INVESTIGATION OF GAS NITRIDING IN PURE FE, AISI 1070 STEEL AND FE-CR ALLOYS

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by

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A Thesis

Submitted to the School of Graduate Studies in Partial Fulfillment of the Requirements for the Degree of

Master of Applied Science

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TITLE:	Investigation of gas nitriding in pure Fe, AISI 1070 steel and Fe-Cr alloys
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NUMBER OF PAGES:	XV, 135

ABSTRACT

Following a review of the gas nitriding process, of the Fe-N system and of the formation of the compound layer, this study investigates the interaction between the diffusing nitrogen and the material to be nitrided.

The formation of the compound layer and diffusion case is discussed for pure iron. AISI 1070 low alloy steel is investigated using different microstructures and the resulting effect on the nitrided microstructure is presented. The interaction of a nitride forming element is studied with a Fe/Fe-5Cr diffusion couple specimen. The strengthening mechanisms resulting from the nitriding process for all these materials are discussed using standard models from the literature. The scale of the precipitates produced in pure iron as well as in the 1070 steel pearlitic and spheroidized microstructure is found to provide marginal hardening. The interaction between N and carbides obtained during the nitriding of the 1070 martensitic microstructure gives rise to a significant hardness increase up to 130HV. The most significant hardening effect (up to 900HV) is obtained with the formation of a high density of fine CrN precipitates in the Fe-Cr specimens.

I would like to dedicate this work to my wife Assunta for embarking by my side on this Canadian adventure aimed at furthering my education. For your continuous support and encouragement over the years and your patience with our young children while I wasn't home, I thank you from the bottom of my heart. I would not have accomplished this without you.

Merci.

ACKNOWLEDGEMENTS

I wish to express my thanks to the following individuals:

Both my supervisors Professor David Embury and Dr. Hatem Zurob for their guidance, continuous support and availability. I particularly beneficiated from Professor Embury dedication in ensuring that I kept focused on the objectives of this research and his extreme patience with a part-time student often diverted from his academic journey.

The Management of Vac Aero International Inc., Oakville, Canada for their financial support, the un-restricted access to the gas nitriding equipment used for this work and for allowing me to flexibly manage my time between work and school commitment during the course of this research.

Glynis de Silveira, Steve Koprich and Chris Butcher of the Brockhouse Institute for Materials Research for their expert advise on sample preparation and use of the Light microscope and SEM instrument.

Dr. James Britten, manager of the McMaster Analytical X-Ray Diffraction Facility for his work in collecting the X-Ray Diffraction information and his help in the interpretation of the raw data.

Dr. Xiang Wang, Research Associate in the Materials Science and Engineering department for his proficient work in the preparation and evaluation of the TEM specimen.

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Chapter 1

1 INTRODUCTION

The nitriding process has been used in the industry since the middle of the last century as a surface treatment for the improvement of wear and corrosion resistance of components made from iron materials.

1.1 Advantages and Limitations of Gas Nitriding

The gas nitriding process has one of the lowest cost (less than \$5/lb) of all the surface hardening processes available (Figure 1.1), which has been a significant factor in its acceptance by the industry.



Figure 1.1: Approximate relative cost of various surface treatments

The main advantages are:

 a) Low temperature treatment when compared to other case hardening process such as carburization (C diffusion) and carbonitriding (C and N diffusion)

- b) No liquid quenching required to obtain the hardness, thus reducing distortion
- c) High hardness obtained with a wide variety of steels, up to 1000HV
 (≈ 3000 MPa)
- d) Resistance to corrosion increased by the compound surface layer (proprietary process also provide post-oxidation treatment at the end of the nitriding, with impregnation of corrosion inhibitor)
- e) No modification of the core properties

Nitrided parts have improved wear and abrasive resistance (high surface hardness) and improved fatigue life (compressive stress at surface). The main applications are in the automotive industry (gears, crankshafts, piston rings, springs), the aerospace industry (misc. parts with surface wear) and commercial applications (hydraulic rods, ...).

The limitations of the process are:

- a) Distortion occurring in the form of growth (compound layer formation) and increase in volume in the case
- b) Brittleness of the compound layer, which makes it inappropriate for impact loading
- c) Nitriding can also act as stress relief / tempering operation if not previously performed, leading to unexpected distortion
- d) Uniform case hardening can only be obtained through continuous controlled circulation (preferably by use of internal fan), accurate control of process gas and temperature and proper part preparation (cleaning, blasting, handling)
- e) Nitriding of SS material requires removal of noble oxide layer (depassivation using ammonium chloride (NH₄Cl)). Nitrided SS components will exhibit a significantly reduced corrosion resistance due to precipitation of CrN

1.2 Objectives of this research

Today's application of the nitriding process by the industry is performed on steel alloys of various composition and containing both elements forming nitrides (Ti, Al, V, Cr) and not forming nitrides (Ni). The complexity of these compositions makes it difficult to account for the interaction of N with the elements present in the material.

The objective of this study was to review the nitriding process and to isolate the interaction between N and materials of known compositions and microstructures. Careful selection and preparation of defined microstructures for a low alloy steel were used to study the effect of the C content and its morphology on the hardness properties of nitrided sample. A similar approach was used to investigate the effect of the addition of Cr alloying element on the microstructure and properties of the nitrided sample. The evolution of the compound nitride layer and diffusion case was related to the process parameters. Chapter 2

2 LITERATURE REVIEW

2.1 Fundamental of Nitriding

Gas Nitriding is a thermo-chemical treatment producing enhanced surface properties (hardness, corrosion resistance) from the bulk material. This case hardening process improves fatigue and wears resistance.

The case hardening is the result of the diffusion of nascent nitrogen into the substrate (solid solution) and precipitation of nitrides (iron and alloy elements nitrides) when holding the metal at a temperature below Ac1 (generally below 575°C). Quenching is not required for the production of a hard case, thus reducing the amount of distortion generally experienced with hardening process relying on rapid cooling. There are three industrial methods of nitriding: gas, liquid (salt bath) and ion (plasma). Table 2.1 illustrates a case depth comparison of these three processes for the same low alloy steel material (AISI 4140).

Material: AISI 4140	Gas	Plasma	Salt Bath
Case Depth [µm] (Process Parameters)	200 (525°C 4brs)	210 (175°C 3brs)	205 (575°C 2brs)
(FIUCESS Faraillelers)	(323 0, 4115)	(475 0, 5115)	(375 0, 2115)

Table 2.1: Case Depth comparison for nitriding processes

For the gas nitriding process, ammonia (NH₃) is the nitrogenous gas typically used in a sealed retort with the parts to treat since it is metastable at nitriding temperature and readily decomposes on contact with iron.

2.2 Gas Nitriding Background

In the early 1900's, two pioneers were experimenting with the diffusion of nitrogen in plain iron and steels. Adolph Machelet (American Gas Company, Elizabeth, NJ, USA) discovered that nitrogen was very soluble in iron. In 1908, he applied for a patent for the "Hardening or Treatment of Steel, Iron" [1] to produce a very hard skin, coating or shell upon the articles by heating them in a retort heated from 900 to 1800° F (480 to 980° C) in a current of ammonia. A parallel research was headed by Dr. Aldoph Fry (Krupp Steel Works, Essen, Germany). From his work in 1906, he developed the iron-nitrogen phase diagram. He also applied for a patent, in 1921, for the "Hardening of Steel Alloys" [2] by nitrogenization at a temperature below the temperature of the peritectoidal transformation to limit the formation of a brittle iron nitride layer and therefore allowing the steel to receive the nitrides in solid solution to a certain depth. Fry was also pioneering the development of steels specifically designed for nitriding (know as the "Nitralloy" group and still specified today) upon his findings that certain elements (AI, Cr, Mn, Si) formed stable nitrides which very much increased the hardness of the nitrided surface.

Dr. Carl F. Floe (MIT professor and with The Nitralloy Corp., NY) presented a paper in 1943 [3] in which he explained that the depth of the nitrided case is largely independent of the ammonia dissociation (up to 65%). The diffusion of the nitrogen is controlled by the iron nitride layer (ϵ and γ') that forms at the surface soon after the nitriding has started. A novel process, know today as the two stage process, is also described. By first nitriding at 30% dissociation for a short period and then allowing the dissociation to increase as high as 85%, the white layer can practically be eliminated with no sacrifice in case depth.

2.3 Liberation of Nascent N

Upon contacting the part to be nitrided, the ammonia gas will dissociate into its fundamental constituents, namely N and H. The H atoms will recombine very rapidly to form molecular H₂. The nascent N will have an opportunity to diffuse into the steel or to recombine to form molecular N₂, depending on the nitriding condition (temperature, atmosphere composition, condition of the steel surface). The rate of dissociation of ammonia is controlled by the step reaction N + N \rightarrow N₂ [4]. Krizman *et al.* [5] also reported that the rate of NH₃ decomposition over iron nitride is about 100x slower than over pure iron.

To summarize, the possible reactions taking place at the surface of the steel are [6]:

 $2NH_3 \text{ (gas)} \rightarrow 3H_2 \text{ (gas)} + 2N \text{ (dissolved in } \alpha\text{-Fe)}$ $\rightarrow 3H_2 \text{ (gas)} + N_2 \text{ (gas)}$ $\rightarrow N_2 \text{ (gas)} + 6H \text{ (dissolved in } \alpha\text{-Fe)}$

which is illustrated by Figure 2.1 below.



Figure 2.1: Possible reactions at steel surface upon dissociation of ammonia molecules (NH₃)

2.3.1 Diffusion Kinetic

The transport of N in the bulk can be described by a nonsteady-state diffusion model. The concentration, which varies with position and time, is represented by plot (a) in Figure 2.2. The flux resulting from the concentration gradient along the x axis is shown by plot (b). To calculate how the concentration varies with time, let's consider a narrow slice of material with an area **A** and a thickness $\delta \mathbf{x}$ as shown by plot (c).



Figure 2.2: Derivation of Fick's second law of diffusion (a) An assumed Concentration(x) plot; (b) Flux (J) for this plot; and (c) elemental volume with flux J₁ entering and J₂ leaving [after 7]

The concentration increase with time within the elemental volume is expressed as:

$$\left(\frac{\partial C}{\partial t}\right)_{x} = -\left(\frac{\partial J}{\partial x}\right)_{t}$$

Eqn 2.1

Using the definition of the diffusion coefficient (Fick's first law) $D \equiv \frac{-J}{(\partial C / \partial x)_{t}}$, Eqn

2.1 can be rewritten as:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial C}{\partial x} \right)$$

Eqn 2.2

If variation of **D** with concentration can be ignored (independent of x), Eqn 2.2 can be simplified to:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}$$

Eqn 2.2 and Eqn 2.3 are referred as Fick's second law of diffusion.

The nitriding process can be modeled as the migration of a change in N concentration in a specimen of infinite length (length >> mean diffusion distance). By adjusting the nitriding atmosphere, the N concentration at the surface of the specimen can be maintained fixed (designated Cs). The concentration profiles normal to the surface that are obtained as time passes are shown in Figure 2.3.



Figure 2.3: Concentration profiles that develop through diffusion at successive time when a surface concentration of C_s is maintained after t = 0 in an infinite specimen of initial composition C_0

Solving Fick's second law (Eqn 2.3) for the following boundary conditions:

• $C_N(x=0) = C_s$

• $C_N(x = \infty) = 0$ (the original N concentration in the specimen)

we obtain:

$$C(x,t) = C_s - C_s \cdot \operatorname{erf}\left(\frac{x}{2 \cdot \sqrt{D \cdot t}}\right)$$
 Eqn 2.4

where "erf" is the Gaussian error function. Since the value of erf $(0.5) \cong 0.5$, the depth at which the N concentration will be half of the nitriding atmosphere concentration is given by:

$$\frac{x}{2} \cdot \sqrt{D \cdot t} \cong 0.5$$
, thus $x = \sqrt{D \cdot t}$ Eqn 2.5

Thus the thickness of the N diffusion case is ~ \sqrt{Dt} and consequently each two fold increase in penetration requires a four fold increase in time.

2.4 Iron-Nitrogen Equilibrium Diagram

The constitutional diagram of Fe-N system is not a true equilibrium diagram (in the sense of equilibrium at any one pressure) but shows the approximate composition limits of the phases (see Figure 2.4) which are produced by the action of ammonia on iron [8]. Below 590°C, the nitrogen austenite decomposes in ferrite and a face centered cubic structure (fcc) named γ' with nominal composition Fe₄N. The other phase readily produced during gas nitriding is named ϵ and has a close-packed hexagonal structure (hcp), with a wide range composition Fe₂N_(1-x) (also reported in the literature as Fe₃N_(1+x) and FeN_y with y=(1+x)/3).



Figure 2.4: Fe-N diagram (metastable), after Wriedt [9]

Fast and Verrijp [10] further studied the stability of the iron nitrides at temperature below 300°C and determined the solubility of α "-Fe₁₆N₂, γ '-Fe₄N and N₂ gas in ferrite (α -iron), as shown in Figure 2.5.



Figure 2.5: Solubility of Fe₁₆N₂, Fe₄N and N₂ gas in ferrite, after Fast and Verrijp [10]

The Fe-N diagram was more recently re-evaluated by Kooi *et al.* [11] to take into account long-range order (LRO) of the nitrogen atoms in the γ ' and ε phases. Their work, which scope is outside this study, showed a major improvement over previously calculated Fe-N phase diagram that did not account for LRO.

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2.5 Phases in the Iron-Nitrogen System

The nitrides shown in Table 2.2 are metastable with respect to one atmosphere of molecular nitrogen, as stated in §2.4. These phases will commonly form during the nitriding of iron, plain-, carbon- or alloyed steels or heat-treatment of nitrogen-austenite.

