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Nitrocarburizing and High Temperature Nitriding of Steels in Bearing Applications

Master of Science Thesis

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Nitrocarburizing and High Temperature Nitriding of Steels for Bearing Applications

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Cover:
Austenitic nitrocarburized sample of 18CrNiMo7-6, 200x, etched in Nital 1.5 %.
For more information on austenitic nitrocarburizing see Section 2.2.5.

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Sammanfattning

Ett antal stål som används i lagerapplikationer utsattes för tre olika värmebehandlingsprocesser – ferritisk och austenitisk nitrokarburering i gas vid 580 °C respektive 620 °C samt högttemperaturnitrering vid 1100 °C. Syftet var att undersöka huruvida processerna kan användas för att öka korrosions- och nötningsmotståndet hos de aktuella stålen samt att utvärdera för vilka stål processerna är lämpligast.

Båda nitrokarbureringsprocesserna resulterade i en tunn föreningszon med en hårdhet på 800–1000 HV för alla testade stål. Diffusionszonen blev hårdast och djupast på de stål som hade lägst kolhalt. Bäst resultat för lagerapplikationer fås med austenitisk nitrokarburering som resulterade i en tjockare föreningszon och ökat nitrokarbureringsdjup jämfört med ferritisk nitrokarburering. Ytterligare en fördel med austenitisk nitrokarburering är att det bildas ett austenitiskt skikt under föreningszonen. Detta skikt kan genom anlöpning vid 300 °C omvandlas till en finkorning struktur med en hårdhet på över 1000 HV. Det konstaterades också att både ferritisk och austenitisk nitrokarburering leder till en signifikant ökning av korrosionsmotståndet i neutral saltdimma.

Högttemperaturnitrering applicerades på en grupp martensitiska rostfria stål och en grupp värmebeständiga stål. Samtliga stål innehöll kväve efter behandlingen. Högttemperaturnitrering ledde till genomhårdning och hög hårdhet för de rostfria stålen, men också till utfällningar i korngränserna. Problemet förvärrades av ökande kolhalt i stålet. Av de värmebeständiga stålen var det endast M50 som uppnådde den önskade hårdheten.

Nyckelord: ferritisk nitrokarburering, austenitisk nitrokarburering, högttemperaturnitrering, lagerstål, rostfritt stål, värmebeständigt stål

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Abstract

A group of steels used in bearing applications were subjected to three different heat treatments – gaseous ferritic and austenitic nitrocarburizing at 580 °C and 620 °C respectively and solution nitriding at 1100 °C. The aim was to improve wear and corrosion resistance of the steels and to evaluate for which steels the processes are most suitable.

Both nitrocarburizing processes resulted in a thin compound layer with a hardness in the range of 800–1000 HV for all investigated steels. The hardest and deepest diffusion zones were obtained on the steels with the lowest carbon content. The best properties for bearing applications were obtained by austenitic nitrocarburizing which resulted in a thicker compound layer and a deeper nitrocarburizing depth than ferritic nitrocarburizing. Another advantage of austenitic nitrocarburizing is that it produces an austenitic layer below the compound layer. By tempering at 300 °C this layer can be transformed to a fine structure with hardness above 1000 HV. It was also established that both ferritic and austenitic nitrocarburizing improve corrosion resistance in neutral salt spray significantly.

Solution nitriding was applied to one group of martensitic stainless steels and one group of heat resistant steels. All the steels were found to contain nitrogen after the treatment. Solution nitriding resulted in high hardness throughout the stainless steels, but also in grain boundary precipitates. The problem increased with increasing carbon content of the steel. Of the heat resistant steels, only M50 achieved the desired hardness.

Keywords: ferritic nitrocarburizing, austenitic nitrocarburizing, solution nitriding, bearing steel, stainless steel, heat resistant steel

Preface

This report is the result of a master thesis in Advanced Engineering Materials performed at SKF Sweden AB during the autumn 2011. The thesis is the concluding part of an engineering degree from Chalmers University of Technology. The project also includes some work which is not presented in this report due to intellectual property rights.

This thesis would not have seen the light of day without the assistance of my supervisors at SKF, Walter Datchary and Staffan Larsson. Thank you for your support and enthusiasm!

I would also like to thank Mats Norell, my examiner at Chalmers, who always has a tricky question at hand.

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Finally I would like to thank my parents for their moral support and Ivar Torstensson for reminding me that sometimes the best solution to a problem is dinner and a good night's sleep.

Göteborg, Sweden, January 2012,

Isabella Flodström

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Definitions

α	Ferrite	
α'	Martensite	
γ	Austenite	
γ'	$\text{Fe}_4(\text{C}, \text{N})_{1-z}$	
ε	$\text{Fe}_2(\text{C}, \text{N})_{1-z}$	
θ	Cementite	
AN	Austenitic nitrocarburizing	
CN	Carbonitriding	
FN	Ferritic nitrocarburizing	
GD-OES	Glow Discharge Optical Emission Spectroscopy	
PRE	Pitting resistance equivalent	
SN	Solution nitriding	
XRD	X-ray diffraction	
A_1	Transformation temperature $\alpha \rightarrow \alpha + \gamma$	(°C)
A_3	Transformation temperature $\alpha + \gamma \rightarrow \gamma$	(°C)
D	Diffusion coefficient	(m ² /s)
M_s	Martensite start temperature	(°C)
M_f	Martensite finish temperature	(°C)
J	Flux	(mol · m ⁻² · s ⁻¹)
P	Partial pressure	(Pa)
RA	Retained austenite	(%)
T	Temperature	(°C)
t	Time	(s)

Chapter 1

Introduction

1.1 Background

Bearings are precision components used for rotation or relative movement of machine parts and have high demands on life length and low friction. They need to sustain wear, fatigue, high loads and sometimes harsh environments. In order to meet the demands of more and more challenging applications and in order to lower costs constant improvement of these properties are needed.

In this project three different heat treatments that could enhance the wear and corrosion resistance of steels in bearing applications are investigated.

Ferritic nitrocarburizing is a surface hardening process in which nitrogen and carbon are supplied to the surface of a ferrous metal. It takes place at relatively low temperature (maximum 580 °C) and therefore the dimensional changes induced are small. This means that post-grinding is not necessary and therefore the process is a cost-efficient way of increasing wear and corrosion resistance of a component. Ferritic nitrocarburizing is a well known process in the industry used on components such as gears and bearing cages. There are however only a few studies [1, 2] made on ferritic nitrocarburizing of the high carbon steels which are used in rings and rolls of bearings.

Austenitic nitrocarburizing is a variant of nitrocarburizing that uses higher temperatures (typically 600–700 °C) than ferritic nitrocarburizing. Nitrogen that has diffused into the surface of the steel lowers the austenitization temperature and a part of the structure transforms to austenite during the treatment. Austenitic nitrocarburizing is not as widely used as ferritic nitrocarburizing, but it presents some interesting properties, such as improved corrosion resistance and higher load bearing capacity. Higher temperatures do however also present an increased risk of distortions during heat treatment.

When bearing applications demand higher corrosion resistance than what can be achieved by low alloy steels, martensitic stainless steels are used. These provide a good combination of hardness and corrosion resistance. Solution nitriding is a relatively new method for case hardening stainless steels using

gaseous nitrogen. The process uses high temperature (1050–1150 °C) and low pressure nitrogen gas to produce a nitrogen rich case which improves corrosion and wear resistance of the material. There are several studies [3, 4, 5] showing that solution nitriding can produce high surface hardness and good corrosion properties on low carbon martensitic stainless steels. The bearing industry normally uses stainless steels with a higher carbon content and it is interesting to evaluate if the solution nitriding process can be used to improve properties also on these steels. A group of heat resistant alloys will also be included in the solution nitriding tests in order to see if they might benefit from the treatment.

1.2 Aim and goals

The aim of the project is to study if solution nitriding and two different nitrocarburizing processes are applicable to a number of commercially available steel grades and evaluate if the obtained properties are suitable for use in the bearing industry.

A number of steel alloys which are used in the bearing industry today have been selected and heat treatments of these will be performed by external partners. Hardness, microstructure, out-of roundness and residual stresses will be investigated on the treated samples. Analyses of nitrogen and carbon distribution by glow discharge optical emission spectroscopy and evaluation of corrosion resistance will also be performed by external laboratories.

The project aims to identify strengths and drawbacks of the three processes with bearing applications in mind and to identify suitable steel candidates for the different heat treatments. Since the focus of the project is to perform a screening of suitable alloys for the respective processes all samples will be treated in the same batch in each process and the process parameters will not be adjusted depending on steel grade.

1.3 Delimitations

The project has a timeframe of twenty weeks and some more time demanding activities will inevitably have to be left out. The following delimitations have been set up:

- The project does not include any development of the heat treatment processes. The processes used are commercially available and heat treatment will be performed by external partners.
- The alloys used in the project are commercially available.
- Corrosion testing and GD-OES measurements will be performed by external partners.
- Tribological properties will be discussed together with hardness, but there will be no wear test included in the study.

- Since the project is aimed at identifying suitable steel candidates for further development all samples will be treated in the same batch in each process.

Chapter 2

Theory

This chapter gives a theoretical background to the project. The first part of the chapter introduces important demands on bearing steels which can be affected by heat treatment. The second half of the chapter deals with the theory behind the three heat treatment processes used in this project – ferritic and austenitic nitrocarburizing and solution nitriding.

2.1 Requirements on bearing steels

Rolling element bearings are subjected to large dynamic stresses, which put high demands on their performance. To fulfill requirements on load bearing capacity and wear and fatigue resistance a clean microstructure and a high hardness are required. The surface hardness needs to be at least 58 HRC for most bearing applications [6].

Small bearings are normally through hardened to a martensitic structure throughout. If large bearings are to be through hardened a steel with a high hardenability is required. The hardenability is increased by increasing the amount of alloying elements. Another alternative is to use a lower alloyed steel in combination with case hardening which produces a hard surface on top of a softer core. Case hardened components can fulfill the requirements on load bearing capacity since the heaviest loads are confined to the surface region. The case must however be thick and hard enough to account for the contact loads. An advantage of case hardening is however that it can produce compressive residual stresses in the case, which improve fatigue properties [6].

In the following sections some properties of special interest for bearings which can be affected by heat treatment are described more in detail.

2.1.1 Fatigue resistance

Ability to resist rolling contact fatigue is a very important property for bearings. Fatigue can be initiated at the surface or below it. Surface fatigue is commonly caused by surface irregularities, whereas subsurface fatigue is caused by subsurface stresses. Knowledge of the stress distribution below the surface is important when working with case hardened steels since these have a yield strength that varies with depth [6, 7].

The local stresses caused by two curved surfaces in contact can be predicted by Hertzian stress theory. The stresses induced at certain depth below the contact surface depend on the contact load, the curvature radius of the two bodies and their modulus of elasticity [6].

The maximal equivalent stress is found below the surface at a depth determined by the contact load. In order to avoid plastic deformations the micro yield stress limit of the material should be higher than the equivalent stress induced by the loading conditions at every depth [7]. In Figure 2.1 an example of acceptable and not acceptable contact loads are shown. If the hardness is too low or the case depth too shallow for an applied load the softer substrate below it will deform plastically. As a result the hard case is bent and the tensile stresses induced can cause it to crack [6].

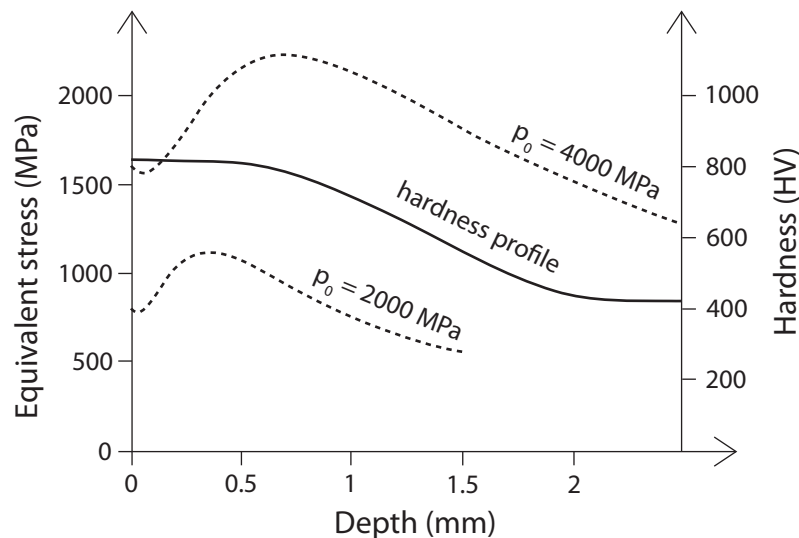


Figure 2.1: A contact load of 2,000 MPa is acceptable according to Hertzian theory, but not a load of 4,000 MPa. Data from [8].

2.1.2 Residual stresses

Residual stresses have an influence on fatigue properties since they affect fatigue crack growth. A crack front that encounters compressive residual stresses is slowed down whereas crack growth is accelerated by tensile residual stresses.

In bearings compressive residual stresses located at the surface of a component are desirable because they can compensate for contact loads. Residual stresses can however also cause distortions, such as out-of-roundness [6].

Residual stresses can be generated in many ways – by rolling, forging, hard machining, welding or heat treatment – but are always a result of misfit in some way. Since the current project focuses on heat treatment, carburizing is used as an example. Carburizing increases the carbon content in the outer region of the specimen. The increased carbon content lowers the martensite start temperature in this region. During cooling, the core, which has a higher martensite start temperature transforms first. The core expands due to the martensitic transformation. The case, which is still austenitic, compensates for the induced stresses by plastic deformation. During the subsequent transformation of the case, the expansion due to martensite formation is resisted by the already transformed core and residual stresses in the case are formed [6].

The amount of residual stresses is affected by the difference in martensite start temperature between the case and the core and by the quenching media and quenching intensity [6].

2.1.3 Retained austenite

Retained austenite is austenite that after heat treatment is not transformed to martensite during quenching. It occurs when the steel has a low martensite start temperature, M_s , for example as a result of high amounts of carbon or other austenite stabilizing elements and therefore retained austenite can become a problem in tool and bearing steels [9].

There are several reasons why one wants to avoid retained austenite – it has a much lower hardness than martensite and since the retained austenite is not in equilibrium at room temperature it can transform to martensite during use. The transformation induces dimensional changes and the martensite that is formed from it is untempered and therefore brittle. There are however ways to get rid of retained austenite. One alternative is deep cooling, another one is tempering, sometimes in several steps [9].

2.1.4 Corrosion resistance

In ordinary bearings common corrosion problems are local corrosion when bearings have been stationary for long periods and corrosion due to contamination. Since the components are moving, fretting corrosion, a combination of wear and corrosion caused by repeated movements between two surfaces, can be a problem. In bearings it can for example occur between the ring and the shaft if these are not properly secured to each other. Wear destroys the protective oxide film on the metal surfaces and causes small metal particles to be detached. The particles oxidize in contact with oxygen and accumulate between the two surfaces, turning into an abrasive medium which causes more particles to detach. Resistance to fretting corrosion can be improved by the use of a more wear resistant alloy [6, 10].

In harsh environments such as paper industry, naval aircraft engines and food processing stainless bearings are used. These martensitic stainless steels have better corrosion resistance than conventional bearing steels, but are still susceptible to pitting corrosion. Pitting corrosion is a type of local corrosion caused by breakdown of the passive film in a small area on passivated metals [6, 10]. The resistance can however be improved by additions of molybdenum and nitrogen and is commonly quantified by the pitting resistance equivalent (Equation 2.1) [11].

$$\text{PREN} = \% \text{Cr} + 3.3 \cdot \% \text{Mo} + 16 \cdot \% \text{N} \quad (2.1)$$

Nitrogen in solid solution also improves the resistance to other types of localized corrosion, whereas manganese and carbon decreases it. A combination of nitrogen and molybdenum creates a synergetic effect and improves pitting corrosion resistance more than what is suggested by Equation 2.1 [12].

2.2 Nitrocarburizing

Nitrocarburizing is a thermochemical process in which nitrogen and carbon are diffused into the surface of a ferrous metal. It produces a thin case consisting of a ceramic iron-nitrocarbide layer and an underlying diffusion zone where nitrogen and carbon are dissolved in the matrix. The treatment is mainly used to improve wear and fatigue properties and to enhance corrosion resistance. Common areas of application include gears and engine parts [13].

Several different types of process medium can be used – gas, liquid or plasma. Gas nitrocarburizing is the most commonly used in the industry today and the only one dealt with in detail here. Besides the process medium nitrocarburizing processes can also be divided according to the temperature at which the treatment takes place. Below the temperature of partial transformation to austenite, A_1 , the process is termed ferritic nitrocarburizing, since at these temperatures the base material is still in the ferritic phase. At higher temperatures ferrite starts to transform to austenite and consequently these treatments are termed austenitic nitrocarburizing [13]. The exact transformation temperature varies depending on composition. Du [14] calculated that the lowest temperature for which it occurs in an alloy of iron, carbon and nitrogen is 586 °C.

2.2.1 Process

The nitrocarburizing process consists of three principal steps: heating, diffusion at the nitrocarburizing temperature and cooling. Pre-heating to accelerate the nitrocarburizing process and post-oxidation to improve corrosion resistance are optional steps. Ferritic nitrocarburizing in gas is commonly carried out at temperatures ranging from 560 to 580 °C [13].

The composition of the atmosphere is a very important parameter in gaseous nitrocarburizing and needs to be closely controlled. The atmosphere consists of nitrogen (N_2), ammonia (NH_3), carbon dioxide (CO_2) and hydrogen (H_2). Ammonia is used as source of nitrogen. Carbon dioxide decomposes into carbon monoxide which together with hydrogen is needed for the transfer of carbon to the steel surface. Sometimes carbon monoxide is used directly instead of carbon dioxide. Hydrogen is not always added separately as it forms from decomposition of ammonia. Nitrogen is used to control the percentage of the other gases and for purging the furnace before and after treatment as ammonia can form an explosive mixture with oxygen. The flow rate of different gases in each process step are plotted in Figure 2.2 [13].

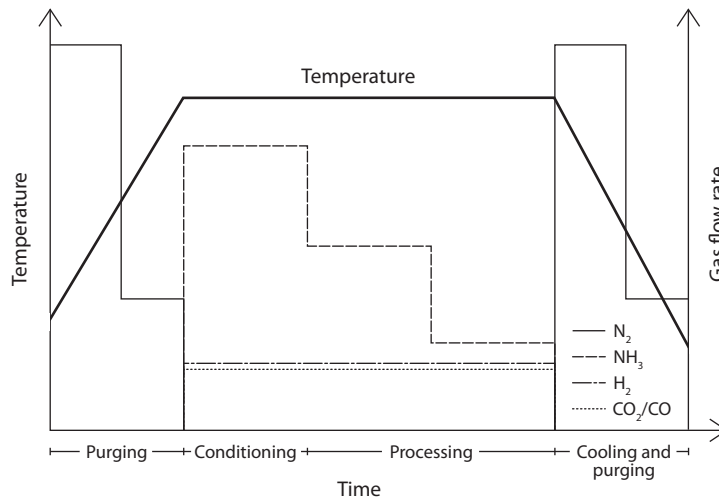


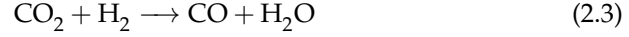
Figure 2.2: Gas ratio per process step. Data from [13].

Diffusion and transfer rates

In gas nitrocarburizing the transfer of nitrogen and carbon atoms can be divided into three steps: deposition onto the steel surface, diffusion in the compound layer and diffusion in the diffusion zone. Ammonia is decomposed into hydrogen and nitrogen at the steel surface, making it possible for the surface to adsorb the nitrogen atoms. The reaction is described by Equation 2.2 [13].



If carbon dioxide is used as carbon source its decomposition takes place in two steps, described by Equation 2.3 and 2.4. First carbon dioxide reacts with hydrogen to form carbon monoxide and water. Thereafter carbon atoms are adsorbed by the steel surface when carbon monoxide reacts with hydrogen to form carbon and water [13].



The adsorption speed of nitrogen and carbon onto the steel surface is governed by equation 2.5. The flux of atoms, J , is proportional to the difference in concentration, c , between the gas and the surface. The reaction rate coefficient is denoted k . The diffusion rate in the compound layer and in the diffusion zone are both governed by Fick's first law of diffusion. Equation 2.6 and 2.7 describes the diffusion rate for the compound layer and the diffusion zone respectively. D denotes the diffusion coefficient. In order to maintain the mass balance the three fluxes need to be equal, as expressed by equation 2.8. The transfer rate is thus governed by the slowest of the three processes [13].

$$J_{surf} = k(c_{gas} - c_{surf}) \quad (2.5)$$

$$J_{comp} = -D_{comp} \frac{dc}{dx} \quad (2.6)$$

$$J_{diff} = -D_{diff} \frac{dc}{dx} \quad (2.7)$$

$$J_{surf} = J_{comp} = J_{diff} \quad (2.8)$$

The diffusion coefficients in equations 2.6 and 2.7 are highly temperature dependent and increase with increasing temperature. The temperature dependence of D in a solid can be predicted by equation 2.9 (the Arrhenius equation), where D_0 denotes the diffusion coefficient at infinite temperature, E_A the activation energy for diffusion, R the gas constant and T the absolute temperature.

$$D = D_0 e^{-E_A/(RT)} \quad (2.9)$$

Since nitrocarburizing is carried out at low temperature compared to for example carburizing, diffusion rates are relatively slow. Thus the case depth that can be achieved in a reasonable amount of time is comparatively shallow.

Cooling

After gaseous nitrocarburizing samples are usually quenched in oil or gas. Oil quenching is the fastest of the two methods. The quenching intensity mainly affects the properties of the diffusion zone. In low alloy steels quick cooling leads to more nitrogen left in solid solution in ferrite and hardness is increased. In high alloy steels the hardness of the diffusion zone depends mainly on precipitation hardening and quenching rate plays a less vital role.

Quick quenching also results in higher compressive residual stresses in the surface region, which improves fatigue resistance. Shortened production time is also an advantage. Too fast quenching can however lead to cracks. Slower cooling rate is preferred if distortions need to be minimized [13].

Post-oxidation

Nitrocarburizing can be followed by a post-oxidation step which is performed to enhance the corrosion resistance of the material. The goal is to create a continuous layer of protective magnetite, Fe_3O_4 , on the surface of the compound layer. The oxide layer thickness is typically in the range of a micrometer and it gives the surface a black appearance [13].

Due to factors such as the process parameters of nitrocarburizing, product demands, intellectual property rights and the need for cost savings, different variants of post-oxidation treatments exist. Figure 2.3 shows some possible variants. The parts can be quenched in an oxidizing medium directly after nitrocarburizing or first quenched and then oxidized [15, 16]. Flash oxidation is done through a few seconds exposure to the air at room temperature directly before quenching [16]. The air exposure has to be limited to a short time since the material cannot be allowed to cool off significantly. The parts need to be quenched from above 550 °C if high hardness and optimal fatigue properties are to be achieved [17]. A notable advantage with flash oxidation is the relatively short process time [16].

Nitrocarburizing in itself has been reported to increase the corrosion resistance of a part [2, 15, 18]. However, the corrosion resistance of the compound layer can be impeded by high amounts of surface porosity. Pores increase the effective surface area of the part and consequently the corrosion rate also increases. Post-oxidation fills and covers the pores in the compound layer with oxide, which is one reason for the increased corrosion resistance seen in post-oxidized samples [19].

The second reason that post-oxidation increases corrosion resistance is that it produces a passivation of the surface similar to that found in stainless steels or aluminium. The oxide film formed on the surface protects the metal from further contact with air and oxidation is slowed down because it can only continue through solid-state diffusion through the oxide layer. Whether a surface will passivate or not can be influenced by the Pilling-Bedworth ratio, R_{PB} , which is defined as the relationship between the volume of the unit cell of the oxide, V_{ox} , to the volume of the unit cell of the metal, V_m (Equation 2.10) [20].

$$R_{PB} = \frac{V_{ox}}{V_m} \quad (2.10)$$

If R_{PB} is less than unity a porous and unprotective oxide is formed. Tensile stresses are developed in the oxide layer and make it crack, exposing the metal surface. If R_{PB} is higher than unity, compressive residual stresses are formed in the oxide layer and passivation is possible. However if the ratio is higher than two, the compressive stresses become too high and cause the oxide to

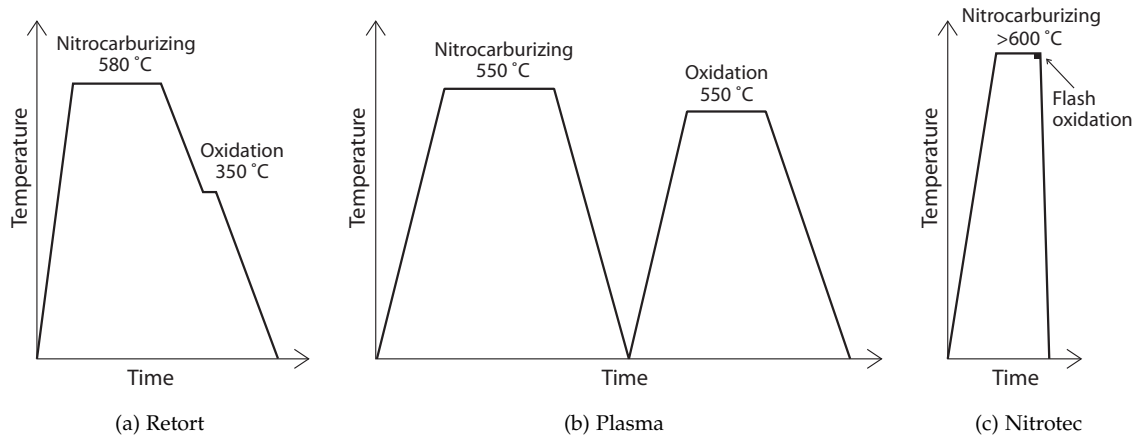


Figure 2.3: Some examples of processes that combine nitrocarburizing with post-oxidation. Many more variants exist [16].

crack and spall, destroying its protective properties [20]. For example magnetite (Fe_3O_4) on ferrite has a Pilling-Bedworth ratio of 2.10 and forms an unprotective oxide layer [21]. In nitrocarburizing the intermediate compound layer between the ferrite and the magnetite layer improves the adhesion of the oxide layer, since the Pilling-Bedworth ratio of each interface becomes lower than two [22]. Table 2.1 summarizes some Pilling-Bedworth ratios of interest for nitrocarburizing.

