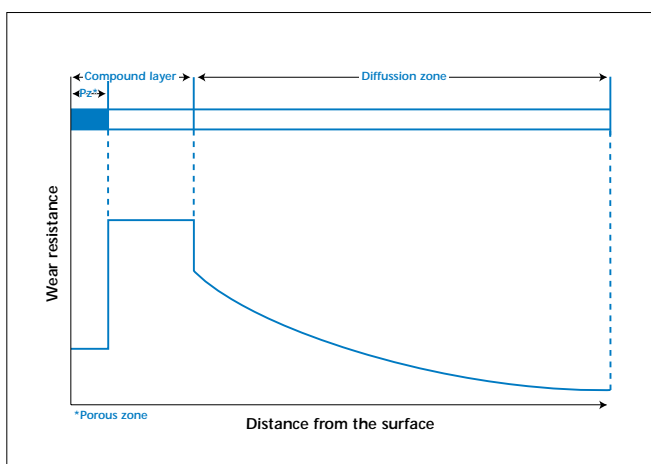


Figure 10. Schematic illustration of wear resistance as a function of the distance from the surface. Ref. 6.

be beneficial to e.g. oxidation wear. The porous zone also has a positive effect on the running in of nitrided components.

Generally the amount of pores increases with treatment time, nitrogen activity and low alloying element content.

Figure 11 shows wear test results under combined rolling-sliding contact traction.

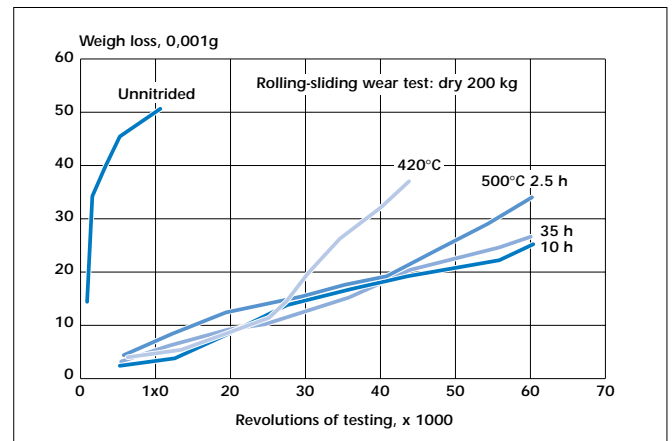


Figure 11. Rolling-sliding wear curves generated for different nitriding treatments. Ref.1.

## 2.4 Corrosion Properties

The compound layer created when nitriding and nitrocarburizing considerably increases corrosion resistance.

There are several ways of improving the corrosion resistance effect of the compound layer by having different additives in the furnace atmosphere e.g. oxygen. These techniques are described in part 3, Nitriding Processes.

Figure 12 shows corrosion resistance of hard chrome plating, chemical nickel plating and nitriding plus post oxidation.

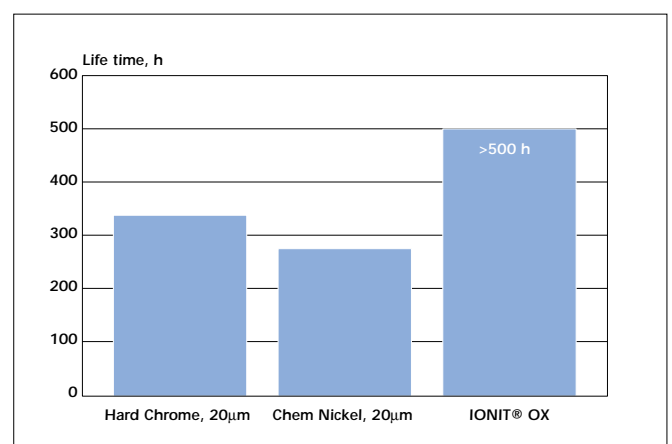


Figure 12. Corrosion resistance of hard chrome plating, nickel plating and nitriding plus post-oxidation in salt spray test according to DIN 50021 SS. Ref. 7.



### 3. Nitriding/ Nitrocarburizing Processes

#### 3.1 Terminology

The terminology often creates confusion to people not directly involved in heat treating and especially the difference between nitrocarburizing and carbonitriding often creates misunderstandings. Nitriding is the term for gas nitriding in ammonia and it is a process where only nitrogen is added to the surface. In nitrocarburizing the main element transferred to the surface is nitrogen but in addition also a small amount of carbon. Carburizing is the term for adding only carbon and in carbonitriding the main element is carbon with the addition of a small amount of nitrogen.