Composition	N [wt. %] ([at. %])	Interstitial atoms / 100 Fe atoms	Bravais lattice	Unit cell dimension [Å]
Fe	0.1 (0.4)	-	b.c.c.	<i>a</i> , 2.8664
Fe	2.8 (11)	12.4	f.c.c.	a, 3.572 + 0.0078(at. %N)
Fe	2.6 (10)	11.1	b.c.tetrag.	a, 2.8664 – 0.0018(at. Ratio %N) c/a, 1.000 + 0.0091(at. Ratio %N)
Fe ₁₆ N ₂	3.0 (11.1)	12.5	b.c.tetrag.	a, 5.72 c, 6.29
Fe₄N	5.9 (20)	25	f.c.c.	a, 3.795
$Fe_2N_{(1-x)}$	4.5 - 11.0 (18 - 32)	22 49.3	h.c.p.	a, 4.6982* c, 4.3789*
Fe₂N	11.14 (33.3)	50	orthorhombic	a, 5.530 b, 4.480 c, 4.425
	Composition Fe Fe Fe Fe ₁₆ N ₂ Fe ₄ N Fe ₂ N _(1-x) Fe ₂ N	CompositionN [wt. %] ([at. %])Fe0.1 (0.4)Fe2.8 (11)Fe2.6 (10)Fe2.6 (11)Fe2.6 (10)Fe_16N23.0 (11.1)Fe_4N5.9 (20)Fe_2N(1-x)4.5 - 11.0 (18 - 32)Fe_2N11.14 (33.3)	CompositionN [wt. %] [wt. %] ([at. %])Interstitial atoms / 100 Fe atomsFe0.1 (0.4)-Fe2.8 (11)12.4Fe2.6 (10)11.1Fe2.6 (10)11.1Fe16N23.0 (11.1)12.5Fe4N5.9 (20)25Fe2N(1-x) $4.5 - 11.0$ (18 - 32)22 - 49.3Fe2N11.14 (33.3)50	CompositionN [wt. %] ([at. %])Interstitial atoms / 100

Table 2.2: Phases in the iron-nitrogen system, adapted from Jack [12] and Jacobs [13]

Figure 2.6 illustrates the different structures of the nitride phases described in Table 2.2.



Figure 2.6: Structure of nitrides phases, after Goldschmidt [14]

The crystal structure of the ε -iron nitride phase requires further description. It is based on a hcp type arrangement of Fe atoms with N in the octahedral interstices. To describe the most commonly observed superstructure (for Fe₃N_(1+x) where 0.00 $\le x \le 0.47$), a hexagonal unit cell with lattice parameters $a = 3^{1/2} a_{hcp}$ and $c = c_{hcp}$ is adopted [15]. The index hcp refers to the unit cell of the hcp arrangement of Fe atoms. An ideally ordered superstructure can occur for the composition ε - Fe₃N, as shown in Figure 2.7. Various composition of the ε -phase have been studied and their respective lattice parameters compiled [16]. A linear dependence of **a** and **c** on **y**_N was reported for the range 0.33 $\le y_N \le 0.47$:

$$a = 0.44709 + 0.0673 y_N (nm)$$
 Eqn 2.6a, b
c = 0.42723 + 0.0318 y_N (nm)

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where y_N denotes the total fractional occupancy of the interstitial sublattice (= at.N/at.Fe) of ε -Fe₂N_{1-z} [$y_N = \frac{1}{2}(1 - z)$]. The relations for the lattice parameters as a function of the composition are very useful since they allow determining the nitrogen content from lattice parameters (for stress-free samples).



Figure 2.7: Crystal structure of ε -Fe3N.

The different octahedral sites are represented by spheres of different size at heights z = 1/4 and 3/4 in the unit cell. The bars represent edge (empty bars in the figure) and face sharing (shaded) contacts between the octahedral sites. The Fe atoms are connected in order to indicate the closed packed layers perpendicular to [001]. In the ideal ϵ -Fe3N configuration only the 2c site is occupied by N; the other two sites remain empty. Disordering is associated with partial transfer of N from the 2c site to the 2b site (after [17])

The appropriate conditions for the formation of the γ' and ε nitrides are shown in the Lehrer diagram [18], Figure 2.8. The equilibria refers to the action of ammonia on pure iron and the concentration of dissolved nitrogen in equilibrium with a given gas mixture is the surface concentration.



Figure 2.8: Lehrer diagram relating the ammonia fraction in nitriding gas atmospheres to the phase present at equilibrium on the surface of pure iron, after Lightfoot [19]

2.6 <u>Nitriding Potential</u>

The properties of the nitrided layer are determined by the phase compositions and the concentration of nitrogen at the surface. The nitrogen solubility at the surface of the iron is determined by the equilibrium:

$$NH_3 \Leftrightarrow \frac{3}{2}H_2 + [N] \text{ (dissolved in Fe)}$$
 Eqn 2.7

hence (for dilute solution of N in Fe, Henry's law)

$$[a_N] = [\% N] = k \cdot \frac{p N H_3}{p H_2^{3/2}}$$
 Eqn 2.8

Where a_N is the nitrogen activity, k is an equilibrium constant at a given temperature and pNH_3 and pH_2 are the partial pressure of ammonia and hydrogen in the gas. The Nitriding Potential K_N is then defined as:

$$K_N = \frac{pNH_3}{pH_2^{3/2}}$$
 Eqn 2.9

A modified version of the Lehrer diagram was experimentally developed by Maldzinski [20] to correlate the concentration of nitrogen in the iron-nitrides phases with the nitriding potential K_N and the temperature. The K_N -T diagram shown in Figure 2.9 also features absorption isotherms for nitrogen.



Figure 2.9: Pure iron K_N-T equilibrium diagram, adapted from Maldzinski [20]

2.6.1 Atmosphere Dilution

The Nitriding Potential K_N can be altered by controlling the amount of ammonia gas injected in the retort. There are practical limitations to this method since it is mandatory to maintain a minimum flow of fresh ammonia to ensure raw gas is available for dissociation. Nascent nitrogen is only available for diffusion for a short time prior to recombining to form molecular nitrogen (N₂).

Another solution is to dilute the inlet atmosphere with hydrogen or "dissociated ammonia" (DA). DA is produced in a separate device (typically another electrical or gas furnace) equipped with a retort lined with a catalyst promoting the dissociation of the NH₃ molecules into N₂ and H₂. When added to the raw ammonia, the DA allows the regulation of K_N while maintaining a good flow of gas in the process retort. This operation needs to be carefully controlled to ensure proper computation of the K_N factor.

To produce effective nitrided cases with thin (or no) compound layers it is necessary to be able to achieve low nitriding potential values through the addition of dilution gases.

2.7 <u>Structure of the Nitrided Case</u>

The nitrided case is made of three distinct zones:

a) Surface Layer:

The surface layer is also called compound or white layer (since it remains "white" when etched with Nital reagent). It is composed of a mixture of ε and γ ' iron nitride phases that are very hard and brittle.

b) Nitrided Case:

Immediately below the compound is located the diffusion zone of solid solution of nitrogen in the matrix as well as stable nitrides resulting from the reaction of nitrogen with nitride forming elements (such as AI, Cr, Mn, Ti, Va). This area exhibits a diminishing hardness gradient as the concentration of nitrides decreases with depth.

c) Core:

The hardness of the nitrided case will eventually decrease to the nominal value of the material prior to nitriding. The total case thickness is typically defined as the depth for which the hardness is 10% greater than the average material core hardness. This indicates the depth of diffusion of nitrogen to a level significantly high enough to alter the hardness properties of the material being treated.

While the compound layer is extremely hard, it is also brittle. Depending on the nitrided component's application and the depth of the compound layer, it may need to be removed by grinding. In most situations it is advantageous to limit the growth of this brittle layer. This can be accomplished by carefully controlling the atmosphere composition. Atmospheres consisting of ammonia only have a high "nitriding potential" and usually create an undesirably thick compound layer. To minimize this condition, the ammonia is often diluted with additions of hydrogen and externally dissociated ammonia ($NH_3 + N_2 + H_2$).

2.8 Development of the compound layer

The formation of a compound layer will depend on the chemical potential of N provided by the nitriding atmosphere. For a selected temperature, a compound layer (if sufficient time is allowed) will form according to the iron-nitride phases in equilibrium with the selected atmosphere, as shown in the Lehrer diagram (Figure 2.8) or its modified version that use the nitriding potential K_N to characterize the atmosphere (Figure 2.9).

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The corresponding N concentration profile normal to the surface can then be described by the diffusion process (§2.3.1) and by local equilibrium at the phases interface, as shown in Figure 2.10. The gas-solid interface equilibrium is given by the N chemical potential from the atmosphere while the solid-solid interfaces are given by the Fe-N phase diagram.



Figure 2.10: Relation between the iron/nitrogen equilibrium diagram and concentration/depth for growth of a bilayer iron nitride into a substrate of α -Fe [after 21]

2.8.1 Nucleation

When the maximum solubility of N in iron in the region adjacent to the surface is exceeded, the nucleation of the γ '-Fe₄N phase will start. The incubation time for the nucleation of γ '-nitride depends on the competition between [22]:

- a) The flux of N arriving at the surface (controlled by ammonia dissociation)
- b) The flux of N leaving the surface (desorbtion of molecular nitrogen gas N_2 + diffusion of N atoms into the bulk)

This competition of N flows and the resulting incubation time are illustrated in Figure 2.11.



Figure 2.11: Evolution of N surface concentration and schematic of γ'-nitride incubation time [after 22]

A quantitative estimate of the incubation time for the nucleation of γ '-nitride is presented in Figure 2.12. The desorbtion of N₂ from the surface, represented as an additional incubation time by dashed line in the figure, has a relatively small effect when the nitriding potential exceeds 1 Pa^{-1/2} (0.3 atm^{-1/2}). These incubation times were compared by the author to experimental work and found to be realistic estimates.



Figure 2.12: Calculated incubation time for nucleation of γ '-nitride as a function of nitriding potential [after 22]

Somers [23] studied the nucleation and growth of the ϵ/γ' bi-layer and showed for T = 843K (570°C) and nitriding potential $K_N \cong 1.9$ (atm^{-1/2}) the following sequence for the formation of the nitride bi-layer (see Figure 2.13 and Figure 2.14):

- 1. Nucleation of γ '-nitride on α -Fe
- 2. Nucleation of ε -nitride on top of γ ' nuclei (prior to the isolation of the substrate by a γ ' layer, Figure 2.13 a)
- 3. Further nucleation and lateral growth of nuclei. In this stage, N can be supplied to growing γ' nucleus via ferrite. Since the diffusion coefficient of N in α -Fe is much larger than in γ' -Fe4N, this by-pass effect can lead to a faster growth of γ' -nitride than by transport of N to the α/γ' interface through the γ' phase only


Figure 2.13: Nucleation and growth of a γ'/ϵ bilayer on iron, Nital etched [after 23] a) after 15 minutes, dual phase nuclei ϵ/γ' have developed at surface b) after 35minutes, an isolating dual layer of ϵ/γ' -nitride has formed at surface c) after 8hrs, porosity has developed in area close to surface of ϵ -nitride sublayer



Figure 2.14: Schematic of of ε / γ' -nitride bilayer formation [after 40]

Experiments reported by Inokuti *et al.* [24] on the nucleation and formation of iron nitride on the surface of highly polished specimens of well refined and coarsened iron grains show a strong dependence on the orientation of the grains. It is suggested that the iron surfaces promoting the growth of the nitrides are those satisfying the coherency relationships between nitrides and iron matrix.

The compound layer thickness uniformity and nitriding kinetics are reportedly improved by an oxidation treatment prior to the nitriding operation. Preoxidation in air at 573K for 1 hr produces a continuous compound layer within 20 minutes, whereas it takes more than 290 minutes to obtain a similar result without pre-oxidation [25]. Friehling and Somers [26] compiled previous work on this subject and proposed two hypothesis to account for this enhanced kinetic:

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- a) The iron oxide promotes the nucleation of the iron nitrides. The presence of an iron oxide layer enhances the density of nuclei and decreases the sensitivity of the nucleation of iron nitrides to the crystallographic orientation of the ferrite grains.
- b) The iron oxide retards the desorbtion of N₂ molecules. Consequently, a higher N concentration is available in the Fe-N phase closest to the surface. More recent work by these authors [27] attributes the enhanced nucleation to an improved dissociation kinetics for ammonia.

2.8.2 Growth

The growth kinetic of the compound layer is usually described by solid-state diffusion of N through the phases constituting the compound layer [21,23,28,29].

