The Effects of Contaminants on the Gas Nitriding of Nitralloy-135

A Thesis

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Abstract

Surface contamination during the heat treatment process can greatly affect the quality of the heat treated parts. Although cleaning the post-heat treated parts is considered a value added process in heat treatment, cleaning parts prior to heat treatment is also important and can influence the outcome of subsequent processes.

A series of experiments has been designed to determine the effects of the surface contaminants on nitriding. Nitralloy-135 steel was selected to evaluate the cleaning methods and the effects on the result of subsequent nitriding process. The samples were contaminated with a variety of contaminants, including rust preventive oil, cutting fluid and rust. The contaminated samples were cleaned using either acid or alkaline cleaner. Both cleaned and contaminated samples were nitride in the furnace. To determine the effect of contaminants on gas nitriding, weight gain and the surface hardness were measured. Nitrogen flux was also calculated. The results show that the acid cleaning effectively removes the rust layer. Rusted parts had lower nitrogen absorption than that of the cleaned samples. The parts contaminated by the oil did not reveal any effect on the nitrogen uptake. The surface hardness (Rc) did not show a significant difference between the heavily rusted sample and the clean sample. It has been observed that the nitrogen flux is smaller due to the rust layer on the heavily rusted samples.

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Chapter 1

Definition of the problem

1.1 Introduction

Surface hardening is the process of hardening the surface of a metal by diffusing carbon or nitrogen atoms into the metal to form a thin layer of a harder alloy. It is also a process to be used to improve the wear resistance of parts without affecting the interior of the part. [1] The surface hardening of steel has an advantage over through hardening or quenching because less expensive low-carbon and medium-carbon steels can be surface hardened without the problems of distortion and cracking. There are two distinctly different ways to perform the surface hardening:

- Methods that involve an intentional buildup or addition of a new layer
- Methods that involve surface and subsurface modification without any intentional buildup or increase in part dimensions [2]

Surface hardening process investigated in the current research focuses on the second set of methods, which is divided into diffusion methods and selective hardening methods. Further, this study investigated the gas nitriding process which is one of the diffusion methods. Diffusion methods modify the chemical composition of the surface with hardening species such as carbon, nitrogen, or boron. [3] Diffusion methods allow effective hardening of the entire surface of a part and are generally used when a large number of parts are to be surface hardened.

The heat treatments are facing tougher specifications for process quality, safety and results in term of reproducibility. That can be achieved only if the metals' surface condition is controlled during the process and, especially, prior to the heat treatment process. It is well known that surface contamination may hinder surface modification processes. Thus, cleaning to provide a residue free surface before a surface treatment such as gas nitriding is important. Since surface contamination during the heat treatment process can greatly affect the quality of the end products, one process to obtain better control is the surface cleaning, to remove the residues from the prior manufacturing processes. Manufacturing residues, like residual coolants, lubricants and anti-corrosives from cold/hot work, cutting or machining operations and mill-scale or rust formed during storage or transit can act as surface contaminant that prevent or hinder the diffusion process. [4]

1.2 Objective

The objective of this study is to determine the effect of surface contaminants on the nitriding behavior of the Nitralloy-135 steel. Microhardness and nitrogen flux after nitriding are used as the parameter to evaluate the heat treatment performance. To determine the effect of contamination on gas nitriding, the weight gained by the parts and the surface hardness were measured.

1.3 Organization of the thesis

The thesis is divided into four chapters. Chapter 1 is an introduction that provides an overview of the research within and why it is important. Chapter 2 is a review of relevant literature and previous work completed by others in the field of heat treating process. The literature review focuses on the classification of surface contaminants and cleaning methods as well as the key aspects of the effect of contamination on the heat treating process. Chapter 3 presents the experimental set-up and testing procedures along with a test matrix that described the experiments to be conducted. Chapter 3 also describes the effect of contaminations on the gas nitriding. In particular, the cutting fluid, the rust preventive oil and the rust were selected to contaminate the samples. The rust samples were cleaned by the acid cleaner, and the oily samples were cleaned by alkaline cleaners. Weight gain was calculated before and after contamination, cleaning and gas nitriding. Surface hardness and hardness profiles were measured after gas nitriding. Nitrogen flux was also calculated after the heat treating process. The results are discussed in terms of the weight gain and microstructures. The final chapter, Chapter 4, presents the summary and future work. In Appendix, the Questionnaire Results from the CHTE Cleaning Project are shown.

Chapter 2

Literature review

2.1 Surface contaminants

Prior to heat treatment, the parts can be handled and treated in different ways, and the surface can be contaminated and then changed. There are two distinct changes: mechanical changes and chemical change of the part's surface. The mechanical changes include deforming, compressing and abrasion. [5] During these processes, auxiliary agents are necessary for cooling, greasing, and corrosion resistance. They assist for a longer life time of the tools, allow faster processing speed and transport splinters away. But they are also responsible for the surface contamination. The chemical change of the part's surface consisted of phosphate layers and adsorption or reaction layers caused by corrosion protection compounds and auxiliaries as cooling compounds, soaps, oils.[6] The schematic of the layers that may form on a work-piece are presented in Figure 1.

As seen in Figure 1, the bulk material may be covered by a deformed boundary layer that is formed during the manufacturing processing of the part. On top of the deformed layer, the reaction layer forms normally due to metal oxides. But it can also contain reaction products of auxiliary compounds used during manufacturing and metal, e.g. metal sulfides or phosphorous compounds. They are thin, but have excellent adhesion and they can be very dense. [7]

On top of the reaction layer is a sorption layer. Compounds of the grease are bound by chemisorption or physisorption. This layer passes into a thicker contamination layer, containing residue of the previous working steps, e.g. oil, grease, cleaner residues or water ingredients.

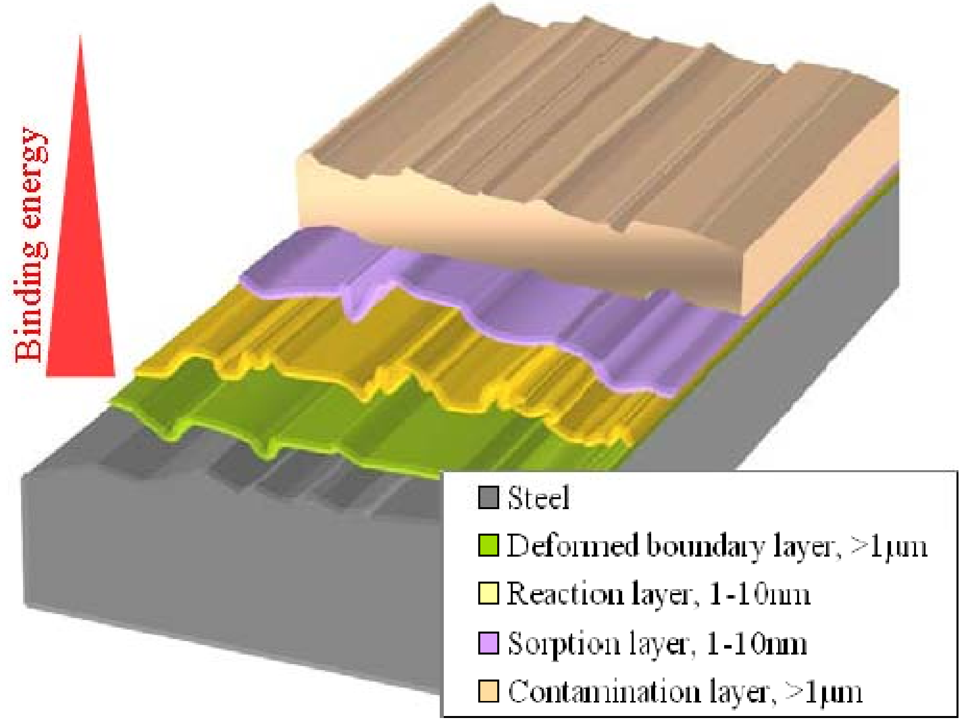

Figure 1. Different layers on the surface of a work piece before the heat treatment. [3]

Reaction layers may form during machining processes also. Reaction layers, however thin, may hinder chemical surface modification processes such as gas nitriding. Haas et al [7] reported that the samples of 42CrMo4 steel milled using mineral oil based cooling agents had reaction layers of oxides and the surfactant cleaner used in the study was unable to remove it.

The top layer is the contamination layer, as shown in Figure.1, which will be investigated in this study. The contamination layer may be loosely deposited, much like ordinary dust, or it may be adhered quite firmly by some chemical or physical means such as chemical bonding, adsorption, adhesion, and so on. This distinction is important, and the surface contamination is classified on the basis of how easily it can be removed. A survey has been conducted among the members of CHTE [8] to identify the surface contaminants that may influence various heat treatment processes.

The results are presented in the Appendix. According to the survey, the most common kinds of surface contamination before the heat treating process are rust preventive oil and cleaner residue. After annealing, normalizing or carburizing, carbon deposits are the most important surface contminants. The oil and carbon deposit also existed after quenching.

2.2 Cleaning methods

The cleaning process is often considered as a non-value-added process, compared to the processes such as plating, coating and heat treatment, etc. The cleaning process consumes time and money. Actually, the cleaning is very important for the quality of the end-products and it may influence subsequent manufacturing processes. [9] Hence, it is quite important to discuss the surface cleaning as being a fundamental step to reach best quality. During the heat treating process, cleaning may not recognized as an issue until after a thermochemical diffusion process (e.g. gas nitriding), even though the parts seemed visually clean.

The processing issues or defects in the part that may arise due to not-cleaned surface are:

- Connecting layers of different thicknesses
- Different concentration profiles
- Partly or complete prevention of nitration in nitriding process
- Bad adhesion of connection layers [10]

Some causes for defects could be type of material, geometry of the parts, positioning of the parts in the furnace, mechanical pretreatment and so on. If these parameters excluded, the defects are caused by non-visible diffusion restricting barrier layers on top of the working piece. [11] On the surface of a visibly clean part if there remain some residue, that may lead to a visible defect after heat treatment process.

The rework of defective parts is difficult; it consumes time and money and, actually, may not always possible. The barrier layers have to be removed mechanically, for example by acid grinding or blasting. Afterwards the parts may need to be heat treated again.

Rust is attached to metal surface; the cleaning method to remove rust often contains metal loss, physically or chemically. For choosing the proper cleaning method for rust, there are several aspects that should be considered. [12]

- Thickness of rust or scale
- Composition of metal
- Allowable metal loss
- Surface finish tolerances
- Shape and size of workpieces
- Production requirements
- Available equipment
- Cost
- Freedom from hydrogen embrittlement

There are various cleaning methods available to remove rust from the part surface [12-13].