One very important difference is that nitriding and nitrocarburizing are low-temperature processes whereas carburizing and carbonitriding are high-temperature processes. “Low temperature” means a temperature below the one where the transformation to austenite starts and “high temperature” is above the same temperature. The advantage of the low-temperature processes is less distortion of the treated parts, which eliminates costly grinding operations, shortens the production cycle and decreases the costs.

There are a lot of nitrocarburizing processes on the market with different trade names and if the heat-treatment terminology creates confusion, the different trade names of the various nitriding/nitrocarburizing processes do not make it easier (Figure 13).

*The processes can be organised into three groups related to the process medium, which may be gas, salt or plasma.*

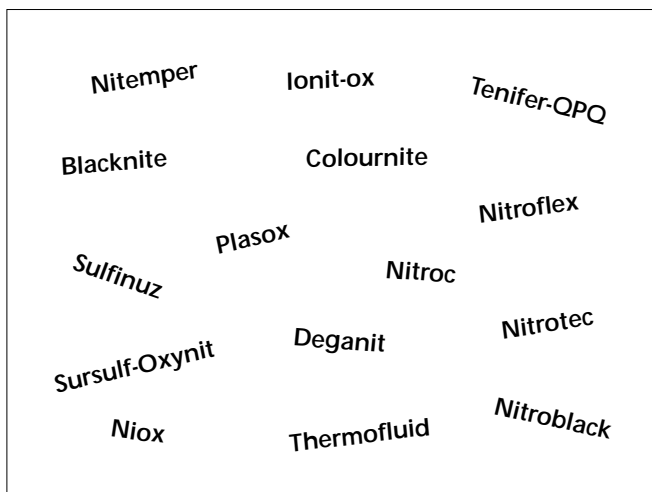


Figure 13. Trade names of some nitriding/nitrocarburizing processes.

#### 3.2 Gas Processes

##### 3.2.1 Nitriding

Nitriding is the term primarily used for the classical gas nitriding in ammonia developed during the 1920s. The process temperature is 500-520°C and to obtain sufficient case depth the nitriding time required is very long, commonly 24-60 h.

The traditional nitriding process is controlled by monitoring the degree of dissociation of the ammonia. There is a risk that the surface can be “over nitrided”, which can result in a brittle compound layer that has to be removed.

##### 3.2.2 Nitrocarburizing

Nitrocarburizing is always done in an atmosphere containing more or less ammonia together with other gases. The gaseous mixture is different between the various commercial processes and for some major technologies the mixture is the following:

Nitemper	$\text{NH}_3 + \text{endogas}$
Nitroc	$\text{NH}_3 + \text{exogas}$
Deganit	$\text{NH}_3 + \text{endogas} + \text{exogas}$
Nitrotec	$\text{NH}_3 + \text{endogas} + \text{air}$
Colournite	$\text{NH}_3 + \text{N}_2 + \text{CO}_2 + \text{H}_2$ (+ air/ $\text{N}_2\text{O}$ / $\text{H}_2\text{O}$ )

The properties of nitrocarburized components depend on the surface microstructure and the hardness. The compound layer is 2-30  $\mu\text{m}$  thick and consist of  $\epsilon$ -phase with variable composition of carbon and nitrogen ( $\text{Fe}_2\text{NC}_{1-x}$ ) and/or  $\gamma'$ -phase ( $\text{Fe}_4\text{N}$ ) depending on atmosphere and steel grade. Tribological properties such as friction, wear and corrosion resistance are mainly determined by the compound layer.

The  $\gamma'$ -phase can cause brittle layers whereas the  $\epsilon$ -phase has higher ductility and it is very important that the process can be controlled in order to optimise the properties in the compound layer. The diffusion zone goes deeper into the steel, 0.1-0.6 mm, and the load bearing capacity, static and fatigue strength are largely determined by this zone.

Normally the same type of furnaces are used for nitrocarburizing as for carburizing and that is pre-heating/tempering furnaces and sealed quench furnaces. To some extent belt furnaces and fluidized beds are also used. The processing temperature is 560-580 °C and the processing time is normally 2-3 h.

### 3.2.3 The Colournite Process

The possibilities to control the gas mixture during the process, in order to vary for example the nitrogen activities and by that be able to design the composition and thickness of the compound layer, are limited with today's standard nitrocarburizing processes.