Interface	R_{PB}
$\text{Fe}_3\text{O}_4 - \alpha\text{-Fe}$	2.10
$\text{Fe}_3\text{O}_4 - \gamma\text{-Fe}_4\text{N}$	1.80
$\text{Fe}_3\text{O}_4 - \epsilon\text{-Fe}_2\text{N}_{1-x}$ (7.3 wt% N)	1.79
$\text{Fe}_3\text{O}_4 - \epsilon\text{-Fe}_2\text{N}_{1-x}$ (11.0 wt% N)	1.69

Table 2.1: Pilling-Bedworth ratios of interest in nitrocarburizing [21, 23].

There are many factors which can affect the effectiveness of a post-oxidation treatment – nitrocarburizing process parameters, steel grade and the process parameters of the post-oxidation itself [24, 25]. Lee et al. [25] investigated the effect of post-oxidation time on plasma nitrocarburized AISI 1020 steel and found that the thickness of the oxide layer decreased with increasing oxidation time, since prolonged oxidation led to undesired spalling of the oxide layer.

2.2.2 Microstructure

Nitrocarburizing introduces more nitrogen atoms than carbon in the steel and the phase compositions found are more similar to the ones found in the Fe-N system (Figure 2.6a) than in the Fe-C system [14]. After ferritic nitrocarburizing the microstructure consists of three zones: a compound layer at

the surface, a diffusion zone just below it and further in the unaffected base material. A schematic view is shown in Figure 2.4a. The compound layer is typically 2–30 μm thick and consists of the iron carbonitrides $\epsilon\text{-Fe}_2(\text{C},\text{N})_{1-z}$ and $\gamma'\text{-Fe}_4(\text{C},\text{N})_{1-z}$. The ϵ -phase has a hexagonal crystal structure whereas γ' is cubic [26]. The diffusion zone can reach 0.1–0.5 mm in thickness and consists of carbon and nitrogen in interstitial solid solution in the base material combined with small carbide and nitride precipitates [13].

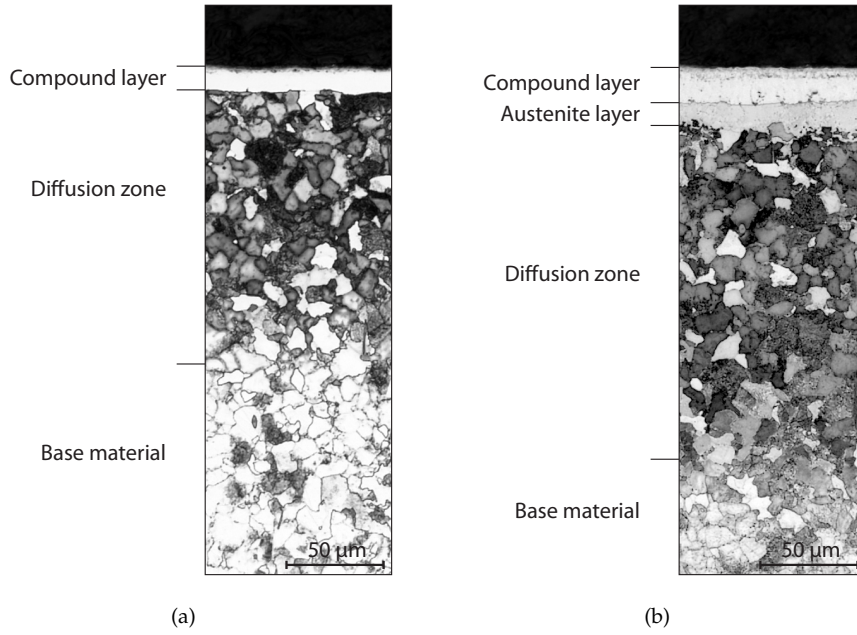


Figure 2.4: Typical microstructure of ferritic (a) and austenitic (b) nitrocarburized samples.

The compound layer

The presence of the different microstructures can be understood by studying the formation of the compound layer. Three factors are important: the temperature, the time and the nitrogen and carbon potentials, r_N and r_C , of the processing medium. The nitrogen and carbon potential are expressed by equation 2.11 and 2.12. P denotes the partial pressure of the respective chemical compounds [13, 26].

$$r_N = \frac{P_{\text{NH}_3}}{P_{\text{H}_2}^{3/2}} \quad (2.11)$$

$$r_C = P_{\text{CO}} \cdot \frac{P_{\text{H}_2}}{P_{\text{H}_2\text{O}}} \quad (2.12)$$

To understand how the partial pressure affects the stability of different phases it is useful to first look at nitriding as an example. Figure 2.5 shows a so called Lehrer diagram where phase boundaries are plotted in a diagram showing nitriding potential versus temperature. As can be seen in the figure utilizing a low nitriding potential results in nitrogen being dissolved completely in ferrite. Increasing the nitriding potential leads first to the formation of γ' and at even higher potentials to the formation of ϵ [13, 26].

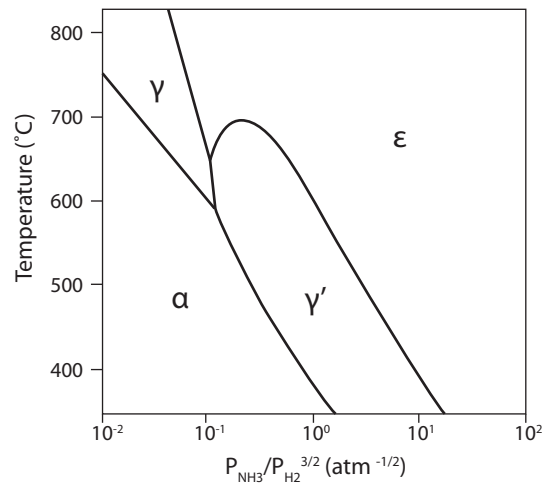


Figure 2.5: Lehrer diagram. Data from [14]

Nitrocarburizing however is affected by the partial pressure of carbon in addition to the partial pressure of nitrogen and would need a 3D-version of the Lehrer diagram. Different reaction rates for the nitriding and carburizing reactions also affect the growth of the compound layer. The carburizing reaction (Equation 2.4) is faster than the nitriding reaction (Equation 2.2) and therefore the first step of compound layer formation is the nucleation of cementite at the surface of the substrate. The ϵ -phase has a crystal structure that is similar to the crystal structure of cementite. Therefore its barrier to nucleation is smaller than the one for γ' and ϵ starts to form directly on cementite. As the treatment continues, cementite transforms to ϵ which results in an almost homogeneous ϵ layer. The next step in the formation of the compound layer is the formation of γ' between ϵ and the substrate. This leads to a redistribution of nitrogen and carbon at the interface and a second ϵ layer forms between γ' and the substrate [13, 26, 27].

The growth rate of the compound layer is governed by which phases it contains. Figure 2.7 shows an isothermal section of the Fe-N-C phase diagram at 580 °C. The γ' -phase is an almost stoichiometric compound with a narrow solubility range for carbon and nitrogen. This makes the growth rate of γ' relatively slow. The ϵ -phase has a higher solubility range for both nitrogen and carbon and a high nitrogen mobility, which lets it grow quicker. Since the ϵ -phase is favored by high nitriding potential and by high alloy content, increasing these parameters makes the compound layer grow faster [27].

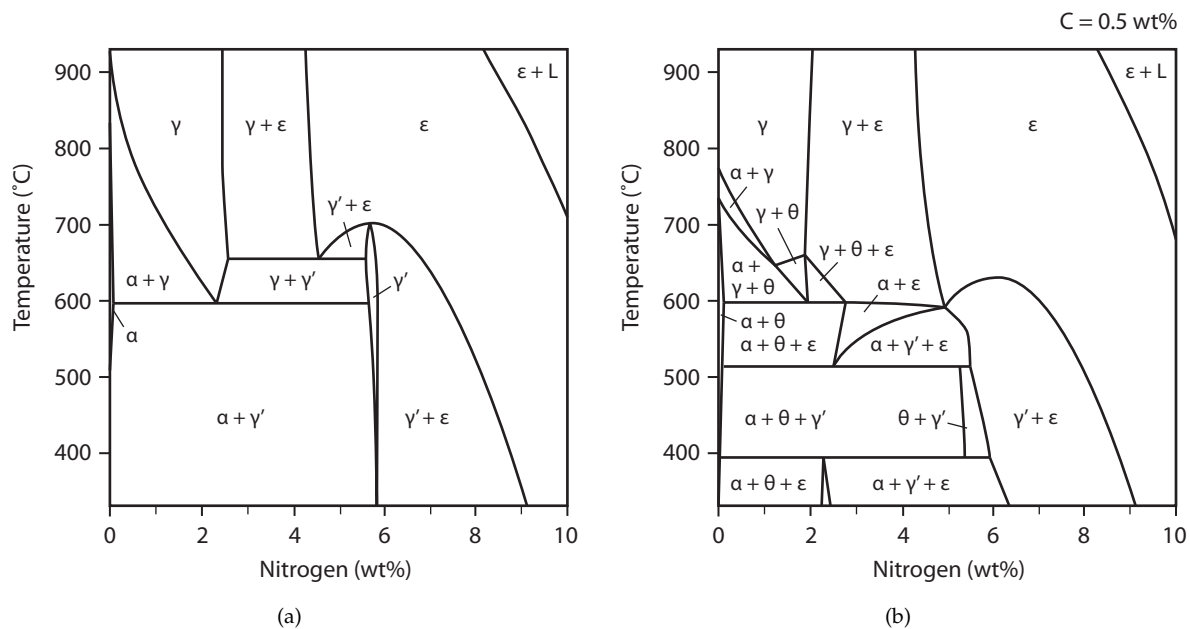


Figure 2.6: Fe-N phase diagram (a) compared to the Fe-N-C phase diagram at 0.5 wt% carbon (b). Data from [14].

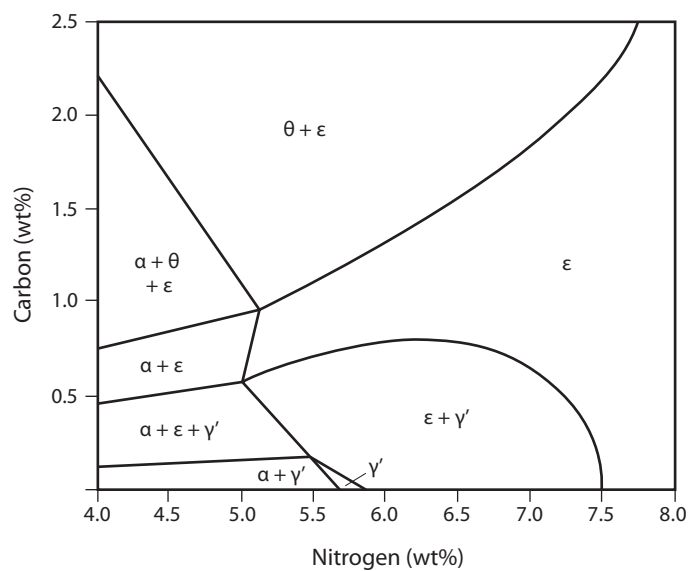


Figure 2.7: Isothermal section of the Fe-C-N phase diagram at 580 °C. Data from [14].

The steel alloy also plays an important role for the composition of the compound layer. For example, when medium or high carbon steels are nitrocarburized, the ϵ -phase in the compound layer can be enriched with carbon from the base material. Small amounts of chromium nitrides (Cr_2N and CrN) have also been reported to occur in the compound layer of salt bath nitrocarburized 100Cr6 [1].

Porosity

The outer part of the compound layer contains pores. Longer process time and high nitrogen potential increases the amount of porosity. On low alloy steels it is not uncommon that 30–40 % of the compound layer is porous. Increasing the alloy content causes the porosity to decrease, likely because the nitrogen activity is lowered by alloying [13].

Pores form by the pressure of gaseous nitrogen as interstitial nitrogen in the compound layer recombines to nitrogen molecules ($2\text{N} \rightarrow \text{N}_2$). The phenomenon occurs particularly at grain boundaries and other discontinuities [13, 28].

The diffusion zone

In the diffusion zone nitrogen and carbon exist either in an interstitial solid solution in the ferritic phase or in alloy nitrides and carbides. The morphology is both alloy dependent and influenced by whether the piece was quenched from treatment temperature or not [28]. Quenching leaves more interstitial elements in solid solution, whereas slow cooling promotes precipitation [13].

Just like the compound layer the diffusion zone increases in thickness with increasing temperature and time. Increasing the amount of nitride and carbide formers in the alloy causes the nitrocarburizing depth to decrease since nitride formers trap nitrogen and carbon and more atoms need to diffuse into the steel to reach a certain nitrocarburizing depth [13].

2.2.3 Influence of prior heat treatment

The hard case produced by nitrocarburizing is relatively thin and cannot withstand heavy loads on its own. In order to improve the load bearing capacity, parts can be hardened and tempered prior to nitrocarburizing. A tempering temperature that is at least 20–30 °C above the nitrocarburizing temperature should be used, otherwise the base hardness will be lost during nitrocarburizing. Nitrocarburizing can however be applied to normalized or annealed parts to increase wear and corrosion resistance [13].

2.2.4 Reported properties

Nitrocarburizing produces a hard but shallow case that can improve wear, fatigue and corrosion resistance. The relatively low process temperature causes limited distortions and leaves a good surface finish. It also has the advantage of short cycle times and comparatively low energy consumption which is favorable both from an economic and environmental perspective [13].

Hardness

One of the main reasons for utilizing nitrocarburizing is that it produces a very hard surface layer which improves both wear and fatigue resistance and load bearing capacity of the nitrocarburized part. Wear resistance is mainly provided by the hardness of the compound layer whereas fatigue resistance is more dependent on the diffusion zone. Load bearing capacity is increased both by increased surface hardness and by increased relative case depth (ie. case depth/part thickness) [13, 29].

The compound layer has a constant hardness throughout most of its cross section. In the outer region it is however lowered by porosity. Its hardness can be related directly to the steel grade of the part and increases as the alloy content increases. The compound layer has been reported to have a hardness of around 700 HV in low alloy steels and about 800 HV for steels with 1.5 wt% chromium content. The hardness of the diffusion zone follows the concentration gradients of nitrogen and carbon. The process temperature together with the nitriding and carburizing potentials determines how much nitrogen and carbon that is dissolved in the material. The case depth increases with increasing process time and decreases with increasing alloy content. The quench rate determines how much of the dissolved nitrogen and carbon that is kept in solid solution [13].

Wear resistance

The tribological properties of a nitrocarburized part are determined mainly by the properties of the compound layer. Resistance to abrasive wear is proportional to surface hardness, which in its turn depend on the steel grade. A favorable state of very low wear rate can be attained if the abrading material is softer than the compound layer [13].

Hardness is not the only factor which influence wear resistance. The ceramic nature of the compound layer lowers friction and prevents surfaces from welding together so that the resistance to adhesive wear is also increased. It has been shown that this effect is favored by the presence of more ϵ -phase [13]. A suggested explanation is that its lamellar crystal structure lowers the amount of heat produced by friction since it allows sliding along the basal plane [1].

However, a drawback with nitrocarburizing is the shallow depth of the compound layer. When the compound layer eventually wears off, resistance to wear deteriorates dramatically. This can be compared to carburizing where

the thicker case can result in longer resistance to wear even if the initial wear rate is higher. Nitrocarburizing is therefore best suited for mild abrasive environments [13].

The initial wear rate of nitrocarburized components is usually higher than steady state wear rate. This is due to porosity [13]. Pores can have a detrimental effect on wear resistance. Qiang et al. [1] investigated the sliding wear behavior of 100Cr6 subjected to salt bath nitrocarburizing alone and to salt bath nitrocarburizing combined with oxidation, polishing and a second oxidation step. They found that nitrocarburizing lowered the wear resistance whereas the combined process increased it compared to the untreated material. They ascribed the lowered wear resistance of the nitrocarburized sample to the presence of more pores. The same authors also found that the friction coefficient was lowered by both treatments, due to that the porosity can contain lubricants. In some applications the lubricant contained in the pores can also lead to that wear resistance is improved [13].

Fatigue

The fatigue strength of a nitrocarburized part is improved by compressive residual stresses created in the diffusion zone as a consequence of the heat treatment (see section 2.1.2). A fast quench rate leads to more residual stresses forming in the diffusion zone, but also to increased distortions [13].

The role the compound layer plays for fatigue strength is not completely understood. A mono phase γ' -layer gives rise to compressive residual stresses whereas tensile stresses have been reported for the ϵ -phase [13, 30, 31].

Corrosion resistance

Nitrocarburized low alloy steels generally show good corrosion resistance compared to the untreated materials. The improved corrosion resistance can be attributed to that the nitrocarbides in the compound layer are noble phases. Since the nitrocarbides form a dense layer, the underlying steel is protected from corrosion [29].

The ϵ -phase has better corrosion properties than the γ' -phase because of its crystalline structure and higher nitrogen content. The quantity of ϵ -phase in the compound layer is the most important factor for improved corrosion resistance. How dense the compound layer is also plays a vital role. High amounts of porosity in the compound layer can have a detrimental effect on the corrosion resistance, since pitting corrosion is promoted by pores [29].

As described in Section 2.2.1, the corrosion resistance of nitrocarburized parts can be further improved by a post-oxidation treatment which creates an oxide layer on top of the compound layer.

Distortions

Nitrocarburizing creates small distortions compared to for example carbonitriding since much lower temperature is used. Phase transformations only occur close to the surface and the dimensional increase associated with the process can be predicted. The dimensional growth has been found to be 30–50 % of the compound layer thickness. Possibility to predict the dimensional changes is an advantage since it removes the need for tolerance adjustments by post grinding after nitrocarburizing [13].

2.2.5 Austenitic nitrocarburizing

Austenitic nitrocarburizing differs from ferritic nitrocarburizing in that it takes place at higher temperature which causes a part of the matrix to transform to austenite due to nitrogen enrichment [17]. After austenitic nitrocarburizing the microstructure is composed of four regions as shown in Figure 2.4b. Just like in ferritic nitrocarburizing a compound layer consisting of ϵ and γ' -phase is formed at the surface. Below the compound layer a zone of austenite enriched with nitrogen and carbon is formed. Below the austenitic region lies the diffusion zone and further in the unaffected base material [29]. If post-oxidation is utilized, an oxide layer on top of the compound layer can also be expected.

The presence of the iron-carbon-nitrogen austenite can be understood by studying the phase diagram presented in Figure 2.8. At temperatures used for austenitic nitrocarburizing the austenite phase is stable for certain concentrations of carbon and nitrogen. These conditions occur right below the compound layer. The high content of both nitrogen and carbon decreases the martensite start temperature, M_s , of the iron-carbon-nitrogen austenite and when the material is quenched the austenite is retained.

Austenitic nitrocarburizing increases the depth of both the compound layer and the diffusion zone compared to ferritic processes [13, 29]. Nitrogen and carbon can diffuse deeper into the material since diffusion speed is increased by the augmented temperature (Equation 2.9). Another reason for the increased thickness of the compound layer is that ϵ -phase is favored by higher temperatures as seen in the phase diagrams in Figure 2.6 and ϵ has a quicker growth rate than γ' [26]. Porosity also increases with increasing process temperature [29]. The thicker case depth means that higher surface loads can be sustained by the material.

Transformation of austenite layer

The hardness of the austenite layer can be increased by transforming it to either martensite or bainite. Martensitic transformation requires deep cooling since the martensite start temperature lies below room temperature [13].

Tempering is carried out at 200–300 °C and causes the austenite to decompose into an upper bainitic structure sometimes referred to as nitrogen bainite or

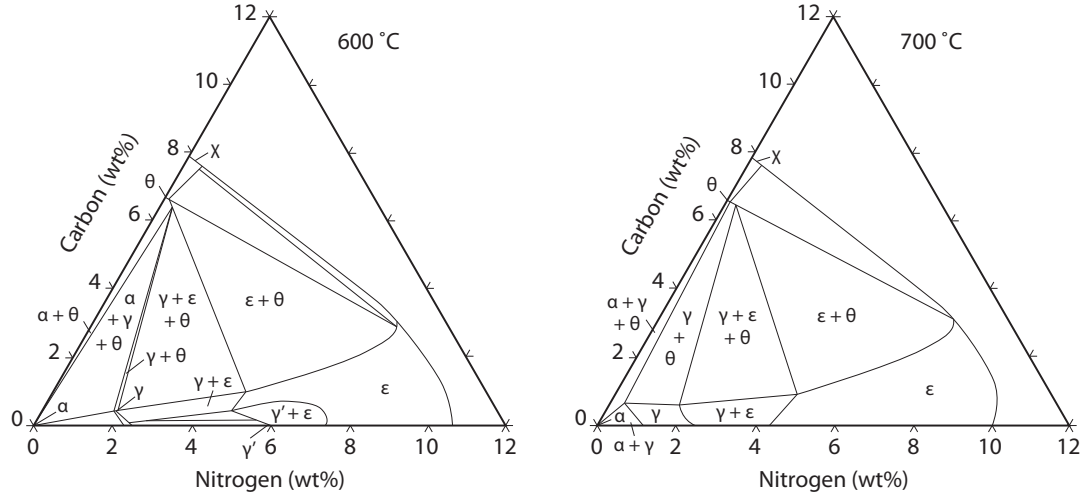


Figure 2.8: Iso-thermal sections of the Fe-C-N phase diagram at 600 °C and 700 °C. Data from [14].

braunite (Equation 2.13) [29]. The new microstructure is composed of γ' and α and has an exceptionally high hardness. Values in the range of 800–1000 HV has been reported [32, 33, 34]. The high hardness is attributed to the fine microstructure which has been explained by the limited diffusivity of carbon and nitrogen in the temperature region in question [32]. Short range ordering of nitrogen atoms and a coherent relationship between precipitates and the parent phase has also been proposed as explanation [33].



The evolution of the phases during tempering and the influence of time and temperature was studied by several authors. The optimal transformation temperature and time varies depending on the base material. Table 2.2 summarizes some results found in literature. As shown in Figure 2.9, Bell et al. [35] also studied the tempering of nitrogen stabilized austenite and found that higher nitrogen content in the austenite increased the hardness after tempering.

Material	Nitriding	Tempering	Maximum hardness	Ref.
Pure iron	645 °C, 6–8 h	225 °C, 5 h	800 HV	[33]
Pure iron	640–650 °C, 6 h	225 °C, 6.5 h	1000 HV0.025	[34]
En32	700 °C, 1 h	250 °C, 2 h	> 1000 HV	[35]

Table 2.2: Tempering treatments found in literature

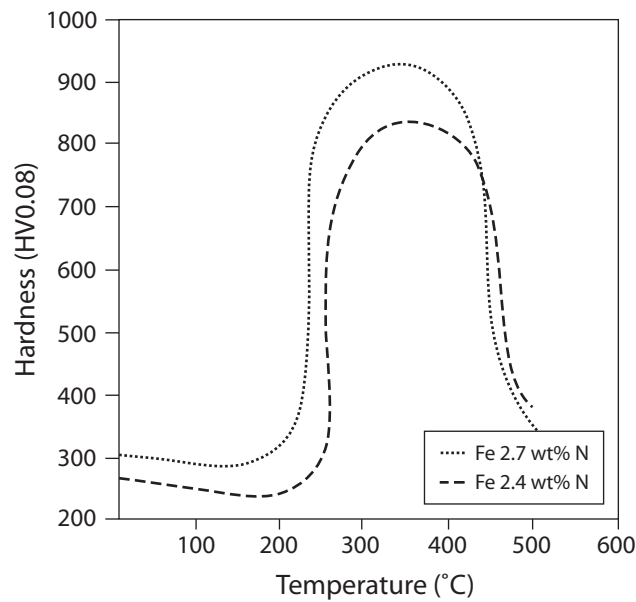


Figure 2.9: Hardness of austenitic iron-nitrogen alloys after tempering for 30 minutes at different temperatures. Data from [35].

2.2.6 Nitrocarburizing of stainless steels

Conventional case hardening processes (eg. nitrocarburizing, carburizing) cannot be utilized for stainless steels. The reason is their high chromium content which interferes with the carbon and nitrogen diffusion in several ways. Firstly, the surface of stainless steel is covered by a chromium oxide layer which is responsible for the corrosion resistance. This oxide acts as a barrier to nitrogen diffusion. In addition, nitrocarburizing of chromium rich steels will lead to the formation of chromium nitrides and chromium carbides. As a consequence the amount of chromium in solid solution decreases and the corrosion resistance of the material deteriorates.

It is possible to avoid these problems by the use of plasma or low temperature nitriding, typically below 500 °C. However these processes produce a very thin case (<20 µm) which is not suitable for heavily loaded applications. It can however be used for increased wear and corrosion resistance [4, 36, 37].