Abrasive Blast Cleaning - Abrasive Blast Cleaning is widely used for removing all classes of scale and rust from ferrous mill products, forgings, castings, welding, and heat-treated parts. Depending on the requirement, abrasive blast cleaning can be the sole process, or combined with pickling, which is applied after to remove the remainder. [12-13,15,18]

Tumbling – Tumbling is the least expensive method. However, the size and shape of parts are the limiting factors for this the process. Tumbling in dry abrasives is often used to clean small work-piece, and the parts with complex shape can not be descaled uniformly. Adding descaling compounds often decrease the required time by 75%. [12-13,16]

Pickling - Pickling in hot, strong solutions of sulphamic, phosphoric, sulfuric, or hydrochloric acid is used for complete removal of scale from mill products and fabricated parts. Pickling is generally used as the second step after abrasive blast cleaning or salt bath descaling. At acid concentrations of about 3% and at temperatures of about 60°C or lower removed the steel. [12-14]

Salt Bath Descaling - Salt bath descaling is an effective way to remove scale on alloys and tool steels. Several types of salt baths either reduce or oxidize the scale. It operates at temperature range of 400 to 525 °C. [12-13,17]

Alkaline Descaling - Alkaline descaling is more costly and slower in its action than acid pickling of ferrous alloys, but no material is lost using this method. The action stops when the rust or scale is removed. Immersion baths are usually operated from room temperature to 71 °C and can also be used between 93 to 99°C with a concentration of 20% alkali compound. [12-13,17]

Acid Cleaning - Acid cleaning is effective to remove light rust, such as the rust forms on ferrous metal in storage under high humidity. In acid cleaning, detergents, liquid glycol ether, and phosphoric acid are effective in removing the heavy oil compounds from the engine parts, even after it dried. By using a power spray, these acid solutions can clean the parts without manual scrubbing. Phosphoric acid cleaners may cause some discoloration, but it will not etch steel. Acid cleaners are usually used in a power spray. Some cleaners remove light blushing rust and form a thin film of protection temporarily. They are high in cost, but still often used in large ferrous parts, such as truck cabs. Phosphoric or chromic acid cleaners, with power spray or soak cleaning are used in removing most cutting fluids. These methods are expensive. But in some cases, they are still used because of their ability to remove light rust. [12-13]

Alkaline cleaning - Alkaline cleaning can remove the light oil compounds by immersion and spray cycles. The size of the parts is limited for alkaline immersion. The recommended minimum spray pressure is 0.10 MPa. The larger parts can be cleaned more effectively by spraying. Alkaline cleaners [19] are efficient and economical for removing light oil and grease and can achieve to a no-water-break surface. They remove oil and grease by saponification, emulsification or both. However, alkali will contaminate paint and phosphate coating systems, so thorough rinsing is necessary. Cold water rinsing is recommended. Parts should be kept wet between stages, and delays before subsequent processing should be kept to a minimum. Alkaline Cleaning is the least expensive method and it also can be used in cleaning all cutting fluids [20].

2.3 Surface hardening methods

Surface hardening is used to improve the versatility of certain steels by producing combinations of properties not readily attainable in other ways. For many applications, wear and the most severe stresses act only on the surface of a part. So surface hardening is the process to improve the wear resistance of parts without affecting the softer, tough interior of the part. Therefore, the part maybe fabricated from a low- or medium-carbon steel, and is surface hardened by a final heat treatment after all other processing has been accomplished. This combination of hard surface and resistance to breakage upon impact is useful in parts which must have a very hard surface to resist wear, and a tough interior to resist the impact as well. [1] Further, the surface hardening of steel has an advantage over through hardening because surface hardening also reduces distortion and eliminates cracking which happens through hardening, especially in large section. There are two distinctly different ways to the methods for surface hardening:

- Methods that involve an intentional buildup or addition of a new layer
- Methods that involve surface and subsurface modification without any intentional buildup or increase in part dimensions [2]

The surface hardening method used in this study focuses on the second set of methods, which is divided into diffusion methods and selective hardening methods. These are two major approaches to surface hardening techniques. First approach changes surface composition and includes the applications of such techniques as carburizing, nitriding, and carbonitriding. The second one does not change composition and consists of hardening the surface by flame or induction heating.

The selective hardening of steel surfaces is typically achieved by localized heating and quenching, without any chemical modification of the surface. However, selective surface hardening can also include chemical modification by such techniques as ion implantation and selective carburization. The more common methods currently used to harden the surface of steels include flame and induction hardening. However, each of these methods has shortcomings that can prevent its use in some applications. For example, the disadvantage of flame hardening include the possibility of part distortion, while induction hardening requires very small part-to-coil distances, which must be precisely maintained**.** [2]

Surface hardening by diffusion will modify the chemical composition of the surface with several variations of hardening species like carbon, nitrogen, or boron. The diffusion methods allow effective hardening of the entire surface of a part and are generally used when large numbers of parts are to be surface hardened. The basic process is thermochemical because some heat is needed to enhance the diffusion into the surface of the part. The depth of diffusion exhibits time-temperature dependence as shown in eqn. (1).

$$\textit{case depth} \propto \mathrm{K}\sqrt{\mathrm{Time}} \tag{1}$$

where the diffusivity constant, K, depends on temperature, the chemical composition of the steel, and the concentration gradient of a given hardening species. Concentration gradients depend on the surface kinetics and reactions of a particular process. The diffusivity constant increases as a function of absolute temperature. [21]

Diffusion methods include different hardening species and process methods which are used to transport the hardening species to the surface of the part. These processes variations generate differences in case depth and hardness as shown in Table 1. It is also important to discriminate between the total case depth and the effective case depth. The effective case depth is usually about two-thirds to three-fourths of the total case depth. [22]

Table 1 Typical characteristic of diffusion treatments [22]

Process	Process temperature (C)	Typical case depth	Case hardness (HRC)
Carburizing			
Gas	815-980	75um-1.5mm	50-63
Liquid	815-981	50um-1.5mm	50-65
Vacuum	815-1090	75um-1.6mm	50-63
Nitriding			
Gas	480-590	125um-0.75mm	50-70
Salt	510-565	2.5um-0.75mm	50-70
Ion	340-565	75um-0.75mm	50-70
Carbonitriding			
Gas	760-870	75um-0.75mm	50-65
Liquid	760-871	2.5-125um	50-65
Ferrite nitrocarburizing	565-675	2.5-25um	40-60

Nitriding

Nitriding is a surface hardening heat treatment in which the nitrogen content of the surface of the steel is increased by exposure to an appropriate atmosphere at a temperature in the ferrite phase field. Hardening can be accomplished with a minimum of distortion and excellent dimensional control, because nitriding does not involve heating into the austenite phase field and a subsequent quench to form martensite.

Nitriding is a ferritic thermochemical method. The diffusion process is based on the solubility of nitrogen in iron, as shown in the iron-nitrogen equilibrium diagram. (Figure 2)

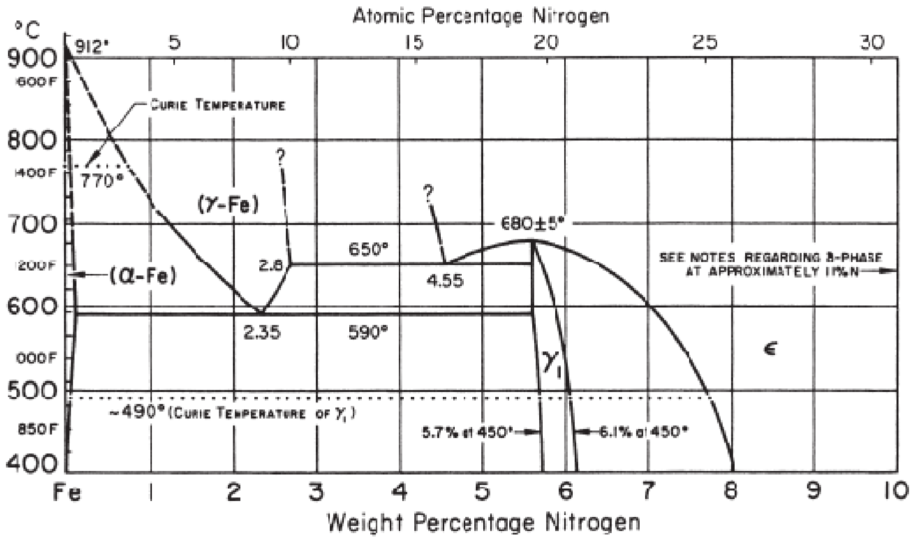

Fig2; Iron-nitrogen equilibrium diagram. [23]

The solubility limit of nitrogen in iron is temperature - dependent, and at 450 ^{o}C the iron-base alloy will absorb up to 5.7% to 6.1% of nitrogen. Beyond this, the surface phase formation on alloy steels tends to be predominantly epsilon phase. The greater the nitrogen content, the more potential for the epsilon phase to form. When the temperature is increased to the gamma prime phase at 490 ^{o}C, the limit of solubility begins to decrease at 680 ^{o}C. [23] The equilibrium diagram shows that control of the nitrogen diffusion is critical to process success.

Several operating process parameters must be adhered to and controlled in order to carry out the nitriding process. Most of them can be controlled with simple instrumentation and methods. Examples of process parameters for gas nitriding include:

- Furnace temperature
- Process control
- Time
- Gas flow
- Gas activity control
- Process chamber maintenance [24]

The factors help to reduce the distortion during the process. Another benefit of nitriding is that it acts as a stabilizing process by providing an additional temper to the processed steel. Control of the process parameters is necessary to ensure formation of an acceptable metallurgical case. [25] Without control, repeatability of the metallurgical requirements cannot be guaranteed.

The process control factors are the elements that will ensure a controlled process and acceptable results:

- Total surface area to be nitrided
- Process pressure inside the sealed process chamber
- Pressurization system and gas delivery into the sealed process chamber
- Exhaust gas system from the sealed process chamber
- Control the preheat treatment procedure prior to nitriding, including stress relief and prehardening and tempering
- Quality and integrity of the steel surface precleaning prior to nitriding [26]

Of the alloying elements, aluminum, chromium, vanadium, tungsten, and molybdenum are beneficial in nitriding because they are strong nitride-forming elements which form stable nitrides at nitriding temperature. Aluminum especially is a very important nitride former and is used in amounts between 0.85 and 1.5% in nitriding steel. [27] Aluminum- containing steels produce a nitrided case of very high hardness and excellent wear resistance. All hardenable steels must be hardened and tempered before being nitrided. Tempering is performed at temperatures between 540 and 750 ^{o}C, usually at least 30 ^{o}C higher than the maximum temperature to be used in nitriding. Tempering above the nitriding temperature provides a core structure that will be stable during nitriding.

Gas nitriding is accomplished with ammonia gas which dissociates on the surface of the steel according to the following reaction: [28]

$$NH_3 \Rightarrow N + 3H$$

The resulting atomic nitrogen is absorbed at the surface of the steel. The schematic of the process is shown in Figure 3.

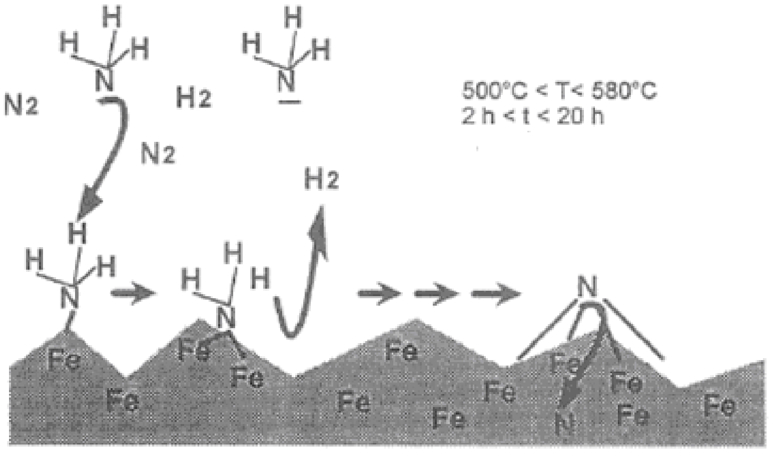

Fig 3: Process steps during nitriding [29]

Gas nitriding is based on a heterogeneous reaction between an ammonia gas atmosphere and a steel surface at temperature between 500 and 580 ^{o}C, with several chemical reactions involved :

- Ammonia is transported to the metal surface by molecular diffusion
- Ammonia molecules absorb at convenient surface locations and dissociate by steps into atomic nitrogen and hydrogen
- Nitrogen diffuses into the surface forming an interstitial solution and iron nitrides Fe_xN
- Hydrogen forms molecular H_2 or reacts with oxygen to form H_2O, both of which desorbed from the surface into the furnace atmosphere [29]

The results are a compound layer at the surface consisting of iron nitrides, as well as a diffusion layer beneath the compound layer consisting of an interstitial solution of nitrogen in the α-Fe lattice which is shown in the Figure 4. The compound layer is responsible for excellent wear and corrosion resistance and the diffusion layer for the increased surface hardness. [30] In the compound layer, nitrogen concentration can reach values of 20 at%. In the diffusion layer, nitrogen concentration is below 8 at%. The boundary region between these layers is characterized by dissolved atomic nitrogen as well as nitride precipitation, usually at the grain boundaries. [31]