2.8.2.1 Single layer growth of γ ' nitride

The growth of a γ '-nitride monolayer is described as the difference between the N flux entering the γ '-phase and the N flux leaving the γ'/α interface. A schematic concentration profile is given in Figure 2.15 and the flux balance equation is given by [28]:

$$\frac{v^{\gamma'\alpha}}{V_N^{\gamma'}}(u_N^{\gamma'\alpha}-u_N^{\alpha/\gamma'})=J_N^{\gamma'}-J_N^{\alpha}$$
 Eqn 2.10

 $v^{\gamma' \alpha}$ is migration rate of $\gamma' \alpha$ interface

 $V_N^{\gamma'}$ is partial volume/mole of N atom of γ' phase

 $u_N^{\gamma'\alpha}, u_N^{\alpha'\gamma'}$ contents of N on the γ' and α side of interface

 $J_N^{\gamma'}, J_N^{\alpha}$ diffusion fluxes of N on the γ' and α side of interface

The following assumptions are made:

- Planar interface parallel to surface
- Growth of new phase obeys parabolic growth (i.e. $l = k\sqrt{t}$ where *l* is thickness of layer, *t* is time and *k* is called growth rate constant)
- α -Fe substrate is saturated with N (i.e. $J_N^{\alpha} = 0$)
- Diffusion in γ' is stationary due to narrow composition range in the phase
- Mobility M_N of N is independent of concentration

Using Fick's first law of diffusion for flux:

$$J_{N}^{\gamma'} = \frac{\tilde{D}_{N}^{\gamma'}}{V_{N}^{\gamma'}} \frac{\partial u_{N}}{\partial z}$$
 Eqn 2.11

The partial Gibbs free energy (i.e. chemical potential) of N is the driving force for diffusion. The chemical diffusivity \tilde{D}_N can be related to the self diffusion coefficient using the thermodynamic factor Ψ :

$$\tilde{D}_{N} = D_{N}^{*} \Psi = D_{N}^{*} \cdot \frac{U_{N}}{RT} \frac{\partial \mu_{N}}{\partial U_{N}}$$
 Eqn 2.12

with u_{N,μ_N} the concentration and chemical potential of N, *R* the gas constant and *T* the absolute temperature.



Figure 2.15: Schematic N concentration profile for γ' monolayer growth into $\alpha\mbox{-Fe}$ during nitriding

2.8.2.2 Dual layer growth of ε/γ' nitride

The growth of the ε/γ' -nitride bilayer is described similarly as the case of monolayer growth, as shown by the schematic N concentration profile in Figure 2.16. Applying flux balance equations at both the ε/γ' and γ'/α interface yields [28]:

$$\varepsilon/\gamma'$$
: $\frac{v^{\varepsilon/\gamma'}}{V_N^{\varepsilon}}(u_N^{\varepsilon/\gamma'}-u_N^{\gamma'/\varepsilon}) = J_N^{\varepsilon}-J_N^{\gamma'}$ Eqn 2.13

$$\gamma'/\alpha: \quad \frac{v^{\gamma'\alpha}}{V_N^{\gamma'}} (u_N^{\gamma'\alpha} - u_N^{\alpha/\gamma'}) = J_N^{\gamma'} - J_N^{\alpha}$$
 Eqn 2.14

with Fick's first law of diffusion for flux:

$$J_{N}^{\phi} = \frac{\tilde{D}_{N}^{\phi}}{V_{N}^{\phi}} \frac{\partial u_{N}}{\partial z} \quad (\phi = \varepsilon, \gamma' \text{ or } \alpha)$$
 Eqn 2.15

The following assumptions are made:

- Stationary diffusion may not be satisfactory for ε phase due to its wide range of composition. The flux balance equations have to be solved numerically
- Self-diffusivity of ε is likely to be concentration dependent for the same reason. Thus the atomic mobility M_N^{ε} is evaluated instead and assumed concentration independent.



Figure 2.16: Schematic N concentration profile for ϵ/γ bilayer growth into α -Fe during nitriding

Chapter 3

3 EXPERIMENTAL METHODS

This section describes the Gas Nitriding Process Control and the Equipment used for this research. The preparation of the sample materials and the selected evaluation methods are also reviewed.

3.1 Gas Nitriding Process Control

Good process control is mandatory to meet customer specification but will also improve:

- Process repeatability and economics
- Metallurgical requirements
- Operator interfacing, data trending and archiving

The procedures and requirements for heat treating low-alloy and tool steels and their subsequent gas nitriding by the use of raw or dissociated ammonia are outlined in specification such as AMS 2759/6 [30]. This standard specifies the maximum acceptable thickness for the white layer, namely 13 μ m for Class 1 and 25 μ m for Class 2 treatment. The key parameters to control the gas nitriding process are:

- Temperature (± 8°F or ± 4.5°C per AMS 2759/6) by means of control thermocouple and set point programmer
- Process gas by means of flow meter. Anhydrous ammonia, hydrogen and nitrogen shall be of the high purity grade (99.98%) with dew point -54°F (-48°C) or lower.
- 3. Atmosphere by means of a dissociation pipette (burette) (± 5% dissociation per AMS 2759/6) or gas analyzer
- 4. Retort pressure slightly above atmosphere to prevent any oxygen from entering the vessel (risk of explosion) and to maintain flow through pipette or gas analyzer

In conventional gas nitriding systems, the primary means of controlling the nitriding atmosphere is by periodic measurements of the percentage of dissociated ammonia in the retort atmosphere exhaust. The measurements are used to set the inlet gas flow required to obtain a desired dissociation rate within the retort. This method of monitoring the dissociation rate requires a manual volumetric measurement that is heavily operator-dependent. The timing of atmosphere analysis and control may be irregular and no continuous monitoring or control of the system can be achieved. Additionally, this approach of measuring dissociation and flow does not provide optimal results as neither parameter directly correlates to the resultant properties of the nitrided layer.

3.1.1 Traditional Burette Method

The measure of dissociation is conducted using a burette (refer to Figure 3.1 below): it is simply the amount of decomposition of the ammonia gas, considering that the exhaust gas is a mixture of $2NH_3 + H_2 + N_2$ and ammonia is the only one soluble in water. It should be pointed out that typical "burette" dissociation measurement in an industrial nitriding installation can have an error of up to 5%.



Figure 3.1: Schematic of dissociation measurement with a burette, from Pye [31]

3.1.2 Nitriding Potential Method

A new specification for a tighter control of the nitriding process was originally published in 1999, AMS 2759/10 "Automated Gaseous Nitriding Controlled by Nitriding Potential" [32]. The automated and precise control of the Nitriding Potential (K_N) allows for a complete elimination of the white layer. For the gas nitriding installation used for the experiments reported in this research, the nitriding potential is calculated based on the H₂ content of the exhaust gas, as described in Figure 3.2 below.





In addition to the requirements mentioned in §3.1.1, a nitriding installation meeting the AMS 2759/10 specification must satisfy the following additional requirements:

- 1. Average K_N value to be maintained within ± 10% of set point
- 2. Minimum of 60% (for short process up to 6hrs) or 85% (longer process) of stage time conducted under stable condition
- 3. Sample reading of outlet gas should be minimum once every 30 seconds

The control of the K_N within 10% of the set point requires both a precise gas analyzer unit and precise control of the inlet gas flow. Figure 3.3 illustrates the influence of the precision for the measurement of hydrogen in the outlet gas as a function of the K_N / ammonia dissociation rate. From this illustration, one can see that the sampling cell need to have a precision better than 1% to meet the requirements of AMS 2759/10. Another important aspect of the K_N control is the inlet gas flow regulation. The original equipment was supplied with motor driven needle valves, which were found to have a precision of about 4% of full scale. This resulted in unstable K_N control compromising both the acceptable 10% deviation from set point and the minimum requirement of stage time under stable condition. A new gas regulation relying on mass flow controllers was installed: the precision is now better than 1% and these units can react very rapidly to set point changes.

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Figure 3.3: Effect of 2% and 1% error on H2 measurement as a function of K_{N} / Dissociation Rate

3.2 Gas Nitriding Equipment

3.2.1 Design

A typical nitriding installation is shown in Figure 3.4.



Figure 3.4: Schematic of typical gas nitriding installation (after Bever [33])

The nitriding furnace used for this research was very similar in principle, except for the following hardware (as illustrated in Figure 3.5 and Figure 3.6):

- Exhaust gas going through a sampling station fitted with a hydrogen and oxygen sensor (to ensure sufficient purging prior to start cycle)
- Internal gas recirculation fan installed in the retort lid

 Retort, baskets and internal liner made of Inconel 600 alloy (Ni super alloy) to minimize dissociation of ammonia on hardware. The internal liner promotes good gas circulation and ensures fresh ammonia is continuously circulated around the components to be nitrided.

The nitriding process control system, model 9200, is manufactured by Super Systems Inc., Cincinnati, OH, USA.



Figure 3.5: K_N controlled Gas Nitriding installation at Vac Aero International Inc.



Figure 3.6: Schematic of nitriding retort showing gas path and internal recirculation fan 1) Fan Motor, 2) Control Thermocouple Port, 3) Retort Lid, 4) Gas Inlet / Outlet, 5) Centrifugal Fan, 6) Retort Shell, 7) Load Basket with Liner

3.2.2 Characteristics

The electric power available with the heat source is 60 KVA (~50 kW). The retort has an internal diameter of 600 mm, a height of 1200 mm and a volume of about 350 L. The process gas is injected in location 4) of Figure 3.6 and then circulated by the centrifugal fan between the retort shell and internal liner (20 mm annular gap) all the way to the bottom of the retort and then sucked back through the center of the baskets where the parts to be nitrided are located. The fan wheel has an outside diameter of 310 mm, rotates at 3600 rpm and can maintain a flow rate of 42 m³/min maximum (more than 2500 retort volume exchange per hour).

The retort is maintained under slight overpressure (10-15 mbar) by means of a regulated butterfly valve installed on the exhaust line. Its main purpose is to prevent any infiltration of oxygen inside the retort (potential of explosion due to the presence of H_2) and to ensure a continuous flow of exhaust gas to the gas sampling station.

The heat control thermocouple is inserted through port 2) and reaches the center area of the retort at mid height.

3.2.3 Instrumentation

The key variables to control during the nitriding process are the temperature, the atmosphere composition (i.e. Nitriding Potential K_N) and the retort pressure, as explained in § 3.1. The documented precision of the instrumentation installed on the gas nitrider used for this investigation is detailed below:

- Temperature uniformity, maximum deviation of ± 4°C. The bottom and center of the retort are slightly above the SP while the top is below, due to heat loss through the lid insulation and water cooled flange as well as the process gas inlet and outlet.
- Ammonia flow regulation (NH₃ Mass Flow Controller), Brooks model 5850i, 0 25 SLPM, precision of 0.8 % of FS or better
- Nitrogen flow regulation (N₂ Mass Flow Controller), Brooks model 5850i, 0 20 SLPM, precision of 0.15 % of FS or better
- Hydrogen (H₂) detection cell, Hitech Instruments, model SSI Katharometer OEM card, 0-100 %H₂, precision of 0.3% of FS or better
- The retort pressure set point regulation is not as critical as the other parameters described above. The precision of the regulation was better than 10% during stable process gas flow condition and as high as 30% during large change in flow

3.2.4 Gas Analysis

Certificates of Analysis for the gases used by the gas nitrider are detailed below:

- Ammonia (NH₃, Liquid Anhydrous), 99.995% minimum (Water < 35 ppm, Oil < 2 ppm)
- Nitrogen (N₂), 99.998% minimum (O₂ < 3 ppm, CO < 2 ppm, Water
 < 0.5 ppm, H₂ < 2 ppm, Carbon bearing gases < 3 ppm)
- Hydrogen (H₂), 99.99% minimum (O₂ < 5 ppm, N₂ < 25 ppm, Water < 3.5 ppm, Carbon bearing gases < 5 ppm). This gas was used for the calibration of the Hydrogen cell

3.3 Samples Material for Gas Nitriding

3.3.1 Sample Material Composition

The 1070 steel material was heat treated prior to the gas nitriding experiments to achieve the following specific microstructures: pearlitic, spheroidized and martensitic. The chemical compositions for the AISI 1070 low alloyed steel and Armco Iron used in this investigation are given in Table 3.1 below.

A Fe-2%Cr sample was produced by repeated (5 times) vacuum melting of Fe and Cr, fast cooling and was eventually cold rolled to achieve about 70% reduction. A diffusion couple Fe/Fe-5%Cr, produced by annealing at 1395°C under protective atmosphere for 4 days was also prepared.

Chemical Composition (%)						
Material	Fe	С	Si	Mn	Р	S
Armco-Fe	Bal.	0.01	0.02	0.015	<0.01	<0.01
AISI 1070	Bal.	0.7	0.22	0.79	0.01	0.015

Table 3.1: Chemical composition of test material

3.3.2 Sample Material Heat Treatment

A typical microstructure for the Armco-Fe, which has a mean hardness of $95HV0.1 \pm 1.5$ is shown in Figure 3.7.



Figure 3.7: Typical microstructure of Armco Iron material prior to Nitriding

The chromium content of the Fe/Fe-5%Cr diffusion sample, determined by EDS, is reported in Figure 3.8. The precision of measurement for all the recorded values is typically \pm 0.2%, but the overall accuracy has not been established due to the lack of a Fe-Cr alloy standard. The EDS detector was calibrated for 100% Fe using a sample of Armco iron. The diffusion bonding heat treatment was performed at a temperature of 1395°C for about 96hrs. The equivalent diffusion depth for a 1.25% Cr concentration in the iron at this temperature and time condition is approximated (using Eqn 2.5) to be about 4 mm. Note that the Cr diffusion coefficient for Fe-Cr alloy is estimated to be about 5*10⁻¹¹ [m²s⁻¹] under the above conditions [34]. For reference, the thickness of the iron side of the diffusion couple was only 2 mm. This clearly confirms the evidence that the Fe/Fe-5Cr sample was fairly advanced into completing its homogenization. The sample was then slowly cooled to room temperature. The mean hardness was measured at 83HV0.1 ± 1.2.

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Figure 3.8: Chromium concentration in Fe/Fe-5%Cr diffusion couple

3.3.2.1 AISI 1070 Steel Heat Treatment

The 1070 steel material was heat treated as described in Table 3.2 to produce specific microstructures (typical microstructures shown in Figure 3.9). The samples were run in a retort filled with a nitrogen atmosphere to prevent oxidation during the heat treatment.