Therefore Brukens has developed a new process together with SKF and AGA called Colournite. The background was new more demanding customer requirements and one product was cages for spherical roller bearings. To meet the requirements, it was not only necessary to find a better nitrocarburizing process, but we also had to design a new furnace, which we did together with Ipsen (*Figure 14*).

With the Colournite process all gases are added and controlled separately which gives very good possibilities to produce tailor-made layers. The reason why the process is called Colournite is because by applying different postoxidation methods very attractive surface colours such as black, yellow/gold, silver and blue can be obtained. AGA is marketing a similar process called Nitroflex.

By combining nitrocarburizing with post-oxidation the improvement in corrosion resistance is considerable. The thickness of the oxidised zone is 1-2  $\mu\text{m}$ , (*Figure 15*).

The treatment time in standard nitrocarburizing processes is limited for low-alloy steels by the fact that porosity and thickness of the compound layer

reach too high values which result in poor adherence, low hardness and lower corrosion resistance. With the Colournite process and similar processes, however, it is possible to control both porosity and compound layer thickness by adjustment of the furnace atmosphere composition.

Today nitrocarburizing in gas is the fastest growing heat-treatment process. Today's techniques provide excellent opportunities to produce tailor-made surface layers that meet the increased property requirements of components.

### **3.3 Salt-bath Processes**

The first salt bath for nitrocarburizing was introduced in 1929 but it was not until the middle of 1960s that the use of the process became more widespread. Initially the bath consisted of cyanide-based salts and the concentration of cyanide could be as high as 50 %. Today the cyanide content in the bath has been reduced to 1-5 %.

Most steels, including stainless steels, high speed steels and cast iron can be nitrocarburized in salt baths but low-alloy and carbon steels show the best results.

The salt-bath processes are rapidly losing market shares to the gas and plasma processes due to environmental factors and the use of salt will continue to decrease.



*Figure 14. Furnace line used for the Colournite process at Bodycote Brukens workshop in Gothenburg, Sweden.*

Oxide layer →  
Compound layer →

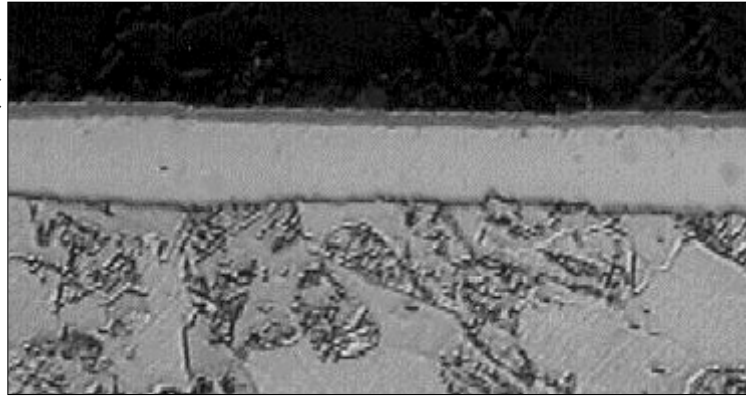


Figure 15. Surface layer after Colournite treatment and postoxidation. Micrograph 500 times magnification.

### 3.4 Plasma Nitriding/Nitrocarburizing

The plasma processes make use of an ionized gas that serves as a medium for both heating and nitriding. The process was developed in the 1930s but it was not until the early 1970s that the method became significantly more widespread due to further development of the process.

The parts to be treated are placed in a vacuum chamber and the furnace is filled with the process gas to a pressure of 10 – 800 Pa. The plasma is created by applying a direct electrical current between the cathodically charged workload and the chamber wall as the anode in the circuit. The applied voltage ( 300 – 800 V ) accelerates the ions towards the workload surface and the layer structure can be adjusted according to the property requirement of the parts, *Figure 16*.

The plasma processes operates at temperatures between 400 and 800°C, which allows a large degree of flexibility. Today's plasma process is mainly used for nitriding and nitrocarburizing (often together with postoxidation) but the plasma technique is also used for producing hard surface layers such as TiN, TiC, TiCN, TiAlN etc. (Plasma CVD).



Figure 16. Plasma Ionitox furnace line at Bodycote's workshop in Ludenschied, Germany.

