SURFACE HARDENING OF
DUPLEX STAINLESS STEEL 2205

by

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\[1\] We certify that written approval has been obtained for any proprietary material contained therein.
...when you have eliminated the impossible, whatever remains, however improbable, must be the truth.

Sherlock Holmes
*The Sign of the Four*
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Nomenclature

Symbols

\( \alpha \)  
Low-temperature ferrite (bcc)

\( \alpha'' \)  
\( \text{Fe}_{16}\text{N}_2 \) (bct)

\( \alpha'_M \)  
Ferrous martensite (bct)

\( \alpha'_\text{Cr} \)  
Cr-rich ferrite (bcc) existing in the Fe–Cr system

\( \alpha_{\text{Fe}} \)  
Fe-rich ferrite (bcc) existing in the Fe–Cr system

\( \vec{g} \)  
Reciprocal lattice vector where \( |\vec{g}| = 1/d_{hkl} \)

\( \beta \)  
CALPHAD parameter related to the total magnetic entropy

\( \chi \)  
\( \text{Fe}_5\text{C}_2 \) (orthorhombic)

\( \delta \)  
High-temperature ferrite (bcc)

\( \epsilon \)  
\( \text{Fe}_{2.4}\text{C} \) (orthorhombic)

\( \epsilon' \)  
\( \text{Fe}_{2}\text{C}_{1-x} \) (hcp)

\( \gamma \)  
Austenite (fcc)

\( \gamma' \)  
\( \text{Fe}_4\text{N} \) (simple cubic)

\( \gamma'_M \)  
Martensitic austenite transformation product (fcc)

\( \gamma_{\text{C}} \)  
Carbon-expanded austenite

\( \gamma_{\text{N}} \)  
Nitrogen-expanded austenite

\( \mu \)  
Linear absorption coefficient
\( \mu_i^\phi \)  
Chemical potential of constituent \( i \) in the \( \phi \) state

\( \tau \)  
\( \text{Cr}_23\text{C}_6 \) (fcc)

\( \tau_C \)  
Critical temperature for magnetic ordering

\( \theta \)  
Fe\(_3\)C (orthorhombic)

\( \varepsilon \)  
Fe\(_2\)N\(_{1-x}\) (hcp)

\( \zeta \)  
Fe\(_2\)N (orthorhombic)

\( iL_{A,B,C}^\phi \)  
\( i \)-th order CALPHAD parameter representing the interaction of constituents A and B with C on the second sublattice

\( a, b, c \)  
Lattice parameters

\( a_{N_2} \)  
Chemical activity of \( N_2 \) gas

\( C_i \)  
Concentration of \( i \) in atomic fraction

\( d_{hkl} \)  
Interplanar spacing of the \( hkl \) planes

\( D_i^\phi \)  
Diffusion coefficient of element \( i \) in the \( \phi \) state

\( G_{M:N}^{h\phi} \)  
Molar Gibbs free energy of a compound in a hypothetical non-magnetic state where all interstitial sites are filled with nitrogen

\( G_{M:Va}^{h\phi} \)  
Molar Gibbs free energy of an element in a hypothetical non-magnetic state

\( G_m^\phi \)  
Total molar Gibbs free energy of a state \( \phi \) on formula unit basis

\( G_m' \)  
Total molar Gibbs free energy on atomic basis

\( H_i^{\text{SER}} \)  
Enthalpy of the stable state of element \( i \) at 298.15 K and 1 atm

\( I_{hkl} \)  
Integrated diffracted intensity of peak \( hkl \)

\( p_i \)  
Partial pressure of \( i \)

\( R \)  
Universal gas constant = 8.3145 J K\(^{-1}\) mol\(^{-1}\)

\( R_{hkl} \)  
Substance- and peak-dependent parameter relating the volume fraction of two phases to the integrated diffracted intensity