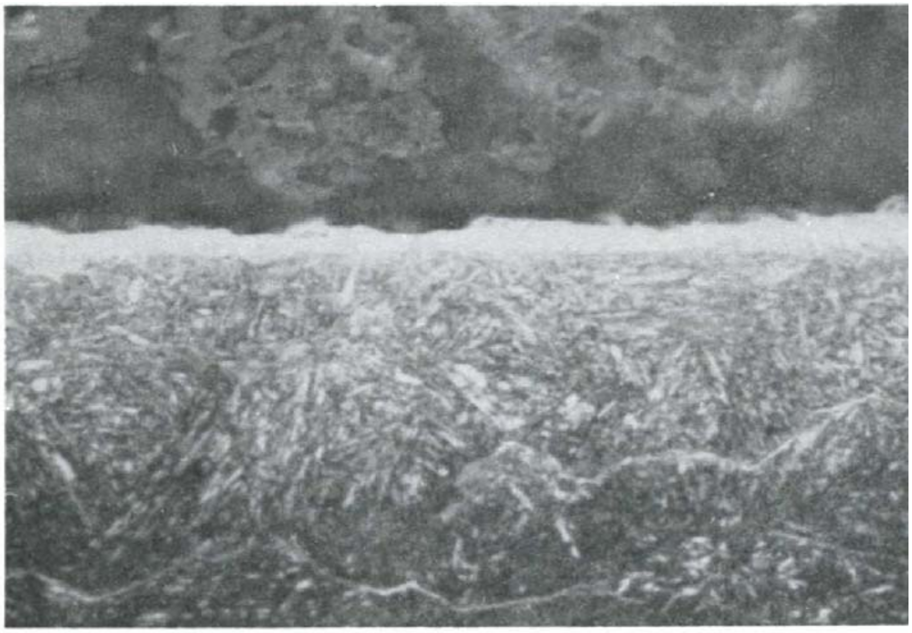

Figure 4: White layer and diffusion zone in nitrided steel. Steel is Nitralloy 135 Modified. Etched in 1.5% nital. Magnification, 500X. [27]

The overall reaction is slow and demands long furnace residence times up of up to 20h. The performance of this process depends on the material. Each step of the process can be hindered by surface contamination from prior manufacturing steps. On the other hand, improvements in nitriding have been reported owing to a preoxidation process taking place in the nitriding furnace at temperatures up to 300 ^{o}C, resulting in the formation of oxide layers. [32]

The nitriding may be accomplished by either a single-stage or double-stage process. In the single-range process, the brittle gamma iron nitride at the temperature in the range of about 500 to 525 ^oC is produced. The dissociation rate of ammonia ranges from 15 to 30%. The double-stage process is known as the Floe process [23] by using a two-stages process. The first stage of the double-stage process is a duplication of the single-stage process. The principal purpose of the second stage is to minimize the depth of the white layer. The dissociation rate of ammonia is increased to 65-85% with the temperature ranges from 550 to 565 ^oC. Since the NH_3 content of the atmosphere is reduced, the iron nitride does not grow as rapidly and in fact dissolves as it supplies nitrogen into the interior of the steel. Nitriding times are quite long, anywhere from 10 to 130h depending on the application, and the case depths are relatively shallow. [23]

2.4 Effects of contaminants on the heat treating process

Heat treatment processes are facing increasing specifications with reference to process quality, safety and results in terms of reproducibility and repeatability. It is well known that the surface contamination may hinder surface modification processes, so they can be met only if the surface condition is controlled during manufacturing and, especially, prior to the heat treatment. Thus, cleaning to provide a residue free surface before the gas nitriding is important. It has been shown that surfactant cleaners which consist of anionic or non-ionic surfactants tend to decrease the rate of nitrogen acceptance. [34] Alternatively, hydrocarbon cleaners can be used which do not form non-volatile adsorption layers and are ideal for removing water insoluble oils and fats. [35] Not all types of surface contaminants interfere with the nitriding or nitrocarburizing process. Generally, the more volatile components are desorbed or vaporised, whereas others can react with the metal to form stable surface films preventing diffusion. If the nitriding process does not lead to satisfactory results in terms of surface hardness, nitrogen depth profile, diffusion or compound layer thickness, etc., the overall reaction rate was too slow, or the reactivity of the surface was low. This surface condition is termed as "passive". [36]

Residual coolants and lubricants from cold or hot work, cutting or machining operations can act as passive layers and prevent or hinder a thermochemical diffusion process. If the contaminants are nonvolatile and do not vaporize completely before the nitriding temperature in the furnace, there will be a passive layer formed. Residues from cleaning must be removed completely from the steel surfaces, so that the rinsing stage with rinsing water composition surveillance and control is an important part of a cleaning installation, especially if aqueous cleaning agents are used.

Not all contaminants are equally effective, which can be seen from Figure 5. The pure paraffin mineral oil does not hinder the formation of the compound layer. In contrast to this, a commercial cutting oil leads to reduced surface hardness and a thinner, non-uniform compound layer, even if its composition is about 95% mineral base oil. [36]

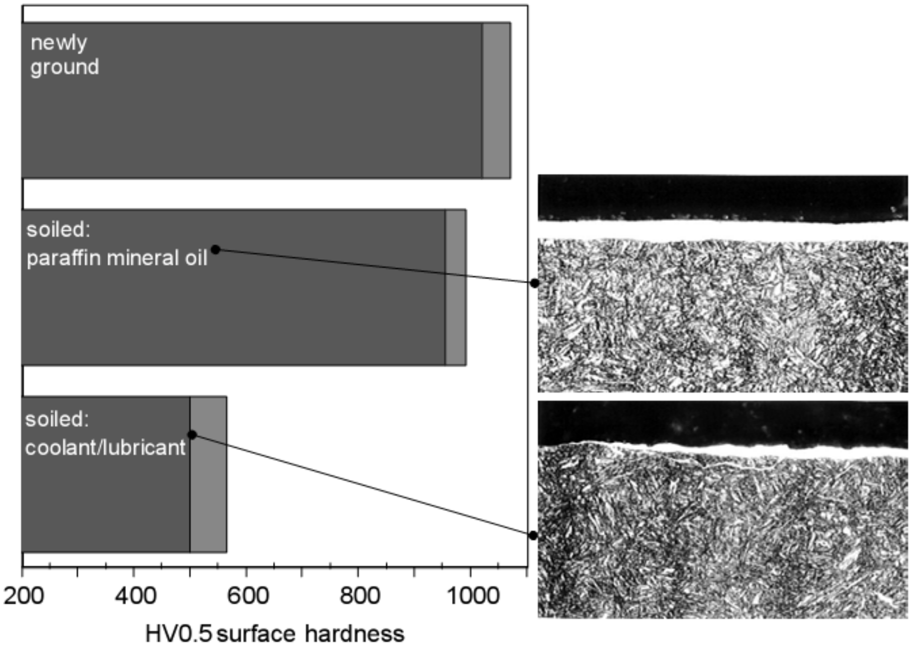

Figure 5 Nitriding results of 42CrMo4 specimens with reference to surface hardness and white layer mophology. [36]

If the cleaning agent residues are not removed by diligent rinsing, they can lead to passive layers. They are adsorbed on the steel surface in contact with the cleaning solution as shown in Figure 6. Their negative effect of surface hardness after nitriding depends on their volatility; inorganic salts like silicates and phosphates have high melting points and do not vaporize at nitriding temperature. However, if a cleaning installation provides rinsing stages, they can be removed completely.

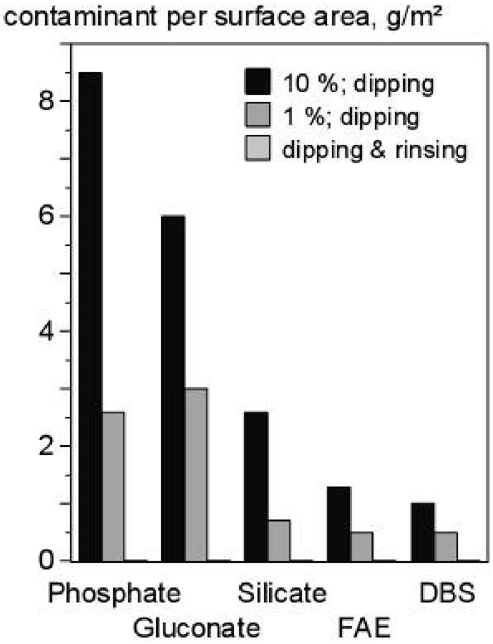

Figure 6 Adsorption of cleaning agent components on a steel surface after rinsing in solutions of different concentrations (FAE=fatty alcohol ethoxylate) [36]

During cold or hot work, as well as during machining, the cooling lubricants, hydraulic oils, and machine grease may form stable reaction layer at the elevated temperatures and pressures which occur during the manufacturing process. Reaction layer can work as barrier layers and inhibit surface modification reactions. Reaction film from lubricant additives can affect the white layer formation and surface hardness, which makes white layer too thin and non-uniform. However, the different additives react differently. Whereas a fatty ester appeared to promote the formation of the hard layer, additives containing sulfur of phosphorous reduced the achievable surface hardness. The most defective result achieved using commercial cutting oil. It should be stressed that the effect is enhanced by vigorous cutting conditions which lead to a great amount of cold work.

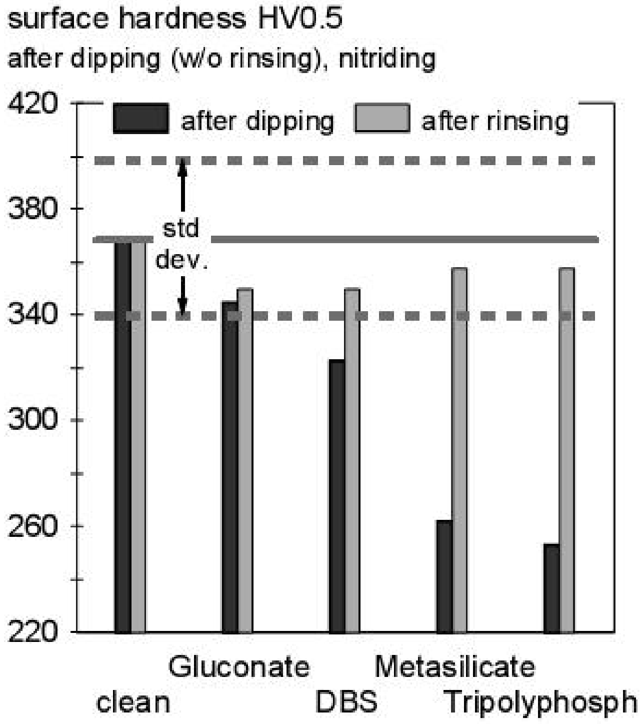

Figure 7 Surface hardness of soiled C15 specimens after nitriding (DBS = dodecylbenzene sulfonate)[36]

Even cleaning agent residues can lead to passive surface layers if not removed by diligent rinsing. They are adsorbed on the steel surface in contact with the cleaning solution as can be concluded from Figure 7. Their negative effect of surface hardness after nitriding depends on their volatility; inorganic salts like silicates and phosphates have high melting points and do not vaporize at nitriding temperature. Furthermore, they form glassy films which can completely prevent diffusion, or nitrogen uptake. However, if a cleaning installation provides rinsing stages, they can be removed completely.