## 4. Ovako Steel Nitriding Steel Grade Ovako 225A

### 4.1 General Information

Ovako Steel has developed a nitriding steel grade which combines a number of beneficial properties:

- Favourable nitriding rate
- Favourable surface hardness
- Favourable machinability
- Favourable weldability
- Favourable matrix mechanical properties

The wide range of good properties makes Ovako 225A a favourable alternative in many different applications:

- In substitution of type 1%Al nitriding steels
- In substitution of hardening and tempering steels
- In substitution of carburizing
- In substitution of induction hardening
- In substitution of tool/bearing steels

### 4.2 Chemical Composition of Ovako 225A

Table 1 shows the principal composition of grade Ovako 225A.

C	Mn	Cr	Mo
0.17	0.85	1.85	0.55

Table 1. Principal chemical composition of grade Ovako 225A.

The carbon content is low compared to most of the traditional steel grades used for nitriding. The advantage of the low carbon content is high nitriding rate, good matrix toughness, good machinability, good weldability, etc.

The *Cr* and *Mo* contents control the surface hardness and give the steel grade good hardenability and tempering resistance.

*Mn* also contributes to a good hardenability and tempering resistance.

### 4.3 Hardenability

The hardenability of Ovako 225A is shown with the Jominy diagram, Figure 17, and the CCT-diagram, Figure 18.

The relatively straight and horizontal shape of the Jominy curve in combination with the low carbon content, makes it possible to harden in water without any risk of hardening cracks. This makes it

possible to use the grade in large diameters. The standard delivery program covers bars of diameters up to 185 mm.

The “straight” and “horizontal” shape of the Jominy curve also indicates that the steel grade has low sensitivity for variations in the quenching velocity.

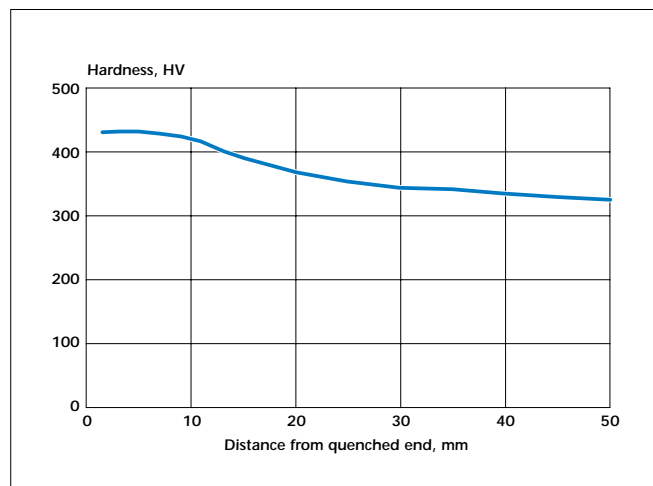


Figure 17. Jominy diagram. Austenitizing temperature 900°C.

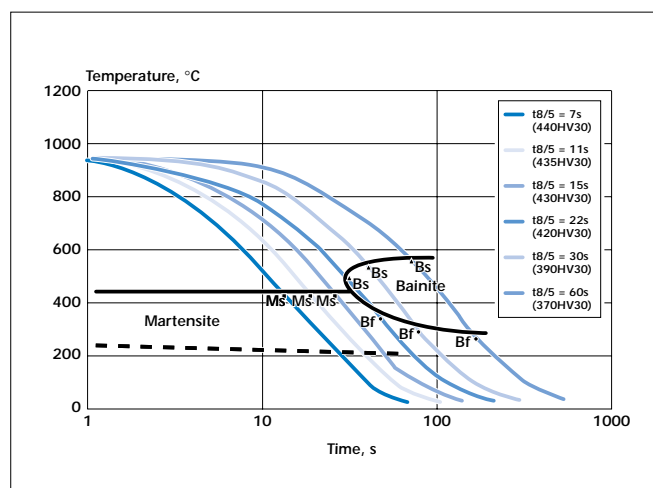


Figure 18. CCT diagram. Austenitizing 950°C, 10 minutes.