	Mean	Heat Treatment Parameters				
Microstructure Hardness [HV _{0.1}] Temperature		Time	Atmosphere	Cooling		
Pearlite	230	850° C	½ hr	Nitrogen (N ₂)	In N ₂ atmosphere, furnace cool <300°C, then forced air	
Martensite (M _s)	345-650	850° C	1⁄2 hr	Nitrogen (N ₂)	Quenched in oil	
Spheroidized	188	700° C	11 hrs	Nitrogen (N ₂)	In N ₂ atmosphere, furnace cool <300°C, then forced air	
Decarburized	150 - 836	1100° C	6 hrs	Wet Hydrogen	Quenched in oil	

Table 3.2: Heat treatment of 1070 steel material

The carbide precipitates formed in the spheroidized microstructure have a size ranging from about 0.5 to 2 μ m, with most of them at about 1 μ m.

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Figure 3.9: Typical microstructures of 1070 steel prior to Nitriding

The sample material that was oil quenched did not transform homogenously: the 25mm diameter bar revealed to be of a too large section for oil quenching. It was noticed later that the AISI 1070 specification recommends to use water or brine quenching media to achieve full hardness on material section greater than 6mm. Evaluation of the microstructure revealed that the sample has a gradient of mainly plate martensite phase (outside edge of round disc) gradually changing to a fully pearlitic structure of very fine lamellar spacing. SEM images of the outside edge and of the center of the specimen confirm the transition of phases, as visible in Figure 3.10.

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Figure 3.10: Typical microstructures for oil quenched 1070 steel prior to Nitriding

The micro-hardness profile taken from the outside edge to the center of the disc sample highlights the phase's transition (see Figure 3.11). It is of interest to point out the high hardness resulting from the very fine pearlite produced by the oil quenching rapid cooling.



Figure 3.11: Micro-hardness Profile for the oil quenched 1070 sample material, starting at the outside edge of the disc

3.3.2.2 AISI 1070 steel - Decarburization Heat Treatment

A sample of 1070 steel was decarburized in a "wet hydrogen" atmosphere (6hrs at 1100° C) and then oil quenched. A micrograph of the resulting microstructure is presented in Figure 3.12.

The corresponding hardness profile, measured from the outside edge of the disc, is given in Figure 3.13. The estimated carbon content has been added on the horizontal axis. It is based on data compiled by Kraus [35, Figure 16.2] to investigate the hardness of martensite as a function of the carbon content in Fe-C alloys and steels. The maximum hardness of about 825HV (as-quenched hardness at room temperature for steel with 0.7% C) is in good agreement with the maximum hardness of 836HV \pm 26 measured at the core of the decarburized sample.



Figure 3.12: Micrograph of typical microstructure for decarburized and oil quenched 1070 steel sample



Figure 3.13: Hardness Profile of Decarburized 1070 steel sample

3.3.3 Sample Preparation for Nitriding

The sample material was carefully sectioned into discs (\emptyset 10 to 20 mm) of 3-4 mm thick and then split in two using an aluminum oxide (Al₂O₃) cut-off wheel. All the faces were freshly polished with silicon carbide (SiC) 320 grit abrasive paper and cleaned with methyl hydrate alcohol prior to the samples being placed in the retort for the nitriding cycle.

3.3.4 Typical Nitriding Cycle

The samples were suspended to the 3^{rd} basket (from bottom of fixture) using stainless steel wire and the retort was loaded in the furnace hot zone. The control system then started to purge the retort with N₂ until the O₂ content dropped below 1%. Full flow of NH₃ was then introduced and the temperature started ramping to the configured set point. Typical heating rates were in the range of 6-8°C/min, considering that it took about 1h15min to reach the nitriding temperature of 500°C.

A sample nitriding cycle is shown in Figure 3.14 below. Once the temperature reached 455°C, the regulation of the nitriding atmosphere was enabled. With the continuous rise in temperature, the dissociation of NH_3 slowly began to happen: the detected %H₂ increased (around 18h00 in the sample chart). The corresponding calculated nitriding potential K_N sharply decreased until the dissociation rate of ammonia reached a stable state for the amount of NH_3 being introduced in the retort.

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Figure 3.14: Typical Nitriding Cycle recorded by Gas Nitrider Interface

Once the soak time at nitriding temperature has elapsed, the controller initiated the purge of the retort with N₂ and the heat was turned off. The retort was then usually allowed to cool down inside the heat source until the temperature dropped below 200°C. The last stage of the cooling happened when the retort was placed in the cooling stand with forced air circulation until it was cool enough to be opened to retrieve the nitrided samples.

The thermal history during cooling was also recorded and compiled for comparison between the different materials. Typical cooling rates achieved with the retort left in position in the furnace hot zone varied from 1.5°C/min (at the beginning of cooling) to less than 0.3°C/min (when the temperature dropped below 200°C). The cooling rates greatly increased when the retort was positioned in the cooling stand with forced air circulation, namely from about 20°C/min at the beginning and decreasing to less than 8°C/min when the temperature dropped below 200°C. Both cases are illustrated in Figure 3.15, where forced air cooling was used on both the 3rd and 5th tests, after an initial cooling in the furnace.

The effect of cooling rate on the final microstructure will be reviewed later in the Experimental Results and Discussion sections.



Figure 3.15: Thermal history recorded during cooling for all nitriding tests

3.3.5 Gas Nitriding Test Cycles Summary

Table 3.3 summarizes the nitriding test cycles run for the different materials evaluated in this research. The error on K_N is computed using the H₂ cell precision of ± 0.3 %H₂.

Cycle #	Samples	Cycle Parameters	Error on KN
1	1070 misc. microstructure	12hrs, 500°C, average K _N =7	+ 0.20 / -0.15
1 - b	Fe	12hrs, 500⁰C, average K _N =7.3	+ 0.20 / -0.18
2	Fe 1070_Spheroidized	2.5hrs, 500°C, average K _N =9	+ 0.28 / -0.25
3	Fe 1070_Decarburized	6hrs, 500°C, average K _N ≖7.5	+ 0.2 / -0.2
4	Fe/Fe-5%Cr Diffusion Couple	6hrs, 500ºC, average K _N =7.1	+ 0.2 / -0.15
5	Fe-2%Cr	13.5hrs, 550ºC, average K _N =4.2	+ 0.1 / -0.09

Table 3.3: Summary of Gas Nitriding Test Cycles

3.3.6 Study of Cooling Rate Effect on Nitrided Iron

Samples of previously nitrided Armco Iron (Test #1, 2 and 3) were placed in a Nitrogen protective atmosphere and slowly re-heated to 500°C (in about 3hrs). There were then rapidly cooled in an oil bath used for oil quenching steels components (oil temperature of about 60°C). The resulting microstructure was compared to the one obtained in Test #1 and 2, which were slowly cooled in the furnace.

3.4 Samples Evaluation

3.4.1 Metallographic Preparation

The nitrided half disc sections were cut in half (see Figure 3.16, step (1)) to obtain a cross-section of the nitrided case (2). The freshly cut section was then hot mounted in an epoxy resin with the metallographic evaluation face up (3).





The mounted samples were prepared following a grinding and polishing technique developed with Struers and using consumables from this supplier. The details of the metallographic preparation are given in Table 3.4 below.

Sample Information:								
Material Gro	up: Nitrideo	Nitrided Steels						
Alloy Descri	otion: Mild St	Mild Steel, Austenitic Stainless Steel						
Sectioning	<u>L</u>							
Equipment: Im		Imptech C-10 manual cut-off saw						
Wheel: Al2O3 with rubber bond, ø9" x ø1.25" x 0.032" (Abrasicorp P/N56831 450001 Avery Abrasives)					(N5083) = PC-			
Mounting: Resin: Struers DuroFast (black epoxy with mineral filler)								
Grinding a	nd Polishing:							
Equipment: Struers Rotopol-2 / Pedemat, no dosing unit								
Disc size:	10" (25	0mm)						
Number & si	ze of samples:up to	o 6x 1_1/4 in (30n	nm)					
Step		1/4	2 / 4	3 / 4	4/4			
Surface	Туре	SiC Disc, 320grit	MD-Plan	MD-Dur	MD-Nap			
	Speed [RPM]	300	150	150	150			
	Туре		Diamond Susp. DiaPro Plan 9μm	Diamond Susp. 3µm	Diamond Susp. 1µm			
Abrasive	Application		Every 1:00 or as required to keep moist	Every 1:00 or as required to keep moist	Every 1:00 or as required to keep moist			
	Туре	Water		DP-Green	DP-Green			
Lubricant	Application	Full wash		Every 0:30 or as required to keep moist	Every 0:30 or as required to keep moist			
	Force/sample [N]	30	30	30	30			
Holder	Direction	>>	>>	>>	>>			
	Speed [RPM]	150	150	150	150			
Time	Time [min:sec] 2x 1:00 5:00 5:00 2:00							

Table 3.4: Sample Preparation Technique

3.4.2 Vickers Micro-hardness Evaluation

A Vickers micro-hardness depth profile was carried out for each of the nitrided sample. The testing was performed on a Mitutoyo MVK-HO tester fitted with a Vickers diamond indenter (see Figure 3.17 below). The applied load was 50gf (Armco Fe) and 100gf (all other materials) for a dwell time of 15 sec.

The Vickers hardness is defined as the ratio between the applied force F [kgf] and the surface area A [mm²] using the average length d of the resulting indentation diagonal. Hence,

$$HV = \frac{F}{A} = \frac{F}{\frac{d^2}{2 \cdot \sin(136^\circ/2)}} \approx \frac{1.854 \cdot F}{d^2} \text{ [kgf/mm^2]}$$
Eqn 3.1

Figure 3.17: Schematic of Vickers Hardness Testing [36]

The indentation size was manually measured using the image acquired by the Clemex CMT (rev 3.1.50) image analysis software and the corresponding hardness was automatically computed by the software. A sample micro-hardness profile report can be seen in Figure 3.18 below. The hardness tester precision was verified using standard calibration blocks. The error on reported hardness varies from about 3% (975HV0.1) to less than 1.5% (525HV0.1) when computed from the measured deviations listed in Table 3.5.

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Figure 3.18: Typical micro-hardness profile report generated with the Clemex CMT software

Calibration Block	976 HV0.1	706 HV0.1	525 HV0.1
Measured error	± 30 HV0.1	± 19 HV0.1	± 8 HV0.1

Table 3.5: Hardness Deviation for selected Calibration Blocks

The Vickers hardness test is an inexpensive and non-destructive method of testing a material. The possibility of using this test to determine the yield strength (plastic material) or the tensile strength (brittle material) has been researched. Tabor [37] showed that hardness measured with a pyramidal (as in the Vickers test) or conical indenters can be related to the material's flow stress. For an ideal plastic material, the relationship between Vickers hardness and yield strength is expressed by the following equation:

$$HV = c \cdot Y \quad [kgf/mm2]$$

$$HV \quad [kgf/mm2] = \frac{3}{9.8} \cdot Y \quad [MPa] \approx \frac{1}{3} \cdot Y \quad [MPa]$$
Eqn 3.2

with **Y** the yield stress and *c* a constant with a value of about 3 at room temperature. Since HV is of $[kgf/mm^2]$ unit, the relation 1kgf = 9.8N is used to express the yield stress in [MPa] unit.

3.4.3 Metallographic Evaluation

The sample microstructure was revealed using 2% Nital reagent (composition of 2ml HNO₃ and 98ml Methanol)). Visual light microscopy evaluation was conducted on a Zeiss Axioplan 2 microscope (both in bright field and differential interference contrast (DIC)). Micrographs were captured using the Northern Eclipse software.

Scanning Electron Microscopy (SEM) was conducted on a Philips 515 instrument equipped with an Energy Dispersive X-ray Spectroscopy (EDS) detector. This detector was used to confirm the presence of Nitrogen in the nitrided samples.

A Philips CM12 Transmission Electron Microscope (TEM) was also used to investigate selected samples at higher magnification.

3.4.4 X-ray Diffraction Analysis

Phase analysis investigations were also conducted on a Bruker SMART 1K diffractometer using a Molybdenum (Mo) rotating anode generator and fitted with a 2D CCD detector. The data collected by the detector was analysed with the Bruker GADDS (General Area Detector Diffraction System) ver. 4.1.27 software to produce the peak intensity vs. 20 diffraction pattern. A sample illustration of detector raw data as well as the corresponding diffraction pattern is shown in Figure 3.19.

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Figure 3.19: X-ray Diffraction data collected by 2D CCD detector and corresponding diffraction pattern for a nitrided Iron sample

The phase analysis of the diffraction pattern was conducted with the Bruker Topas ver. 2.1 software. A sample diffraction pattern for the Armco iron sample is shown in Figure 3.20. The collected spectrum is in red color while the calculated pattern for α -Fe (ferrite) is fitted in blue color. The difference between the two patterns is shown in grey on a separated trace.




Chapter 4

4 EXPERIMENTAL RESULTS

This section compiles the results collected for the three groups of material investigated: Armco Iron, AISI 1070 low alloyed steel and Fe-Cr alloys.

The diffusion depth has been estimated visually from the metallographic samples after etching (whenever possible). The total diffusion depth is also defined (see AMS2759/6B, [30]) as the depth at which the hardness is 10% higher than the core hardness computed from the micro-hardness depth profile report. The diffusion depth calculated using the method is also reported for comparison.

The micro-hardness data has been expressed as the increase in hardness with respect to the core hardness of each sample. This approach ensures that the observed hardness increase can be attributed solely to the nitriding process by removing the influence of possible changes attributable to the thermal treatment.