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Chapter 3

The Effects of surface contaminations on Gas nitriding process

3.1 Introduction

Surface cleaning should be employed prior to the thermochemical heat treatments. Manufacturing residue on parts and components soil the furnace and may lead to corrosion and harmful exhaust components. Furthermore, they affect the result of the thermochemical treatment. Manufacturing residues, residual coolants, lubricants and anti-corrosives from cold/hot work, cutting or machining operations can act as passive layers and prevent or hinder the diffusion process. Nonvolatile contaminants do not vaporize completely before the heat treatment temperature is reached in the furnace. Cleaning/degreasing agents will also leave some inorganic salt residues which are hard to volatilize, so they must be removed completely from the steel surfaces prior to heat treating. The rinsing stage becomes an important part of a cleaning process, especially if aqueous cleaning agents are used. [1]

During cold or hot work, as well as during machining, the cooling lubricants, hydraulic oils, and machine grease may form stable reaction layer at the elevated temperatures and pressures which occur during the manufacturing process. Reaction layer can work as barrier layers and inhibit surface modification reactions. Reaction film from lubricant additives can affect the white layer formation and surface hardness, which makes white layer too thin and non-uniform. [2]

Not all types of surface contaminants interfere with the nitriding. Generally, the more volatile components are desorbed or vaporized, whereas others can react with the metal to form stable surface films, preventing diffusion. Furthermore, Haas et al [3] presents that steels containing chromium as alloying element tend to form passive oxide surface films even if free from contaminants. In common cleaning procedures liquid cleaners are applied, either water- or solvent based. However, these cleaners are limited in their capability with respect to the removal of passive chemisorption or reaction layers. Electrochemical methods allow distinguishing types of surface contamination which do not interfere with the thermochemical process from passive layers which do, and thus must be removed - or prevented from formation during manufacturing.[3]

In the present work, Nitralloy-135 steel samples have been contaminated with the cutting fluid, rust preventive oil and rust. The objective of this study is to understand the effect of surface contaminants on the nitriding behavior of steel. Microhardness and nitride flux after nitriding are used as the parameters to evaluate the heat treatment performance. To determine the effect of contamination on gas nitriding, weight gained by the parts and the surface hardness were also measured.

Nitriding Process

Gas nitriding is based on a heterogeneous reaction between an ammonia gas atmosphere and a steel surface at temperatures between 500 and 580°C. Residence times for the steel components to be treated are between 2 to 20 hours. Ammonia content, furnace temperature and residence time control the process result with respect to the hard layer morphology.

Usually the hard layer can be divided into a "white layer" and a compound layer consisting of metal nitrides of thickness 20 um or less, and a diffusion layer below, containing nitride precipitation at grain boundaries and dissolved atomic nitrogen in the ά-iron lattice of some mm thickness.[4]

As seen in Figure 1, the reaction is the typical heterogeneous reaction between a gas and the steel's surface. As ammonia is not thermodynamically stable at nitriding conditions with respect to the formation of nitrogen and hydrogen, the reaction is kinetically controlled. Several chemical reactions that control the overall reaction rate and thus, the growth rate of the hard layer:

- The molecular transport of ammonia
- The adsorption of ammonia molecules
- The stepwise dissociation into atomic N and H
- The combination of H and N atoms to form H_2 and N_2, and/or, in competition with the combination reactions
- The removal of atomic nitrogen from the surface owing to the formation of the interstitial solution representing the diffusion layer and at higher nitrogen content.
- The removal of H_2 (and N_2 if present) by desorption and molecular transport into the bulk gas phase. [5]

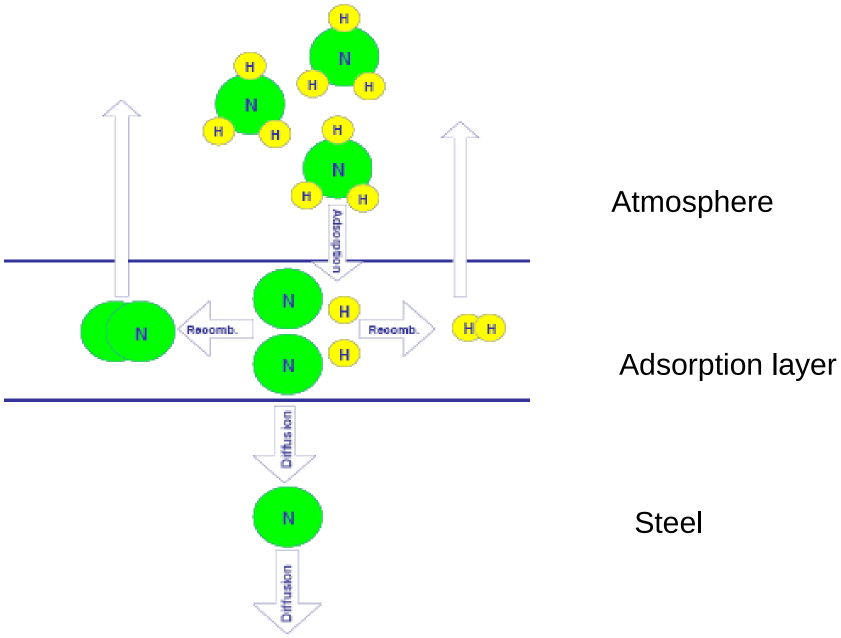

Figure 1 The sketch for the liberation of nascent N [5]

The results are a compound layer at the surface consisting of iron nitrides, as well as a diffusion layer beneath the compound layer. The compound layer is responsible for excellent wear and corrosion resistance and the diffusion layer for the increased surface hardness. In the compound layer, nitrogen concentration can reach values of 20 at% and more. In the diffusion layer, nitrogen concentration is below 8 at%. [6]

The overall reaction is slow and demands long furnace residence times of up to 20 hours. The performance of this process depends on the material, on surface shape and condition, and on the pretreatment of the work-piece, as well as the nitriding process parameters. Each step of the process can be hindered by surface contamination from prior manufacturing steps. [7]

3.2 Experimental procedure

Sample preparation and test matrix

The Nitralloy-135 alloy was used in this study. It is a modification of AISI 4140 specifically designed to be nitrided for high surface hardness and abrasion resistance to develop the case-hardened products, such as gears, bushings and pinions. [8] The composition of the material is presented in Table 1.

Table 1 Composition of the Nitralloy-135 in wt%

C	Mn	Si	Cr	Mo	Al	Fe
0.4	0.6	0.3	1.6	0.35	1.15	balance

This alloy is supplied for nitriding in a prehardened condition, about 26/30 HRC. Further heat treatment is generally not required. The nitriding treatment is undertaken after all grinding and polishing on the part has been completed. [8]

Disks used in this experiment were about 1.43 cm in diameter and 0.56 cm in thickness with an identifying mark on the side. The schematic of the sample and its loading configuration for the nitriding experiments can be seen in Figure 2.

Figure 2 Sample shape and workload used for the nitriding experiments

Four sample sets were settled for characterization using several analysis measurements. Sample set 1 was ground by using 240 grit SiC paper to create a standard surface finish. Sample set 2 was placed in a controlled environment of 25℃ and 80% humidity to form rust. The times that were chosen are 7 days, 4 days and 2 days. Sample set 3 was contaminated in cutting fluid (Castrol Clearedge 6519). Sample set 4 was contaminated in rust preventive oil (Houghton Rust Veto 4225). All the sample sets can be seen in table 2.

Table 2 Test matrix for the effect of contaminant on the heat treatment performance test

Material	Contaminant		No.of trials
Nitralloy-135	As-polished		4
	Rust	2 days	2
		4 days	4
		7 days	2
	Cutting fluid		2
	Rust preventive oil		2

The experimental plan flowchart is shown in Figure 3. The samples which were polished were divided into two groups for each contamination: cleaned and non-cleaned. The samples were nitrides in the same batch to ensure the same nitriding condition. The workload used in nitriding experiment is shown in Figure 4. Each sample was weighed before and after the nitriding using a Mettler AB54-S scale to calculate the nitrogen uptake and the total flux into the steel. The surface hardness-HRc and Vickers hardness were also measured. One sample for each condition was heat treated and analyzed. By comparing the as-polished and non-cleaned samples, the effect of contamination on gas nitriding can be studied. By comparing the cleaned and non-cleaned samples, the cleaning method for contamination removal can be evaluated.

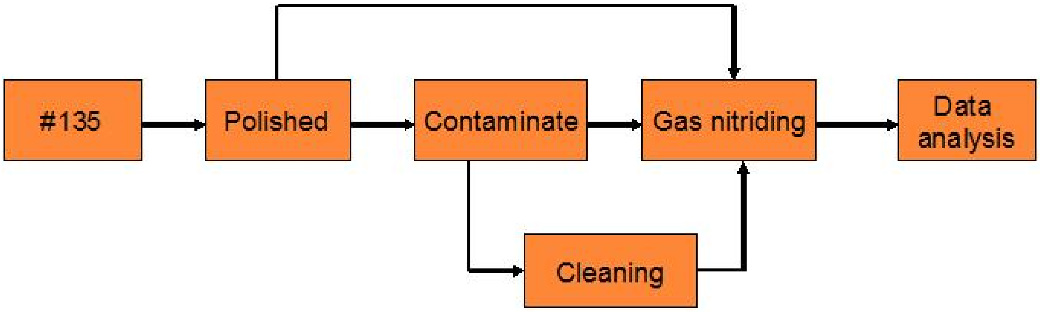

Figure 3 The flowchart for the experiment

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Contamination methods

Rust

As evident in Figure 4, the samples were placed in a controlled tank of 25℃ and 80% humidity to form rust. The corrosion times which were chosen are 7 days, 4 days and 2 days, as presented in Table 2.

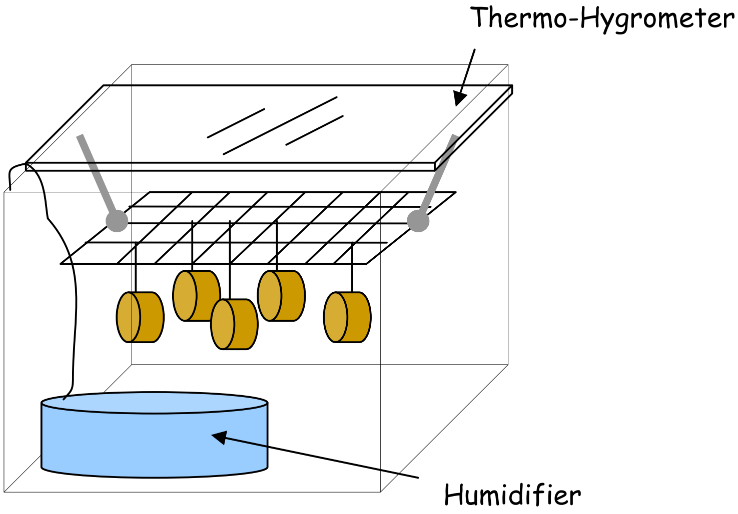


Figure 4 the sketch for the experimental set-up.

Cutting fluid

The cutting fluid used in the experiment was Castrol Clearedge 6519 [9], a high performance cutting and grinding fluid. It is chlorine free and formulated to eliminate time consuming maintenance problems associated with traditional semi-synthetic coolants, particularly regular additive additions, dumping and recharging, and cleaning foam-outs. It can be used in aluminum and ferrous alloy machining. The emulsion is 5% Concentrate + 95% tap water, which has the pH value of 9. The used cutting fluid was taken from the WPI machine shop is CNC machines.

The samples contaminated with cutting fluids were prepared as follows – immersed in room temperature oil and then heated to 300^{o}C for five minutes, then immediately immersed in the fluid to simulate the cutting condition.

Rust preventive oil

The rust preventive oil used in the experiments was Houghton Rust Veto 4225 [10]. It is water displacing, light solvent-based rust preventive that leaves a soft film to provide good long term indoor protection [11]. It can release displaced water within minutes and leave a very thin transparent protective film. It can provide indoor protection for steel, if parts are packaged. It contains mineral oil and paraffin wax.

To apply the rust preventive oil contamination, the immersion was performed at room temperature. New rust preventive oil was used in this experiment.

Cleaning methods

Acid cleaning

Acid cleaning was selected due to its ability to remove the rust from sample. It is effective to remove light rust, such as the rust forms on ferrous metal in storage under high humidity. Hydrochloric acid cleaner: 50 vol% HCl was used as the cleaner. The samples were dipped in acid cleaner for 1min at room temperature, rinsed in distilled water twice for 3 min each time, dried and kept in a cool and dry environment. Visually, the brown rust layer disappeared after immersion.