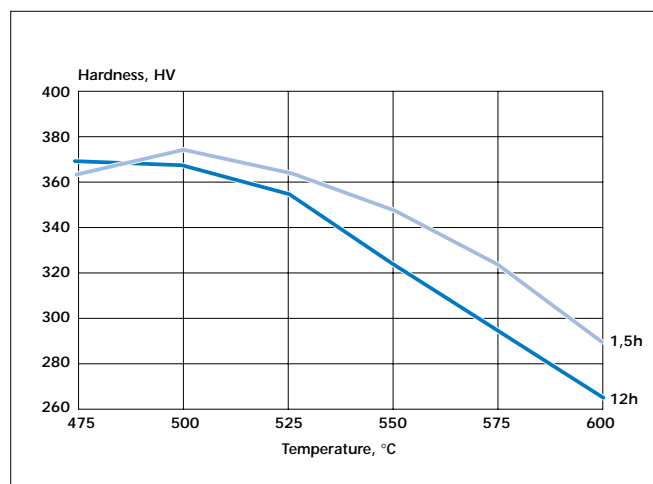


Figure 19. Hardness as a function of the tempering temperature. 1.5 and 12 hours holding time.



#### 4.4 Hardening and Tempering.

Ovako 225A is usually supplied in hardened and tempered condition. Hardening temperature 900-930°C and quenching in water. A normal tempering temperature for attaining a tensile strength of about 950 Mpa is 590°C.

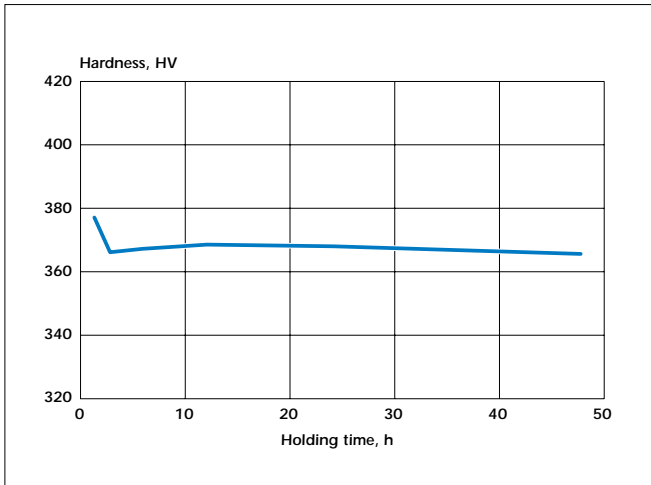


Figure 20. Hardness as a function of the holding time at 500°C.

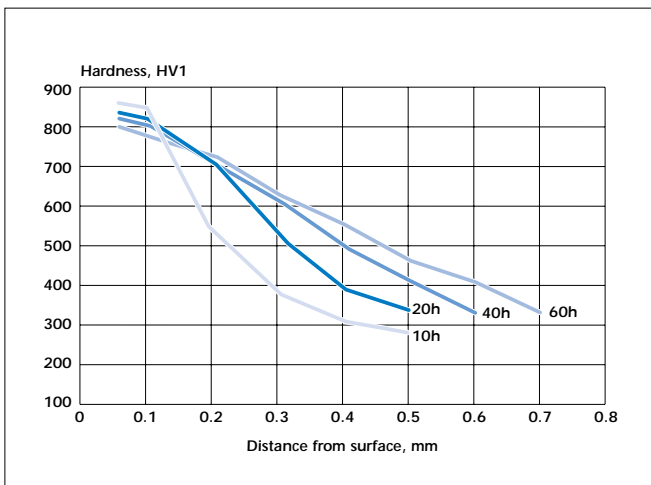


Figure 21. Surface hardness profiles of grade Ovako 225A. Plasma nitriding 510°C, 10, 20, 40 and 60h nitriding time.

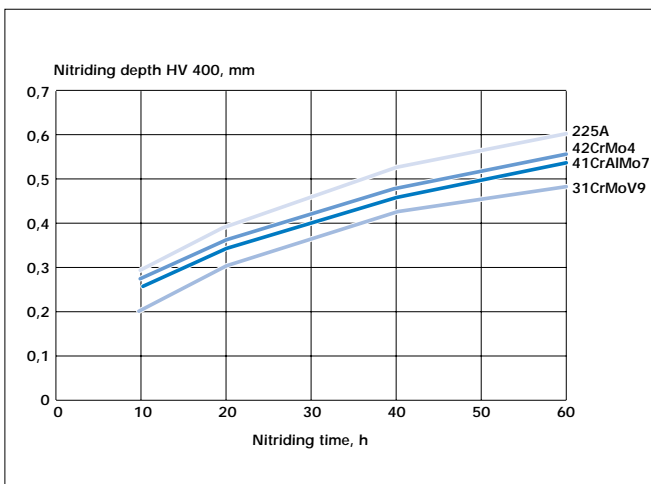


Figure 22. Nitriding depth, 400HV1, as a function of the nitriding time. Plasma nitriding 510°C.