The compound layer, defined as the iron nitride layer growing at the surface of the sample, is also reported.

4.1 Nitrided Armco Iron (Fe) Samples

The Armco Iron samples were nitrided with three different sets of parameters. The corresponding maximum hardness increase, diffusion depth and compound layer thickness are summarized in Table 4.1.

Test	Gas Nitriding Parameters	Maximum Hardness Increase [HV0.05]	Diffusion Depth (Micro-hardness) [µm]	Diffusion Depth (Visual) [μm]	Compound Layer Thickness [μm]
1	12hrs, 500°C, average K _N =7.3	28	1000	~ 1000	13
2	2.5hrs, 500°C, average K _N =9	34	650	~ 500	4
3	6hrs, 500°C, average K _N =7.5	8 (Location A) 27 (Location B)	940	~715	6.5

 Table 4.1:
 Maximum Hardness Increase, Diffusion Depth and Compound Layer Thickness in Armco Fe Samples for three Different Nitriding Cycles

4.1.1 Micro-hardness Profile

The increase in micro-hardness for each nitriding test is presented in Figure 4.1. Two hardness profiles taken from different locations are displayed for the nitriding test #3. The noticeable change in hardness profile can be related to the specific microstructure of the area tested, as shown in Figure 4.2.



Figure 4.1: Increase in micro-hardness for Nitrided Armco Iron Samples

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Hardness indentations micrograph for test #3, Location B - magnified Figure 4.2: Hardness indentations micrographs for nitrided iron

4.1.2 Microstructures Evaluation

4.1.2.1 1st Nitriding Test – Light Microscopy and SEM

The microstructure obtained with the Armco Iron nitrided for 12hrs is shown in Figure 4.3 below, with a magnified view taken closer to the surface. Three regions can be clearly identified, moving from the surface inwards (from bottom up in the micrographs):

- Surface iron nitride compound layer
- Region of large "plate-like" precipitate with size ranging from less than 5 μm (just below the surface) up to 150 μm or more.
- Region of fine "needle-like" precipitate with sub-micron size for the smallest and up to 3-4 μm for the largest one

One can also noticed in the area of high density large "plate" precipitates, the surrounding areas are free of the smaller "needle" precipitates. In contrast of other areas where both low density of large "plates" and a "cloud" of "needle" precipitates co-exist.



Figure 4.3: Micrographs of Armco iron nitrided for 12hrs (Test #1), Nital etched

The SEM evaluation did not unveil significantly more information about the microstructure and Figure 4.4 is shown for reference. It is of interest to point out that some "plate" precipitates are connected to the surface compound layer.



Figure 4.4: SEM image of the Armco iron nitrided for 12hrs (Test #1), Nital etched

4.1.2.2 2nd Nitriding Test – Light Microscopy and SEM

The microstructure obtained with the Armco Iron nitrided for 2.5hrs is shown in Figure 4.5 below, with a magnified view taken closer to the surface. The microstructure is very similar to the 12 hrs sample, except for the significantly smaller size of the three regions depicted for Test #1.



Figure 4.5: Micrographs of Armco iron nitrided for 2.5hrs (Test #2), Nital etched



The SEM evaluation is shown for reference in Figure 4.6.

Figure 4.6: SEM image of the Armco iron nitrided for 2.5hrs (Test #2), Nital etched

The sample nitrided in the Test #2 was also evaluated with the EDS detector on two selected locations to confirm the presence of Fe-nitride phases. These areas were a large "plate-like" precipitate and the compound layer visible at the surface. Figure 4.7 shows the SEM image with the EDS target marked (star symbol) and the corresponding X-ray spectrum for each location.

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Figure 4.7: EDS X-Ray analysis of compound layer and large "plate" precipitate in nitrided Armco iron, Test #2

4.1.2.3 3rd Nitriding Test – Light Microscopy

The microstructure obtained with the Armco Iron nitrided for 6 hrs is shown in Figure 4.8 below, with a magnified view taken closer to the surface. The microstructure differs significantly from the 12 hrs and 2.5 hrs samples: there is almost no evidence of the large "plate" precipitate, except for a small number of fine ones present at the interface with the surface compound layer.



Figure 4.8: Micrographs of Armco iron nitrided for 6 hrs (Test #3), Nital etched

It should also be pointed out the significant density disparity of the fine "needle" precipitates from one grain to another and also the complete absence of any visual evidence of them in certain grains, as illustrated in Figure 4.9.



Figure 4.9: Micrographs of Armco iron nitrided for 6 hrs (Test #3) showing disparity in precipitates size and density between grains, Nital etched

4.1.2.4 3rd Nitriding Test – TEM Evaluation

A TEM foil was produced at a depth of about 175 μ m below the surface of the sample nitrided during the 3rd test. Figure 4.10 shows a TEM magnified view of the "needle-like" precipitates observed in light microscopy, with spacing of 0.2 -0.4 μ m and size ranging from 0.5 to 2 μ m.



Figure 4.10: TEM image of the "needle-like" precipitates of nitrided iron, Test #3

The precipitates observed in Figure 4.10 are seen in a cross-section orientation. Further evaluation of the samples with different foil orientations revealed that they are "disc-shaped" precipitates, as illustrated in Figure 4.11. Their thickness is estimated to range from about 50 to 150 nm.



Figure 4.11: TEM image of the "needle-like" precipitates of nitrided iron, Test #3 revealing a "disc-shaped" morphology

4.1.3 X-Ray Diffraction Analysis

A standard Armco Iron (in annealed condition) and one sample each of nitriding Test #1 and #2 were evaluated by X-Ray diffraction. The corresponding diffractograms were analyzed with the Topaz software (§3.4.4) to determine which iron nitride phases could be fitted to the pattern. Each sample was evaluated for α -Fe (ferrite), α "-, γ '- and ε -nitride phases. The standard Armco iron sample was used to verify the equipment setup and calibration. The diffractograms, first collected at the surface and then at a depth of 25-30 µm (after removing the compound layer and some of the diffusion case by mechanical polishing) are shown in Figure 4.12 and Figure 4.13 respectively.



Figure 4.12: X-Ray Diffractograms obtained from surface of nitrided Armco iron samples





The lattice cell parameters calculated by the Topaz software for the selected iron nitride phases, along with the corresponding errors are summarized in Table 4.2. Standard cell sizes for the phases evaluated during the fitting operation were obtained from the ICDD database [38].

Sample I.D.	Description	Phases	Measured cell size [Å]	Error	Comments	
			a = 2.8669	0.00013		
Fe	Armco iron (baseline)	α-Fe	a = 2.867		Standard cell size for α-Fe (Ferrite)	
		α-Fe	a = 2.8674	0.0007		
		ε-Fe₃N	a = 4.7258	0.0006		
			c = 4.3969	0.0011		
			a = 4.6982		Standard cell size	
Fe_1NA	Armco Iron,#1 Nitriding (at surface)		c = 4.3789		for ε-Fe ₃ N	
		α"-Fe ₁₆ N ₂	a = 5.7552	0.003		
			c = 6.219	0.006		
			a = 5.72		Standard cell size	
			c = 6.29		for α "-Fe ₁₆ N ₂	
	Armco Iron,#1 Nitriding (~30µm below surface)	α-Fe	a = 2.8668	0.0001		
Fe_1NB		α"-Fe ₁₆ N ₂	a = 5.7542	0.0004		
			c = 6.292	0.004		
	Armco Iron,#2 Nitriding (at surface)	α-Fe	a = 2.8707	0.00002		
		ε-Fe ₃ N	a = 4.7307	0.0001		
			c = 4.3935	0.0001		
Fe_2NA		γ'-Fe₄N	a = 3.8183	0.00007		
_			a = 3.795		Standard cell size for γ'-Fe₄N	
		α"-Fe ₁₆ N ₂	a = 5.705	0.0006		
			c = 6.333	0.0005		
	Armon Iron #2 Mitridian	α-Fe	a = 2.86668	0.00007		
Fe_2NB	(~30um below surface)	9 α"-Fe ₁₆ N ₂	a = 5.7485	0.0004		
			c = 6.189	0.001		

Table 4.2: Lattice cell parameters resolved for X-Ray diffractograms of various iron samples

4.2 Nitrided Armco Iron (Fe) Samples – Oil Quenched

Samples of previously nitrided Armco Iron (Test #1, 2 and 3) were reheated and quenched to study the effect of the cooling rate on the microstructure. The corresponding maximum hardness increase, diffusion depth and compound layer thickness are summarized in Table 4.3. There is no visual evidence of the transition area between the diffusion case and the core area that can be used to determine the depth of diffusion.

Test	Gas Nitriding Parameters	Maximum Hardness Increase [HV0.05]	Diffusion Depth (Micro-hardness) [µm]	Compound Layer Thickness [µm]
1 - OQ	12hrs. 500°C, average K _N =7.3	65	975	11
2- OQ	2.5hrs, 500°C, average K _N =9	71	775	4.5
3- OQ	6hrs, 500°C average K _N =7.5	75	600	6

 Table 4.3:
 Maximum Hardness Increase and Compound Layer Thickness for Oil Quenched

 Armco Fe Samples for three Different Nitriding Cycles

There is a significant increase in hardness and no significant changes in compound layer thickness when compared to the results presented in Table 4.1.

4.2.1 Micro-hardness Profile

The increase in micro-hardness for the Oil Quenched samples is presented in Figure 4.14. The micro-hardness indentation patterns and related microstructures are revealed in Figure 4.15 for samples from Test #1 and #3.



Figure 4.14: Increase in Micro-Hardness for Nitrided Armco Iron Samples, after Oil Quenching



Figure 4.15: Hardness indentations micrographs for oil quenched nitrided iron

4.2.2 Microstructures Evaluation

4.2.2.1 Light Microscopy and SEM

The microstructure obtained with the nitrided Armco Iron samples that were subsequently re-heated and oil quenched is very similar for all three test samples. There are only few small size "plate-like" precipitates visible, all located in the area directly under the surface compound layer. Figure 4.16 shows this typical microstructure for test sample #2-OQ and #3-OQ.





Further investigation under the SEM (up to 5000x) did not reveal more information about the microstructure (Figure 4.17).



Figure 4.17: SEM image of oil quenched nitrided iron, sample #2-OQ, Nital etched

4.3 <u>AISI 1070 Steel Sample – Pearlite and Spheroidized</u> microstructure

Samples of 1070 steel with pearlite and spheroidized microstructure were nitrided in Test #1 and #2. The corresponding maximum hardness increase, diffusion depth and compound layer thickness are summarized in Table 4.4. There is no visual evidence of the transition area between the diffusion case and the core area that can be used to determine the depth of diffusion.

Test	Gas Nitriding Parameters	Maximum Hardness Increase [HV0.1]	Diffusion Depth (Micro-hardness) [µm]	Compound Layer Thickness [μm]
1 – Pearlite	12hrs, 500°C, average K _N =7.3	29	400	12
1 - Spheroidized	12hrs, 500°C, average K _N =7.3	34	600	11
2 - Spheroidized	2.5hrs, 500°C, average K _N =9	49	325	5.5

 Table 4.4:
 Maximum Hardness Increase and Compound Layer Thickness for Nitrided 1070

 Steel of Pearlite and Spheroidized Microstructure

4.3.1 Micro-hardness Profile

The increase in micro-hardness for the pearlitic and spheroidized nitrided samples is presented in Figure 4.18. The micro-hardness indentation patterns and related microstructures are revealed in Figure 4.19 for the spheroidized sample nitrided in test #2.



Figure 4.18: Increase in Micro-Hardness for Nitrided 1070 Steel, Pearlite and Spheroidized Samples



Figure 4.19: Hardness indentations micrographs for 1070 steel, spheroidized sample, nitriding test #2

4.3.2 Microstructures Evaluation

4.3.2.1 Pearlitic Sample – Light Microscopy and SEM

The microstructure obtained with the pearlitic 1070 steel nitrided for 12hrs is shown in Figure 4.20 below, with a magnified view taken closer to the surface. The pearlitic microstructure doesn't exhibit noticeable change when compared to the microstructure prior nitriding. It is interesting to note the presence of fine "plate-like" precipitates within the first 400 μ m or so below the surface. They are extending through multiple grains and can be clearly resolved in the ferrite grains (highlighted in magnified view of Figure 4.20)



Figure 4.20: Micrographs of pearlitic 1070 steel, nitrided for 12hrs (Test #1), Nital etched

The SEM image taken immediately below the surface compound layer and shown in Figure 4.21 confirms the presence of these precipitates.



Figure 4.21: SEM image of the pearlitic 1070 steel nitrided for 12hrs (Test #1), Nital etched

4.3.2.2 Spheroidized Sample – Light Microscopy and SEM

The microstructure obtained with the spheroidized 1070 steel nitrided for 12hrs is shown in Figure 4.22, with a magnified view taken closer to the surface. The spheroidized microstructure doesn't exhibit noticeable change when compared to the microstructure prior nitriding. It is interesting to note the presence of fine "plate-like" precipitates within the first 300 μ m or so below the surface. They are very similar to the one observed in the pearlitic microstructure, but of shorter size and higher density.



Figure 4.22: Micrographs of spheroidized 1070 steel, nitrided for 12hrs (Test #1), Nital etched

The image shown in Figure 4.23, produced by darkfield illumination and the use of a polarized filter amplifies the height difference between the carbides / "plate" precipitates and the ferrite matrix resulting from the Nital etching. The carbides within the first 100 μ m or so from the surface are networked with "plate" precipitates.



Figure 4.23: Darkfield Micrographs of Spheroidized 1070 Steel, Nitrided for 12hrs (Test #1), Nital etched

The SEM image taken immediately below the surface compound layer and shown in Figure 4.24 confirms the presence of "plates" precipitates.