Alkaline cleaning

Alkaline cleaning was selected to remove the oil contamination from the sample. The alkaline cleaner was diluted in hot water which temperature was about 80°C, in which 5 vol% cleaner was used. The samples were dipped in the solution for a few minutes at room temperature, rinsed in distilled water twice for several minutes each time, dried and kept in cool and dry environment. Visually, the surfaces of the sample were shiny after cleaning.

Nitriding Experiments

After cleaning, the samples were placed in the nitriding furnace at the Bodycote [12] facility in Worcester. The reaction temperature has an effect on the ammonia dissociation and diffusion rates and reaction progress is determined by the residence time. The furnace was flushed with nitrogen and the reaction temperature was established.. Furnace residence time started when ammonia was introduced into the system.

The nitriding process done by Bodycote is double-stage process. In the first stage of a temperature of 526°C (980°F) is used, and the dissociation rate ranges from 24 to 28%. This process produces a brittle, nitrogen-rich layer known as the white nitride layer at the surface of the nitrided case. The second stage proceeds at the nitriding temperature which may be increased to 549°C (1020°F) and the dissociation rate in the second stage is increased to 78 to 80%. External ammonia dissociation is necessary for obtaining the required higher second-stage dissociation. The principal purpose of double-stage nitriding is to reduce the depth of the white layer produced on the surface of the case.

Measurements

Weight test

The weight of samples was tracked during these experiments. The weight of samples before and after rust process has been recorded and subtracted by original weight to obtain the rust gain during rust forming step by using the lab balance, Mettler H54AR.

Hardness test

Surface hardness was measured with Wilson Rockwell Hardness Tester. The Rockwell scale characterizes the indentation hardness of steel through the depth of penetration of an indenter, loaded on a sample and compared to the penetration in some reference material. The HR_c was measured on each sample for 5 times.

Microstructure

Surface composition and layer thickness after nitriding was analyzed qualitatively and quantitatively by using an optical microstructure and scanning electron microscope (SEM). The SEM signals result from interactions of the electron beam with atoms at or near the surface of the sample. SEM micrographs have a very large depth of field yielding a characteristic three-dimensional appearance that is useful for understanding the surface structure of a sample. A wide range of magnifications is possible, ranging from about 25X (about equivalent to that of a powerful hand-lens) to about 250,000X, approximately 250 times the magnification limit of the best light microscopes.

3.3 Results and Discussion

Flux of nitrogen vs. contaminants

The total flux of nitrogen atoms that have diffused in the work-piece can be presented from the equation of the change of the total weight gain by the steel over the surface area by nitriding time. The flux of nitrogen J was calculated by using the equation 1.

$$J = \frac{\Delta M}{A \cdot t} \qquad (1)$$

where J is the nitrogen flux (g/cm^2*s), ΔM is the total weight gain (g), A is the surface area (cm^2) and t is the carburizing time(s).

As seen in Figure 11, the total flux for the samples including the as-polished samples was plotted along with contaminated samples. In the case of the samples that were contaminated in the cutting fluid and rust preventive oil, the total flux did not show a significant difference with the one of as-polished samples. In the contrast of the rust samples, the difference for the flux can be seen in Figure 9. Furthermore, the more time the samples were allowed to oxidize, the lower total flux of nitrogen, as shown in Figure 9 and table 3. For this reason, the following experiments will be focused on the effect of rust on the gas nitriding.

Table 3 The total flux of nitrogen vs. Contaminants

Samples			Weight gain after nitriding (g)	J(g/cm^2 hour)
As-polish			0.02229	8.67E-05
			0.02178	8.91E-05
Rust	2 days	C	0.02253	7.89E-05
		NC	0.01897	6.64E-05
	4 days	C	0.00962	4.77E-05
		NC	0.0137	3.37E-05
	7 days	C	0.02338	8.16E-05
		NC	0.00048	1.69E-05
Rust preventive oil		C	0.02432	8.49E-05
		NC	0.02388	8.48E-05
Hot cutting fluid		C	0.02546	8.88E-05
		NC	0.02491	8.70E-05

*C: cleaned sample; *NC: non-cleaned sample

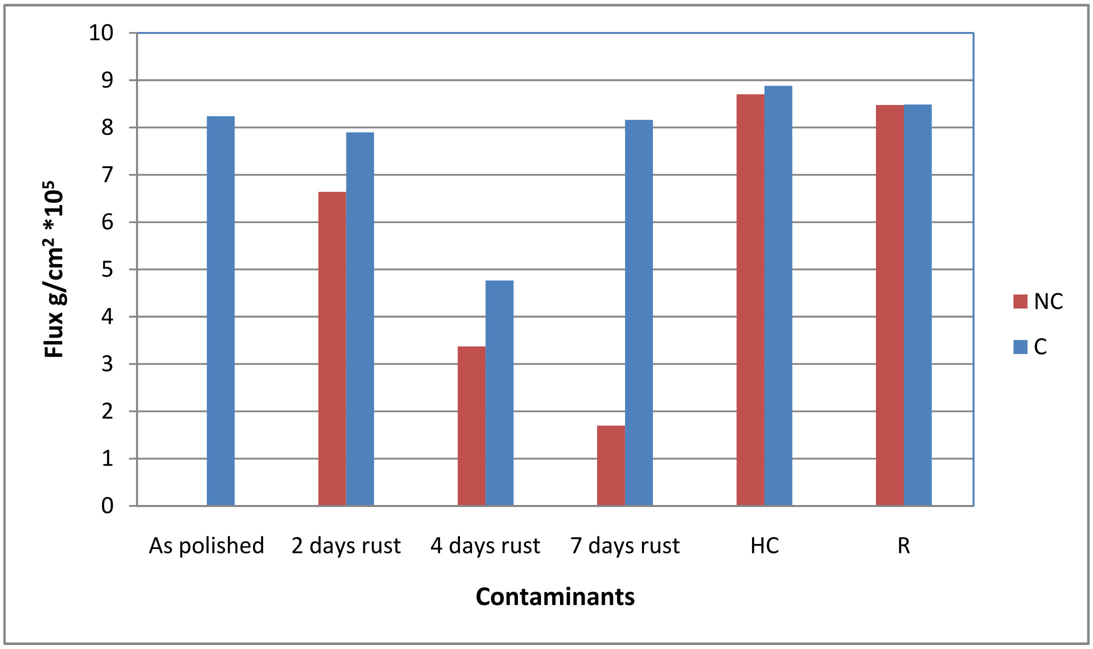


Figure 9 The total flux of nitrogen vs. contaminants

Weight gain

The weight of samples before and after the rust process was recorded and subtracted by the original weight to obtain the rust gain during the rust forming step. Weight increased when time increased, shown in Figure 10. The thickness of the rust was calculated by equation 2.

$$Thickness = \frac{m}{\rho \cdot A} \qquad (2)$$

Where m is the weight gain after rust (g), ρ is the density of the rust, A is the surface area (cm^2).The thickness of the rust vs. Corrosion time is shown in Figure 11.

The weight after nitriding was also measured. The weight gain after nitriding was observed to decrease as the rust layer becomes thicker, as shown in Figure 12. The blue diamond represents the weight difference between rusted sample and nitrided sample. Compared to 0.0024 - 0.0034 mg/cm^2 weight gain for other rusted samples, only 0.0001 mg/cm^2 of nitrogen diffused into the 7 days rust sample. Because the rust layer prevents the nitrogen absorption, less nitrogen was diffused into sample when the rust layer thickness increased. The green triangle in Figure 12 shows the weight gain between as received sample and nitrided sample, which got the same conclusion: less nitrogen is diffused into sample when the rust layer thickness is increased. After cleaning, the weight gain varies in a small range, from 0.0039 - 0.0041 mg/cm^2, except for the sample in 4 days rust set. The rust layer has been removed effectively by the acid cleaner.

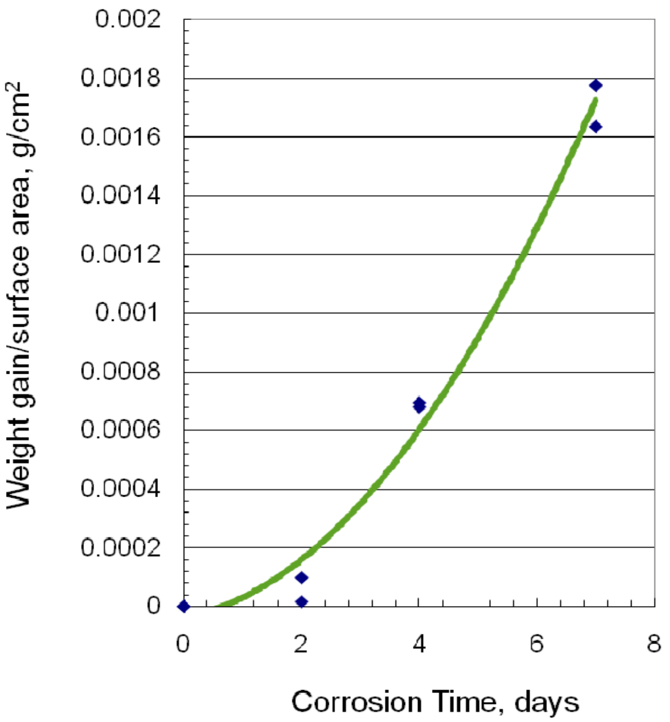


Figure 10 Average weight gain of rust sample due to rust vs. time curve.

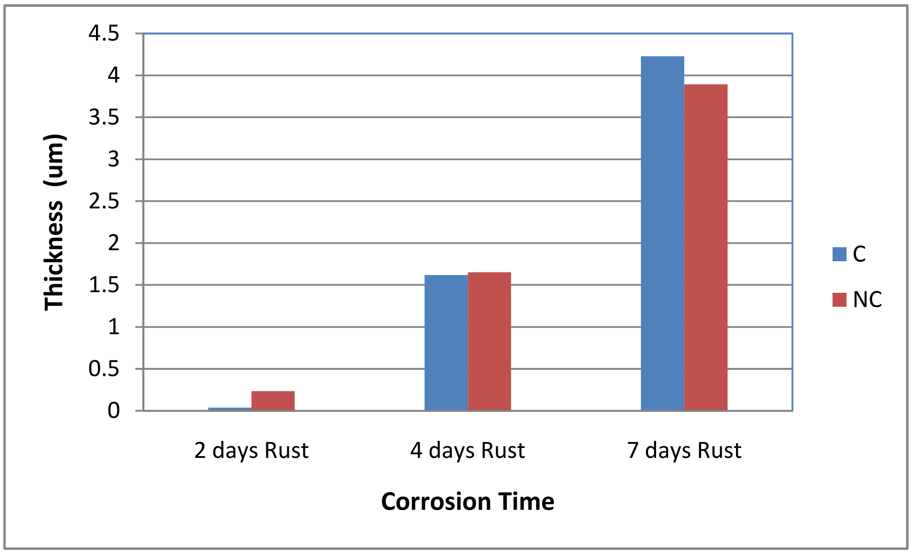


Figure 11 The thickness of the rust vs. corrosion time

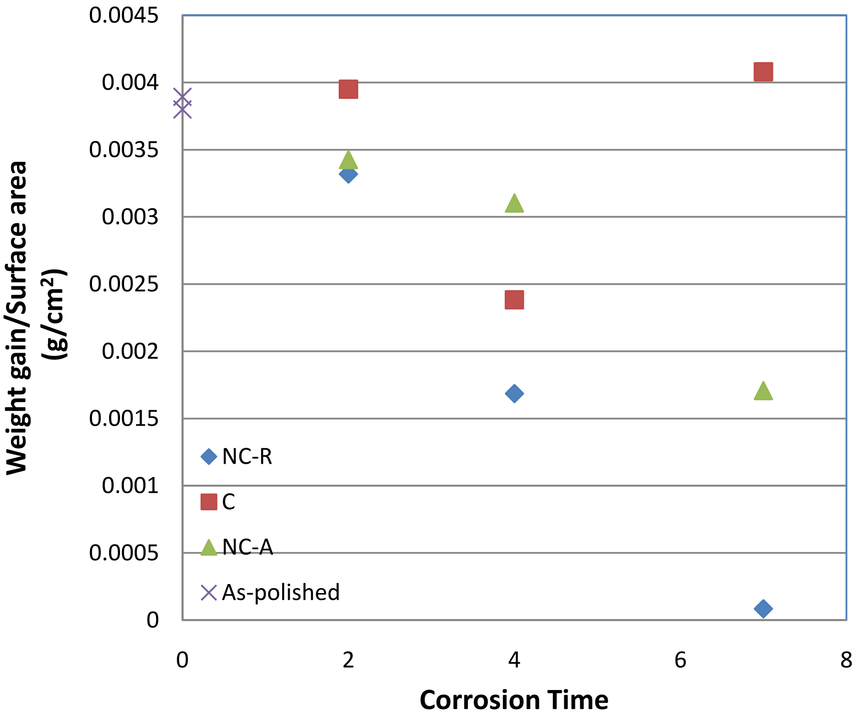


Figure 12 Average weight gain/cm^2 of rust sample after nitriding vs. corrosion time.