2.3 Solution nitriding

Solution nitriding is a high temperature thermochemical treatment that utilizes nitrogen (N_2) to case harden stainless steel. It is a relatively new process that was developed to overcome the inherent problems of conventional carburizing and nitriding of stainless steels. It also presents an alternative to expensive high nitrogen steels (HNS), that require high alloy contents or powder or pressure metallurgy to reach a high content of nitrogen [5, 38].

Solution nitriding utilizes high temperatures to dissolve nitrogen in austenite and quick cooling so that nitrogen remains in solution and does not form precipitates [4].

Solution nitriding can be applied to austenitic, martensitic and duplex stainless steels [3]. Since hardness is an important property for applications such as bearings and tools, only martensitic stainless steels are dealt with in this project.

2.3.1 Process

Typically the solution nitriding process consists of four steps – solution nitriding at 1050–1150 °C, a fast quenching in high pressure nitrogen, deep freezing and tempering [3].

The solution nitriding takes place in a vacuum furnace filled with nitrogen gas to desired partial pressure. The partial pressure of nitrogen is in the range of 0.1–3 bar depending on steel type. An advantage of using nitrogen is that it is neither toxic nor explosive. The temperature of the treatment is chosen so that the desired case depth is reached in a reasonable time. A higher temperature is used if a thick case is desired or if the steel contains high amounts of chromium or other alloying elements which slows down diffusion of nitrogen. Diffusion times of up to 24 hours are sometimes used [3, 4, 38].

With longer nitriding times comes an increased risk of grain growth. In some cases secondary hardening is needed to refine the grain size [39].

Reaction

The principle behind solution nitriding is the much higher solubility of nitrogen in austenite than in ferrite, as seen in Figure 2.10. Nitrogen that is diffused into the material at high temperature is kept in solid solution in martensite if quenching from the treatment temperature is sufficiently quick [12, 38].

The transfer of nitrogen to the steel can be divided into two steps: adsorption of nitrogen on the steel surface and diffusion into the material [3].

At temperatures above 1000 °C gaseous nitrogen (N_2) cracks by itself to form free nitrogen atoms, which can be adsorbed by the steel surface. The reaction is described by equation 2.14 [12].

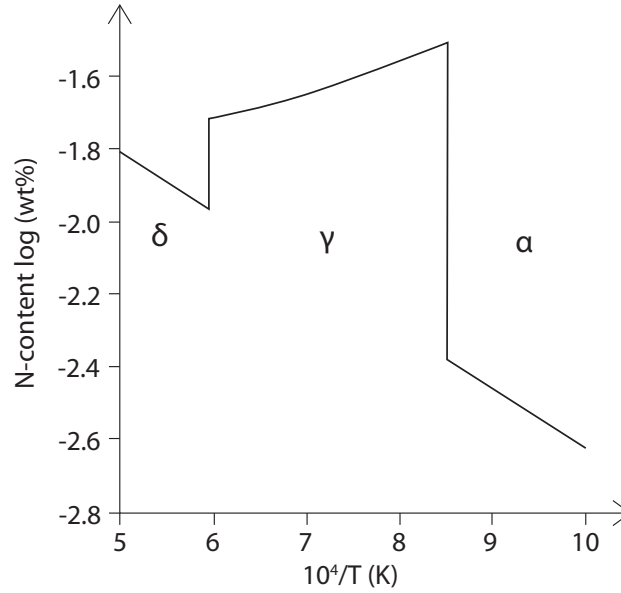


Figure 2.10: The solubility of nitrogen in α , γ and δ -iron at 1 atm pressure of N_2 gas. Data from [3].

$$\frac{1}{2} N_2 = [N] \quad (2.14)$$

The equilibrium content of nitrogen at the steel surface, N_s , is given by Equation 2.15. It depends on three factors – treatment temperature, T_N , partial pressure of nitrogen in the atmosphere, p_{N_2} , and the alloy composition. The term f_N^x represents the influence of an alloying element X on the activity of nitrogen [12].

$$\ln [N]_{Fe-X} = \ln \sqrt{p_{N_2}} - \ln f_N^x - \frac{\Delta H_0}{RT} + \frac{\Delta S_0}{R} \quad (2.15)$$

Increasing the partial pressure of nitrogen increases the equilibrium surface content of nitrogen. So does alloying with an element that attracts nitrogen, such as chromium or molybdenum, which decreases f_N^x . Increasing the temperature also increases the solubility of nitrogen if the heat of solution, ΔH_0 , is positive. In pure iron ΔH_0 is positive for α - and δ -ferrite, but negative for austenite, which corresponds well to the solubility profile seen in Figure 2.10. In ternary high chromium alloys ΔH_0 is negative for all phases. Hence, for a given phase, N_s decreases with increasing temperature in stainless steels. This means that a rise in treatment temperature to increase the diffusion speed must be accompanied by a concurrent increase of the partial pressure of nitrogen in order to keep nitrogen adsorbed on the steel surface [3, 38].

Diffusion into the case is governed by Fick's second law for a semi-infinite body (Equation 2.16) [4].

$$\frac{N_x - N_c}{N_s - N_c} = 1 - \operatorname{erf} \left(\frac{x}{2\sqrt{D_N \cdot t}} \right) \quad (2.16)$$

Quenching

Solution nitriding utilizes pressurized nitrogen gas (N_2) with pressures up to 10 bar for quenching. Gas quenching can be used since the steels utilized have a high hardenability due to high amounts of alloying elements.

The quenching is usually fast enough to keep nitrogen in solid solution. However if higher cooling rates are needed a liquid quenchant can be used, but this requires a change of furnace [4]. Slower quenching rate has the advantage of minimizing distortions [39].

Deep cooling and tempering

Nitrogen is an austenite stabilizer and lowers the martensite start temperature, M_s . In order to transform all the austenite in solution nitrided stainless steels to martensite they have to be deep frozen to -80°C and tempered, typically at 450°C . The tempering also promotes secondary hardening in both case and core [38].

So called “two stage tempering” can be used lower the core hardness. The solution nitrided specimen is quenched to a temperature right above the martensite start temperature of the case. At this temperature parts or all of the core has already transformed to martensite. The quenching is followed by tempering at $550\text{--}580^\circ\text{C}$ which softens the partially transformed core. The austenitic case is thereafter transformed to martensite during cooling, deep freezing and tempering at 450°C [38].

2.3.2 The role of nitrogen

Nitrogen has a higher solubility in austenite than carbon. Isothermal sections of the Fe-Cr-C and Fe-Cr-N phase diagrams at 1050°C are compared in Figure 2.11. It can be seen that the solubility of nitrogen in austenite increases with increasing chromium content whereas the solubility of carbon decreases. Solution nitriding is thus a more suitable process than carburizing for case hardening stainless steels since carburizing tends to produce carbides and ferrite, which deteriorates the mechanical properties [38].

Exchanging carbon for nitrogen increases the amount of free electrons in austenite which makes the interatomic bonds more metallic in character. The increase in free electrons also promotes short range atomic ordering which in turn increases the stability to phase transformations. Carbon on the other hand increases the ionic-covalent character of interatomic bonds and promotes atomic clustering. In stainless steels clustering of carbon and chromium leads to precipitation of chromium carbides which results in a low solid solubility of carbon in austenite as seen in Figure 2.11a. In contrast, the ordering effect

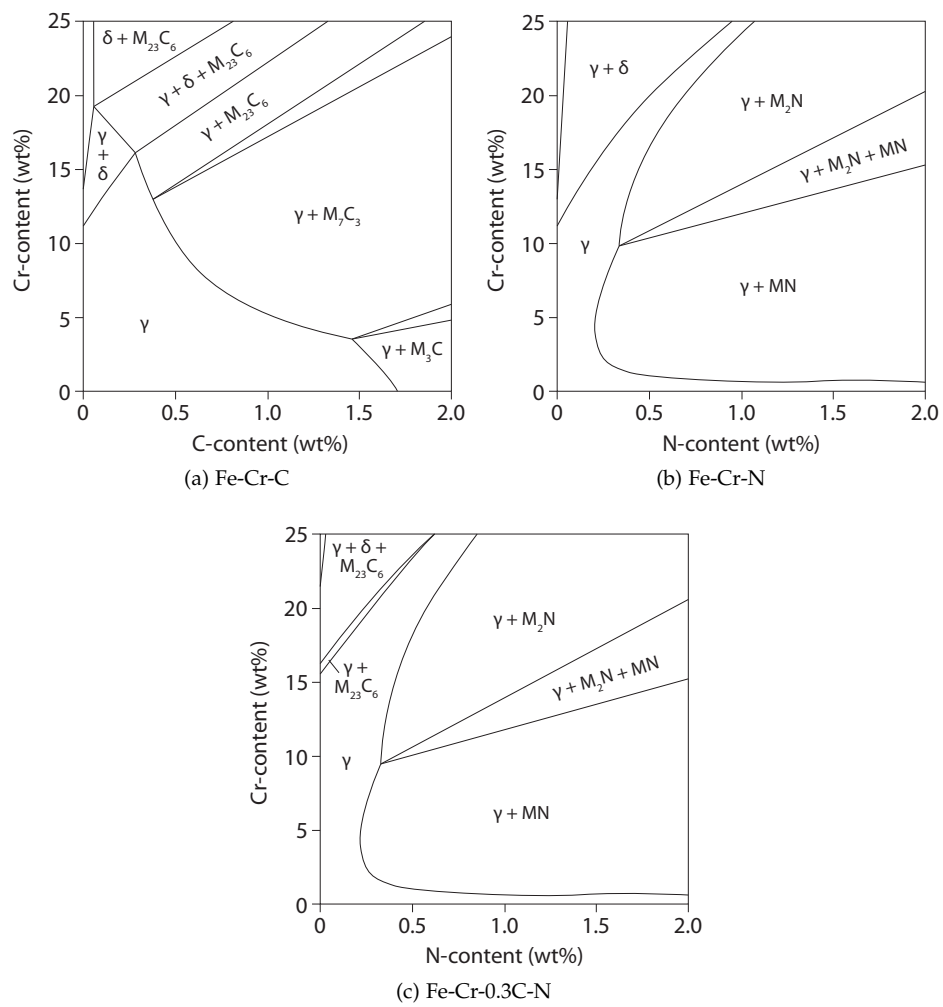


Figure 2.11: Iso-thermal sections at 1050 °C. Data from [14]

of nitrogen leads to a more homogenous distribution of chromium and makes the solubility of nitrogen in stainless austenite higher (Figure 2.11b) [40].

A combination of carbon and nitrogen increases the concentration of free electrons further and promotes short range atomic ordering even more. As seen in Figure 2.11c a combination of carbon and nitrogen enlarges the austenitic field of stainless austenite [40].

2.3.3 Suitable steels

The suitability of different martensitic stainless steels for solution nitriding was investigated by Berns [38], who found that the best results were achieved on steels with a relatively low carbon content, a chromium content of 13–15 wt% and less than 1 wt% molybdenum. Two commercially available alloys were suggested as good alternatives – X12Cr13 and X20Cr13. The material considerations were based on the need for a good combination of case and core properties.

In ternary alloys the solubility of nitrogen increases in the order of tungsten, molybdenum, manganese, chromium, niobium, vanadium and titanium [38]. Out of these elements chromium, manganese and possibly molybdenum are the most interesting for increasing nitrogen solubility. Niobium, vanadium and titanium tend to form nitrides rather than leaving nitrogen in solid solution. Tungsten and molybdenum are expensive [3, 41]. Silicon, nickel, cobalt and copper lowers the solubility of nitrogen [38].

To get a martensitic case with a hardness of 58 HRC or higher the total amount of carbon plus nitrogen in solid solution needs to be above 0.5 wt%. However, to avoid grain boundary precipitates, the nitrogen plus carbon content needs to be kept below a certain value, $(N + C)_{max}$, which is alloy dependent. As described in the previous section ordering is stronger if the stainless austenite contains both carbon and nitrogen. The presence of carbon increases the interstitial solid solubility of nitrogen and a higher $(N + C)_{max}$ is attained. However, high carbon content increases the hardness not only of the case but also in the core, making it less ductile. If a high ductility in the core is desired, carbon content needs to be kept low [38].

Low carbon content and high contents of chromium and molybdenum increases the risk of formation of δ -ferrite in the core. Alloying with chromium is preferred over alloying with molybdenum since chromium is cost effective and increases the solubility of nitrogen more than molybdenum does. Molybdenum does however contribute more to pitting corrosion resistance [38].

Formation of δ -ferrite in the core can be avoided by adding nickel, manganese or cobalt to the alloy. However, nickel and cobalt also lower the solubility of nitrogen in austenite and nickel and manganese promote formation of retained austenite in the case. Deep freezing and tempering are used to reduce the amount of retained austenite, but the amount of substitutional elements still needs to be limited, which is the reason for the upper limit of chromium and molybdenum content [38].

2.3.4 Microstructure

After solution nitriding the microstructure is composed of two regions. The case where nitrogen is found in interstitial solid solution and the core which has just been affected by the temperature cycle of the heat treatment.

The case depth is affected by alloy content and by the process parameters temperature, time and partial pressure. Case depth of up to 3 mm have been reported [4].

Grain growth

The high chromium content and the strong attraction between chromium and nitrogen makes diffusion of nitrogen slower in stainless steels than in pure iron. The more chromium the steel contains, the higher process temperature is needed to limit process time. An undesirable effect of the increased temperature is grain growth. This problem is more pronounced when a thick case is desired since this increases process time [4, 5].

There are several ways to avoid large grains. In a martensitic case the grains can be refined by a second hardening at the same temperature as solution nitriding or at a lower temperature. Another alternative for grain size refinement is alloying with vanadium or niobium which produce a fine dispersion of nitrides which are not dissolved at solution nitriding temperatures and thus inhibits grain growth [38].

Grain boundary precipitates

If the solubility of nitrogen in austenite is exceeded during solution nitriding of stainless steels, brittle chromium M_2N nitrides will start to precipitate along grain boundaries. This occurs most rapidly in the range of 800–1000 °C [4]. At higher nitrogen levels, precipitates will also form discontinuously within the grains. Besides reducing toughness of the material, the precipitates also lead to a lowered corrosion resistance since chromium is depleted from the matrix [12].

Chromium nitrides can be avoided by increasing the solubility limit of nitrogen in austenite by providing a suitable combination of carbon and nitrogen as described in Section 2.3.3. Microalloying with niobium, which promotes intragranular precipitation instead of precipitation along grain boundaries, is an alternative for preserving toughness [38].

Formation of M_2N precipitates can also be avoided by adjusting the process parameters. Increasing the solution nitriding temperature or the partial pressure of nitrogen leads to an increased solubility of nitrogen. However, the solubility of nitrogen and chromium decreases upon cooling and the critical cooling time, $t_{8/5}$, needed to avoid precipitates during quenching becomes shorter with increasing nitrogen content. Figure 2.12 shows an example of critical cooling time for ferritic-martensitic X14CrMo16 [3].

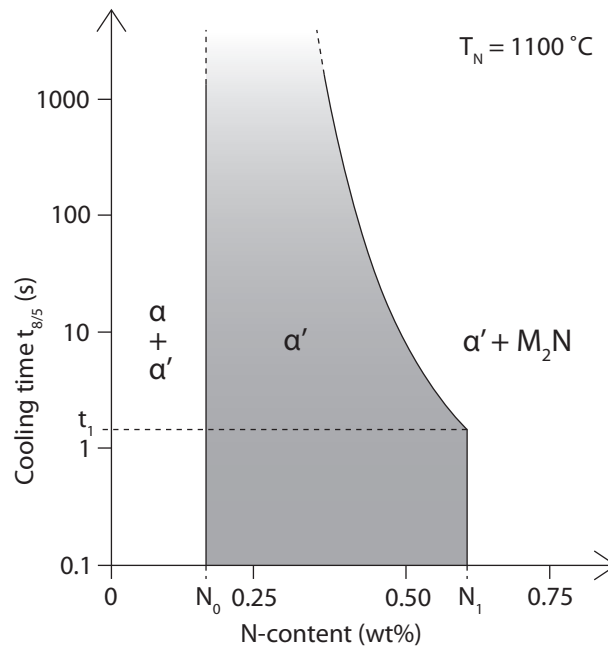


Figure 2.12: Critical cooling time for ferritic-martensitic X14CrMo16. Data from [3].

Another problem with increasing temperature and partial pressure is that it promotes grain growth and ferrite formation in the core. The grain size can be reduced by the use of “double quench hardening”, a second hardening at the same temperature as solution nitriding [38].

2.3.5 Reported properties

After solution nitriding the surface content of nitrogen is in the range of 0.3 to 0.9 wt%, resulting for most martensitic stainless steels in a hard martensitic case on top of a martensitic core [38].

Hardness and wear resistance

Nitrogen in interstitial solid solution increases the hardness of steel much in the same way as carbon in solid solution [3].

Solution nitriding of ferritic X20Cr13 has been reported to produce a martensitic case with a hardness of 58 HRC and in ferritic-martensitic X12Cr13 a martensitic case with a hardness of 60 HRC was produced. This can be compared to through hardened X46Cr13, which has a surface hardness of about 56 HRC [39].

Resistance to wear can be significantly improved by solution nitriding. Berns et al. [4] investigated the wear resistance of solution nitrided ferritic-martensitic X14CrMo16 and found that the mass loss due to vibratory wear was reduced 100 times compared to the conventionally heat treated material. The resistance to sliding wear was also improved and the friction coefficient was lowered in both air and water.

Residual stresses and fatigue properties

Solution nitriding produces compressive residual stresses in the case, which can improve fatigue properties of the treated steel. The higher nitrogen content in the case stabilizes austenite in this region during cooling so that the core transforms to martensite before the case. When the volume of the case expands due to the martensitic transformation, this expansion is resisted by the already transformed core and the case is put in compression [38].

Retained austenite

Nitrogen stabilizes austenite so that deep freezing is needed to transform it to martensite [38]. The Koistinen-Marburger relation, Equation 2.17, can be used to predict the volume fraction of martensite, $V_{\alpha'}$, found in a specimen at a certain temperature, T , provided that the martensite start temperature, M_s , is known [42]. However M_s varies with the nitrogen content which is highest at the surface in solution nitrided specimens. Therefore most retained austenite will be found close to the surface.

Manganese, cobalt and nickel are austenite stabilizer and alloying with these elements lead to more retained austenite [38].

$$V_{\alpha'} = 1 - \exp \beta (M_s - T) \quad \beta \approx 0.011 \quad (2.17)$$

Transformation of retained austenite to martensite during service of a component should be avoided since the volume increase associated with the transformation can cause shape changes. The retained austenite that may remain after deep freezing and tempering is however quite stable at room temperature. Another problem with retained austenite is that it lowers both hardness and residual stresses. Retained austenite transformed during service has however been reported to have a positive effect on wear and fatigue properties [38].

Corrosion resistance

Nitrogen in solid solution improves the corrosion resistance of stainless steel. Compared to carbon, nitrogen lowers the susceptibility to localized corrosion since nitrogen causes a more homogenous distribution of chromium. If nitrides are allowed to precipitate during solution nitriding the corrosion resistance is lowered. However the sensitization around nitride precipitates is

smaller than around carbide since nitrogen modifies the surface chemistry of the passive film and improves passivation [4, 41].

Berns et al. [4] made immersion test on solution nitrided martensitic-ferritic X14CrMo16 in ferritic sulfate + sulphuric acid and in 5 % hydrochloric acid and found that solution nitriding lowered the mass loss in the former but increased it in the latter.

Manufacturing advantages

One advantage of solution nitriding from a product development perspective is that narrow and blind holes can be solution nitrided evenly. This is difficult to achieve with standard nitriding or case hardening. The reason why solution nitriding works better is that the cracked nitrogen constantly recombines to nitrogen gas and thus the gas stays active [39].

Another interesting feature of solution nitriding is that it allows machining of parts to be replaced by cold forming. The hardness of martensitic stainless steels increases with increasing carbon content which makes them hard to cold form. Solution nitriding after cold forming allows the use of stainless steel with a lower initial carbon content [39].

Chapter 3

Method

The first part of this chapter discusses which steels that were selected for the project and why. It also gives some background on the conventional heat treatment of these steels and what properties can be expected from them. The second part of the chapter describes the heat treatment parameters of the different heat treatments used in the project. The third part of the chapter is dedicated to methods used to evaluate the effect of the processes on different materials. Finally a compilation of the test pieces and what processes and which test were applied to each of them is presented.

3.1 Steel selection

The study includes one group of martensitic stainless steels, one group of heat resistant steels and one group of bearing steels. Two criteria were considered when selecting the steels to include in the study:

- The steels should be of interest for the bearing industry.
- The steels should be suitable for the processes.

Solution nitriding was developed as a process for case hardening stainless steels and a group of martensitic stainless steels were included in the study. The reason for choosing only martensitic stainless steels and not for example austenitic ones is that high hardness is required if the steels are to be of interest for bearing applications. Martensitic stainless steels are the only stainless steels that can fulfill that requirement.

A group of heat resistant steels were also selected. Three of these steels have a chromium content of 3–5 wt% and the fourth one is a martensitic stainless steel. Thermodynamic calculations have shown that chromium improves the solubility of nitrogen in austenite (see Figure 2.11b). It is interesting to investigate if the chromium found in the heat resistant steels is high enough for the solution nitriding process to work.

For ferritic and austenitic nitrocarburizing five bearing steels were selected – two alloys with a high carbon content that are normally through hardened, one grade with medium carbon content and two low carbon grades that are usually case hardened.

3.1.1 Bearing steels

The five bearing steels included in the study are: 100Cr6, 100CrMo7-4, 50CrMo4, 18CrNiMo7-6 and 16MnCr5. Their compositions are given in Table 3.1.

100Cr6

100Cr6 is a high carbon steel, which is very common in bearing applications. It is normally through hardened to a martensitic or bainitic structure with a hardness in the range of 58–65 HRC [43]. One sample of through hardened 100Cr6 was included in the austenitic nitrocarburizing process.

100CrMo7-4

100CrMo7-4 is also a through hardening, high carbon, bearing steel. The main difference from 100Cr6 is that it contains molybdenum and higher amounts of chromium and manganese.

In the present study 100CrMo7-4 was used in the annealed condition for both ferritic and austenitic nitrocarburizing.

50CrMo4

50CrMo4 is a medium carbon bearing steel. It was ferritic and austenitic nitrocarburized in the soft condition.

18CrNiMo7-6 and 16MnCr5

18CrNiMo7-6 and 16MnCr5 are case hardening steels with a relatively low carbon content. The main difference between the two is that 18CrNiMo7-6 has a much higher nickel and molybdenum content. Both materials were ferritic and austenitic nitrocarburized in the soft condition.

3.1.2 Martensitic stainless steels

Alloying steel with chromium increases its corrosion resistance. Chromium is more prone to oxidation than iron and in an alloy it selectively corrodes, forming a protective film of Cr_2O_3 on the steel surface. The film protects the steel from further corrosion. This is the fundamental idea of stainless steel [42].

Steel	C (wt%)	Si (wt%)	Mn (wt%)	Cr (wt%)	Ni (wt%)	Mo (wt%)
100Cr6	0.93–1.05	0.15–0.35	0.25–0.45	1.35–1.60	-	max 0.10
100CrMo7-4	0.93–1.05	0.15–0.35	0.60–0.80	1.65–1.95	-	0.40–0.50
50CrMo4	0.46–0.54	max 0.40	0.50–0.80	0.90–1.20	-	0.15–0.30
18CrNiMo7-6	0.15–0.21	max 0.40	0.50–0.90	1.50–1.80	1.40–1.70	0.25–0.35
16MnCr5	0.14–0.19	max 0.40	1.00–1.30	0.80–1.10	-	-

Table 3.1: Typical composition of selected bearing steels

Steel	C (wt%)	Si (wt%)	Mn (wt%)	Cr (wt%)	Ni (wt%)	Mo (wt%)
X46Cr13	0.43–0.50	max 1.00	max 1.00	12.50–14.50	-	-
X65Cr13	0.60–0.70	max 1.00	max 1.00	12.50–14.50	-	max 0.75
X105CrMo17	0.95–1.20	max 1.00	max 1.00	16.00–18.00	max 0.75	0.40–0.80

Table 3.2: Typical composition of selected stainless steels

Steel	C (wt%)	Si (wt%)	Mn (wt%)	Cr (wt%)	Ni (wt%)	Mo (wt%)	Co (wt%)	V (wt%)
M50	0.77–0.85	max 0.25	max 0.35	3.75–4.25	max 0.15	4.00–4.50	-	0.90–1.00
M50NiL	0.11–0.15	0.10–0.25	0.15–0.35	4.00–4.25	3.20–3.60	4.00–4.50	max 0.25	1.13–1.33
32CrMoV13	0.29–0.36	0.10–0.40	0.40–0.70	2.80–3.30	-	0.70–1.20	-	0.15–0.35
Pyrowear 675	0.05–0.09	0.10–0.70	0.50–1.00	12.00–14.00	2.00–3.00	1.50–2.50	4.00–7.00	0.40–0.80

Table 3.3: Typical composition of selected heat resistant steels

Martensitic stainless steels contain 11–18 wt% chromium and up to 1 wt% carbon. They are magnetic and can be heat treated to achieve a martensitic structure, much in the same way as carbon and low alloy steels. Compared to other stainless steels, martensitic stainless steels have a relatively low corrosion resistance owing to the fact that a martensitic structure cannot be achieved if the amount of alloying elements is too large. They do however present a good combination of strength, hardness, toughness and moderate corrosion resistance making them attractive for uses such as pipes in oil production, cutlery and applications where stability at elevated temperature is of importance. Some alloys have been tailored specifically for use in turbines [42].

In this study three martensitic stainless steels were included – X46Cr13, X65Cr13 and X105CrMo17. Their compositions are given in Table 3.2. The two first contain chromium and carbon as main alloying elements. The latter is also alloyed with molybdenum. X105CrMo17 is the hardest of all stainless steels owing to its martensitic structure in combination with its many carbides [44].