Figure 4.24: SEM image of the spheroidized 1070 steel nitrided for 12hrs (Test #1), Nital etched

4.4 AISI 1070 Steel Sample – Oil Quenched microstructure

As reported in §3.3.2.1, the microstructure obtained after oil quenching was mainly martensite on the outside edge with an increasing content of very fine pearlite as we move towards the center of the disc.

The corresponding maximum hardness increase, diffusion depth and compound layer thickness are summarized in Table 4.5. The compound layer thickness was fairly consistent along the entire length of the specimen (i.e. from the martensite microstructure on the outside to the fine pearlite at the center of the sample). There is no visual evidence of the transition area between the diffusion case and the core area that can be used to determine the depth of diffusion.

Sample	Gas Nitriding Parameters	Maximum Hardness Increase [HV0.1]	Diffusion Depth (Micro-hardness) [µm]	Compound Layer Thickness [µm]
625μm (mainly Ms)	12hrs, 500ºC, average K _N =7.3	134	430	
1875µm		132	350	
4375µm		105	325	10.5
6875μm (~100% P)		88	275	

 Table 4.5:
 Maximum Hardness Increase and Compound Layer Thickness for Oil Quenched and Nitrided 1070 Steel Sample

4.4.1 Micro-hardness Profile

The increase in micro-hardness for the oil quenched and nitrided sample is presented in Figure 4.25. The hardness prior nitriding is reported in the legend box for reference.



Figure 4.25: Increase in micro-hardness for Nitrided Oil Quenched 1070 Steel Sample

The micro-hardness indentation patterns and related microstructure are revealed in Figure 4.26 for the sample reading taken at the distance " 6875μ m" from the edge of the disc (almost 100% fine Pearlite).



Figure 4.26: Hardness indentations micrographs for 1070 steel, oil quenched sample, fine Pearlite microstructure, Nital Etched

4.4.2 Microstructures Evaluation

4.4.2.1 SEM Microscopy

The martensite and fine pearlite microstructures produced in the oil quenched sample used for the nitriding test #1 require high magnification to resolve their details. The nitrided samples were therefore mainly evaluated in the SEM. Figure 4.27 exhibits both microstructure (martensite and fine pearlite) obtained after the nitriding operation. None of these two microstructures reveals noticeable change when compared to the ones prior nitriding.

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Figure 4.27: SEM image of 1070 steel, oil quenched sample, Martensite and fine Pearlite microstructure, Nital etched

4.4.2.2 TEM Microscopy

A TEM foil was produced at a depth of about 125 μ m below the surface of the nitrided 1070 oil quenched steel sample. The micrographs presented in Figure 4.28 are from the center of the sample, in the fine pearlite region. The lamellar spacing, measured on the right hand side magnified view, ranges from 50 to 100 nm.



Figure 4.28: TEM image of nitrided 1070 oil quenched steel sample, fine pearlite region from center of sample

4.5 <u>AISI 1070 Steel Sample – Decarburized and Oil</u> Quenched microstructure

The decarburized, oil quenched and nitrided sample was evaluated at different depths from the decarburized edge. The equivalent estimated carbon content (corresponding to the "as-quench" hardness, see §3.3.2.2) has been added along with the distance from the decarburized edge.

The corresponding maximum hardness increase, diffusion depth and compound layer thickness are summarized in Table 4.6. There is no visual evidence of the transition area between the diffusion case and the core area that can be used to determine the depth of diffusion.

Sample	Gas Nitriding Parameters	Maximum Hardness Increase [HV0.1]	Diffusion Depth (Micro-hardness) [µm]	Compound Layer Thickness [µm]
635μm (~0.05%C)		126	420	1
800μm (~0.1%C)		84	215	1
1500μm (~0.3%C)	6hrs, 500⁰C, average K _N =7.5	119	420	1.5
1900μm (~0.4%C)		88	250	2.5
4500μm (0.7%C)		123	250	3

 Table 4.6:
 Maximum Hardness Increase, Diffusion Depth and Compound Layer Thickness for Decarburized 1070 Steel, Oil Quenched and Nitrided Sample

4.5.1 Micro-hardness Profile

The increase in micro-hardness for the decarburized, oil quenched and nitrided sample is presented in Figure 4.29.



Figure 4.29: Increase in micro-hardness for Nitrided Decarburized - Oil Quenched 1070 Steel Sample

4.5.2 Microstructures Evaluation

4.5.2.1 Light and SEM Microscopy

Figure 4.30 reveals the microstructure obtained after the nitriding of an area very close to the edge of the decarburized and oil quenched sample. The carbon content is estimated to be lower than 0.05%. Refined equiaxed ferrite grains with carbide precipitates can be resolved.


Figure 4.30: Micrographs of decarburized 1070 steel, oil quenched and nitrided sample, low carbon area (<0.05%), Nital etched

The microstructure obtained after the nitriding of an area about 2 mm from the edge of the decarburized and oil quenched sample is shown in Figure 4.31. The carbon content is estimated to be around 0.45%. The matrix structure show little change from the appearance of the as-quenched martensite, except for the presence of cementite platelets within the larger martensite lath.



Figure 4.31: Light and SEM micrographs of decarburized 1070 steel, oil quenched and nitrided sample, medium carbon area (~0.45%), Nital etched

4.5.2.2 TEM Microscopy

A TEM foil was produced at a depth of about 300 μ m below the surface of the nitrided 1070 decarburized steel sample. Unfortunately, the foil didn't thin out homogeneously and only very limited area could be evaluated in the TEM. The micrographs presented in Figure 4.32, from the center of the sample (nominal C content of 0.7%), exhibit a tempered martensite microstructure with precipitates (probably cementite and/or carbide).



Figure 4.32: TEM image of 1070 decarburized steel (nominal 0.7%C area), oil quenched and nitrided sample

4.6 Fe / Fe-5Cr Diffusion Couple

The corresponding maximum hardness increase, diffusion depth and compound layer thickness are summarized in Table 4.7. The sample identification is given as the distance from the Fe / Fe-5Cr interface, with the approximate %Cr (obtained by EDS X-Ray analysis in the SEM).

Due to the high Cr content of this material, the preparation of the sample required a stronger etching reagent. The microstructure of the diffusion case was revealed using 10% Nital. The compound layer thickness was fairly consistent along the entire length of the specimen. The diffusion depth was estimated visually from the strong transition between the area immediately below the surface and the core area.

Sample	Gas Nitriding Parameters	Maximum Hardness Increase [HV0.1]	Diffusion Depth (Micro-hardness) [µm]	Diffusion Depth (visual) [µm]	Compound Layer Thickness [µm]
-1500μm (1.6% Cr)		664	460	140	
-200μm (2.25% Cr)		821	460	130	
0 (2%)	6hrs, 500°C, average K _N =7	787	525	130	_ 11.5
200μm (2.6% Cr)		800	450	100	
1300μm (3% Cr)		891	340	110	

 Table 4.7:
 Maximum Hardness Increase and Compound Layer Thickness for Nitrided

 Fe/Fe-5Cr Diffusion Couple Sample

4.6.1 Micro-hardness Profile

The increase in micro-hardness for the nitrided Fe/Fe-5Cr diffusion sample is presented in Figure 4.33. The measured chromium content has been added in line with the distance from the Fe / Fe-5Cr interface.

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4.6.2 Microstructures Evaluation

4.6.2.1 Light Microscopy

As stated at the beginning of this section, a more concentrated (10%) solution of Nital was used to reveal the microstructure. Figure 4.34 exhibits the interface area (large void at top of image represent the interface) between the originally pure Fe sample (left) and the Fe-5Cr alloy (right). The chromium content was measured to be about 2% in this area. The microstructure did not get attacked beyond ~100 μ m from the surface. One can suspect the chromium distribution beyond that limit remained comparable to the core area, allowing the formation of a chromium oxide layer that resisted the Nital reagent chemical attack. It is of interest to mention the two combination of phases present in the surface iron nitride layer. A thicker, porous layer on the outer part and a thinner, fully dense phase on the inner side can be clearly distinguished.



Figure 4.34: Micrograph of Nitrided Fe/Fe-5Cr Diffusion Sample at the interface area, Nital etched

The views presented in Figure 4.35 are taken from both side edges of the sample:

- 1. On the left is the original Fe sample (Cr content measured at 1.25%)
- On the right is the original Fe-5Cr sample (Cr content measured at 3.25%).

The surface iron nitride layer is separated from the sample material and some significant voids are visible at this interface (on the right micrograph). However, it should be pointed out that this surface was not prepared prior to the nitriding cycle. The surface appeared oxidized prior to be placed in the retort.

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Figure 4.35: Micrograph of Nitrided Fe/Fe-5Cr Diffusion Sample, highest Cr content area, Nital etched

The last micrograph presented, Figure 4.36, highlights an interesting observation made in the corner of the Fe-5Cr sample side, where the amount of nitrogen diffused in the bulk sample is increased by the "edge effect". Here, two faces are contributing to the diffusion of N, resulting in a greater diffusion depth as confirmed by the thickness of the etched area. The "plate-like" precipitates, observed mainly in the nitrided Armco iron (see §4.1.2), are shown "growing" out of the surface iron nitride layer towards the bulk material.



Figure 4.36: Micrograph of Nitrided Fe/Fe-5Cr Diffusion Sample, corner of highest Cr content area, Nital etched

4.7 Fe-2Cr Alloy

The Fe-2Cr alloy, unlike any of the other materials, was nitrided in a "cold worked" condition (about 70% reduction). The corresponding maximum hardness increase, diffusion depth and compound layer thickness are summarized in Table 4.8.

Sample	Gas Nitriding Parameters	Maximum Hardness Increase [HV0.1]	Diffusion Depth (Micro-hardness) [µm]	Diffusion Depth (visual) [µm]	Compound Layer Thickness [µm]
Fe-2Cr alloy	13.5hrs, 550°C, KN=4	595	1000	330	32

 Table 4.8:
 Maximum Hardness Increase, Diffusion Depth and Compound Layer Thickness for Nitrided Fe-2Cr Sample

4.7.1 Micro-hardness Profile

The increase in micro-hardness for the nitrided Fe-2Cr sample is presented in Figure 4.37.



Figure 4.37: Increase in micro-hardness for Nitrided Fe-2Cr Sample

4.7.2 Microstructures Evaluation

4.7.2.1 Light Microscopy

As stated at the beginning of this section, this sample was in a cold worked condition prior to be nitrided. Clear evidence of deformed grains is exhibited in Figure 4.38. The two combinations of phases present in the surface iron nitride, as observed in the Fe/Fe-5Cr sample described in §4.6.2.1, are clearly visible in this sample as well.



Figure 4.38: Micrographs of Nitrided Fe-2Cr Sample, Nital etched

4.7.2.2 TEM Microscopy

Two TEM foil were produced: one at a depth of about 200 μ m below the surface and another one at the core of the nitrided Fe-2Cr sample. The grain morphology shown in Figure 4.39 clearly indicates recrystallization at the core where the nitrided area below the surface still exhibits deformed grain.



Figure 4.39: TEM images of nitrided Fe-2Cr sample, grain morphology at the core vs. surface area

The images presented in Figure 4.40 (from the surface area as well) reveal the presence of a very high density of fine chromium nitride precipitates. The larger "streaks" visible on the magnified view are less than 20 nm in length while the smaller spots are less than 5nm. Note that the magnified view is not from the same area as the image on the left.



Figure 4.40: TEM images of nitrided Fe-2Cr sample, CrN precipitates

4.7.3 X-Ray Diffraction Analysis

Two samples taken from the nitrided Fe-2Cr alloy were evaluated by X-Ray diffraction:

- One from the core to use as a baseline
- One from about 100 μ m below the nitrided surface

The corresponding diffractograms, shown in Figure 4.41, were analyzed with the Topaz software (ref. §3.4.4) to determine which chromium nitride phases could be fitted to the pattern. The core sample was used to verify the cell size for a 2% Chromium alloyed iron, after cold working and nitriding treatment. There was no significant unit cell size change when compared to pure iron ferrite. The diffractogram produced from the nitrided area exhibited very similar diffraction peaks, with the addition of a small peak on each side of the main ferrite peak ($2\theta = 20.15^{\circ}$). These added diffraction peaks have not been fitted to any phase that could be expected in this alloy. There was no detectable evidence of the presence of the CrN precipitates.

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Figure 4.41: X-Ray Diffractograms obtained from nitrided Fe-2Cr samples

The lattice cell parameters calculated by the Topaz software for the ferrite and chromium nitride phase (for reference), along with the corresponding errors are summarized in Table 4.9.