Softening as a function of the holding time at 500°C is shown in Figure 20.

#### 4.5 Nitriding Rate

The chemical composition of grade Ovako225A is designed to give a high nitriding rate in combination with good mechanical properties. Figure 21 shows the surface hardness profiles for 10, 20, 40 and 60 hours nitriding times.

Figure 22 shows the nitriding depth as a function of the nitriding time for grade Ovako 225A, 42CrMo4, 31CrMoV9 and 41CrAlMo7. All the grades were plasma nitrided 510°C on the same occasion.

Figure 22 shows that grades 31CrMoV9 and 41CrAlMo7 need about a 30-50% longer nitriding time for reaching the same nitriding depth as Ovako 225A.

#### 4.6 Surface Hardness

The nitride-forming elements, Cr and Mo, are balanced such that their contents are not so high that they cause negative effects, but high enough to give a surface hardness which is sufficient for most applications.

As described in part 2.2.1, nitriding hardness depends on many factors. Normally the surface hardness is HV1=800-950. This is a hardness range which makes Ovako 225A an interesting alternative in substitution of carburizing.

The big advantage with nitriding compared to carburizing and many other heat-treatment methods is the fact that nitriding causes only minor dimensional changes and distortion.

An application which requires small dimensional changes in heat treatment and good fatigue properties is for example the gear axles in hydraulic gear pumps, Figure 23.

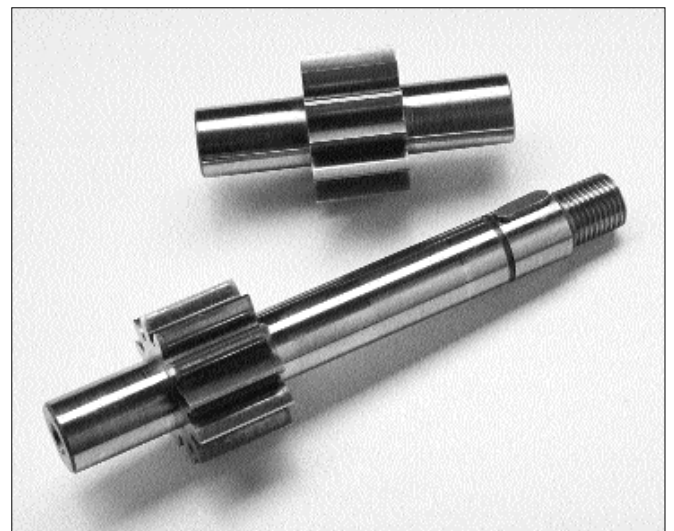


Figure 23. Gear axle in a hydraulic gear pump

#### 4.5 Machinability

The machining operation cost is often a very big part of the total component manufacturing cost. Good machinability is therefore very important for reducing the manufacturing cost.

Figure 24 shows the tool life as a function of the cutting speed in the ISO 3685 single-point cemented-carbide length turning test.

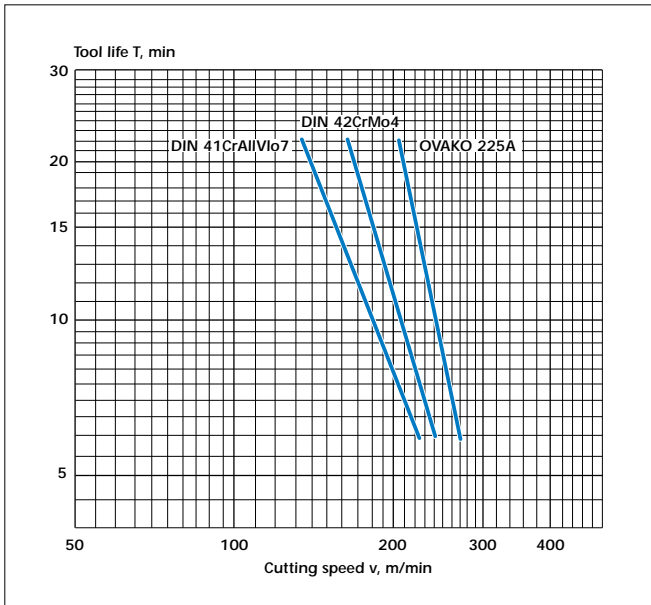


Figure 24. VT-diagram showing the tool life as a function of cutting speed for the grades Ovako 225A, 42CrMo4 and 41CrAlMo7. Hardened and tempered material, hardness 280 HB.