3.1.3 Heat resistant steels

The heat resistant steels included in the study are: M50, M50NiL, 32CrMoV13 and Pyrowear 675. Their chemical compositions are given in Table 3.3.

M50

M50 is a tool steel that was developed in the 1950's. It is commonly used in aircraft engine bearings and can withstand high operating temperatures due to good hot hardness provided by molybdenum carbides [6, 45].

M50 has a high hardenability and is usually through hardened. A common heat treatment cycle consist of pre-heating to 500 °C, heating to 800 °C and austenitizing at 1100 °C whereafter the material is quenched to 560 °C and air cooled to room temperature. Not all carbides are dissolved at the austenitizing temperature so that after cooling the microstructure is composed of martensite, 20–30 % retained austenite, and primary carbides (mainly molybdenum-rich M_2C , vanadium-rich MC and possibly some chromium-rich M_6C). Deep cooling to -70 °C is used to transform the retained austenite to martensite. Thereafter a secondary hardening at 540–550 °C for 2 hours followed by air cooling is performed. The deep cooling step can be omitted and replaced by several tempering cycles at approximately 550 °C [6].

After hardening, M50 has a hardness of approximately 60 HRC and can withstand operating temperatures up to approximately 310 °C. High temperature strength also makes the material able to sustain shorter periods of starved lubrication without failure. M50 also has a good wear resistance due to the large primary carbides [6].

The rolling contact fatigue life of M50 can be improved by using so called duplex hardening in which the normal hardening treatment is followed by nitriding at 500 °C for 40–70 hours. This results in a surface hardness of 1000–1250 HV and compressive residual stresses in the case [6].

M50NiL

M50NiL is a carburizing version of M50. The main differences between the materials is that M50NiL has a much lower carbon content and that it contains nickel. Since M50NiL is not through hardened it has an increased fracture toughness compared to M50. Another advantage of M50NiL is that case hardening creates compressive residual stresses in the surface so that excellent rolling contact fatigue properties are obtained [6].

The heat treatment commonly applied to M50NiL is similar to the one for M50, except that it is preceded by carburizing at 840–950 °C for 4–30 hours. Several tempering cycles are applied and after the heat treatment the case of M50NiL has a microstructure similar to M50 with a low content of retained austenite. The core consists of fine tempered martensite, with a distribution of small carbides, less than 1 µm in diameter. In M50 the carbides can be several tens of micrometers. Duplex hardening can also be applied to M50NiL [6].

The maximum service temperature of M50NiL is 315 °C and the material owns its hot hardness to carbides (M_6C , $M_{23}C$ and MC) precipitated during secondary hardening [6].

32CrMoV13

32CrMoV13 is a deep nitriding steel used in bearings for aerospace applications. Typically it is found in turbine engines, where bearings operate at high speed and temperature [7, 46].

Nitriding is performed at 525–575 °C for about 100 hours. Within this time a case depth of about 600 µm is reached. The compound layer is usually removed by grinding since it is brittle. The diffusion zone contains nitrogen in interstitial solid solution and fine, semi-coherent CrN precipitates with a diameter of about 10 nm. Both the interstitial nitrogen and the precipitates contribute to the increased hardness of the diffusion zone. The formation of CrN precipitates in the case also expand the ferritic matrix causing residual stresses that improve fatigue properties through inhibition of crack growth [7, 46]. Precipitation of chromium nitrides does however deplete the matrix of chromium and thereby the corrosion resistance decreases.

The case hardness achieved by the nitriding treatment depends on the presence of nitride forming elements (Cr, Mo and V in this specific case) and on the hardness of the starting structure. Therefore an initial heat treatment is carried out before nitriding in order to obtain a suitable core hardness (380–420 HV). During this treatment the steel is hardened by oil quenching from 900–950 °C followed by a tempering at 625–650 °C. The treatments result in a steel with low sensibility to aging and hardness is maintained after 100 hours at 450 °C [7, 46].

Since nitriding is carried out at relatively low temperatures the distortions induced by it are small and little subsequent processing is needed, making it easier to manufacture complex parts. The quench and temper treatment also contributes to the minimization of shape changes since it keeps the base material from softening during nitriding [7, 46].

The 32CrMoV13 samples used in this study were delivered in a quenched and tempered condition. They had also been subjected to a 80 hours nitriding treatment.

Pyrowear 675

Pyrowear 675 is a carburizing martensitic stainless steel used for bearings and gears in aerospace applications. It was developed in the beginning of the 1990's to meet the need for an alloy which combine good corrosion resistance with toughness and high temperature capability. Case hardened steels generally provide superior toughness compared to through hardening grades [47].

Pyrowear 675 has a very low carbon content for high core toughness. It contains chromium for corrosion resistance and molybdenum for secondary hardening and resistance to pitting corrosion. Vanadium is also added for formation of carbides which improves wear resistance of the case. Nickel and cobalt are added to avoid formation of δ -ferrite in the core [47].

The recommended heat treatment for Pyrowear 675 is summarized in Table 3.4. A relatively low carburizing temperature and a long carburizing time is used to avoid formation of coarse carbides. Annealing and normalizing is used to break up carbide necklacing and diffuse excess carbon in the case inwards. Thereafter the specimens are austenitized at a temperature high enough to dissolve the carbides but low enough to minimize retained austenite in the case followed by step quenching. Finally the material is deep frozen to transform retained austenite in the case and thereafter tempered [47].

Treatment	Temperature	Time	Cooling/warming
Pre-oxidizing	1038 °C	0.5 h	Air
Carburizing	871 °C	24 h	Oil
Annealing	649 °C	12 h	Air
Normalizing (x 2)	1038 °C	0.5 h	Air
Austenitizing	1038 °C	0.25 h	Quenching to 204 °C + air cooling
Deep freezing	-73 °C	1 h	Air warming
Tempering (x 2)	316 °C	2 h	Air

Table 3.4: Recommended heat treatment of Pyrowear 675.

After the heat treatment cycle Pyrowear 675 has a surface hardness of 62 HRC and a hardness of above 50 HRC in the outer 0.89 mm. At 200 °C a hardness of 61.5 HRC is maintained. The final case microstructure consist of a martensitic matrix with well distributed carbides and no retained austenite [47].

3.2 Heat treatment parameters

3.2.1 Ferritic nitrocarburizing

Samples of 100Cr6, 100CrMo7-4, 50CrMo4, 18CrNiMo7-6 and 16MnCr5 were ferritically nitrocarburized in a seal quench furnace using a standard nitrocarburizing process. Figure 3.1 shows a schematic view of the process. Before heat treatment samples were cleaned using a three step alkaline washing and pre-heated to combust possible remaining contaminants. The samples were nitrocarburized at 580 °C for 2.5 hours in an atmosphere of 60% NH₃, 35% N₂ and 5% CO₂. Thereafter they were quenched in oil at 60 °C and tempered at 180 °C.

3.2.2 Austenitic nitrocarburizing

The austenitic nitrocarburizing parameters were the same as for the ferritic process, except that the temperature was raised to 620 °C. The temperature was selected high enough so that an austenite layer would be formed below the compound layer in all alloys, but as low as possible to minimize distortions. A schematic view of the process is shown in Figure 3.2. Just before quenching the samples were exposed to the atmosphere for a few seconds. This so called flash oxidation produced a thin oxide layer on the surface of the samples. The test included same materials as the ferritic process plus an additional sample of through hardened 100Cr6.

Tempering

As discussed in Section 2.2.5, the retained austenite layer formed by austenitic nitrocarburizing can transform to a very hard bainitic structure when tempered. Since the austenite layer was not transformed after the first tempering included in the austenitic nitrocarburizing process a second tempering was performed in an air circulating tempering furnace. Based on the data presented in Table 2.2 and Figure 2.9 a treatment at 300 °C for 1 hour followed by air cooling was decided upon. Two materials were selected – 18CrNiMo7-6 with a low carbon content and 100Cr6 with a high carbon content. The first material was chosen because it had a thick austenite layer and thus more accurate hardness measurements could be made. The second material was selected because it is very common in bearing applications.

3.2.3 Solution nitriding

Samples of the stainless and heat resistant steels were solution nitrided at 1100 °C 2.5 hours in a partial pressure of nitrogen gas (N₂). The samples were quenched in gaseous nitrogen and deep cooled to –80 °C. Thereafter they were tempered at 150 °C for 2 hours. A schematic representation of the process is shown in Figure 3.3. The total process time was 6.5 hours. All samples were

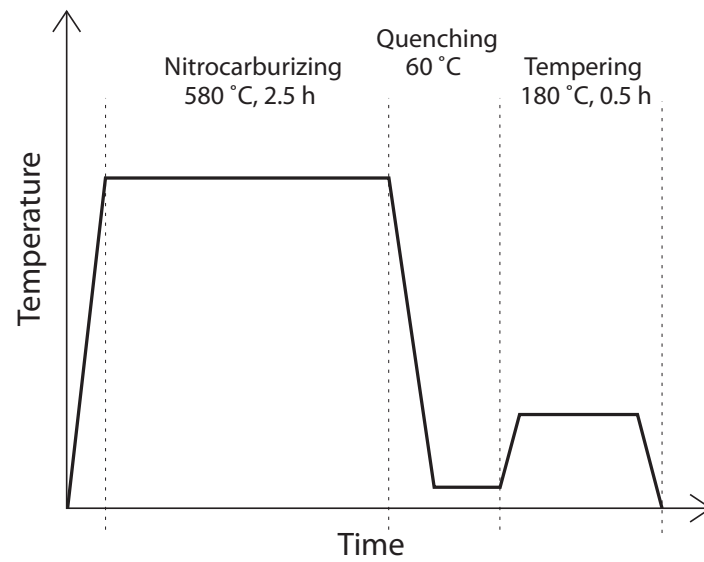


Figure 3.1: The ferritic nitrocarburizing process

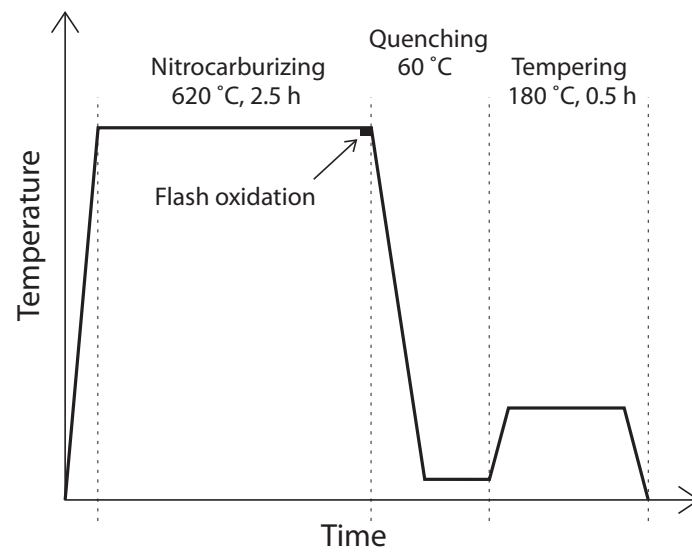


Figure 3.2: The austenitic nitrocarburizing process

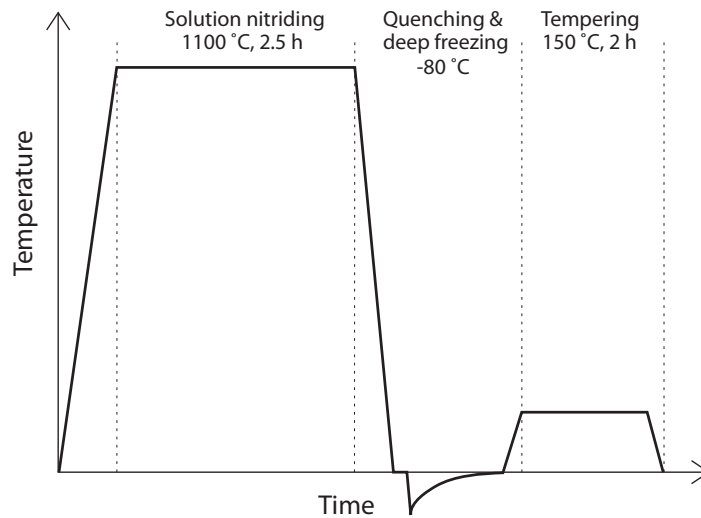


Figure 3.3: The solution nitriding process

heat treated in the same process and the process parameters were adapted to X46Cr13.

3.3 Sample preparation

Sample preparation for microhardness testing and microscopic examination consisted of three steps – cutting, mounting and grinding/polishing. After cutting, the samples were mounted in MultiFast resin. The nitrocarburized samples were covered in aluminum foil prior to mounting. This was done to support the compound layer so that the edges would stay sharp and not spall during polishing. After mounting, the samples were ground and polished using a semi-automatic system. The nitrocarburized samples were polished for longer times with a lower pressure to protect the compound layer from spalling.

Etching was done using 1.5 % Nital for the bearing steels and for M50 and 32CrMoV13. The stainless steel samples and M50NiL were etched using Kalling's reagent No. 1 (1.5 g CuCl_2 , 33 % HCl , 33 % $\text{C}_2\text{H}_5\text{OH}$, 33 % H_2O [48]).

3.4 Microstructure examination

Microscopic investigation was performed using a light microscope with a maximum magnification of 1000x.

Thickness of compound layer

The thickness of the compound layers on the nitrocarburized samples were examined in unetched condition using light microscopy. Both the full depth and the depth of the porous zone were measured using 1000x magnification. Figure 3.4 shows how the compound layer measurements were performed. On the austenitically nitrocarburized samples the thickness of the retained austenite zone was also measured. This was done in the etched condition. On each sample the thickness was measured in ten locations to minimize the influence of local variations and measurement errors. The numbers presented in this report are the arithmetic mean values of the measurements.

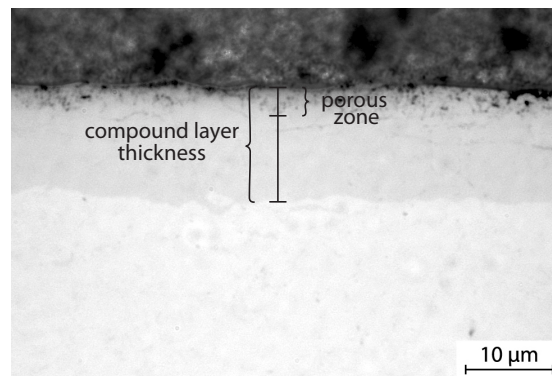


Figure 3.4: Method for measuring compound layer thickness.

3.5 Hardness

As explained in Section 2.1 the hardness distribution in a material affects properties such as load bearing capacity and fatigue resistance. A semi-automatic Vickers indenter was used to measure the micro hardness profiles on the treated samples. For the solution nitrided samples a load of 1 kg was used and for the nitrocarburized samples a load of 500 g was used. The reason for using a lower force on the nitrocarburized samples is that some of the nitrocarburized samples have a soft core. Indents produced with 1 kg load in this region become too big to measure with the available equipment.

The load utilized could have an effect on the result and should always be specified, but the difference between measurements made with 500 g and 1 kg load is considered nonsignificant [49].

The microhardness measurements were utilized to evaluate the nitrocarburizing depth. There are several ways to specify nitrocarburizing depth. It could be defined either as the depth below the surface at which the hardness is 400 HV [50] or as the depth at which the hardness is 50 HV above the core hardness. Since some materials in the present study were nitrocarburized in the soft condition the first method gives misleading results and the second alternative was used.

The compound layer and the austenitic layers found in the nitrocarburized samples are very thin and it was not possible to measure their hardness with the Vickers indenter. Instead a Knoop indenter with a force of 15 gf was used. The difference between Knoop and Vickers is the shape of the diamond indenter. Vickers utilizes a square based pyramidal indenter with equally long sides. Both diagonals are measured and their mean value is used to calculate the hardness according to Equation 3.1. A Knoop indenter has an oblong diamond shape, where only the long diagonal is measured and used to calculate the hardness according to Equation 3.2.

$$HV = \frac{1.85P}{d^2} \quad (3.1)$$

$$HK = \frac{14.2P}{l^2} \quad (3.2)$$

A comparison of the Knoop and Vickers indenters can be seen in Figure 3.5 [44]. Since the Knoop diamond has little extension in one dimension it is suitable for measurements on thin layers. The longer diagonal makes it possible to use less force with the Knoop indenter [49]. However, the fact that only one diagonal is measured makes Knoop measurements more sensitive to measuring faults.

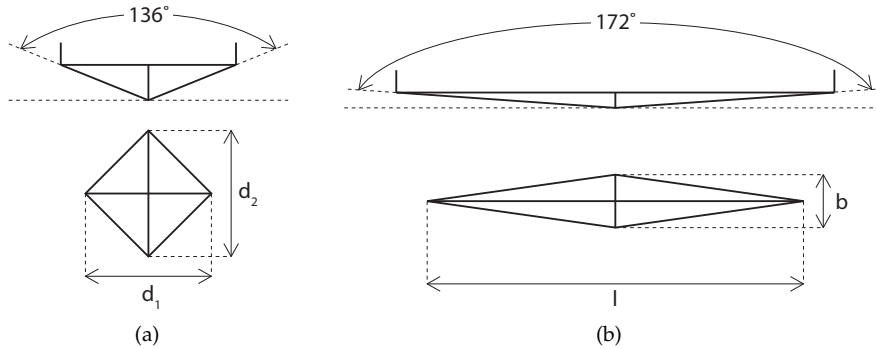


Figure 3.5: Comparison of the Vickers (a) and the Knoop indenter (b)

The Knoop measurements are presented together with a Vickers conversion scale. The scale is based on measurements on the same hardness blocks with a Knoop and a Vickers indenter. A load of 15 gf was applied to the Knoop indenter and a load of 1 kgf was applied to the Vickers indenter. It is however difficult to translate Knoop hardness into other hardness scales correctly when low loads are applied and therefore the conversion scale should not be interpreted as representing absolute values and should be used for indication only.

Surface hardness

The surface hardness of the solution nitrided samples was measured with a Rockwell hardness tester and hardness was reported in Rockwell C, HRC. Rockwell C uses a diamond cone indenter and a load of 150 kgf. The depth of the indent is measured [44]. The method could not be used on the nitrocarburized samples since the indenter breaks through the hard surface layer and into the softer base material so that hardness values below the lower bound of the HRC-scale are attained. Instead the surface hardness of the nitrocarburized samples is given as microvickers hardness at 100 μm depth. This means that surface hardness of the solution nitrided samples and the nitrocarburized samples are not directly comparable.

3.6 Out-of-roundness

Roundness is an important parameter to measure on circular rotating components since failure to fulfill this criterion might shorten the lifespan of the component drastically. Noise can also be a problem caused by large out-of-roundness [51].

Heat treatment always induces thermal distortions, but the question is how large. Out-of-roundness measurements is an important tool in assessing whether post grinding is needed to compensate for the thermal distortions induced by a certain heat treatment.

In this project, out-of-roundness was measured before and after ferritic and austenitic nitrocarburizing on rings of a high carbon bearing steel with a diameter of 75 mm and before and after solution nitriding on a 32CrMoV13 ring with a diameter of 164 mm. The equipment used a stylus to trace the perimeter of the part and the measurement data was printed on a polar chart.

On a perfectly round part all points on the perimeter lies at an equal distance from the central axis. Of course, this perfectly round part only exists in theory. It is however possible to specify how much a shape deviates from ideal roundness. There are several ways to do this [52]. In this project, VDp , the outside diameter variation of a ring was measured. It is a two point method where the difference between the smallest and largest diameter in a single radial plane are compared [43].

3.7 Residual stress measurement

Residual stresses affect the fatigue properties of bearing components and compressive residual stresses in the surface region can significantly improve fatigue life. Therefore it is important to assess the residual stresses induced by heat treatment.

Residual stresses were measured by X-ray diffraction (XRD) on three rings of a high carbon bearing steel. One was carbonitrided for 8 hours, one was

ferritic nitrocarburized and one was austenitic nitrocarburized. The measuring equipment parameters are summarized in Table 3.5.

Machine	XTRESS3000 (by Stresstech)
X-ray tube	CrK α
X-ray voltage	30 kV
X-ray current	6.7 kV
Collimator	3 mm
Detector angle	156.4°
Calibration	Stress free ferritic powder

Table 3.5: X-ray equipment parameters for residual stresses measurements

Residual stresses cannot be measured directly. Instead X-ray diffraction is used to measure the distance between crystal lattice planes in a solid. The method utilizes that residual stresses increase or decrease the distance between lattice planes and assumes a linear elastic distortion of the crystal lattice [53].

As X-rays of a specific wavelength collide with the material they are diffracted at an angle determined by the lattice spacing. The diffraction angle is measured and the distance between crystal lattice planes are calculated using Bragg's law, Equation 3.3, where n is an integer determined by the order of diffraction, λ is the wavelength of the X-rays, d is the distance between crystal lattice planes and θ denotes the diffraction angle. The calculated lattice spacing is compared to the lattice spacing in a stress free powder and the residual stresses can be determined [53].

$$n\lambda = 2d \sin \theta \quad (3.3)$$

Electrochemical etching with a NaCl electrolyte was used to allow measurements of residual stresses at different depths below the surface. If residual stresses in a specific location are of interest measurements have to be alternated with stepwise etching in the same hole. Otherwise etching to different depths can be done in several geometrically equivalent locations prior to the residual stresses measurements. Etching times to reach a certain depth are usually selected based on experience. However in this project it was not known if and how the compound layer on the nitrocarburized samples would affect the etching depth. Therefore it was important to be able to measure the etching depth and consequently etching was done in several locations.

It was not possible to measure the residual stresses in the compound layer. Partly because no suitable stress free powder was available, partly because the compound layer contains two phases, γ' and ϵ , which have different crystal structures and different lattice spacing. This complicates matters since it might become difficult to attribute a certain diffraction peak to the right phase.

3.8 Corrosion resistance test

Evaluation of corrosion resistance was done in neutral salt spray according to SS-ISO 9227. The tests were carried out by an external laboratory. Neutral salt spray testing is an accelerated corrosion test method that utilizes test chamber with controlled conditions. In the test chamber the temperature is elevated and a saline fog is produced continuously from a 5 % solution of NaCl.

The samples were documented in the unexposed condition, after 3, 18, 42, 66, 80 and 104 hours and finally after cleaning. Visual inspection was used to evaluate the percentage of the surface area that had corroded.

The aim of the corrosion test was to evaluate the relative corrosion resistance of heat treatments and materials and for this purpose neutral salt spray testing is an adequate method. It should however be noted that the correlation between the result of neutral salt spray testing and actual life length of a product can be weak, since corrosion is a complex process that can be affected by other factors than the ones taken into account in the test.

3.9 Glow discharge optical emission spectroscopy

Glow discharge optical emission spectroscopy, GD-OES, was used to analyze the chemical composition in the near surface of the nitrocarburized and solution nitrided samples. Profiles for each element were made from the surface to a depth of 35–50 μm . The aim was to reach a better understanding of how the heat treatments affect the concentration of carbon and nitrogen at different depths and to relate this to properties such as hardness and corrosion resistance. The measurements were done by an external laboratory.

GD-OES uses glow discharge, a plasma created by passing a current through a low pressure noble gas at 100–1000 V, to sputter elements from the sample. The noble gas used is normally argon. During the discharge the sample serves as a cathode and is bombarded by positive ions from the noble gas. The bombardment removes atoms from the sample and an atomic vapor is formed. The sputtered material emits photons, with specific wavelengths that are characteristic of the element the photon comes from – characteristic spectral lines. The concentration of different elements in the sample can be determined by measuring the intensity of the spectral lines [54, 55].

The main advantages of GD-OES is the simple sample preparation and the short measurement duration, typically in the range of 10 s/ μm [56]. All elements are measured simultaneously and the method works for light elements such as oxygen, carbon and nitrogen. This makes it possible to obtain good quantitative data on composition in relatively short time [55].

Since GD-OES measurement are performed at low pressure the sealing between the apparatus and the sample needs to be tight, which makes it difficult to measure on curved surfaces [57]. In the present study, measurements on rings were excluded due to this reason. Another limitation of the method is that the analyzed area is relatively large, typically in the range of 4 mm [56].

This was however not a problem in the present case. The depth of the measurements are limited by build-up of recondensed sputtering products around the analyzed area which eventually reaches the anode and causes short circuiting [55]. The maximum measurement depth is about 100 μm and thus the penetration depth of interstitial elements could not be assessed in this way [56].

It should be noted that the data presented in this report have been filtered for readability purposes and that only major alloying elements and alloying elements relevant for the discussion are shown in the GD-OES graphs. It should also be taken into consideration that the GD-OES measurements were optimized for nitrogen contents in the range of what is normally present in compound layers of nitrided and nitrocarburized steels. The sensitivity of the method to low amounts of nitrogen is limited and below 0.3 wt% the results are uncertain.

3.10 Summarized test plan

The heat treatments and analyses applied to each material are summarized in Table 3.6.