Sample I.D.	Description	Phases	Measured cell size [Å]	Error	Comments
Fe	Iron (baseline)	α-Fe	a = 2.867		Standard cell size for α -Fe (Ferrite)
Fe-2Cr	Fe-2Cr alloy, nitrided, core (baseline)	α-Fe	a = 2.8675	0.00013	
Fe-2Cr_A	Fe-2Cr alloy, nitrided, ~100μm below surface	α-Fe	a = 2.8653	0.00043	
		CrN	a = 4.149		Standard cell size for CrN (could not be detected)

Table 4.9: Lattice cell parameters resolved for X-Ray diffractograms of Fe-2Cr samples

Chapter 5

5 DISCUSSION

5.1 Diffusion of N

5.1.1 Total Case Depth

A qualitative comparison of the measured diffusion depth for all nitrided microstructures and the theoretical depth (based on Eqn 2.4) is presented in Figure 5.1. The $2^*\sqrt{(Dt)}$ plots (both for 500 and 550°C) give the nominal N diffusion depth in α -Fe for about 15% of the nitriding atmosphere N concentration and will be used as a baseline for this review. This approach has been selected to take into account that a small N concentration is sufficient to enhance the mechanical properties of most specimens. The diffusion coefficient **D** for N in α -Fe (estimated to be constant for a given temperature since the α phase is a dilute solution of N) is calculated using the relation:

$$D = D_0 \exp \frac{-Q}{R \cdot T}$$

Eqn 5.1

where **R** is the gas constant, **T** is the absolute temperature [K], with **Do** = 7.8*10-7 [m²s⁻¹] and the activation enthalpy **Q** = 79.1 [kJmol⁻¹] [from 39]. The diffusion coefficient **D** was calculated to be $3.52*10^{-12}$ [m²s⁻¹] at 773 K (500°C) and 7.44*10⁻¹² [m²s⁻¹] at 823 K (550°C).

The diffusion depth is defined as the depth for which the measured hardness increase is 10 HV. This approach is preferred over the "Total Case Depth" defined in §4 to account for the large range of core hardness between all the microstructures. Using the definition of the Total Case Depth, the diffusion depth for pure iron (core hardness of ~100HV) would be estimated for a hardness increase of 10HV versus 45HV for the 1070 steel oil quenched microstructure (core hardness of ~450HV).

From the depth vs. \sqrt{t} (square root of time) profiles given in Figure 5.1, the following comments can be made:

- The diffusion distance predicted is of the right order of magnitude when compared to the measured diffusion depth for each specimen
- Both the pure Iron and the spheroidized 1070 specimen show a clear trend and relate closely to the calculated diffusion distance
- The other material exhibit some level of interaction with the diffusing N since the measured depth is significantly smaller than the predicted value.

It is evident from the above comments that more data would be required (particularly in pure iron after oil quenching) to properly interpret the interaction between N and the specimen microstructure.



Figure 5.1: N Diffusion Depth for all nitrided material

5.1.2 Compound Layer Thickness

The formation of the compound layer, as described in §2.8, will depend of the temperature, the nitriding atmosphere and the time of treatment. The thickness of the compound layer vs. \sqrt{t} for all the specimens is presented in Figure 5.2.



Figure 5.2: Compound Fe-nitride layer thickness for all nitrided material (all 500°C, except Fe-2Cr at 550°C)

The iron-nitride surface layer(s) thickness also shows it's dependency to the square root of time, confirming the solid state N diffusion models discussed in §2.8. For the specimen run at 500°C, the decarburized and oil quenched 1070 steel data point is the only one not following the \sqrt{t} regression. Upon detailed review of the surface nitride layer, no particular evidence could be found to explain this "discrepancy". The iron specimen nitrided with this sample produced a surface iron nitride layer of expected thickness.

As expected, the ε/γ -nitride bilayer produced on the Fe-2Cr sample at 550°C shows a significant thickness increase from the other samples produced at 500°C. This layer is also exhibiting heavy porosity in the ε sub-layer, which could have contributed to the enhanced layer growth.

The calculated incubation time for our nitriding parameters, according to Figure 2.12, is less than 10 minutes. The kinetic of the compound layer formation can therefore be described by the growth model only. This is supported by the data collected for the 2.5 hrs cycle ($\sqrt{t} = 1.6 \ h^{1/2}$): the thickness lies closely on the \sqrt{t} linear regression.

Since all cycles at 500°C were produced with a nitriding potential of $K_N = 7$ atm^{-1/2}, the surface iron nitride layer should be made of both the ε/γ' -nitride sublayers. This has been confirmed on all the cycles, as well as on the Fe-2Cr alloy nitrided at 550°C and $K_N = 4.2$ atm^{-1/2} (but still sufficient to produce ε -nitrides).

5.1.3 Porosity in surface iron nitride layer

Upon review of the compound layer microstructure, it should be mentioned that most specimens exhibit porosity in the outer iron nitride sub-layer. For the specimen nitrided for 2.5 hrs, the porosity is resolved in the SEM, where as for the longer treatment, observation under light microscopy is sufficient to detect it. This is more pronounced for samples nitrided 6hrs and more and on the Fe-2Cr sample nitrided at a higher temperature (550°C).

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Porosity has been reported by numerous researchers [23,40,41] who investigated the formation of the compound iron-nitride layer. At the surface, the apparent partial pressure of N₂ (pN_2) in equilibrium with ε -nitride amounts to about 250,000 atm [40]. However, within the growing nitride (mono or bi-) layer, there is no contact with the gas atmosphere which imposes the large pN_2 . As a result, the layer is only stable at the surface. The Fe-nitrides are metastable compounds with an enthalpy of formation close to zero. Within the layer, simultaneous formation and decomposition of Fe-nitrides take place. With increasing temperature, the decomposition of the nitrides to Fe + N₂ releases energy (Gibbs free energy) and is therefore more favorable.

When nitrides decomposition takes place more quickly than local transport of atomic N through the layer, the N₂ bubbles will coalesce to form pores (see Figure 5.3). The rate limiting step in the decomposition is the recombination of the N atoms into N₂ molecules, which becomes significant above 400°C [4]. This temperature acts as a high kinetic barrier in the decomposition of the unstable ironnitrides [42]. After prolonged treatment time, the porosity will also develop within grains. Pores formation is observed especially in the near surface region, where most N is present (enhancing the thermodynamic driving force for N₂ formation). Coalescence of individual pore leads to the formation of channels that connect the interior of the compound layer with the surface atmosphere. The nitriding potential is now imposed to a certain depth in the newly created channel surfaces, leading to a layer growth increase. As the ammonia dissociates in the channels, this enhanced N diffusion kinetic slow down due to poor gas replacement at the bottom of the channels. Somers and Mittemeijer [23] also suggest that nitrides formed on pure iron become porous very quickly where as samples with impurities (oxygenrich iron from a pre-oxidation treatment in their experiment) at grain boundaries may explain the delayed nucleation of pores in these locations.

During application of gas nitriding to industrial applications, it may be advantageous to optimize the nitriding potential K_N and treatment temperature to achieve the required compound layer and case thickness while minimizing the amount of porosity developing in the region near the surface. While porosity might be beneficial for sliding wear application (retention of lubricants), it will most likely increase cracking and spalling of the brittle iron nitride layer under impact loading. The presence of porosity will also significantly reduce the enhanced corrosion protection offered by a dense compound layer.



Figure 5.3: Development of N₂ pores at grain boundary in ε-layer and coalescence into channels. Internal pores formation occurs too [after 40]

5.2 <u>Review of Nitrided Case in Pure Iron</u>

5.2.1 Microstructure

The microstructure of the nitrided case is made up two distinctive regions (refer to §4.1.2):

- Area closer to the surface compound layer, exhibiting mainly large "plate-like" precipitates with dissolving clouds of fine "needle-like" precipitates
- 2. Area deeper in the bulk exhibiting a dense and homogeneous distribution of fine "needle-like" precipitates.

The large "plate-like" precipitates have been identified as the γ '-Fe₄N nitrides and the "needle-like" (provided evidence that they are actually discs, see Figure 4.10) as α "-Fe₁₆N₂. This identification was confirmed with comparable microstructures reported in the literature [24,27].

The γ' -phase precipitates first from the supersaturated ferrite during slow cooling and depletes the γ' -precipitate surrounding areas of N. This is clearly visible in the magnified view of Figure 4.3 and Figure 4.5. Using the cooling profiles discussed in Figure 3.15, we can estimate the N mean diffusion length around γ' -precipitates to be about 45 μ m (conservatively assuming 350°C for 3hrs for \sqrt{Dt}). This distance is of the right order of magnitude when compared to the spacing between γ' -precipitates and the surrounding "clouds" of α "-precipitates. As the temperature continue to decrease, the α "-phase precipitates from the supersaturated ferrite.

Recent work [42] suggest that for temperature below 214°C (487K), the γ' phase is no longer stable with respect to the α and ε -phase (see new Fe-N phase diagram in Figure 5.4). But in order to achieve this new equilibrium, the system needs to be allowed sufficient time to reach this state. This annealing condition can be extremely long, since Malinov *et al.* [43] showed an enrichment of the γ' -phase and the development of new α'' -precipitates after annealing 28 days at 214°C (413K). The reported diffusion distance (\sqrt{Dt}) in the γ' -phase under this condition was about 50 nm.



Figure 5.4: Complete Fe-N phase diagram with additional equilibrium information at low temperature [after 42]

5.2.2 Microstructure for increased cooling rate

A significantly different microstructure was observed for the nitrided iron specimen that was rapidly cooled (test #3). Only α "-precipitates are visible in the nitrided case. A review of the thermal history suggests that the sample spent about 1/2hr above 450°C prior to be rapidly cooled (more than 15°C/min). This condition did not allow sufficient time for the N to diffuse from the supersaturated ferrite and form γ '-precipitate, but instead formed a fine dispersion of α "-precipitates, as shown in Figure 4.10.

To verify this model, nitrided iron specimens from test #1, 2 and 3 were reheated to 500°C (ramp rate of about 3°C/min) and then oil quenched. The resulting microstructures, presented in §4.2.2, confirmed that no nitride precipitates had time to form in the nitrided case. Only fine γ' -precipitates, formed during the nitriding operation are visible attached to the γ' -sublayer or along grain boundaries immediately underneath the compound layer. The microstructure obtained, a N supersaturated α -Fe phase called nitrogen martensite α' , is therefore not an equilibrium phase and will decompose to α -Fe + γ' or ε if reheated to a sufficient temperature and time to allow the reaction to complete.

5.2.3 Hardening mechanism

The measured hardness increase for the nitrided iron specimen varies between 8 and 34 HV0.1, depending on the location of the indentation (i.e. finely dispersed α "-precipitates vs. large and spaced γ '-precipitates). The precipitate hardening effect can be described by the interaction between dislocation and precipitate obstacles, such as the Orowan model. This model describes the force balance required for a dislocation to loop around undeformable particles spaced by distance L, as shown in Figure 5.5 [44].



Figure 5.5: Balance of force between particle resistance to dislocation movement and line tension of dislocation

The balance of force between the particle resistance F to the dislocation movement and the line tension T of dislocation is given by:

$$F = 2T\sin\theta$$
 Eqn 5.2

and the bowing force *B* is expressed as:

$$B = \Delta \tau \cdot b \cdot L$$
 Eqn 5.3

where $\Delta \tau$ is the increased shear stress due to the presence of particle, **b** the Burgers vector and **L** the spacing between particles. Combining these equations with the definition of the line tension for dislocation $T \cong Gb^2/2$ where **G** is the shear modulus and considering the resisting force is maximized when $\sin\theta = 1$ gives:

$$\Delta \tau = \frac{G \cdot b}{L}$$
 Eqn 5.4

Converting this model to the macroscopic tensile yield strength using the Taylor factor M [45]:

$$\Delta \sigma_{y} = \frac{M \cdot G \cdot b}{L}$$
 Eqn 5.5

The hardening effect produced by the α "-precipitates, with a particle spacing L ranging from 300 to 500 nm (from Figure 4.10) can be estimated using Eqn 5.5. Considering G=82 GPa and b = 0.248 nm (Burgers vector in the slip direction) for iron [46], the corresponding increase in yield strength $\Delta \sigma_y$ is calculated to be between 125 and 210 MPa. The equivalent stress calculated using Eqn 3.2 is about 40 to 64 HV. This is of the right order of magnitude when compared to the measured increase in hardness. The hardening effect to be expected from the γ '-precipitates can be neglected, since the particle spacing is at least one order of magnitude greater.

Another strengthening model to consider is the solid solution effect, where the strengthening coefficient is attributed to the lattice expansion due to the solute addition. For N in solution in α -Fe, the coefficient ($\Delta \sigma_y$ /1at%) is reported to be about 1000 MPa/1at% [44]. No data for the N content of the α -Fe produced during the nitriding experiments was collected. However, it is of interest to mention that for the region below the compound layer (assumed to be a N saturated α -Fe during nitriding), the solid solution hardening could range between 10 and 50 MPa (for N solubility of 0.01% and 0.05% at 200 and 300°C respectively, according to Figure 2.5). The solid solution hardening will therefore not account for any significant increase in hardness for iron that underwent slow cooling after the nitriding operation.

5.2.3.1 Hardening of annealed and oil quenched specimens

A significant hardness increased ranging from 65 to 75 HV was recorded for the nitrided iron specimens that were annealed and oil quenched. The microstructure is described as nitrogen martensite. Assuming that the region below the compound layer achieved equilibrium during nitriding, the maximum N solubility at 500°C is about 0.2 at.% (according to Figure 2.5). The corresponding solid solution strengthening is estimated to be about 200 MPa (using strengthening coefficient of 1000Mpa/1at% discussed in previous paragraph). The equivalent hardness increase is 61 HV, which is in good agreement with the measured data.

5.3 <u>Review of Nitrided Case in 1070 Steel – Pearlite /</u> Spheroidized Microstructure

5.3.1 Microstructure

Very little changes were observed under light microscopy and SEM evaluation of the nitrided samples when compared to the microstructure prior nitriding. The pearlite sample exhibits fine γ' -precipitates in the region below the compound layer (Figure 4.20, Figure 4.21). These precipitates are seen going through ferrite grain and continuing in adjacent pearlite grain in Figure 5.6. The ε/γ' -bilayer can be distinctively resolved at the surface. A significant amount of channel and intergranular porosity is visible in the ε -sublayer and also extend in the γ' -sublayer. Some "wedge-shaped" ε -nitride phase is seen growing into the γ' -sublayer of Figure 4.21.