Hardness

Surface hardness vs. corrosion time

HR$_c$ was measured and plotted with corrosion time, which has been shown in Figure 13. The hardness of samples is between 55 and 57. The non-cleaned samples have lower hardness when compared to clean samples.

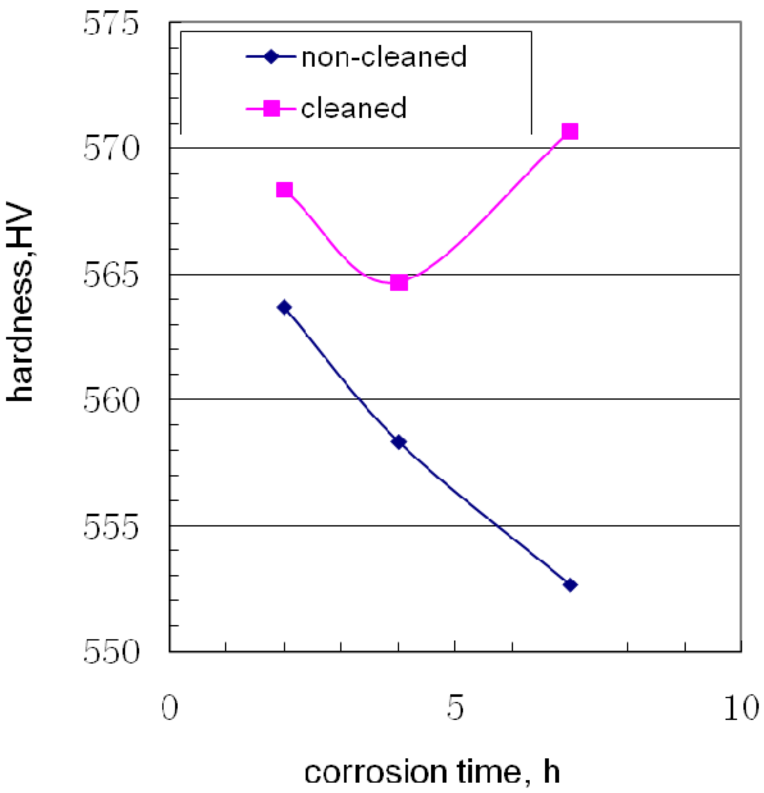


Figure 13 Surface hardness vs. corrosion time.

Cross-section hardness vs. corrosion time

The Vickers hardness test was used in testing the cross-section micro hardness. The samples were cut, polished with 800 grit sand paper and then a 200gf load and 15s loading time was used in Shimadzu HMV-2000 Micro Hardness Tester. The measurements started at 100µm depth from the edge, and an increase of 100µm per measurement was taken at 100-1000µm depth, 200µm per measurement was taken at 1000µm-2000µm. Figure 14 shows the diamond shape made by the indenter with a square-based pyramid and an angle of 136° between opposite faces.

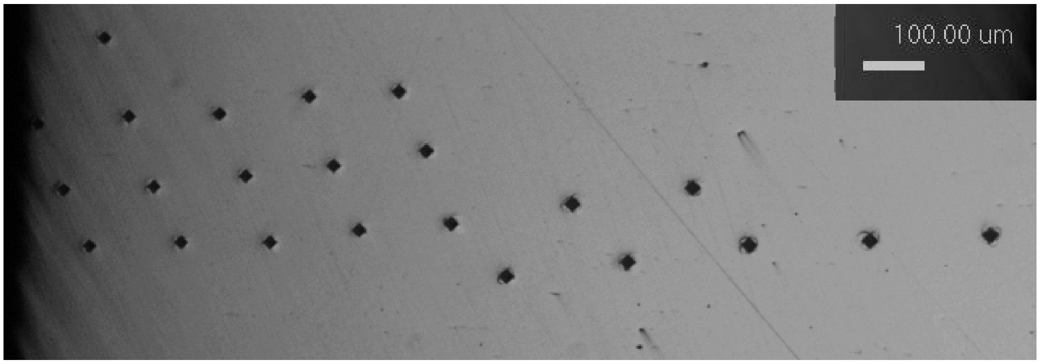


Figure 14 The optical image of the diamond shape holes made by the indenter under 200gf for 15s for Vickers Hardness test.

The results of the Vickers hardness were collected and plotted in Figure 15-17. In the case of 2 days rust samples, the hardness variation can be seen clearly from 100 um to 500 um case depth. For the range from 500 um to 1000 um, there is no significant hardness difference for the samples. In Figure 15, the hardness for the non-cleaned sample is smaller than the one of cleaned sample and as the polished sample. The large difference was found about the 400 um case depth. In the case of 4 days rust samples, the hardness variation can also be seen from 100 um to 500 um case depth in Figure 16. After the 500 um case depth, there is no significant hardness difference. As it can be seen in Figure 17, there is large difference between the non-cleaned sample and cleaned sample from the 100 um and 500 um case depth. After the 500 um case depth, there is the same situation for the hardness because the depth for the nitrogen diffusion layer is about 500 um from the surface of case.

As shown in Table 4, the cross-section hardness of non-cleaned sample is lower than cleaned sample. The total and effective case depths data, given in Table 4, were obtained from the micro hardness data (to 420HV). Comparing data from the Figure 15-17 and Table 4, the data clearly suggests that nitriding the parts of the same steel grade in the same workload, and therefore, the same nitriding process parameters will be affected by the rust layer.