Material	TH	FN	AN	SN	Temp	HV	HK	Micro	OOR	GD-OES	Corrosion
100Cr6	X					X		X	X		X
100Cr6	X		X			X		X	X		X
100CrMo7-4						X		X			
100CrMo7-4		X				X	X	X		X	
100CrMo7-4			X			X	X	X		X	
50CrMo4						X		X			X
50CrMo4		X				X	X	X		X	X
50CrMo4			X			X	X	X		X	X
18CrNiMo7-6						X		X			
18CrNiMo7-6		X				X	X	X		X	
18CrNiMo7-6			X			X		X		X	
18CrNiMo7-6			X		X	X	X	X			
16MnCr5						X		X			
16MnCr5		X				X	X	X		X	
16MnCr5			X			X	X	X		X	
X46Cr13						X		X			X
X46Cr13				X		X		X		X	X
X65Cr13						X		X			X
X65Cr13				X		X		X		X	X
X105CrMo17						X		X			X
X105CrMo17				X		X		X		X	X
M50						X		X			X
M50				X		X		X		X	X
M50NiL						X		X			
M50NiL				X		X		X		X	
32CrMoV13						X		X			
32CrMoV13				X		X		X		X	
Pyrowear 675						X		X			
Pyrowear 675				X		X		X		X	

Table 3.6: Test plan (TH = through hardened, FN = ferritic nitrocarburized, AN = austenitic nitrocarburized, SN = solution nitrided, Temp = extra tempering, HV = Vickers hardness profile, HK = Knoop hardness profile, Micro = microstructure examination, OOR = out-of-roundness measurements, GD-OES = GD-OES measurements, Corrosion = corrosion test)

Chapter 4

Results

The results of the different analyses are presented in the following chapter, which is divided into two main parts. The first part presents the result of the ferritic and austenitic nitrocarburizing, whereas the second part focuses on solution nitriding.

4.1 Nitrocarburizing

The ferritic nitrocarburized specimens have a dark grey surface. On the austenitic nitrocarburized specimens the surface has a brownish tint due to the formation of an oxide layer.

4.1.1 Hardness

The micro Vickers hardness profiles of the nitrocarburized samples are shown in Figure 4.1 through 4.4. Generally it can be said that the difference in hardness between ferritic and austenitic nitrocarburizing is small. Ferritic nitrocarburizing produces a somewhat higher hardness close to the surface, whereas austenitic nitrocarburizing results in a deeper nitrocarburizing depth. The difference in nitrocarburizing depth is more pronounced in the samples with lower carbon content. The core hardness is slightly lower than the hardness of the reference samples after both ferritic and austenitic nitrocarburizing. In general it is lower for the austenitic samples than the ferritic ones.

The composition of the base material has a large impact on the hardness profiles. A lower carbon content in the substrate leads to a higher hardness close to the surface, but also to a softer core. The highest hardness at 100 μm depth is found in ferritic nitrocarburized 18CrNiMo7-6 and the deepest nitrocarburizing depth is found in austenitic nitrocarburized 16MnCr5.

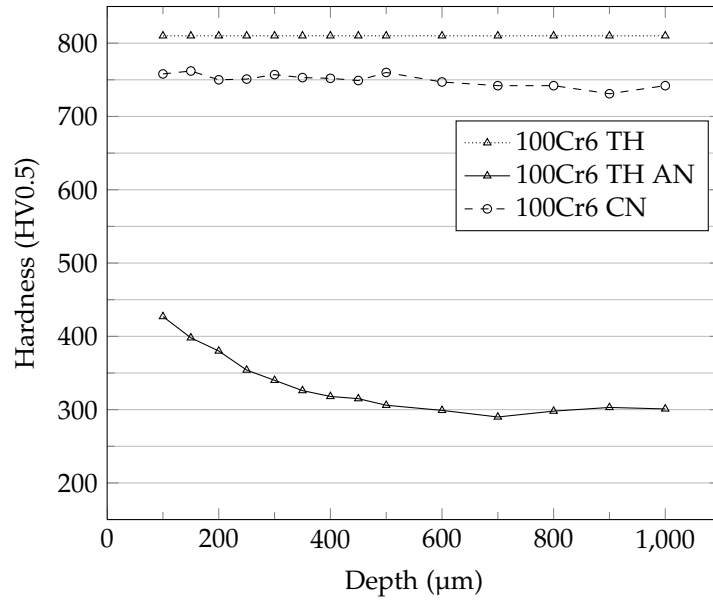


Figure 4.1: Hardness profile of nitrocarburized 100Cr6 samples (TH = through hardened, CN = carbonitrided, AN = austenitic nitrocarburized).

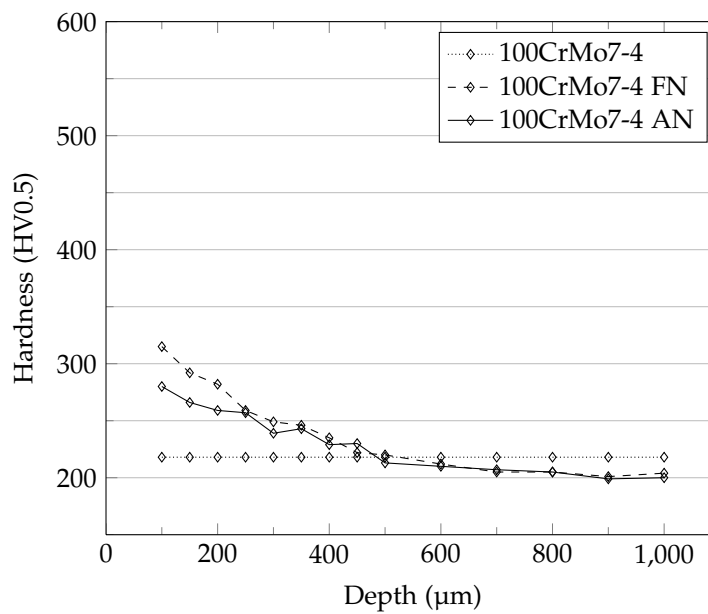


Figure 4.2: Hardness profile of nitrocarburized 100CrMo7-4 samples (FN = ferritic nitrocarburized, AN = austenitic nitrocarburized).

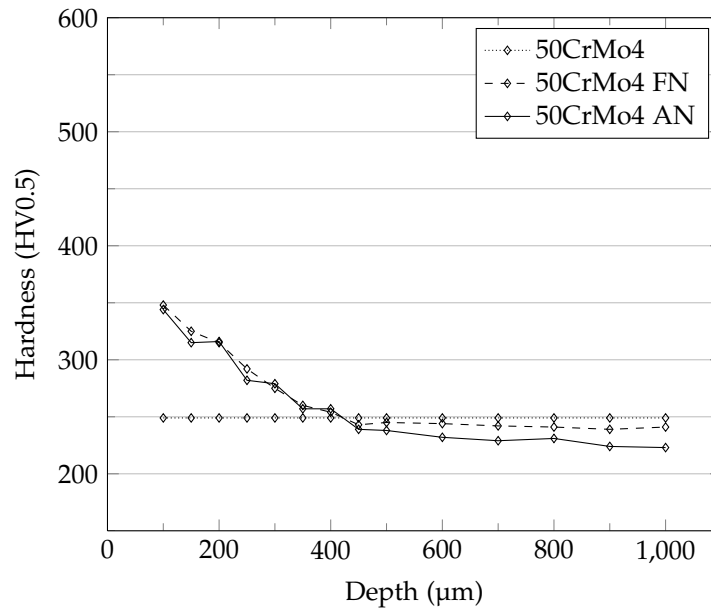


Figure 4.3: Hardness profile of nitrocarburized 50CrMo4 samples. (FN = ferritic nitrocarburized, AN = austenitic nitrocarburized)

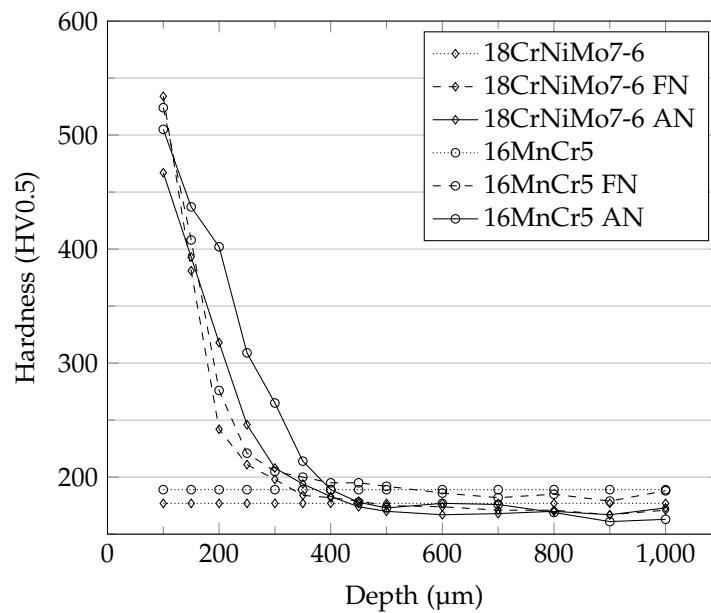


Figure 4.4: Hardness profile of nitrocarburized low carbon samples. (FN = ferritic nitrocarburized, AN = austenitic nitrocarburized)

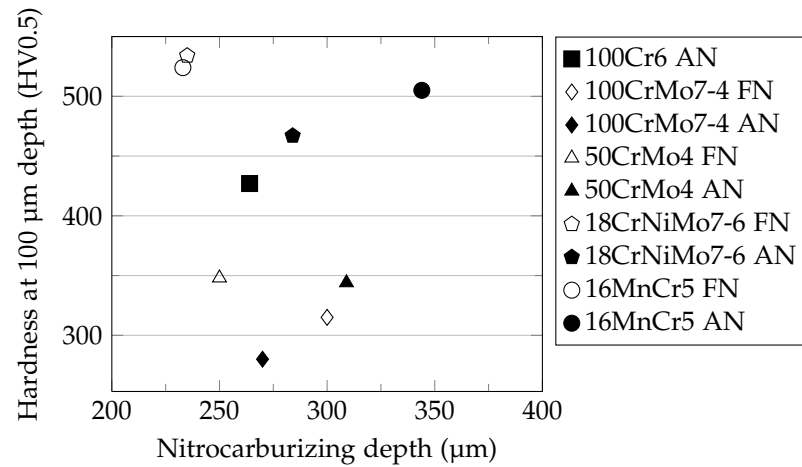


Figure 4.5: Hardness at 100 µm depth versus nitrocarburizing depth of nitrocarburized samples.

As can be seen in Figure 4.5 there is no evident correspondence between the hardness at 100 µm depth and nitrocarburizing depth. However it seems that for ferritic nitrocarburizing surface hardness decreases with increasing nitrocarburizing depth. This does not seem to be the case for austenitic nitrocarburizing.

Knoop hardness

Knoop hardness was measured close to the surface of the nitrocarburized samples. Measurements in the porous part of the compound layer were however avoided. The result of the measurements are shown in Figure 4.6. The hardness of the compound layer is in the range of 1400–1500 HK0.015 (approximately 875–940 HV1) for all materials with the exception of ferritic nitrocarburized 100CrMo7-4. For this material a lower hardness was measured in the compound layer of the ferritic nitrocarburized sample than in the austenitic nitrocarburized sample. In the other materials no difference in compound layer hardness could be detected between the different processes. The compound layer is however thicker in the austenitic nitrocarburized samples.

The hardness in the diffusion zone is higher for the low carbon samples than for the high and medium ones. Ferritic and austenitic nitrocarburizing produce approximately the same hardness in the diffusion zone.

The scatter of the data is quite large, especially for the low carbon samples. This is an effect of the low load used for the measurements since the small indents make it possible for individual grains to affect the hardness values.

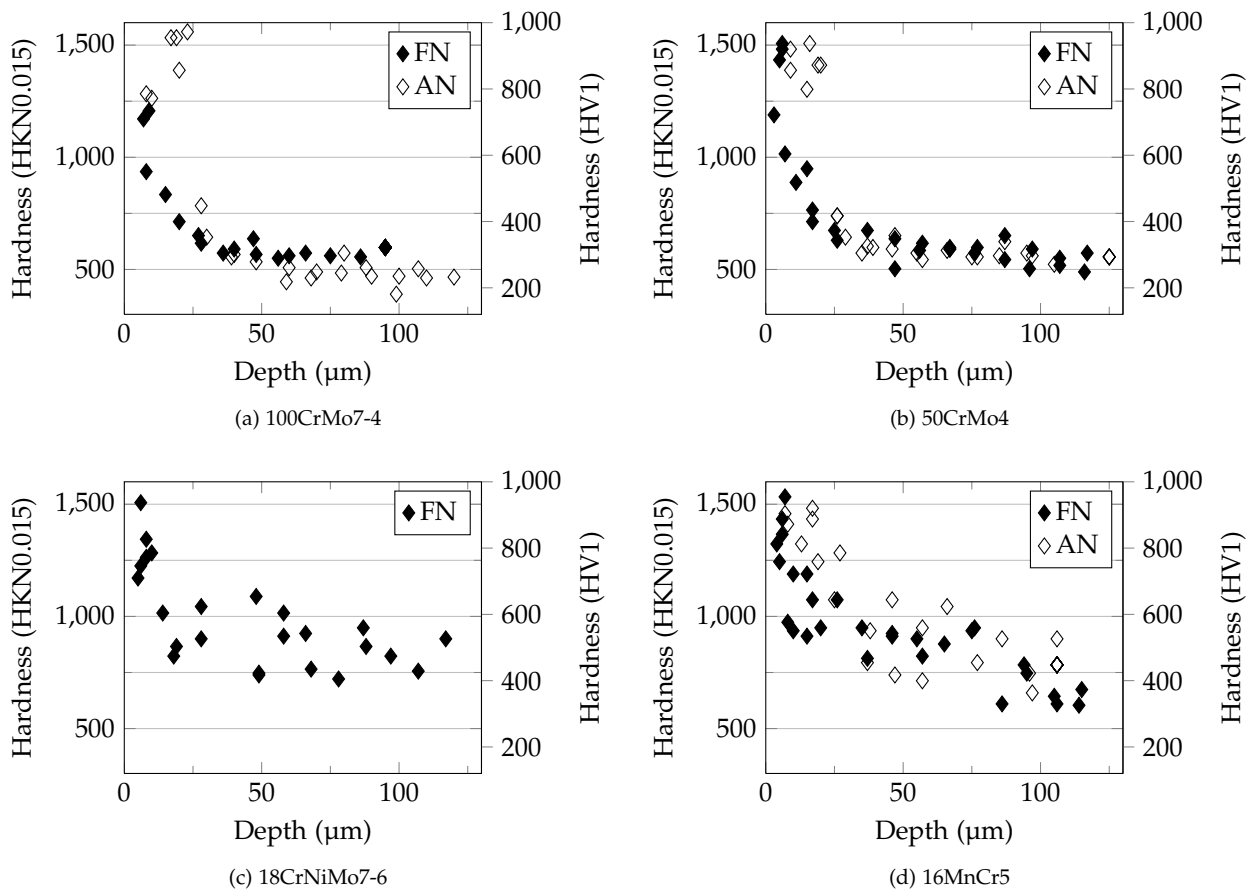


Figure 4.6: Knoop hardness close to the surface of the nitrocarburized samples.

4.1.2 Compound layer thickness

The compound layer thickness of different materials after ferritic and austenitic nitrocarburizing are shown in Figure 4.7. Two important differences between the processes can be seen – austenitic nitrocarburizing produces an austenite layer below the compound layer and the compound layer thickness becomes thicker than for ferritic nitrocarburizing. These differences are an effect of increased temperature alone since temperature was the only process parameter that was changed between the processes.

The thickness of the compound layer varies between 10 and 14 μm for the ferritic process and between 17 and 25 μm for the austenitic process. The thickest compound layer is seen on through hardened and austenitic nitrocarburized 100Cr6. For the ferritic process the thickest compound layer is found on 100CrMo7-4.

The thickness of the austenite layer varies between 5 and 13 μm . The thickest austenite layer was found in the 18CrNiMo7-6 sample.

As seen in Figure 4.8 the thickness of the compound layer seems to increase with increasing carbon content of the substrate for both process, even though the correspondence is better for the ferritic process. However, if the thickness of the austenite layer is added to the thickness of the compound layer, a good fit is obtained also for the austenitic process. No correspondence between the total alloy content and the compound layer thickness could be seen.

The porosity in the compound layer varies between 21–34 % depending on material. The relative thickness of the porous layer is approximately the same for both processes. The exception is 18CrNiMo7-6 where the relative thickness of the porous layer increases by 11 percentage points when the treatment temperature was increased.

4.1.3 Microstructure

The microstructure of the nitrocarburized samples are shown in Figures 4.9 to 4.13. As discussed in the previous section, the main difference seen when increasing the process temperature from ferritic to austenitic nitrocarburizing is the increased compound layer thickness and the appearance of a layer in between the compound layer and the substrate in the austenitic nitrocarburized samples.

Pores are visible in the outer part of the compound layer after both ferritic and austenitic nitrocarburizing. More and larger pores can be seen in the austenitic nitrocarburized samples, but the relative thickness of the porous zone does not increase.

Except for the porous zone the compound layers have a homogenous appearance and different phases cannot be distinguished. The thicknesses of the compound layers are rather uniform, but larger variations of thickness can be seen for 50CrMo4 and 16MnCr5 than for the other samples.

The austenite layers in the austenitic nitrocarburized samples are not as homogenous in thickness as the compound layers. The interface between the

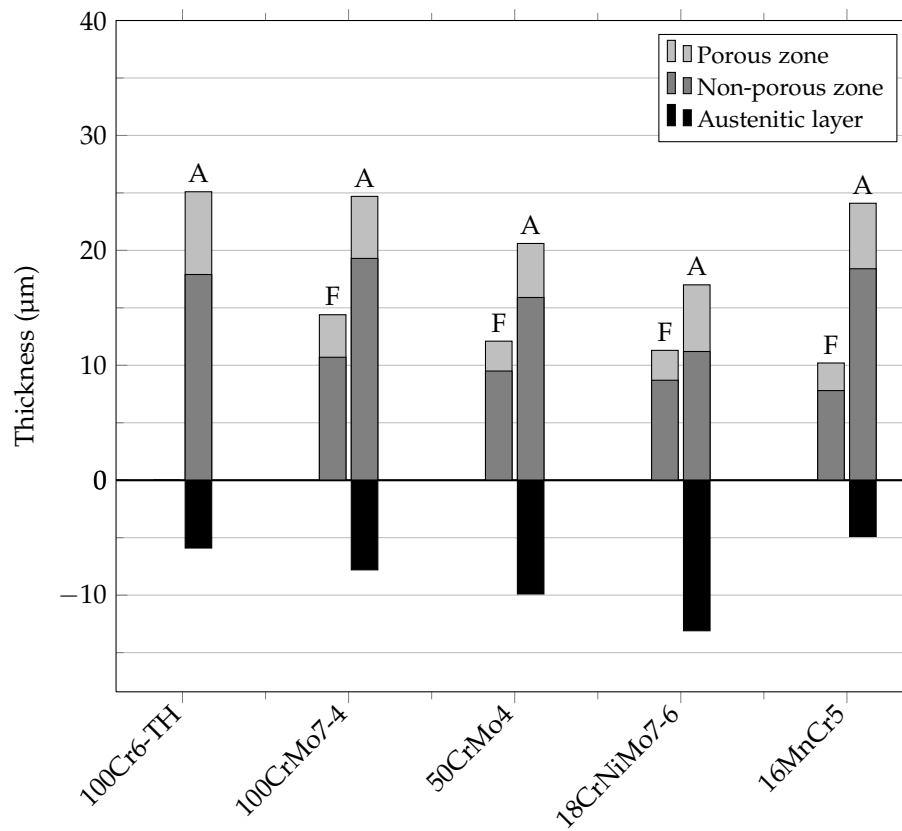


Figure 4.7: Compound layer thickness of bearing steels. Ferritic nitrocarburizing to the left and austenitic nitrocarburizing to the right. No through hardened 100Cr6 sample was included in the ferritic process.

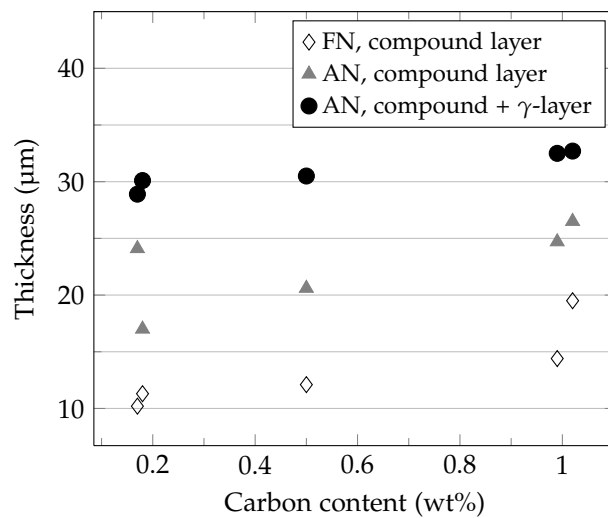


Figure 4.8: Compound layer thickness versus carbon content in the substrate.

austenite layer and the diffusion zone is jagged. In Figure 4.12c and 4.13c it can be seen that the transformation appears to start from grain boundaries. In the high carbon samples, 100Cr6 (4.9b) and 100CrMo7-4 (4.10c), nitrocarbides are visible in the austenite layer.

The microstructures in the diffusion zones and in the cores are similar to the microstructure found in the untreated reference samples after both ferritic and austenitic nitrocarburizing.

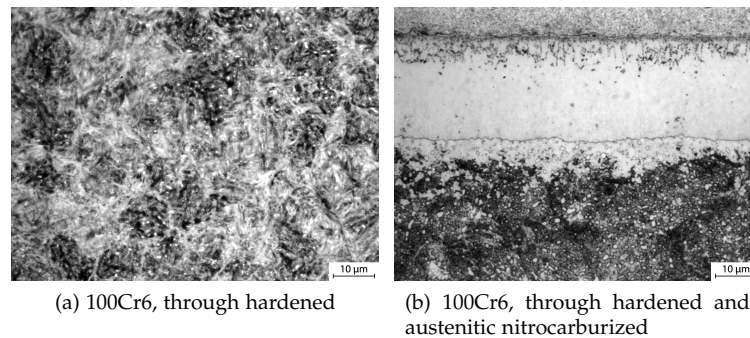


Figure 4.9: 100Cr6, through hardened (a) and thereafter austenitic nitrocarburized (b), 1000x, etched in Nital 1.5 %

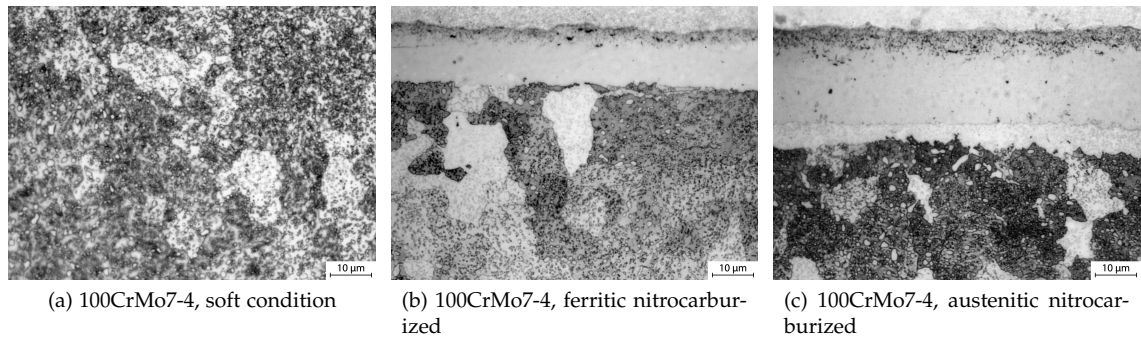


Figure 4.10: 100CrMo7-4, in soft condition (a), ferritic nitrocarburized (b) and austenitic nitrocarburized (c), 1000x, etched in Nital 1.5 %.

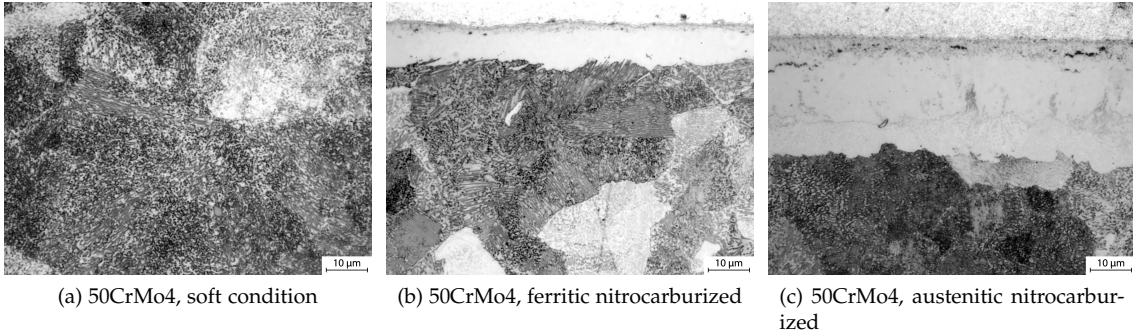


Figure 4.11: 50CrMo4, in soft condition (a), ferritic nitrocarburized (b) and austenitic nitrocarburized (c), 1000x, etched in Nital 1.5 %.

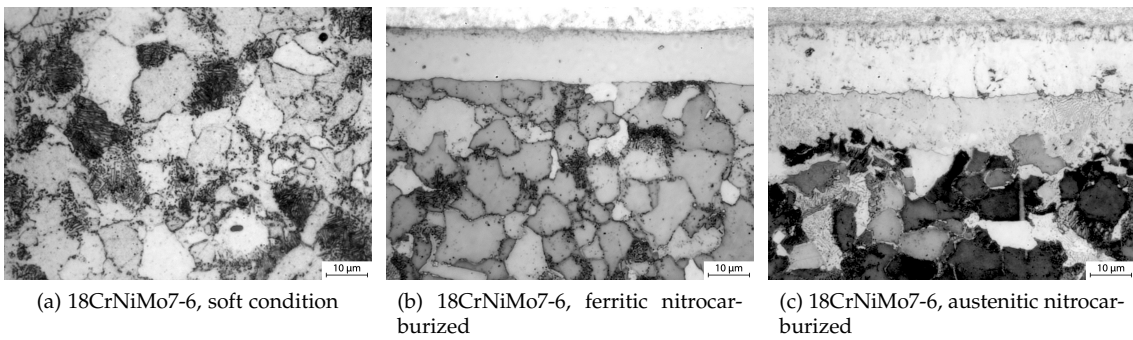


Figure 4.12: 18CrNiMo7-6, in soft condition (a), ferritic nitrocarburized (b) and austenitic nitrocarburized (c), 1000x, etched in Nital 1.5 %.