Figure 5.6: Micrographs of pearlitic 1070 steel in the region adjacent to the compound layer, nitrided for 12hrs (Test #1), Nital etched

The spheroidized samples also feature a significant amount of γ' precipitates in the region below the compound layer (Figure 4.22 and Figure 4.24). The darkfield illuminated micrograph (Figure 4.23) reveals a higher density of γ' precipitates immediately below the compound layer. There is no strong evidence of coarsening of the spheroidized carbides during the nitriding operation.

5.3.2 Hardening mechanism

The recorded hardness increase for both the pearlitic and spheroidized microstructure ranges from 29 (pearlitic) to 49 HV (spheroidized). The low hardening effect of the nitriding on these microstructures is similar to the case of the pure iron: a combination of weak precipitation and solid solution strengthening. The higher density of fine γ '-precipitates in the spheroidized sample most likely account for the higher hardness increase. The addition of Mn (0.8% in the 1070 alloy) doesn't influence the hardness, which is an indication that Mn is not a nitride forming element. The addition of C (0.7% in the 1070 alloy) did not promote the formation of carbonitrides either. This can be explained by the fact that the carbon is not available in the matrix to form carbonitride precipitates. It is already taken up as Fe₃C lamellas in the pearlite and spheres in the spheroidized microstructure.

5.4 <u>Review of Nitrided Case in 1070 Steel – Oil Quenched</u> <u>Microstructure</u>

5.4.1 Microstructure

As detailed in §3.3.2.1, the oil quenched sample did not produce the expected fully martensitic microstructure but a mixture gradient of martensite and fine pearlite (from outside periphery to center of bar). Small region of fine carbides precipitates starts appearing in the tempered Martensite microstructure present on the outer edge of the sample. They are mainly visible in the bottom area of Figure 4.27. At the center of the sample, in the fine pearlite area, the microstructure looks unchanged when compared to the prior nitriding condition.

The rapid cooling treatment (oil quenching) forces the transformation of γ -Fe (austenite) to pearlite to begin at a lower temperature, leading to smaller interlamellar spacing. This refined pearlite exhibits an average hardness of 340 HV0.1. The hardening effect of the pearlite inter-lamellar spacing in eutectoid steel was studied by Heller [47] and he proposed the following equation:

$$\sigma_{y(0.2\%)} = -85.9 + 8.3 \cdot S_p^{-1/2}$$
 Eqn 5.6

with S_p (mm) the inter-lamellar spacing. The inter-lamellar spacing of the "oil quenched" pearlite was measured to range from about 50 to 100 nm (Figure 4.28). The equivalent yield strength σ_y is about 745 to 1090 MPa, which can be converted to 230 to 335 HV. This is in good agreement with the measured hardness.

5.4.2 Hardening mechanism

The recorded hardness increases for the mixture of microstructure range from 134 (mainly martensitic) to 88 HV (fine pearlite).

The strengthening observed in the fine pearlite phase is significantly higher than the one measured on the pearlite produced by slow cooling (29 HV). This would indicate that the diffusing N was able to interact with carbides to form carbonitride precipitates. The explanation might be related to the very fast cooling produced by the oil quenching: the microstructure did not have enough time to reach equilibrium (i.e. to complete the transformation γ -Fe to α -Fe + cementite). During the nitriding cycle, the high temperature and treatment time allow carbides to precipitate from a small fraction of retained austenite. It is also possible that precipitates were already present in the ferrite as un-dissolved carbides (remained as precipitate during the austenitizing treatment). The nitriding thermal process acts as a tempering treatment of the martensite microstructure. The formation of transition carbides will initially start at lower temperature (100 to 250°C), followed by the transformation of low-carbon martensite and the replacement of the transition carbides by ferrite and cementite (θ -carbide) at higher temperature (250 to 350°C) [35]. The strengthening mechanism leading to the observed hardness increase is therefore assumed to be carbonitrides precipitation. The equivalent particles spacing obtained for a hardness increase of about 130 HV is calculated to be about 15 nm (Eqn 5.5). No TEM foil was produced in the martensite area of the sample to evaluate the microstructure at high magnification and to confirm the presence of these precipitates.

5.5 <u>Review of Nitrided Case in 1070 Steel – Decarburized</u> and Oil Quenched Microstructure

5.5.1 Microstructure

The hardenability of a Fe-C alloy as a function of the C content has been described in [35]. This information was used to correlate the as-quench hardness with the C content as a function of the depth from the edge of the decarburized sample (Figure 3.13). Using this information, the carbon content of the microstructure located about 600 μ m from the edge is estimated to be about 0.05%. After nitriding, this area exhibits a ferrite microstructure with a fine dispersion of large carbide / carbonitride precipitates (Figure 4.30). As we move towards the inner core of the sample, the carbon content increases and the microstructure revealed after nitriding appears more like tempered martensite with cementite platelets precipitating within the large martensite laths (Figure 4.31).

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5.5.2 Hardening mechanism

The recorded hardness increase for the decarburized sample ranges from 84 to 126 HV. This variation doesn't relate to the increase in C content, as shown in Table 4.6. Careful review of the microstructure at the specified depths used for the micro-hardness profiles did not provide an explanation for the observed disparity in data.

The strengthening observed is of the same order of magnitude as the one discussed for the martensite microstructure in §5.4.2. This is expected since the microstructures are similar, with the exception of the carbon content. Only one TEM foil of this sample was evaluated (Figure 4.32). It has not been confirmed if the particles visible in these micrographs are indeed carbide / carbonitride precipitates.

It is important to emphasize the significant hardness increase obtained by adding 0.05% C to pure iron (~30 HV for pure iron vs. 125 HV for Fe-0.05C). Gladman [44] expressed the particle strengthening effect as:

$$\Delta \sigma_{y} = \left(\frac{10.8 \cdot f^{1/2}}{r}\right) \cdot \left(\ln \frac{r}{6.125 \cdot 10^{-4}}\right)$$
Eqn 5.7

with **f** the volume fraction of precipitates and **r** the precipitate diameter (μ m). The effect of the particle size on the increase in $\Delta \sigma_y$ clearly shows the dominance of the **1**/**r** term over the **In** (**r** / **cst**). The addition of C to pure iron gives rise to a high number density of particles (n = number of particles / unit volume) while further increase in the C content augments the volume fraction. The increase in $\Delta \sigma_y$ is proportional to **f**^{1/2}, which is not as pronounced as the addition of C to pure iron.

5.6 Review of Nitrided Case in Fe-Cr Alloys

5.6.1 Microstructure

An early study by Lightfoot and Jack [19] reviewed the interaction between common nitride forming elements and the diffusing N. Table 5.1 list the commonly occurring nitride phases for these elements. The heat of formation is related to the strength of the interaction between the N and the alloying elements. The crystal structure of the nitrides gives an indication of the ease of nucleation of the precipitates in a ferrite matrix. Face-centered cubic phases can form with coherent or semi-coherent plates on the cube planes of ferrite [19].

Phase	Bravais Lattice	Unit cell dimensions [Å]	Heat of formation [kJ/mol nitride]
TiN	fcc	a = 4.244	-334
AIN	hex	a = 3.110 c = 4.975	-301
VN	fcc	a = 4.139	-218
CrN	fcc	a = 4.149	-125
Mo ₂ N	fcc	a = 4.169	-82
W ₂ N	fcc	a = 4.126	-71

Table 5.1:
 Characteristics of nitrides phases for common alloying elements in nitrided steels [adapted from 14]

Three types of interactions were studied and confirmed by observation in the work published by Lightfoot and Jack:

1. Strong interaction with easy nucleation

A uniform subscale, characterized by the complete reaction of all the alloying elements with the diffusing N, advances progressively into the core as the nitriding reaction proceeds. The solubility product ($K_s = N$ concentration x alloy element concentration) for homogenous precipitation of the alloy nitride is negligibly small. This behavior is accurately observed with nitrided Fe-Ti alloys and under certain condition with Fe-Cr alloys.

2. Weak interaction or difficult nucleation

Stable precipitate nuclei only occur when a substantial supersaturation is achieved. The solubility product Ks for homogenous precipitation of the alloy nitride is high. This behavior has been observed in Fe-Al and Fe-Mo alloys

3. Intermediate interaction – behavior of Fe-Cr alloys

Depending on the Cr concentration, Fe-Cr alloys can show nitriding responses characteristic of strong or weak interaction. The solubility product Ks = $(\%N) \times (\%Cr)$ is higher than for TiN but not as high as the one characterizing the Mo₂N nitride phase. The diffuseness of the interface between nitrided and non-nitrided area will increase with temperature (Ks increases). Increasing the N concentration at the surface (higher nitriding potential) or the alloy content will produce a sharper interface (Ks decreases).

The change in interaction between alloy element and diffusing N is clearly visible in Figure 5.7. The profile measured on the Fe edge of the diffusion couple (with %Cr measured at 1.6%) is characteristic of an intermediate interaction while the profile recorded on the Fe-5Cr edge of the specimen (with %Cr measured at 3.0%) exhibits a strong interaction with a sharp interface. The interface between the nitrided and non-nitrided area is visible in Figure 4.34 and Figure 4.35. It should also be mentioned that the visual depth of diffusion reported in Table 4.7 is in agreement with the depth of the sharp drop in hardness.

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Figure 5.7: Micro-hardness profiles for nitrided Fe/Fe-5Cr diffusion couple

The nitriding of the Fe-2%Cr shows the characteristic of a weak interaction, as expected from the "low" alloy content, lower nitriding potential K_N and higher temperature treatment. The visual depth of diffusion reported in Table 4.8 is in agreement with the depth of the interface resulting from the micro-hardness profile.

Recent reviews [48,49] of the precipitation of CrN in nitrided pure Fe-Cr alloys revealed the presence of both continuous precipitation (individual precipitates) and discontinuous precipitation (lamellae growth behind moving grain boundaries). The later precipitation was mainly observed with higher alloy content. Samples micrographs of these two types of precipitation are shown for reference in Figure 5.8.



Figure 5.8: TEM micrographs of nitrided Fe-Cr alloys (823K, 14hrs), after [48]

TEM micrographs of the nitrided Fe-2Cr alloy revealed continuous precipitation as well (Figure 4.40), although the magnification used doesn't allow resolving the morphology to the level shown in Figure 5.8. The estimated size of precipitates from the magnified view of Figure 4.40 correlates well with the one visible in Figure 5.8.

5.6.2 Hardening mechanism

The recorded hardness increase for the Fe-Cr alloy sample ranges from 664 to 891 HV and is related to the increase in Cr content (from 1.6 to 3% respectively). The model of precipitation hardening presented in §5.2.3 applies to the microstructure of finely dispersed precipitates observed with the Fe-Cr alloy. The estimated particles spacing giving rise to the observed hardness increase is about 20 to 30 nm (Eqn 5.5). This dimension is of the right order of magnitude when compared to the estimated size of the fine precipitate from Figure 4.40. A better estimate of the strengthening effect would require careful examination with TEM to determine the precipitate size and density to be used with Eqn 5.7. The reduced hardness at the surface of the Fe-2Cr sample has been noticed but can not be explained at this time.
The potential strengthening effect of precipitation during nitriding is clearly established when considering the gain realized by adding about 1.6% Cr to pure iron (which exhibits a hardness increase of ~30HV after nitriding). The increase in alloy content gives rise to a continuous increase in maximum hardness (Figure 5.7), as the volume fraction **f** of precipitates increase with the alloy content. A rough estimate for doubling the alloy content (1.6 to 3%) corresponds to a strengthening increase of $\sqrt{f} = \sqrt{2}$ (Eqn 5.7, assuming strong interaction for precipitation), which is closely followed by the hardness increase (664 vs. 891 HV).

Chapter 6

6 CONCLUSIONS

The objectives of this work were to review the principles of nitriding for iron and steel materials and to establish how the diffusion of N is affecting the microstructure of the material being treated. Careful selection of defined microstructures for a specific low alloyed steel enabled the study of the interaction between the diffusing N and the steel alloying elements. The nitriding of a Fe-Cr alloy of continuous Cr gradient was used to assess the role of nitride forming elements.

6.1 <u>Pure Iron</u>

Two different phases of iron-nitride precipitates (γ '-Fe₄N and α "-Fe₁₆N₂) were observed in the diffusion case area and the effect of higher cooling rate was found to be detrimental to the formation of these phases. The surface compound layer exhibited significant porosity, which was explained by the decomposition of the metastable nitrides and the desorbtion of molecular N₂. The measured hardening effect produced by the nitriding process was found to be very marginal, unless the metastable α ' phase (N martensite) was produced by rapid cooling (liquid quenching) from the nitriding temperature.

6.2 <u>1070 Alloy Steel</u>

Three different microstructures were evaluated after nitriding. The pearlitic and spheroidized microstructures did not significantly beneficiate from the diffusion of N. This was explained by the limited amount of carbide precipitates available to form carbonitrides. The strengthening mechanism for these microstructures was very similar to pure iron.

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The martensitic microstructure was tempered during the thermal treatment provided by the nitriding operation. Carbides formed during this tempering treatment were available to react with the diffusing N to form carbonitrides. The resulting hardening was as high as 130 HV. Similar hardening effect was also observed for the addition of as low as 0.05%C.

6.3 <u>Fe-Cr Alloy</u>

The Fe-Cr alloy highlighted the extraordinary hardening effect resulting from the formation of a high density of fine precipitates, leading to a maximum hardness increase of about 900HV. The interaction between the alloy element and the diffusing N was studied as a function of the nitriding potential, temperature and alloy content.

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