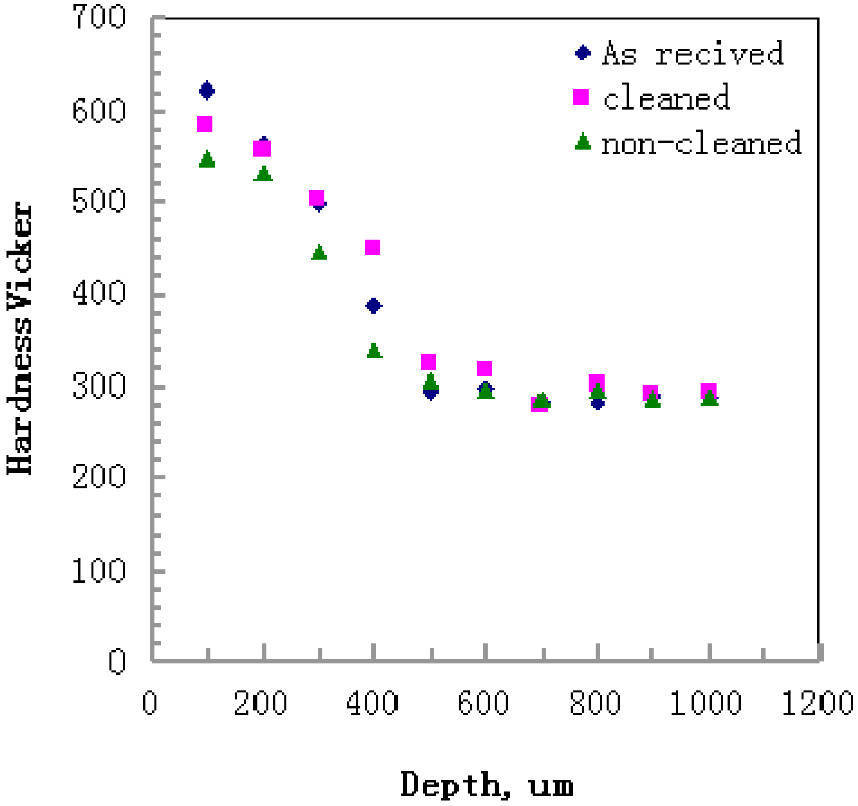


Figure 15 The HV profile for the samples rusted for 2 days

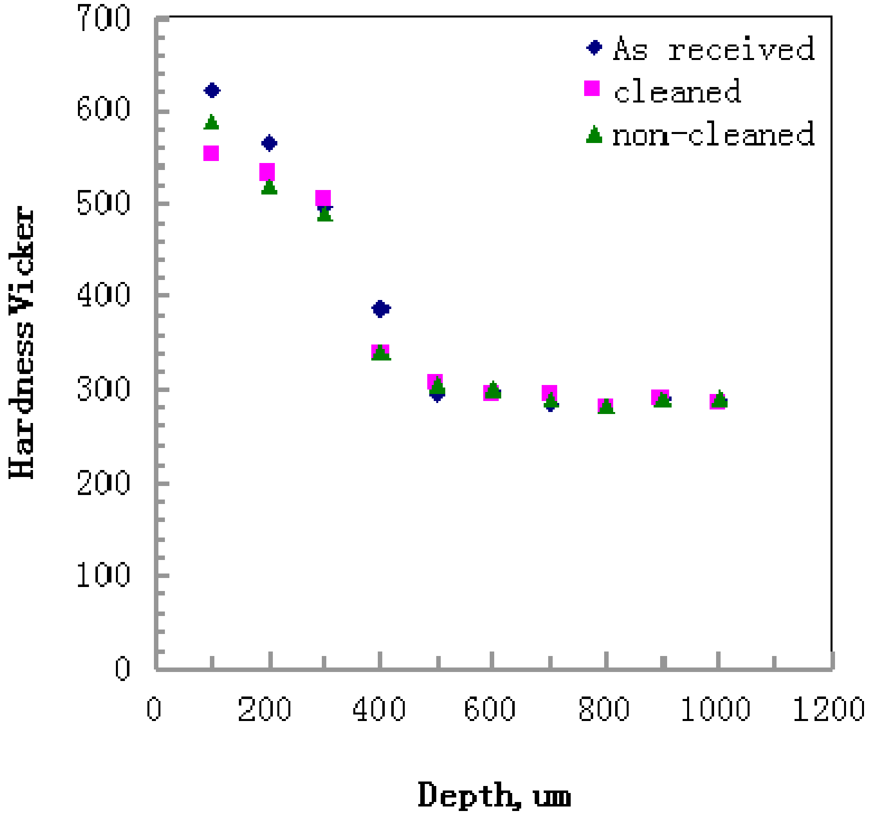


Figure 16 The HV profile for the samples rusted for 4 days

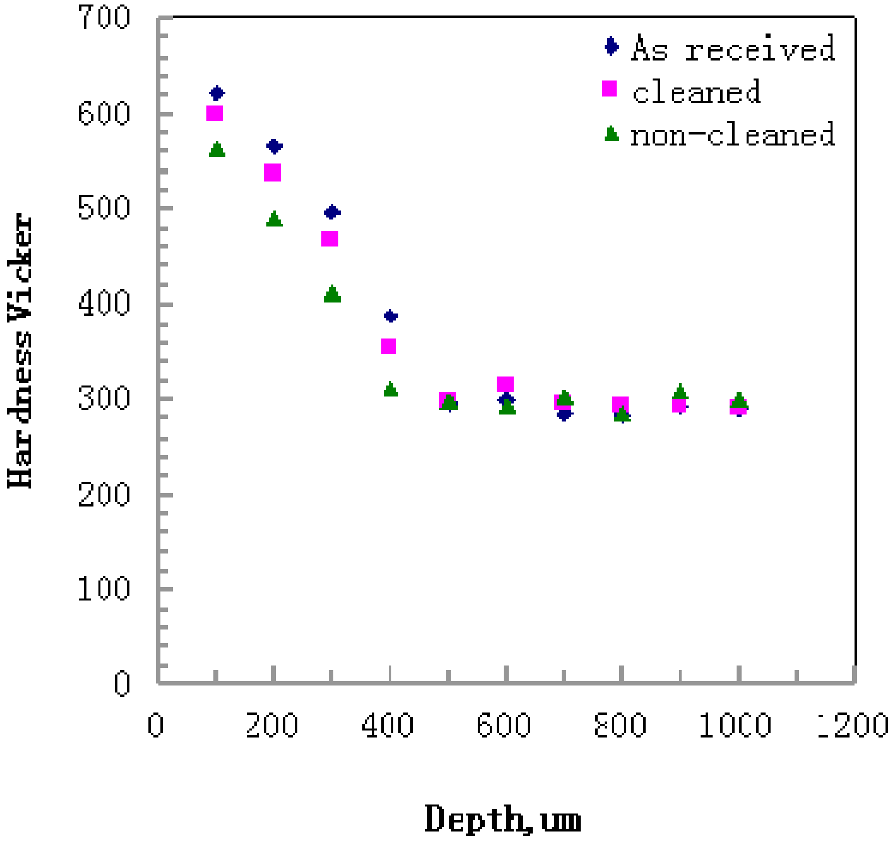


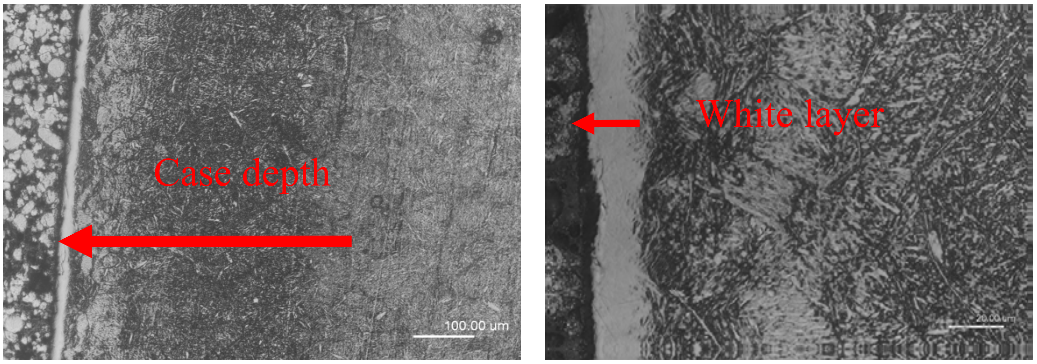
Figure 17 The HV profile for the samples rusted for 7 days

Table 4 Case depth based on microhardness measurements.

Case depth for Cleaned sample (um)		Case depth for Rusted sample (um)	
Rust time	420HV	Rust time	420HV
7days	400	7days	315
4days	400	3days	400
2day	480	1day	370
As-polished	410	--	--

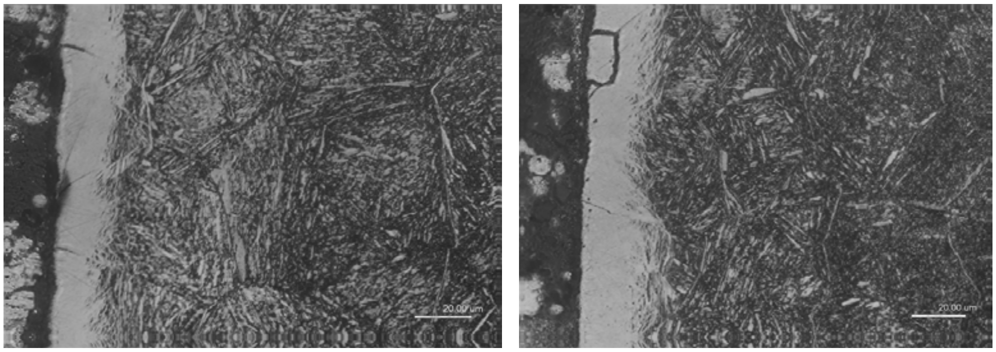
Micrographs

Figures 18-21 present the photomicrographs of nitralloy-135 steel after nitriding. Cleaned and rusted samples both show fine grains in the edge due to the nitriding treatment. The same grain boundary condition was observed for all samples. The difference of the diffusion layer between cleaned and non-cleaned samples can be clearly seen from the Figure 23-25 which are micrographs under magnitude 10 X magnification. The same result can also be concluded from Figure 9: the more time the sample was corroded, the lower was the flux of total nitrogen. The diffusion layer and white layer were identified by red arrows in Figure 18. The thickness slight variation of the diffusion layer for each sample can be seen in Figure 22. For each non-cleaned sample, the more time the sample was rusted, the lower thickness of the diffusion layer the micrograph showed.



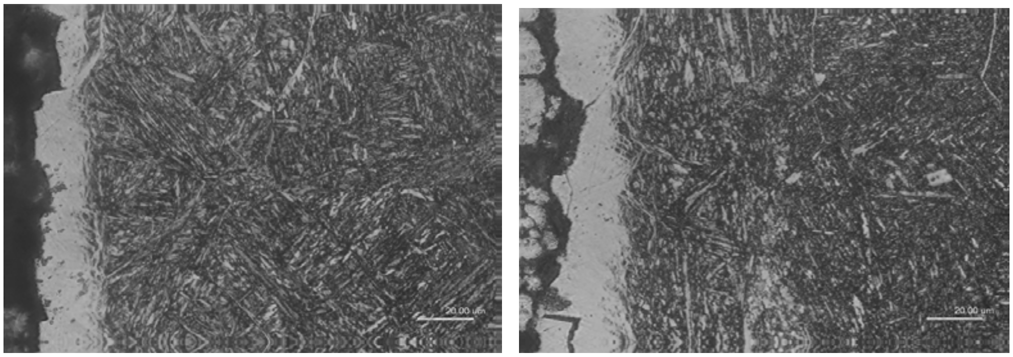
(b) 50X

Figure 18 Photomicrograph of the as-received #135 steel's edge, etched with 2% nital solution. (a) the photomicrograph 10X magnification. (b) the photomicrograph 50 X magnification



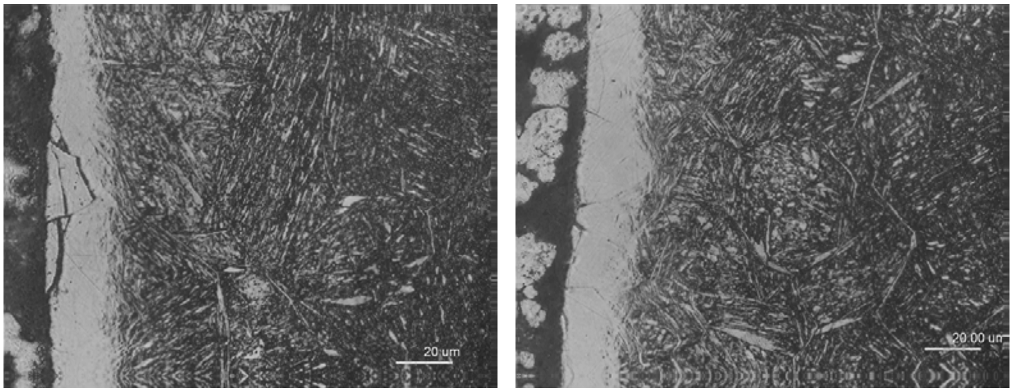
(a) cleaned (b) contaminated

Figure 19 Photomicrograph of the 2 days rust samples, etched with 2% nital solution.



(a) cleaned (b) contaminated

Figure 20 Photomicrograph of the 4 days rust samples, etched with 2% nital solution.



(a) cleaned (b) contaminated

Figure 21 Photomicrograph of the 7 days rust samples, etched with 2% nital solution.

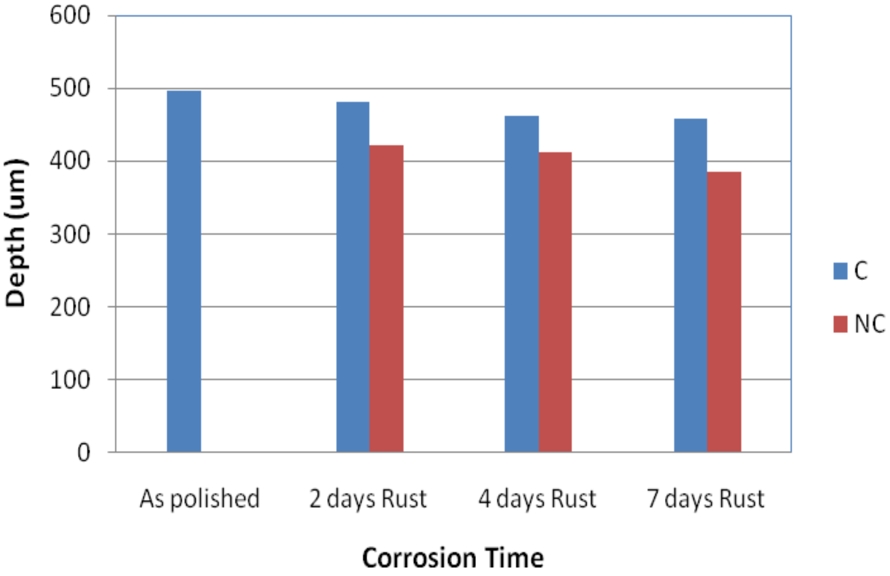
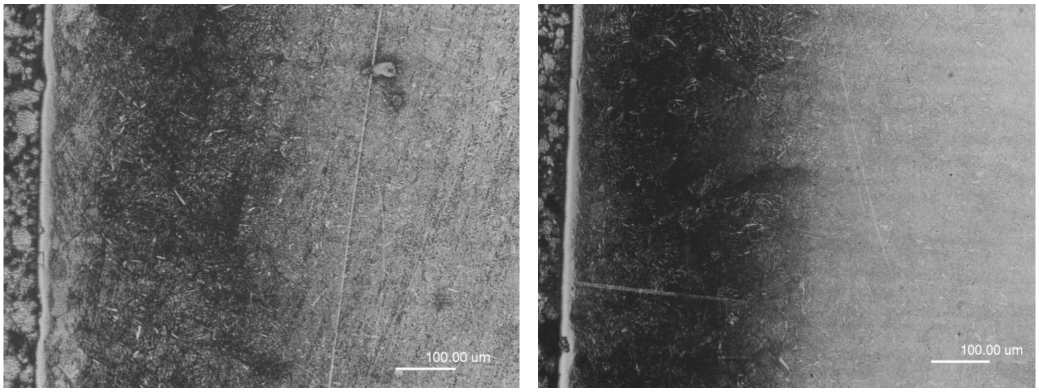
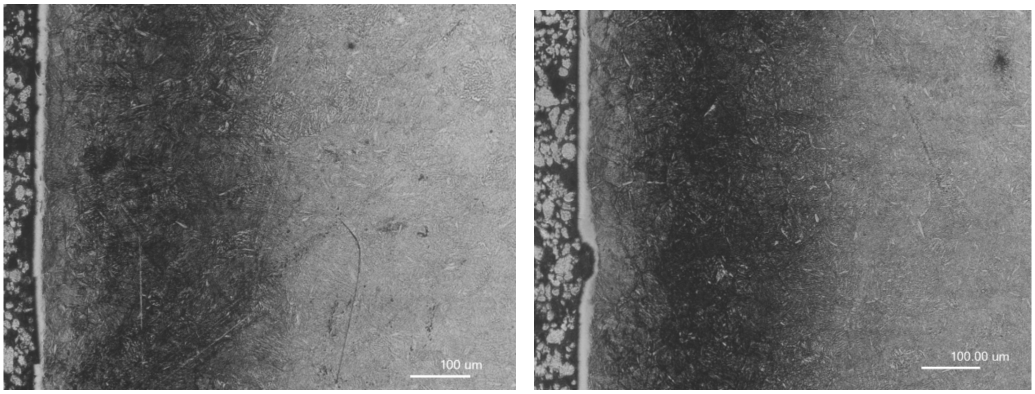


Figure 22 The thickness of the diffusion layer for each sample.