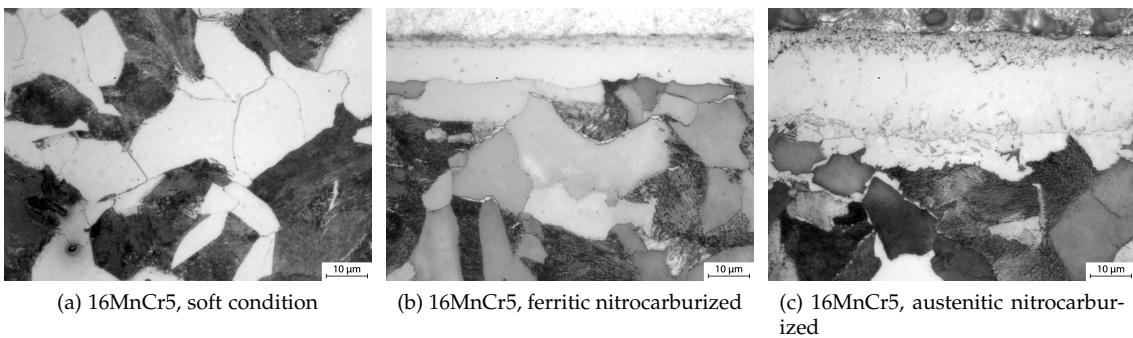


Figure 4.13: 16MnCr5, in soft condition (a), ferritic nitrocarburized (b) and austenitic nitrocarburized (c), 1000x, etched in Nital 1.5 %.

4.1.4 GD-OES

GD-OES measurements of the ferritic and austenitic nitrocarburized samples are shown in Figures 4.14 through 4.17. It should be noted that the carbon concentration is weighted 10 times compared to the other elements in order to be able to display both carbon and nitrogen content in the same diagram.

Generally it can be seen that the nitrogen content is highest towards the surface and decreases with increasing depth for all samples. The compound layer is seen as a plateau in the nitrogen graph. This plateau is wider in the austenitic nitrocarburized samples than in the ferritic ones. In some of the austenitic nitrocarburized samples a second plateau, which is related to the nitrogen austenite layer, can also be distinguished. This is most clearly visible in Figure 4.16b, since austenitic nitrocarburized 18CrNiMo7-6 showed the thickest nitrogen austenite layer. The nitrogen content in the compound layer generally decreases from the surface and inwards and is higher in the ferritic nitrocarburized samples than the austenitic ones.

In contrast to the nitrogen content, the carbon content in the compound layer increases from the surface and inwards. It shows a peak at the interface between the compound layer and the substrate in the case of ferritic nitrocarburizing and at the interface between the compound layer and the nitrogen austenite layer in the case of austenitic nitrocarburizing. The peak is higher for the ferritic nitrocarburized samples. Whether the carbon content increases or decreases through the nitrogen austenite layer varies between alloys. In the diffusion zone the carbon content equilibrates at the carbon content found in the base material before treatment. The exception is austenitic nitrocarburized 18CrNiMo7-6 and 16MnCr5, where the base materials have a low carbon content. In these samples the carbon content has dropped to almost zero at 50 μm depth.

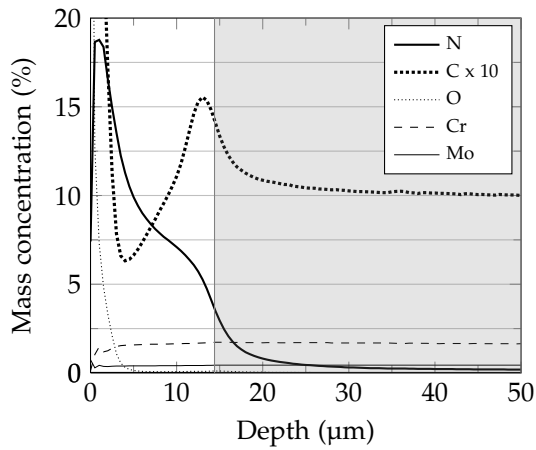
4.1.5 Tempering of austenitic nitrocarburized samples

Tempering for one hour at 300 °C transformed the austenite layer in the austenitic nitrocarburized samples and increased its hardness.

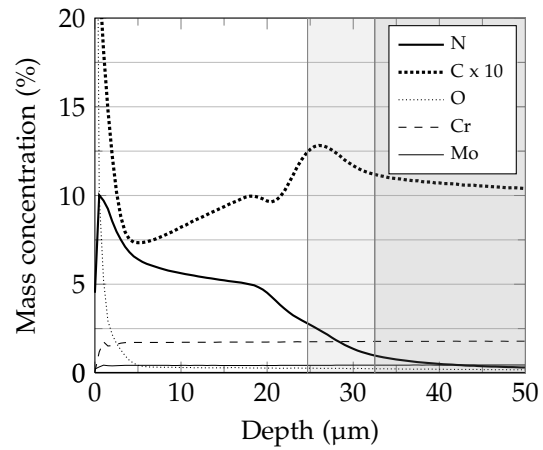
In Figure 4.18 a comparison of the microstructure before and after tempering of a low carbon steel is shown. It can be seen that the austenite layer has transformed to a fine structure, which according to literature [34] is a bainitic structure composed of α and γ' -phase containing nitrogen.

Microstructural changes can also be found in the compound layer. Precipitation of a darker phase can be seen in the inner part of the compound layer.

The hardness of the austenite layer increased drastically due to the transformation to nitrogen-bainite. In Figure 4.19 Knoop hardness profiles close to the surface of the tempered and untempered samples are shown. The compound layer retains its hardness after tempering, except in the outermost part where a loss of hardness can be seen. Below 100 μm depth the hardness was basically unaffected by tempering as seen in Figure 4.20.

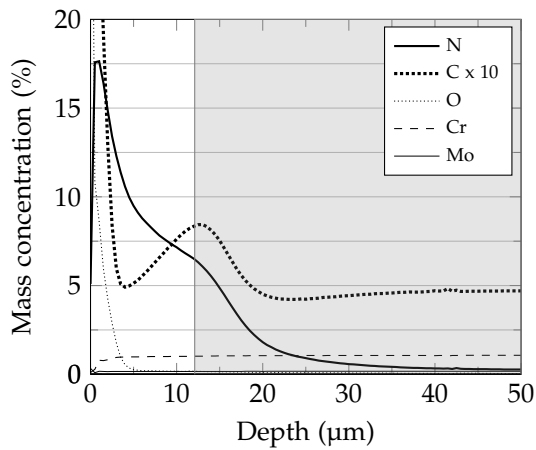


(a) 100CrMo7-4, ferritic nitrocarburizing

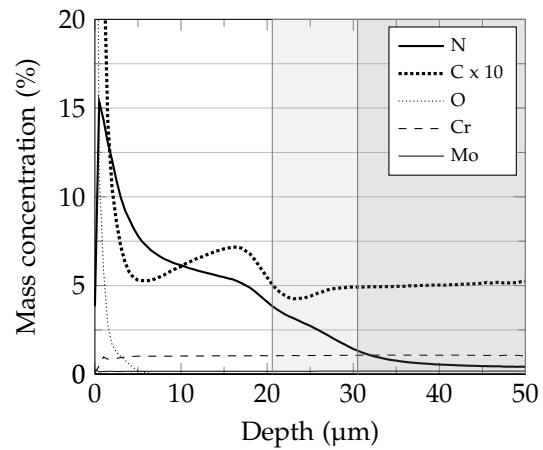


(b) 100CrMo7-4, austenitic nitrocarburizing

Figure 4.14: GD-OES measurements of 100CrMo7-4. The white area marks the compound layer, the light grey area marks the austenite layer and the darker grey area marks the diffusion zone.

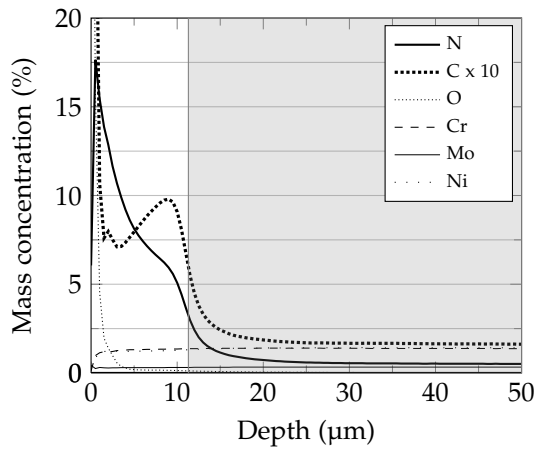


(a) 50CrMo4, ferritic nitrocarburizing

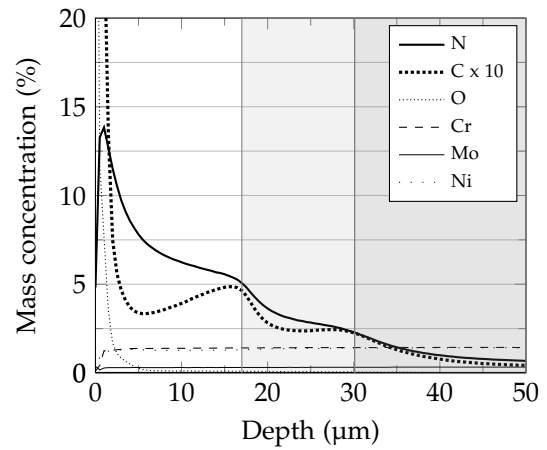


(b) 50CrMo4, austenitic nitrocarburizing

Figure 4.15: GD-OES measurements of 50CrMo4. The white area marks the compound layer, the light grey area marks the austenite layer and the darker grey area marks the diffusion zone.

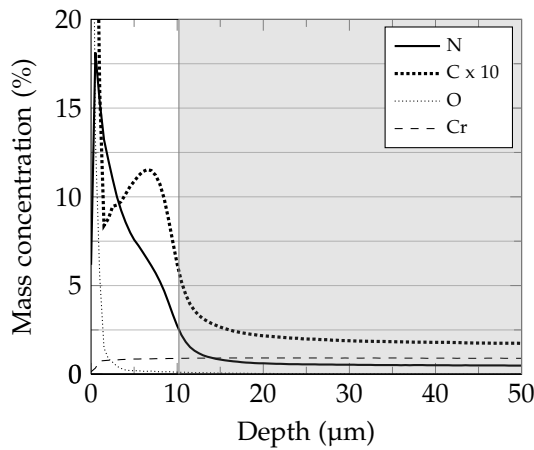


(a) 18CrNiMo7-6, ferritic nitrocarburizing

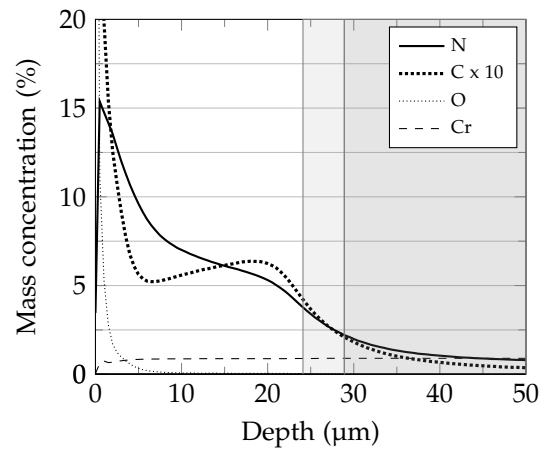


(b) 18CrNiMo7-6, austenitic nitrocarburizing

Figure 4.16: GD-OES measurements of 18CrNiMo7-6. The white area marks the compound layer, the light grey area marks the austenite layer and the darker grey area marks the diffusion zone.



(a) 16MnCr5, ferritic nitrocarburizing



(b) 16MnCr5, austenitic nitrocarburizing

Figure 4.17: GD-OES measurements of 16MnCr5. The white area marks the compound layer, the light grey area marks the austenite layer and the darker grey area marks the diffusion zone.

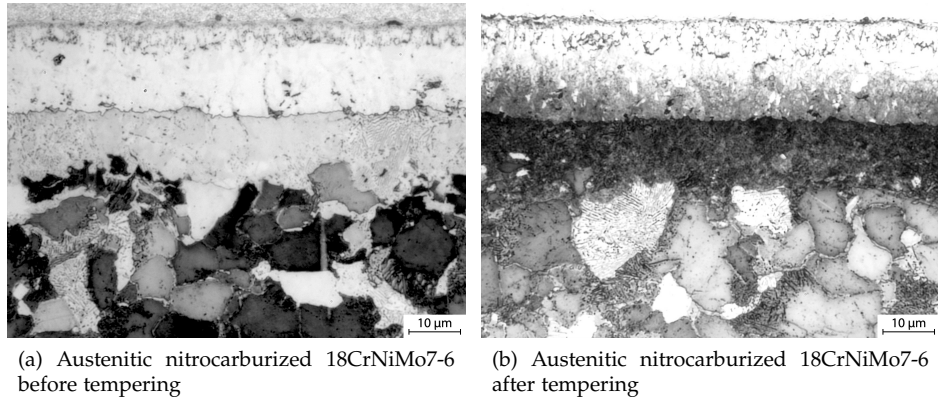


Figure 4.18: Low carbon steel before (a) and after (b) tempering at 300 °C for 1 hour, 1000x, etched in Nital 1.5 %

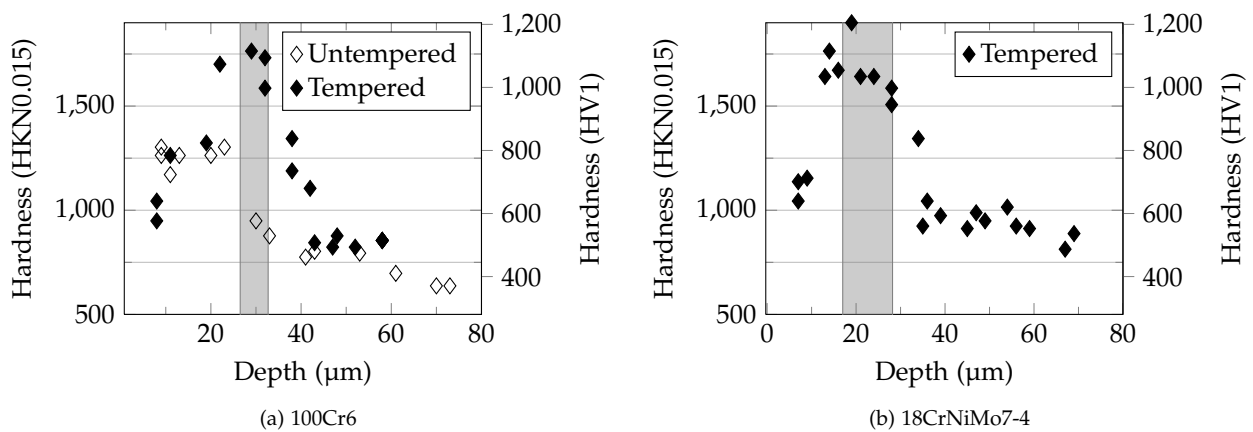


Figure 4.19: Hardness profile before and after tempering. The grey area marks the position of the austenite layer prior to tempering.

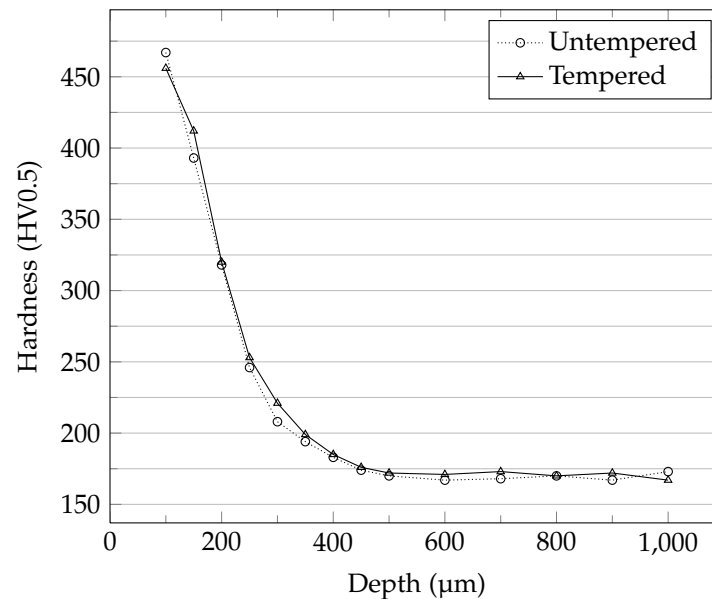


Figure 4.20: Hardness profile of austenitic nitrocarburized 18CrNiMo7-6 in tempered and untempered condition.

4.1.6 Residual stresses

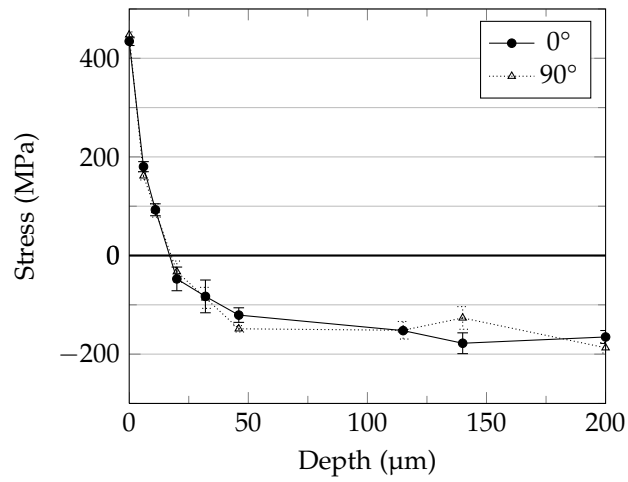
Residual stresses were measured on three 100Cr6 rings. One that had been carbonitrided, one that had been ferritic nitrocarburized and one that had been austenitic nitrocarburized. The results are shown in Figure 4.21.

The carbonitrided reference sample showed tensile residual stresses in the outermost 20–25 μm. Deeper down into the material the residual stresses were compressive.

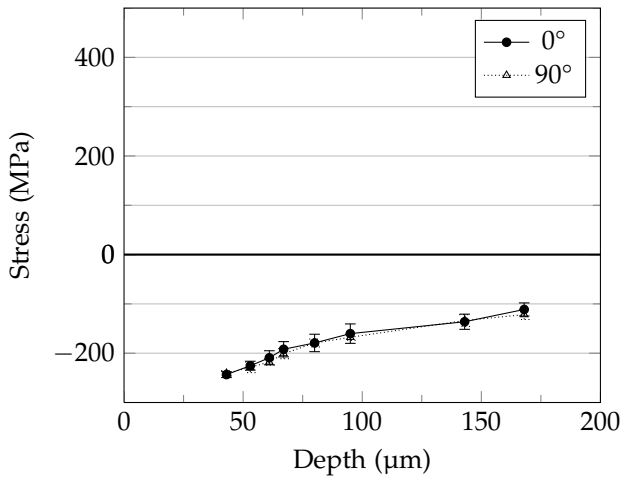
Due to limitations of the method and equipment it was not possible to measure the residual stresses in the compound layer of the ferritic and austenitic nitrocarburized samples. Below the compound layer however the residual stresses were found to be compressive.

4.1.7 Out-of-roundness

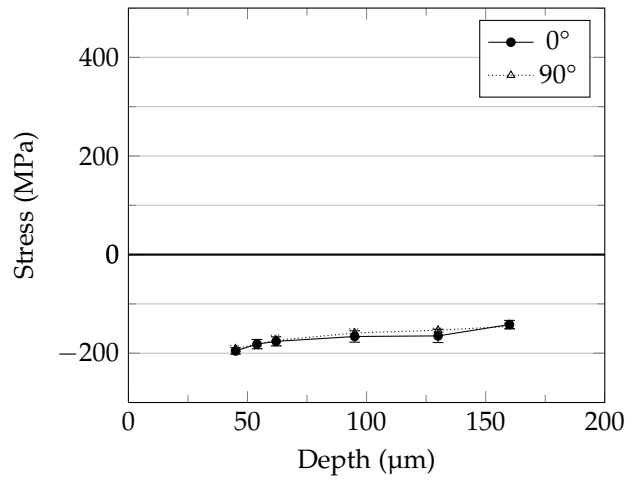
Results of the out-of-roundness measurements are summarized in Table 4.1. It can be established that both the ferritic and the austenitic nitrocarburizing added little out-of-roundness compared to heat treatments at higher temperatures. For one sample the out-of-roundness increased after ferritic nitrocarburizing and for one it decreased. The austenitic nitrocarburizing increased the out-of-roundness for two samples and decreased it for one. Since the data is limited it is not possible to draw any conclusion on whether ferritic or austenitic nitrocarburizing result in the most out-of-roundness. Measurements on the through hardened and ground specimen, A, after austenitic nitrocarburizing does however show the effect of austenitic nitrocarburizing alone.



(a) Carbonitrided



(b) Ferritic nitrocarburized



(c) Austenitic nitrocarburized

Figure 4.21: Residual stresses in 100Cr6 rings.

Sample	VDp before NC (μm)	VDp after FN (μm)	VDp after AN (μm)
A	2.0	-	24.5
B	46.3	57.8	40.5
C	166.7	63.7	180.2

Table 4.1: Out-of-roundness of nitrocarburized samples

4.1.8 Corrosion resistance

The result of the corrosion test on the nitrocarburized steels is shown in Figure 4.23. Ferritic nitrocarburizing resulted in lowered corrosion attack on 50CrMo4 compared to the reference. The 104 hours in neutral salt spray resulted in 10 % of the surface being corroded. Austenitic nitrocarburizing resulted in even better corrosion resistance, 5 % of the surface had corroded at the end of the test. Figure 4.22 shows a comparison between the three cleaned 50CrMo4 test pieces after the test.

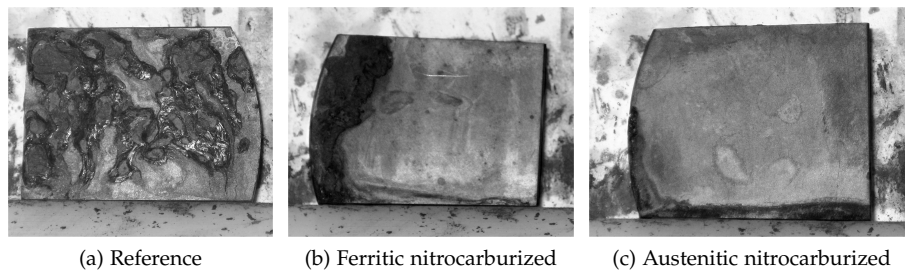


Figure 4.22: Corrosion attack on 50CrMo4 after 104 hours in neutral salt spray, cleaned samples.

A carbonitrided 100Cr6 sample was also included in the corrosion test as a reference. This sample does not show any large improvements compared to the through hardened sample. It should however be taken into consideration that the through hardened sample was ground and had a fine surface finish compared to the carbonitrided samples which had a porous surface as it was tested in the as treated condition. Austenitic nitrocarburizing on the other hand improved the corrosion resistance of the through hardened 100Cr6 sample significantly.

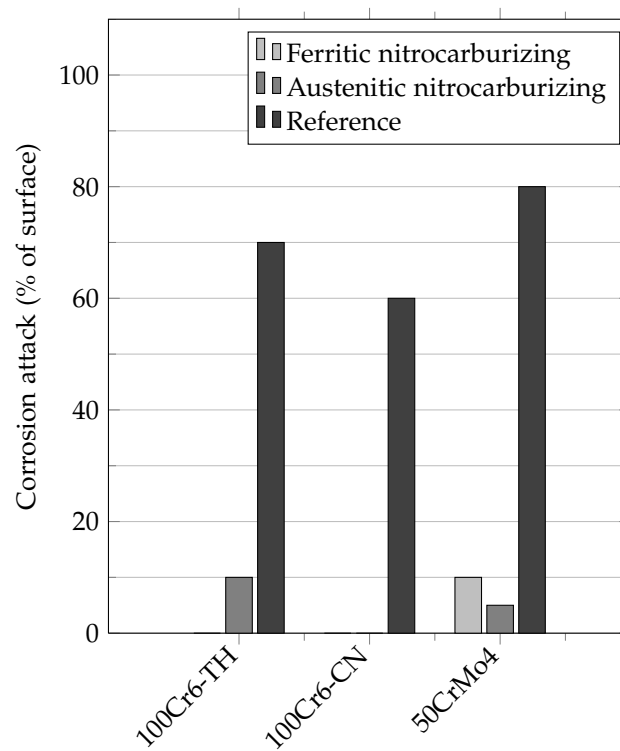


Figure 4.23: The percentage of the surface that was attacked by corrosion after 104 hours in neutral salt spray.

4.2 Solution nitriding

The solution nitriding trials included one group of stainless steels and one group of heat resistant steels. The two groups are treated separately in the following sections.

4.2.1 Stainless steels

Hardness

The hardness profiles of the solution nitrided stainless steels are shown in Figure 4.24. After solution nitriding the samples are through hardened with a hardness of 750–800 HV1. The highest core hardness is found in X65Cr13 and the lowest in X46Cr13. In the outermost 300 μm the hardness decreases compared to the core for all three samples. The largest reduction in hardness is found in X105CrMo17.