Figure 24 shows, as also does our customer experience, Ovako 225A has a very competitive machinability.



Figure 25. Hydraulic piston with a friction-welded end part.

#### 4.8 Weldability

Ovako 225A is used in many welding applications.

In many applications it is a great cost advantage if welding can be used in component manufacturing. A high carbon content in the material is often the factor which restricts the use of welding.

Ovako 225A has a low carbon content which gives a martensite of proportionately low hardness and “good” toughness and thereby a low crack risk.

Applications may for example be hydraulic pistons with friction welded end parts Figure 25.

#### 4.9 Matrix Mechanical Properties

The chemical composition of Ovako 225A possesses good mechanical properties up to large bar diameters.

Table 2 on top of next page, shows the standard mechanical properties in hardened and tempered condition which are guaranteed for bar diameters up to 185 mm.

Figure 26 shows the impact strength as a function of the test temperature for a hardened and tempered bar of 25 mm Ø. As the figure shows, the impact strength is very high down to very low temperatures.

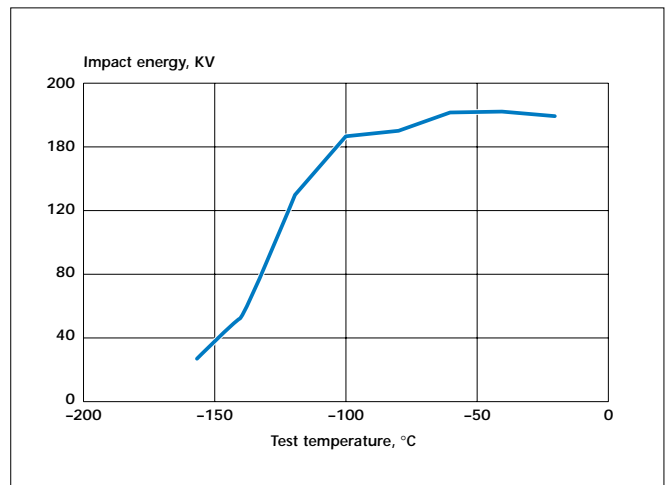


Figure 26. Impact strength as a function of the test temperature. Hardened and tempered bar 25 mm Ø.

#### 4.10 Steel Cleanliness

The steel cleanliness is of vital importance to fatigue behaviour. Ovako 225A is available in different cleanliness levels (Table 3).

The normal stock material of the Ovako grade 225A is in the BQ-quality.

If the application is very highly fatigue loaded it is recommended to use the PBQ quality which is a very clean steel.

Yield strenght MPa	Tensile strength Mpa	Elongation A <sub>5</sub> %	Area reduction Z %	Impact strength + 20°C      -40°C
≥750	880 – 1050	≥ 12	≥ 50	≥ 60      ≥ 27

Table 2. Standard mechanical properties of grade Ovako 225A.

Specification	Macro inclusions mm/dm <sup>2</sup>	Oxygen content (ppm)			Titanium content (ppm)	Macro inclusions							
						A		B		C		D	
		C* < .5%	. 5 < C < .8	C* < .8%		Th	He	Th	He	Th	He	Th	He
CQ		According to customer requirements											
Q	5	15	15	15	–	2.5	1.5	1.0	0.5	0	0	0.5	0.5
BQ	2.5	11	9	7	30	2.0	1.5	0,5	0.1	0	0	0.2	0.1
PBQ	1	9	8	7	30	1.0	0.5	0.5	0	0	0	0.2	0
* The carbon content of the steel grade													

\* The carbon content of the steel grade

Table 3. Ovako Steel cleanliness specification. Ref 8.

## 5. Summary

Knowledge of how the chemical composition of nitriding steels influences nitriding behaviour and component properties is continuously increasing. This knowledge improvement has made it possible to design steel grades for attaining specific properties.

The Ovako Steel nitriding steel grade Ovako 225A is designed to be a multipurpose steel grade with many favourable properties which can be utilised in a great variety of applications.

There has also been a dramatic improvement in how to perform and how to control nitriding/nitrocarburizing processes for attaining specific properties.

This combined increase in knowledge of how steel chemical composition and the nitriding process influence the properties of a nitrided component has made it possible for nitriding/nitrocarburizing to be an attractive alternative in many applications.

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