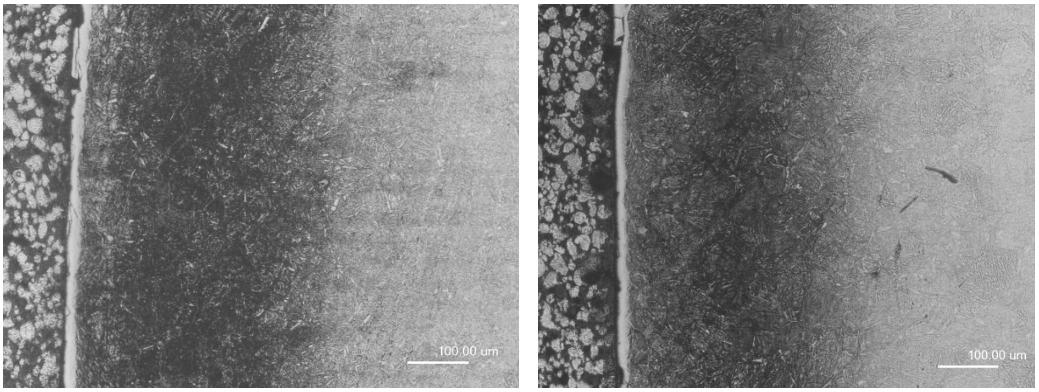
(a) cleaned (b) contaminated

Figure 23 Photomicrograph of the 2 days rust samples 10 X, etched with 2% nital solution. (a) sample cleaned before nitriding (b) sample non-cleaned before nitriding



(a) cleaned (b) contaminated

Figure 24 Photomicrograph of the 4 days rust samples 10 X, etched with 2% nital solution. (a) sample cleaned before nitriding (b) sample non-cleaned before nitriding



(a) cleaned (b) contaminated

Figure 25 Photomicrograph of the 7 days rust samples 10 X, etched with 2% nital solution. (a) sample cleaned before nitriding (b) sample non-cleaned before nitriding

Figure 26 presents the scanning electron microscopy (SEM) image of Nitralloy-135, which shows the white layer and diffusion layer. To identify the type of scales on the nitralloy-135, X-ray diffraction (XRD) pattern had been collected by Panalytical Inc [13]. The peaks of epsilon-iron nitride (Fe_3N), and gamma-iron nitride (Fe_4N) were identified as shown in Figure 28

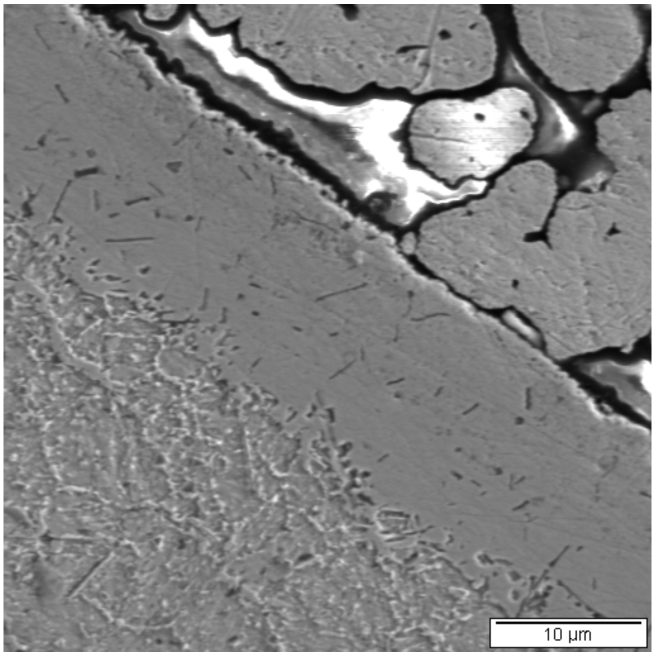


Figure 26 SEM image of nitrided #135 alloy etched by 2% nital.

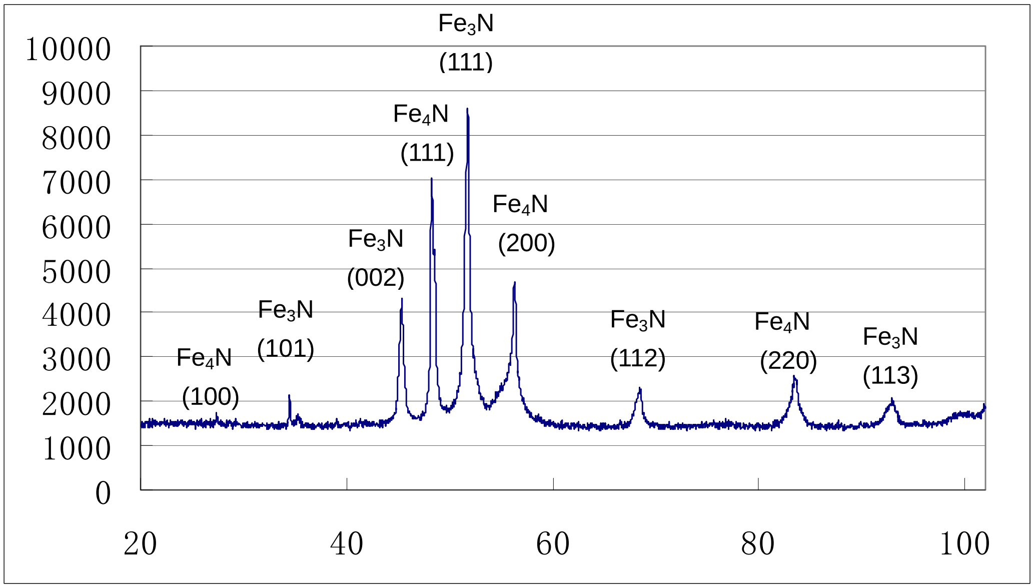


Figure 28 XRD diffraction pattern of nitralloy-135 surface after gas nitriding

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Chapter 4

Summary

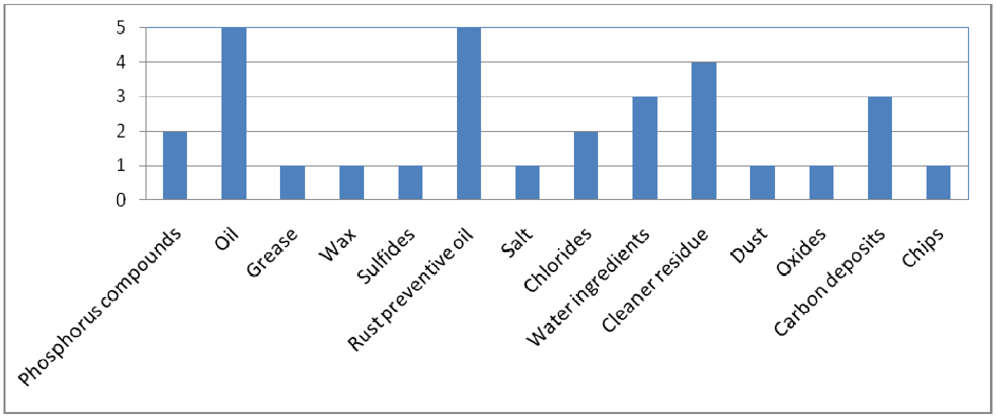
Gas nitriding is a complex process which leads generally to increased surface hardness, and improved wear behavior and corrosion resistance. One problem is that the process is not yet fully understood, especially the influences of surface contamination. The experimental results presented indicate that there is a strong influence of surface contaminants on the rate of nitrogen acceptance. The effects of rust layer on the hardness were experimentally investigated. The results are summarized as below:

- Nitrogen flux is smaller due to rust layer for the heavily rusted sample.
- The surface hardness (R_c) didn't show a significant difference between the heavily rusted sample and clean sample. The hardness of samples nitrided at 526^{o}C and 549^{o}C for 50 hrs is between 55 and 57 HR_c .
- Acid cleaning can remove the rust layer effectively. Hydrochloric acid cleaner: 50 vol % HCl is used. Rinsing completely in distilled water is necessary to remove the cleaner residue.

Appendix

CHTE Cleaning Project Questionnaire Result

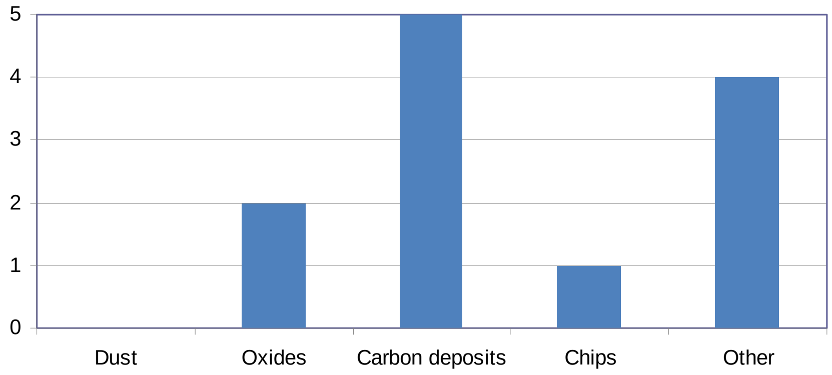
1. What type of surface contaminants do you find on your steel work piece before heat treatment (from upstream operations)?



*Other: Cutting fluids, Lubricants, Soap, Drawing compounds, Fine blanking oils, NaOH, KOH, Borates, and Silicates Salt.

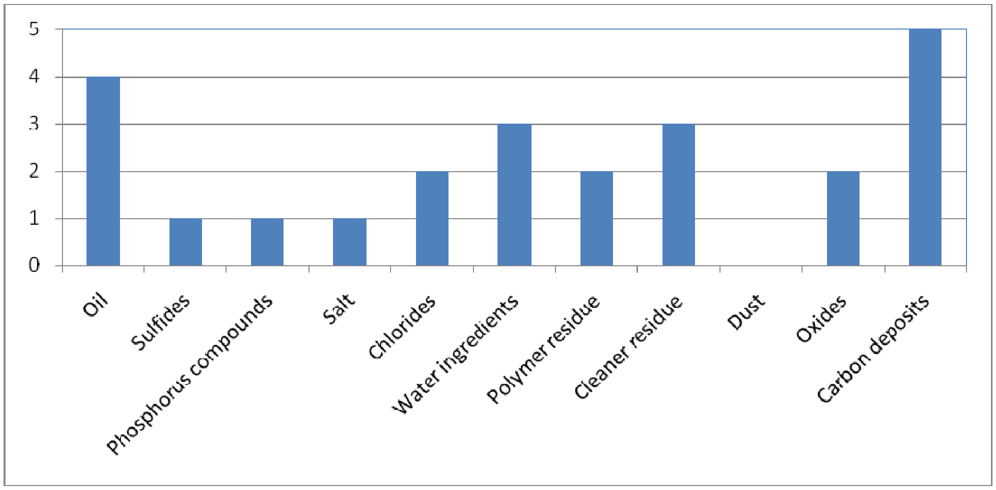
**What must be removed: Hard water, NaOH, KOH, Borates, Silicates Salt, Oil, Chips, Scale from forging?

2. What type of surface contaminants is on your steel work piece after annealing/normalizing/carburizing?



*Other: quench oil,

3. What type of surface contaminants is on your steel work piece after quenching/cooling?



*Other: Rust Preventive, Boron.

**What must be removed: Salt, Oil, Chips, Carbon deposits, [4]

According to the survey result, the most common kinds of surface contamination before the heat treating process are oil, rust preventive oil and cleaner residue. After annealing, normalizing or carburizing, carbon deposits are the most important surface contaminants. The oil and carbon deposits are left after quenching.