The surface hardness of the stainless steels are summarized in Table 4.2. All three samples have high surface hardness that meet the requirements on steels for bearing applications.

Steel	Surface hardness
X46Cr13	62 HRC
X65Cr13	63 HRC
X105CrMo17	61.5 HRC

Table 4.2: Surface hardness of solution nitrided stainless steels.

Microstructure

The microstructure of the solution nitrided stainless steels are compared to the untreated material in Figures 4.25 through 4.27. Generally it can be seen that after solution nitriding the martensitic microstructure consists of two regions and is coarser close to the surface than in the core. The amount of carbides increases with increasing carbon content of the steel and for X65Cr13 and X105CrMo17 the size of the carbides has increased after the treatment. Precipitates are also visible along the grain boundaries in all three samples.

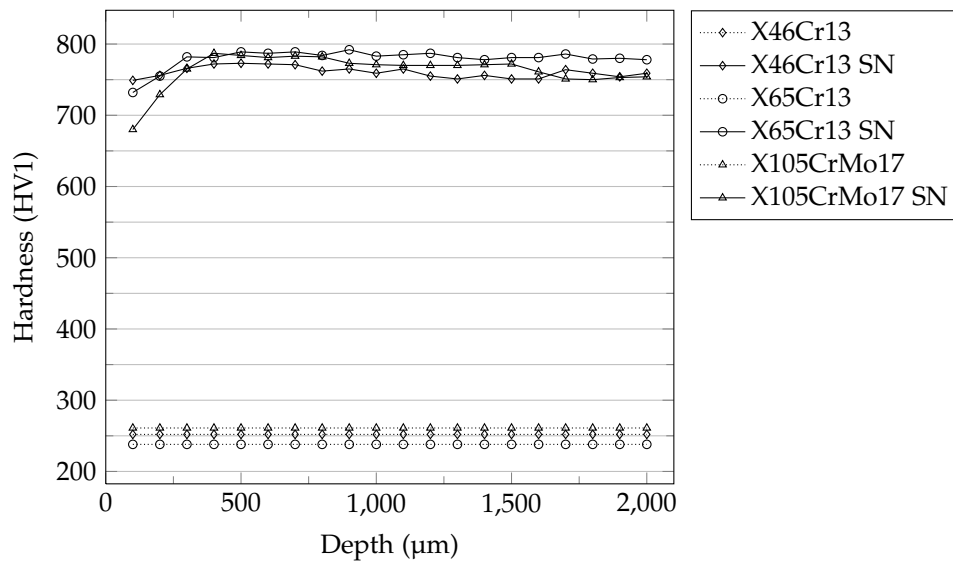


Figure 4.24: Hardness profiles of solution nitrided stainless steels.

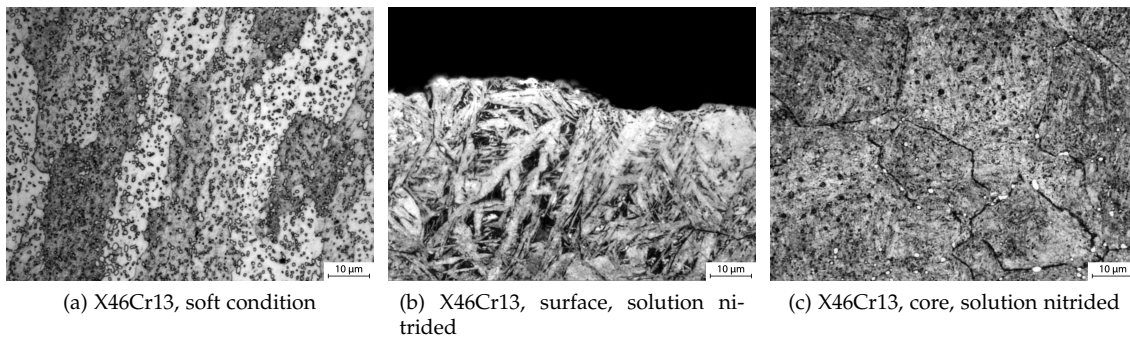


Figure 4.25: Solution nitrided X46Cr13 (b) and (c) compared to the untreated reference (a), 1000x, etched in Kalling's No. 1.

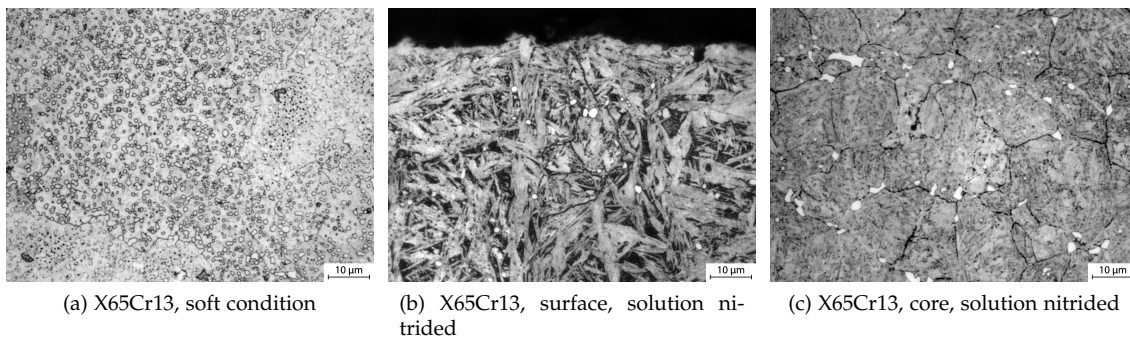


Figure 4.26: Solution nitrided X65Cr13 (b) and (c) compared to the untreated reference (a), 1000x, etched in Kalling's No. 1.

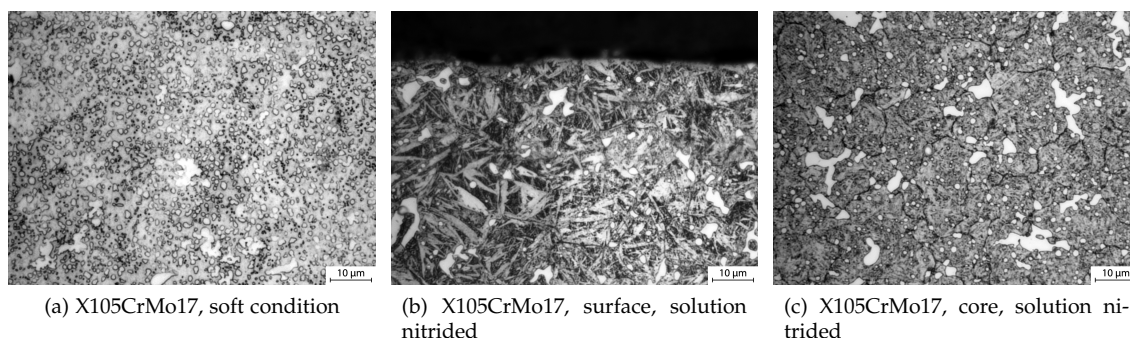


Figure 4.27: Solution nitrided X105CrMo17 (b) and (c) compared to the untreated reference (a), 1000x, etched in Kalling's No. 1.

GD-OES

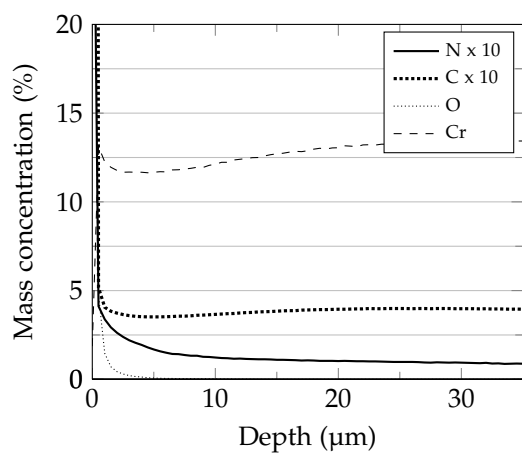
The result of the GD-OES measurements on the solution nitrided stainless steels are shown in Figure 4.28. The nitrogen content decreases from the surface and inwards in all three samples, but stays around 0.1 wt% in the analyzed volume.

In contrast to nitrogen, the carbon content decreases towards the surface. At 30 μm depth it is comparable to the carbon content in the untreated material for X46Cr13 and X65Cr13. In X105CrMo17 the carbon content at 30 μm depth is somewhat lower than in the untreated material. The total amount of nitrogen + carbon at 30 μm depth is approximately 0.5 wt% for X46Cr13, 0.7 wt% for X65Cr13 and 0.9 wt% for X105CrMo17. The chromium content also decreases towards the surface in X46Cr13 and X65Cr13.

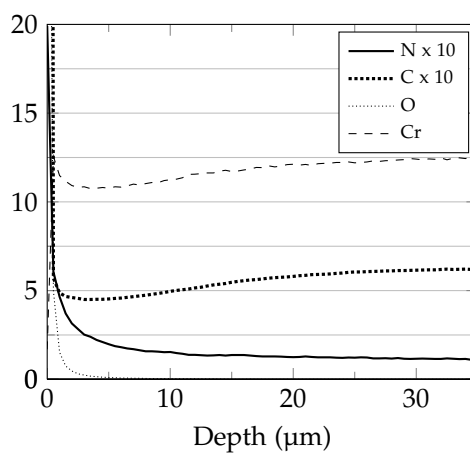
Corrosion resistance

The corrosion attack on the solution nitrided stainless steels after 104 hours in neutral salt spray and cleaning are shown in Figure 4.29. An increased corrosion attack by 10 percentage points after solution nitriding can be seen for all three materials. The corrosion resistance increases in the order of X46Cr13, X65Cr13 and X105CrMo4.

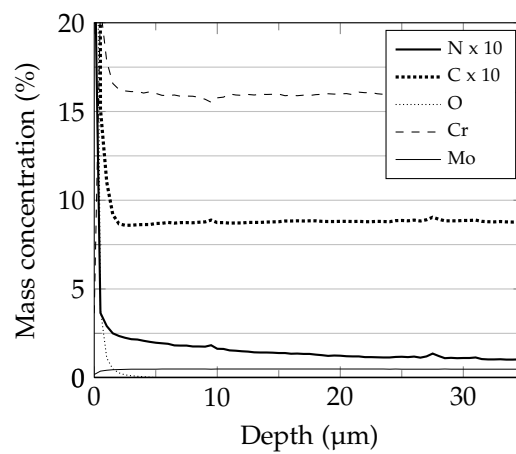
It is also interesting to note that the performance of the reference X46Cr13 sample is comparable to that of carbonitrided 100Cr6 in Figure 4.23, and that there are ferritic and austenitic nitrocarburized bearing steels that perform much better than the solution nitrided stainless steels included in this project from a corrosion perspective.



(a) X46Cr13, solution nitrided



(b) X65Cr13, solution nitrided



(c) X105CrMo17, solution nitrided

Figure 4.28: GD-OES measurements of solution nitrided stainless steels.

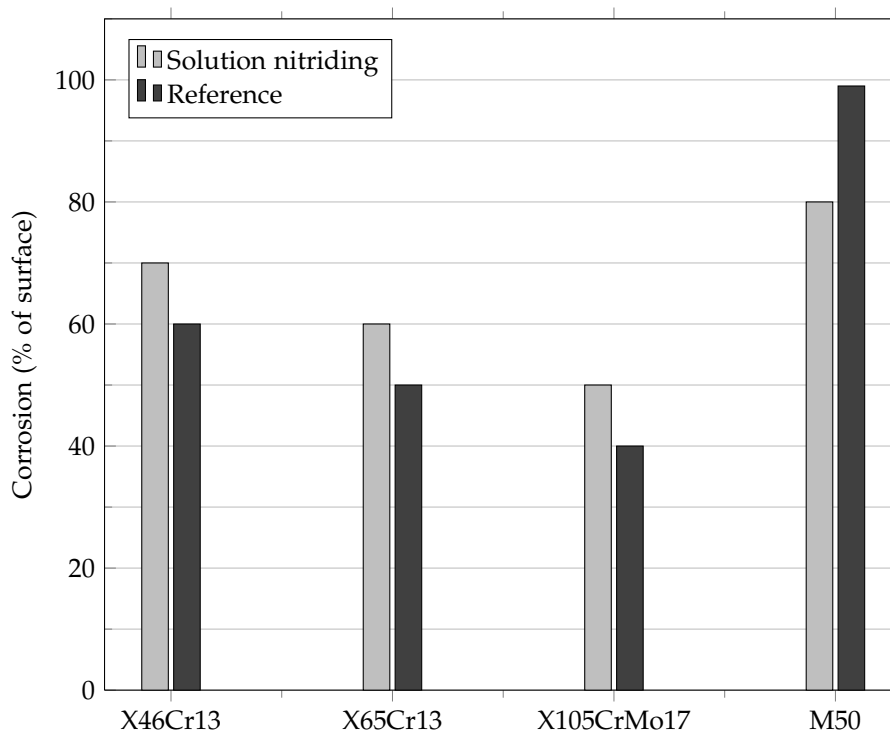


Figure 4.29: Corrosion attack on solution nitrided steels.

4.2.2 Heat resistant steels

Hardness

The hardness profiles of the solution nitrided heat resistant steels are shown in Figure 4.30. The M50 and 32CrMoV13 samples were through hardened by the treatment, whereas for the case hardening steels M50NiL and Pyrowear 675 an increase in hardness close to the surface can be seen. The increase is highest for Pyrowear 675, where the difference in hardness is 100 HV1 between 100 μm depth and the core.

As seen in the figure there is a large difference in hardness between M50 and M50NiL after solution nitriding. The materials have a similar chemical composition, but M50NiL contains nickel and has a lower carbon content. In the GD-OES measurements (Figure 4.35a and 4.35b) it can also be seen that they contain comparable amounts of nitrogen at 30 μm depth. The difference in hardness is therefore related to the difference in carbon content.

Pyrowear shows a much lower hardness than the other stainless steels (Figure 4.24) after solution nitriding. This can also be related to lower carbon content.

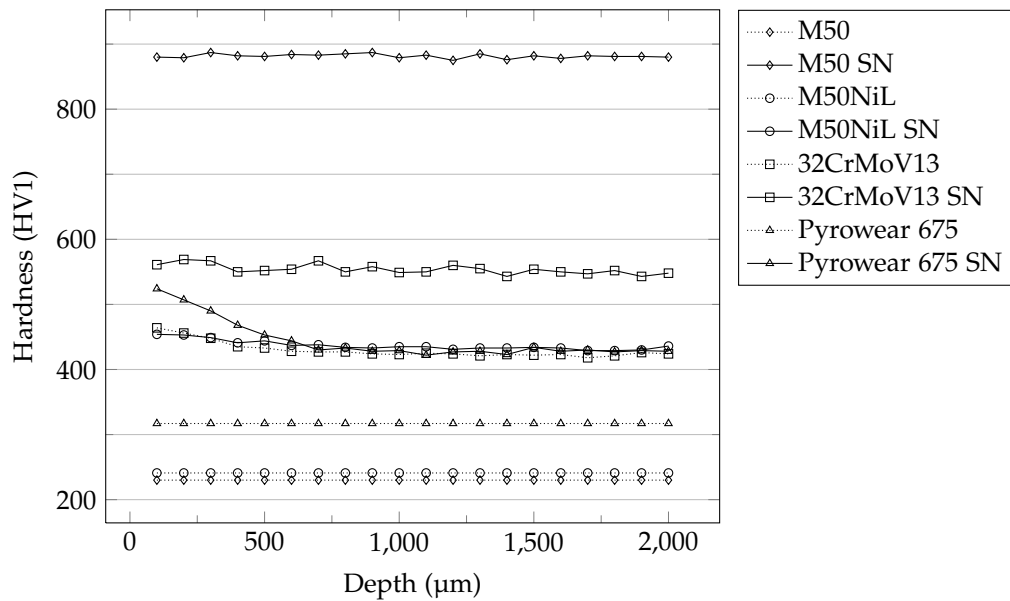


Figure 4.30: Hardness profiles of heat resistant steels before and after solution nitriding.

Steel	Surface hardness
M50	66.5 HRC
M50NiL	44.0 HRC
32CrMoV13	54.5 HRC
Pyrowear 675	48.5 HRC

Table 4.3: Surface hardness of solution nitrided heat resistant steels.

Also 32CrMoV13 shows a lower hardness than the stainless steels, owing both to lower carbon and nitrogen content as seen when comparing the GD-OES measurements of X46Cr13 (Figure 4.28a) and 32CrMoV13 (Figure 4.35c).

The surface hardness of the stainless steels are summarized in Table 4.3. The M50 sample is the only material that has a hardness above 58 HRC, which is the lower limit for bearing applications.

Microstructure

The microstructures of the heat resistant steels pre and post solution nitriding are shown in Figures 4.31 through 4.34. In M50 and 32CrMoV13 no difference could be seen between the microstructure in the case and in the core. For the case hardening alloys M50NiL and Pyrowear 675 the microstructure is finer close to the surface than in the core. In the solution nitrided M50 sample precipitations can be seen along the grain boundaries.

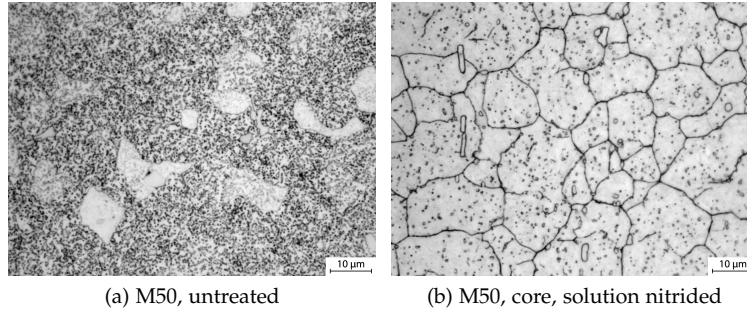


Figure 4.31: Solution nitrided M50 (b) compared to the untreated reference (a), 1000x, etched in Nital 1.5 %.

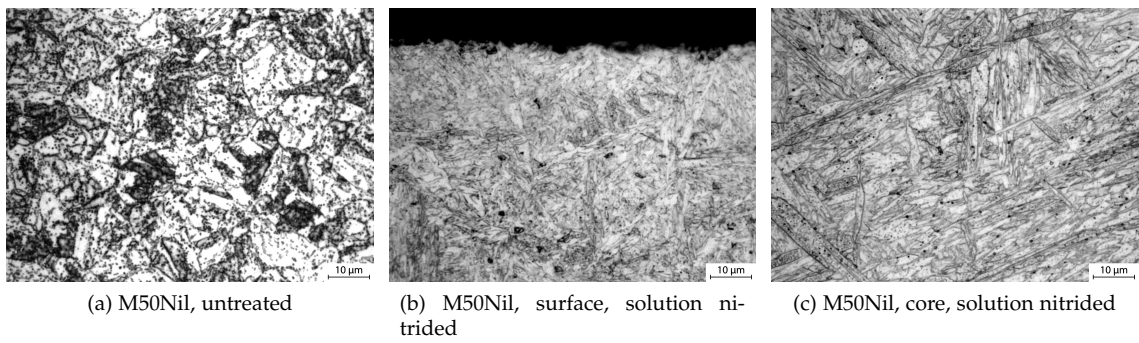


Figure 4.32: Solution nitrided M50NiL (b) and (c) compared to the untreated reference (a), 1000x, etched in Kalling's No. 1.

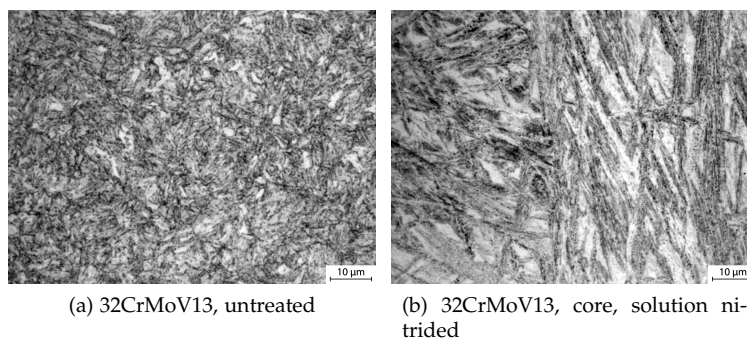


Figure 4.33: Solution nitrided 32CrMoV13 (b) compared to the untreated reference (a), 1000x, etched in Nital 1.5 %.

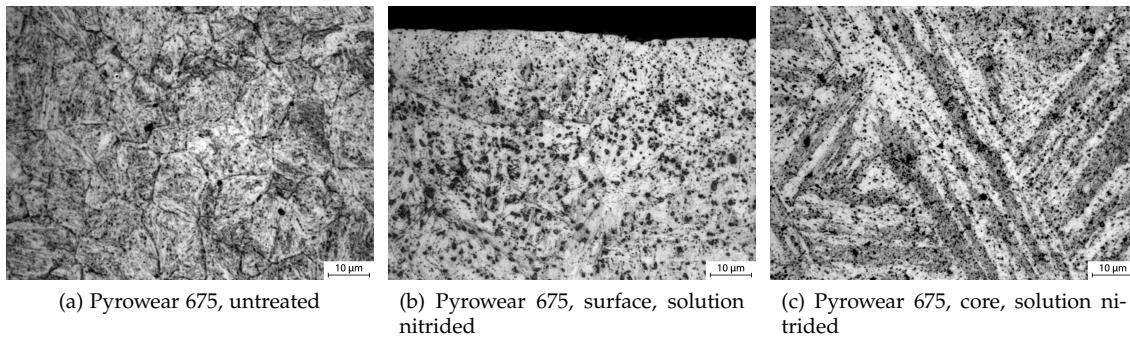


Figure 4.34: Solution nitrided Pyrowear 675 (b) and (c) compared to the untreated reference (a), 1000x, etched in Kalling's No. 1.

GD-OES

GD-OES measurements on the solution nitrided heat resistant steels are shown in Figure 4.35. The nitrogen content is highest at the surface and decreases with increasing depth for all samples. Pyrowear 675 has the highest nitrogen content and 32CrMoV13 has the lowest. For these four steels the nitrogen content increases with increasing chromium content. The carbon content is constant throughout the analyzed volume for all four samples.

The high hardness of M50 after solution nitriding can be explained by its high carbon + nitrogen content – it contains 0.85 wt% (N + C) at 30 µm depth compared to 0.2 wt% (N + C) for M50NiL.

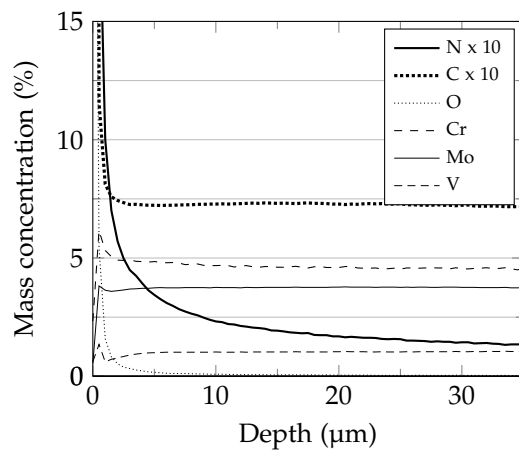
Out-of-roundness

Out-of-roundness was measured before and after solution nitriding on one 32CrMoV13 ring. It increased drastically due to the process – from 5 µm to 278 µm.

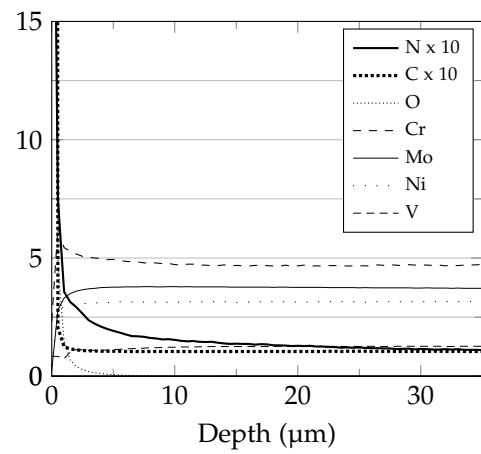
Corrosion resistance

Corrosion resistance was only investigated for M50 since the other heat resistant steels displayed rather low hardness after solution nitriding. It was not worthwhile to make a corrosion test on them since they could not be used for the intended application in their current state.

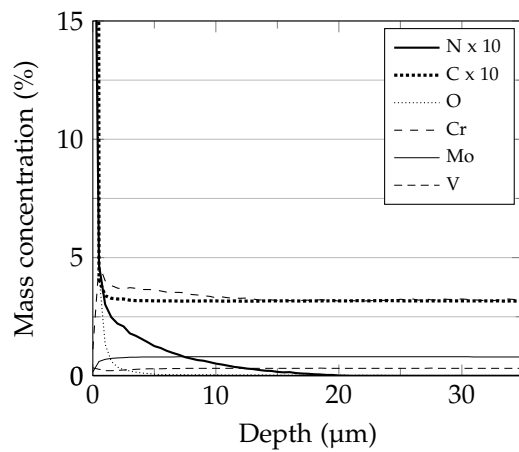
The result for M50 is displayed together with the results for the stainless steels in Figure 4.29. The corrosion resistance of M50 was improved by the treatment, but the sample still shows 80 % corrosion attack after solution nitriding, which is comparable to the worst performing bearing steels.



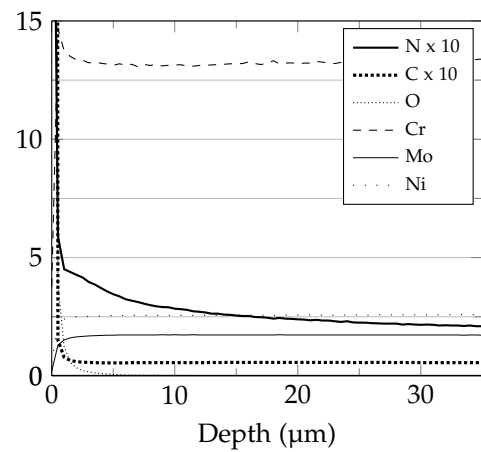
(a) M50, solution nitrided



(b) M50NiL, solution nitrided



(c) 32CrMoV13, solution nitrided



(d) Pyrowear 675, solution nitrided

Figure 4.35: GD-OES measurements of solution nitrided heat resistant steels.

Chapter 5

Discussion

The chapter consists of two parts. The first part focuses on nitrocarburizing and emphasizes the difference between the ferritic and the austenitic process. It also discusses which phases are found in the different layers and how the selection of steel and process affects different properties which are of interest for bearing applications.

The second half of the chapter discusses the solution nitriding process. It focuses on identifying which of the investigated steels that are suitable for the process and which improvements could be made to the process to achieve better results.

5.1 Ferritic and austenitic nitrocarburizing

In general the properties of the nitrocarburized samples are consistent with the results found in literature. As expected the ferritic nitrocarburized samples consist of a hard compound layer on top of a diffusion zone below which the base material can be found. In the austenitic nitrocarburized samples an austenite layer is found between the compound layer and the diffusion zone. The austenitic nitrocarburized samples also have an oxide layer on top of the compound layer. This was expected since the samples were flash oxidized.

In accordance with literature [13, 29] thicker compound layers and deeper nitrocarburizing depth were found in the austenitic nitrocarburized samples than in the ferritic nitrocarburized ones. The thickness of the compound layer and the diffusion zone were found to be both material and treatment temperature dependent.

Both ferritic and austenitic nitrocarburizing resulted in a slight softening in the core. The softening was larger in the austenitic nitrocarburized samples. This was an expected outcome since this part of the material was unaffected by the diffusing carbon and nitrogen and basically just tempered.

5.1.1 The compound layer

The hardness of the compound layer is in the range of 800–1000 HV1 for all samples, which is somewhat higher than the values found in literature (see Section 2.2.4). It is likely that the discrepancy originates from the measuring method since Knoop measurements were made with a low load which produces very small indents and their size is difficult to measure accurately. The Knoop measurements were thereafter translated to Vickers hardness, but such a translation is difficult to make correctly for small loads and high hardness values.

It was not possible to relate the hardness of the compound layer to the total alloy content of the material, which should be the case according to literature [13]. It is likely that certain alloying elements contribute more to the hardness of the compound layer than others and that a more complex model is needed to predict the compound layer hardness.

The thickness of the compound layer measured in the micrographs is marked in the GD-OES graphs in Figures 4.14a to 4.17b. It can be seen that the depth of the compound layer corresponds rather well to the depth of the plateau in the nitrogen graph and to the local maxima of the carbon graph. The deviations that are seen in for example 16MnCr5 can be explained by considering that the compound layer varies slightly in thickness within the sample. The measured thickness of the compound layer is an average from ten different locations whereas the GD-OES data originates from a relatively small area ($\sim 10 \text{ mm}^2$).

The phases present in the compound layer cannot be distinguished in the micrographs. For this a different etching method would be needed. Wells [28] suggested an addition of 0.1 % concentrated hydrochloric acid to 5 % Nital to be able to distinguish ϵ from γ' . This was not done in the current project due to time and lab equipment limitations.

It is however possible to reason about which phases that are present in the compound layer based on the GD-OES data. In Figure 5.1 the nitrogen and carbon content in the compound layer of the ferritic nitrocarburized samples are plotted on top of the isothermal section of the equilibrium Fe-C-N phase diagram. An isothermal section at 580 °C was chosen since the samples were nitrocarburized at this temperature for 2.5 hours and thereafter quenched. It should however be considered as a base for the discussion rather than an absolute representation of the phases present since the samples were not in perfect equilibrium at the nitrocarburizing temperature and since the samples were subsequently tempered.

The figure does however suggest that the compound layer of 18CrNiMo7-6 and 16MnCr5 consists mostly of ϵ -phase, whereas the compound layer of 100CrMo7-4 contains ϵ -phase and, in the inner region of the compound layer, some cementite (θ). The compound layer of 50CrMo4 contains ϵ -phase and possibly some γ' -phase, since the stability range of ϵ -phase decreases with decreasing temperature. High amounts of ϵ -phase is advantageous for the intended application since it has a higher wear resistance than the γ' -phase [13] and improves corrosion resistance [29].

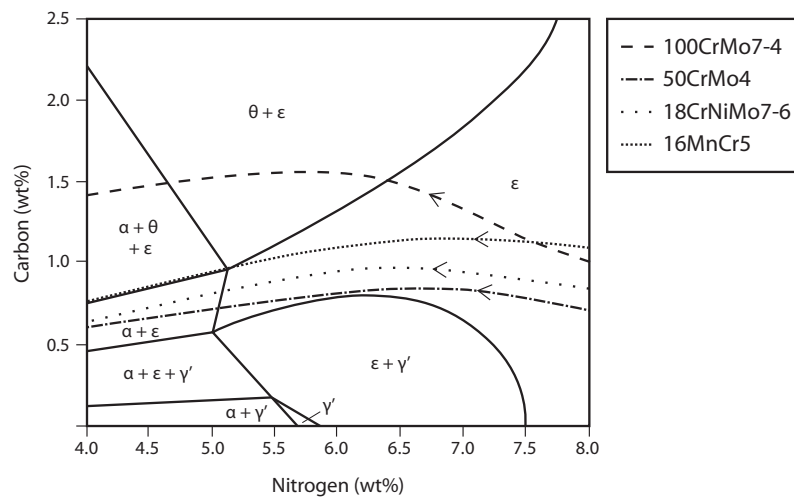


Figure 5.1: Carbon and nitrogen content in the compound layer plotted on the isothermal section at 580 °C of the equilibrium Fe-C-N phase diagram. The arrow indicates the direction from the surface and inwards.

Cementite in the compound layer might affect corrosion resistance negatively. This has however not been verified since the 100CrMo7-4 samples were not included in the corrosion tests.

According to literature [27] higher alloy content favors ϵ over γ' and ϵ grows faster than γ' . This suggests that the compound layer should increase in thickness with increasing alloying content. No such correspondence was however seen in the present study and it is likely that certain alloying elements influences compound layer thickness more than others. Higher carbon content in the substrate could for example be related to an increase in compound layer thickness for ferritic nitrocarburizing this study.

5.1.2 Porosity

The relative thickness of the porous part of the compound layer is approximately the same for both ferritic and austenitic nitrocarburizing. The exception is 18CrNiMo7-6 where the relative amount of porosity increased when the treatment temperature was increased. The variation could however be related to that the compound layer is thinner in this sample due to the thick austenite layer. Thus it can be concluded that for the materials and processes studied the composition of the substrate influences porosity more than the process temperature.

5.1.3 The austenite layer

According to literature (see Section 2.2.5) the layer below the compound layer seen in the austenitic nitrocarburized samples contains nitrogen stabilized

austenite. This is supported by a combination of hardness measurements and GD-OES analysis. The Knoop measurements show that the layer has a low hardness compared to the compound layer which should be the case for austenite. In the GD-OES diagrams it can be seen that the layer is connected to a nitrogen content of 2–4 wt% whereas the carbon content varies between 0.2 and 1.2 wt% in the layer depending on the material. This corresponds rather well to the stability range of austenite in the isothermal sections of the Fe-C-N phase diagrams shown in Figure 2.8.

No investigation of how the alloying elements in the substrate affect the thickness of the austenite layer was found in literature. In this project, several different materials were treated in the same process and from the results in Figure 4.7 it can be concluded that the composition of the base material affects the thickness of the austenite layer, although a more detailed study is needed in order to relate the thickness of the austenite layer to any single alloying element.

5.1.4 Tempering of austenitic nitrocarburized samples

The tempering of the austenitic nitrocarburized samples resulted in a drastic hardness increase in the austenite layer. After tempering it reached a hardness of approximately 1070 HV1 in both the low and the high carbon sample. This is consistent with the results found in literature [34] for nitrogen bainite formed by tempering of nitrogen enriched austenite. According to the same publication the nitrogen bainite consists of α and γ' phase. The cited study was however conducted on pure iron, whereas this investigation is done on steels containing up to 1 wt% carbon. Therefore it is quite possible that the tempering product also contains carbides.

Tempering also introduced changes in the compound layer. The darker region that can be seen in the inner part of the compound layer of the tempered 18CrNiMo7-6 sample is thought to be γ' precipitating in ϵ . As seen in the phase diagrams of the Fe-N and Fe-N-0.5C systems in Figure 2.6 the ϵ -phase has a larger stability range at higher temperatures. For the nitrogen and carbon contents present in the inner part of the compound layer the ϵ -phase is stable at nitrocarburizing temperature and it is retained to room temperature by quenching. It is however metastable and upon tempering some of it can decompose to γ' .

5.1.5 Process improvement

One way to minimize distortions after ferritic nitrocarburizing would be to cool the material slowly instead of quenching. However, since the ϵ -phase has a bigger stability range at higher temperatures there is a risk that some of the compound layer might transform to γ' during slow cooling. This might lead to lowered wear and corrosion resistance since ϵ has better wear and corrosion properties than γ' . Development of CCT-diagrams for the ϵ -phase at different nitrogen contents could facilitate selection of optimal cooling time after nitrocarburizing.

The stability range of the ε -phase could also be an argument against tempering after ferritic nitrocarburizing. Although the diffusion speed at 180 °C is much lower than at 580 °C precipitations of γ' might occur if the samples are tempered for too long time. The subject does however need further investigation.

5.1.6 Load bearing capacity

The load bearing capacity depends on the hardness profile of the sample which must match the Hertzian stress profile (see Section 2.1.1). Austenitic nitrocarburizing provided better load bearing capacity than ferritic nitrocarburizing for the low carbon steels since it resulted in both a thicker compound layer and deeper nitrocarburizing depth. For the samples with a higher carbon content the difference between the processes is smaller. Austenitic nitrocarburizing results in a thicker compound layer, but ferritic nitrocarburizing provides higher hardness in the diffusion zone and retains the hardness of the substrate better.

Tempering of the austenitic nitrocarburized samples could be used to increase the load bearing capacity since the hardness in the austenite layer increases.

Through hardening before nitrocarburizing resulted in a higher core hardness than what is found in the samples that were only nitrocarburized. This suggests that through hardened samples will sustain loads better.

5.1.7 Wear resistance

Even though the wear resistance has not been experimentally evaluated, it can be discussed based on properties of the compound layer. Compound layer hardness was found to be 800–1000 HV in all samples, which suggests a high resistance to abrasive wear. Based on GD-OES measurements it was theorized that the compound layers contain mostly ε -phase which implies good resistance also to adhesive wear. The austenitic nitrocarburized samples probably have better wear resistance than the ferritic nitrocarburized samples since the thicker compound layer formed on these samples will wear off more slowly.

In literature [1, 13] porosity has been reported to have both positive and negative effects on wear resistance and it is therefore difficult to make any accurate predictions of how the pores found in the present study will affect wear resistance without testing it. Important to consider is whether periods of starved lubrication are present in the intended application, since porosity will almost certainly lower the wear resistance in this case. For such applications one should consider removing the porous part of the compound layer.

5.1.8 Fatigue resistance

According to literature (see Section 2.2.4) fatigue resistance is improved by nitrocarburizing. The reason is the presence of compressive residual stresses

in the diffusion zone, which were confirmed on both ferritic and austenitic nitrocarburized 100Cr6 samples in the current project.

When comparing the results in Figure 4.21b and 4.21c it can be seen that ferritic nitrocarburizing results in higher compressive residual stresses right below the compound layer than austenitic nitrocarburizing does. However the curve for the residual stresses in the austenitic nitrocarburized sample has a milder slope, which suggests that compressive residual stresses are present at deeper depth in this sample. This is consistent with the deeper nitrocarburizing depth established for austenitic nitrocarburizing. Which process that is preferable from a fatigue resistance perspective thus depends on the load case.

The residual stresses in the compound layer could not be assessed. However, in contrast to the carbonitrided sample the residual stresses curves (Figure 4.21) have a positive slope for the nitrocarburized rings, which could suggest that the stresses are compressive also closer to the surface. On the other hand, the compound layers presumably contain mostly ϵ -phase, which has been reported to cause tensile stresses, but not to lower fatigue resistance [31].

5.1.9 Out-of-roundness

It is difficult to draw any conclusions about differences between ferritic and austenitic nitrocarburizing from the out-of-roundness measurements since out-of-roundness was not measured on the same rings prior to and after ferritic nitrocarburizing and since large out-of-roundness was present already before nitrocarburizing in four out of five samples. It does however appear that austenitic nitrocarburizing adds somewhat more out-of-roundness than ferritic nitrocarburizing which is to be expected since the temperature of the austenitic process was higher.

The out-of-roundness that can be tolerated depends on the application and the size of the bearing. Grinding or polishing to remove out-of-roundness after austenitic nitrocarburizing should if possible be avoided so that the oxide layer is maintained.

5.1.10 Corrosion resistance

Austenitic nitrocarburizing resulted in better corrosion resistance than ferritic nitrocarburizing. The improved corrosion resistance of the austenitic nitrocarburized samples can be ascribed to the thin oxide layer formed by flash oxidation, which was only performed on the austenitic nitrocarburized samples. It is likely that without the flash oxidation step the ferritic nitrocarburized samples would have outperformed the austenitic nitrocarburized samples since the ferritic nitrocarburized samples were found to have higher nitrogen content in the compound layer.

According to literature [29] porosity can have a negative effect on corrosion resistance. Such effects could however not be seen in the present study and it can be concluded that the improvement in corrosion resistance from nitrocarbur-

izing is much larger than the possible negative effects of the pores introduced by the process. To assess the influence of porosity on corrosion resistance of nitrocarburized materials a comparison between two nitrocarburized samples of the same material with different porosity is needed.

One instance where the result of the corrosion test might have been affected by porosity is however in the comparison of carbonitrided and through hardened 100Cr6. The through hardened specimen was ground and polished to a fine surface finish whereas the carbonitrided samples had a porous surface. It would have been more fair to compare two ground and polished samples to each other and this would likely have improved the corrosion resistance of the carbonitrided sample.

5.1.11 Suitable steels

None of the steels included in the study were found to be unsuitable for nitrocarburizing, but in general the low carbon samples achieved somewhat better hardness properties.

The deepest nitrocarburizing depth and the highest hardness in the diffusion zone was found in austenitic nitrocarburized 16MnCr5. The 18CrNiMo7-6 sample does however provide a thicker austenite layer, which could be tempered to achieve a hard layer supporting the compound layer.

As a means to improve corrosion resistance, nitrocarburizing was found to be effective regardless of carbon content in the substrate.

5.2 Solution nitriding

5.2.1 Stainless steels

All the investigated stainless steels obtained a high hardness and were found to contain nitrogen after the solution nitriding treatment. Drawbacks such as grain boundary precipitates and lowered hardness close to the surface were however also identified, but could possibly be overcome by adjustments of the process parameters.

Since the process parameters of the solution nitriding process were adapted to X46Cr13 the other stainless steels did not get the optimal heat treatment for their respective compositions. This could be one factor contributing to that a reduced hardness can be seen close to the surface in these samples. However, the same behavior can be seen also for X46Cr13, but to a smaller extent.

The decreased hardness towards the surface of the stainless steels could be explained by an increased amount of retained austenite in this region. This is supported by the fact that nitrogen was present in the surface region of the samples according to the GD-OES measurements. These do however not reveal how much of the nitrogen that is in solid solution, neither can the presence of retained austenite be seen in the micrographs.

The coarse martensite seen in the surface region of the samples is likely due to overheating, since the size of the martensite plates depend on the austenite grain size, which increases with treatment temperature and time.

If retained austenite is the cause of the lowered hardness it could be transformed to martensite by deep cooling to even lower temperatures or by tempering at a higher temperature than what was used in the current process. In literature [38], tempering at 450 °C is suggested, though a risk of tempering is that more carbides and nitrides precipitate along grain boundaries.

The decreased hardness close to the surface is however not a large problem since the parts will be ground after heat treatment in a real manufacturing cycle.

The carbon content of the selected stainless steels was high compared to what is recommended in literature (see Section 2.3.3). This leads to an increased risk of grain boundary precipitates, which can also be seen in the microstructure. These precipitates increase the risk of brittleness and can cause decreased corrosion resistance. To avoid precipitates, faster cooling from the treatment temperature is needed.

The corrosion resistance of the stainless steels decreased after the treatment. It should however be taken into account that it was compared to the corrosion resistance of a soft sample and not to a through hardened one, which would have given a more fair result. If further investigations are to be undertaken it is suggested that through hardened samples are used as references.

The nitrocarburized samples had far better corrosion resistance in neutral salt spray than the stainless samples due to the presence of the nitrogen rich compound layer in the nitrocarburized samples. The nitrocarburized samples do however have a lower load bearing capacity than the stainless steels. This makes it hard to compare their performance since they would be used for different applications.

It should also be pointed out that the surface of the martensitic stainless steels could not be expected to maintain an intact passive layer in neutral salt spray and that the environment in a neutral salt spray chamber is quite different from the one found in a bearing. Combinatory effects from corrosion and wear cannot be assessed in this way and therefore full scale tests are needed for a fair view.

5.2.2 Heat resistant steels

Due to the large compositional difference between the heat resistant materials, they are treated one by one in the following discussion. A general remark is however that according to the GD-OES measurements nitrogen was present in the surface region of all four materials.

Another general observation is that the tempering temperature used in the solution nitriding process in this project is far too low for the heat resistant steels since these will be used at temperatures higher than 150 °C. The aim of the project was however to make a screening of which materials might

benefit from the solution nitriding process and in this context the tempering temperature is of lesser importance.

M50

In the micrographs of the solution nitrided M50 it can be seen that the sample was held at high temperature for too long time since most carbides have dissolved or segregated to the grain boundaries. M50 is normally austenitized at 1100 °C, but just for long enough to reach temperature. It is important that the carbides are not dissolved since they are needed for hot hardness of the material. There are also other negative effects of overheating the material – grain boundary precipitates may cause brittleness and can lower the corrosion resistance of the material. The corrosion resistance did however improve after the treatment, but only slightly and M50 was still the worst performing material in the corrosion test.

Considering that nitrogen was found in the surface region of the material, solution nitriding could be an interesting alternative to normal nitriding of M50 provided that the problems with dissolved carbides can be avoided by shortened solution nitriding time or a lowered treatment temperature. It is however necessary that the treatment temperature exceeds 1000 °C so that the nitrogen gas cracks. One alternative could be to combine a short solution nitriding treatment with a tempering at lower temperature to diffuse the nitrogen deeper into the material.

M50NiL

It is interesting to compare M50NiL to M50 since the two materials have similar chemical composition with the difference that M50NiL contains nickel and much less carbon. According to the GD-OES measurements (Figure 4.35b and 4.35a) the difference in nitrogen content at 30 µm depth between M50 and M50NiL is small. The M50NiL sample does however have a much lower hardness which can be related to the much lower carbon content.

In contrast to M50 the hardness of M50NiL increases slightly towards the surface. The augmented hardness is likely caused by nitrogen. The reason that the same behavior cannot be seen for M50 is probably that the M50 sample already contain high amounts of carbon and adding some additional nitrogen will not affect the hardness much.

32CrMoV13

According to the GD-OES measurements 32CrMoV13 is the heat resistant steel with the lowest nitrogen levels after solution nitriding. A possible explanation could be that this material contains the lowest levels of chromium, molybdenum and vanadium which are all elements that attract nitrogen.

One factor which might have influenced the result is that the 32CrMoV13 sample had already been nitrided at a low temperature in the delivery condition.

The large distortions induced in the 32CrMoV13 ring were expected since the process uses high temperature. It confirms that post-grinding of solution nitrided parts is needed.

Pyrowear 675

Pyrowear 675 was the only solution nitrided sample which displayed a distinct hardened case. There are probably three factors contributing to this – the low carbon content, the presence of cobalt and the high chromium content. The main reason why hardness decreases towards the surface in the other stainless steels is thought to be retained austenite. The low carbon content of Pyrowear 675 reduces this problem since carbon lowers the martensite start temperature. Cobalt also contributes to the reduction of retained austenite since it increases the martensite start temperature.

The other heat resistant steels do not show any hard case. The reason is likely lower nitrogen content, possibly in combination with either retained austenite or that nitrogen is not in solid solution in these samples. A high chromium content such as the one found in Pyrowear 675 increases the solubility of nitrogen in austenite (Figure 2.11b) and thus aids the formation of hard nitrogen martensite upon quenching.

Unfortunately the etching procedure utilized was not optimized for Pyrowear 675 and resulted in local over-etching as seen in the micrographs. McCaffrey and Wert [47] used Vilella's reagent for etching Pyrowear and switching to this etchant is suggested if further investigations are to be undertaken.

The solution nitriding process was optimized for a material with medium carbon content. Possibly better results could have been obtained on Pyrowear 675 by using longer treatment time to increase the case depth and lower temperature and partial pressure to increase the solubility of nitrogen in austenite. The material is normally subjected to a complex set of heat treatments and it is not surprising that solution nitriding alone cannot provide optimal properties. It would however be interesting to investigate if the carburizing step in Table 3.4 could be replaced by or combined with solution nitriding and if this could lead to improved corrosion resistance and shortened production time.

Chapter 6

Conclusion

The main difference between ferritic and austenitic nitrocarburizing is that the austenitic process results in a thicker compound layer, below which an austenite layer can be found. The austenite layer can be transformed to a bainitic structure with high hardness. The hardness of the compound layer and the relative amount of porosity is the same for both processes. The austenitic process produces a somewhat deeper nitrocarburizing depth but also softens the substrate slightly more than the ferritic process.

The hard layer achieved by nitrocarburizing materials in the soft condition is not thick enough to sustain the loads in rings or rolls, but the improved corrosion resistance could be of interest in other applications.

Both ferritic and austenitic nitrocarburizing can be used to increase the corrosion resistance of bearing steels. The austenitic process contained a flash oxidation step that produced a thin oxide layer on the surface of the samples. The corrosion resistance of the austenitic nitrocarburized samples is somewhat better than the resistance of the ferritic samples.

The solution nitriding process generally resulted in better properties for the stainless steels than the heat resistant alloys. Overall the process parameters needs optimization for each alloy.

The process resulted in high hardness throughout the stainless steel samples but also in grain boundary precipitates and somewhat reduced corrosion resistance in neutral salt spray. The hardness of the samples was found to decrease close to the surface, probably due to retained austenite. To compensate for these problems, lowered treatment temperature and faster quenching are suggested. If these changes are made the process will likely be applicable at least to X46Cr13.

Nitrogen was found to have penetrated both in the stainless steels and the heat resistant steels, although it was not possible to determine how much of it that was in solid solution with the selected measuring method.

The solution nitriding process was not found to be applicable to the heat resistant steels in its current design. Suggestions were however made on how it could be adapted to M50 and Pyrowear 675.

Chapter 7

Recommendations

In the following section some suggestions for improvements and further work are given.

7.1 Nitrocarburizing

- One of the main advantages of using nitrocarburizing is that wear resistance is improved. The wear resistance after ferritic and austenitic nitrocarburizing were not directly compared in this project. It would however be interesting to do so, since the thicker case depth obtained in austenitic nitrocarburizing suggests an improved wear resistance.
- Dimensional changes due to heat treatment were only touched upon briefly in this project. If the austenitic process is to be implemented a thorough investigation of the subject is suggested. A model for dimensional growth is needed so that the need for dimensional corrections after austenitic nitrocarburizing is avoided.
- The extra tempering of the austenitic nitrocarburized samples in this project was performed in order to show that you can transform the austenite layer to a hard bainitic phase. Optimization of time and temperature is needed to obtain optimal properties. GD-OES analysis of the tempered samples could lead to improved understanding of the redistribution of carbon and nitrogen during tempering. The effect of tempering on corrosion resistance also needs to be evaluated since corrosion resistance is one of the main advantages of austenitic nitrocarburizing.
- Performing austenitic nitrocarburizing at slightly higher temperatures could increase the thickness of the austenite layer and improve the load bearing capacity. However this could also lead to increased distortions.
- Due to limitations of the equipment and method the residual stresses could not be measured in the compound layer on the nitrocarburized samples. It would be valuable to be able to measure the residual stresses

also in this region since it might affect the fatigue properties. Other methods might however be more appropriate than XRD.

7.2 Solution nitriding

- There are studies that suggest that a solution nitrided martensitic stainless steel with a relatively low carbon content such as X12Cr13 and X20Cr13 could match the surface hardness of through hardened X46Cr13. It would be interesting to verify this and at the same time investigate if these steels can fulfil the other demands on a bearing steel. Lowering the carbon content of the substrate would most likely reduce the problem of precipitates along grain boundaries and high core hardness.
- The stainless steels appear not to have received an optimal heat treatment. Lowering the solution nitriding temperature is suggested in order to refine the microstructure in the near surface region. Quicker cooling could also be used for these steels in order to avoid grain boundary precipitates.
- The penetration depth of nitrogen in most of the solution nitrided samples is too deep to be assessed by the GD-OES measurements. Estimations can be made by regression analysis, but measurements on sectioned or turned samples are needed to confirm the estimations. An alternative way of assessing the nitrogen penetration depth would be to find an etching method that reveals it.
- The solution nitriding process utilized in this project is not directly applicable on the heat resistant steels. It is however interesting to note that there is nitrogen present in the near surface region also in the steels with a chromium content in the range of 3–5 wt%. This suggests that high temperature low pressure nitriding could be adapted also to these steels as a faster alternative to conventional nitriding. However, the subject needs further investigation.

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