\( T \)  
Absolute temperature
NOMENCLATURE

\[ T_A \] Activation temperature

\[ t_A \] Activation time

\[ t_C \] Carburization time

\[ T_N \] Nitriding temperature

\[ t_N \] Nitridation time

\[ V_\alpha \] Ferrite volume fraction

\[ V_\gamma \] Austenite volume fraction

\[ W_i \] Concentration of \( i \) in weight fraction

\[ X_i \] Concentration of \( i \) in mole fraction

\[ Y_i \] Site fraction of \( i \)

\[ excess G_m^\phi \] Excess energy of mixing contribution to the molar Gibbs free energy

\[ ideal G_m^\phi \] Ideal entropy of mixing contribution to the molar Gibbs free energy

\[ mag G_m^\phi \] Magnetic contribution to the molar Gibbs free energy of a solution

\[ mech G_m^{h\phi} \] Mechanical mixture of pure components contribution to the molar Gibbs free energy

\[ pres G_m^\phi \] Pressure contribution to the molar Gibbs free energy of a solution

Acronyms

AES Auger electron spectroscopy

AFM Atomic force microscopy

APT Atom probe tomography

ASS Austenitic stainless steel

\( bcc \) Body-centered cubic

\( bct \) Body-centered tetragonal

BF Bright-field
BSE Back-scattered electrons
CALPHAD CALculation of PHAse Diagram
CBED Convergent-beam electron diffraction
CCT Critical crevice corrosion temperature
CPT Critical pitting temperature
Cr_{eq} Chromium equivalent
DBT Ductile-brittle transition
DF Dark-field
DSS Duplex stainless steel
EBSD Electron back-scatter diffraction
fcc Face-centered cubic
FIB Focused ion beam
FSS Ferritic stainless steel
GI-XRD Glancing incidence X-ray diffraction
HAADF High-angle annular dark field
hcp Hexagonal close-packed
HR High-resolution
K-S Kurdjumov-Sachs orientation relationship
LEAP Local electrode atom probe
L/LT/ST L = longitudinal; LT = longitudinal transverse; ST = short transverse directions in wrought material
MFM Magnetic force microscopy
MSS Martensitic stainless steel
Ni_{eq} Nickel equivalent
NT Non-treated
<table>
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<tr>
<th>Abbreviation</th>
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<tr>
<td>N-W</td>
<td>Nishiyama-Wassermann orientation relationship</td>
</tr>
<tr>
<td>PHSS</td>
<td>Precipitation-hardening stainless steel</td>
</tr>
<tr>
<td>PIII</td>
<td>Plasma immersion ion implantation</td>
</tr>
<tr>
<td>ppm</td>
<td>Parts per million</td>
</tr>
<tr>
<td>PREN</td>
<td>Pitting resistance equivalent number</td>
</tr>
<tr>
<td>ROI</td>
<td>Region of interest</td>
</tr>
<tr>
<td>SAED</td>
<td>Selected-area electron diffraction</td>
</tr>
<tr>
<td>SCC</td>
<td>Stress-corrosion cracking</td>
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<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
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<tr>
<td>SER</td>
<td>Standard element reference at 298.15 K and 1 atm</td>
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<td>SE</td>
<td>Secondary electrons</td>
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<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>TGF</td>
<td>Total gas flow</td>
</tr>
<tr>
<td>TKD</td>
<td>Transmission Kikuchi diffraction</td>
</tr>
<tr>
<td>TTT</td>
<td>Time–temperature–transformation</td>
</tr>
<tr>
<td>XEDS</td>
<td>X-ray energy-dispersive spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
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Surface Hardening of Duplex Stainless Steel 2205

Abstract

by

JOHN CHRISTIAN DALTON

Increased use of second-generation duplex stainless steels is expected as demands for tougher, more economical, and corrosion resistant alloys increase. A novel gas-phase carburizing and nitriding procedure operating in the temperature range of 325 °C to 440 °C was utilized with the intent of improving both the tribological and electrochemical performance of the 2205 duplex alloy (22Cr–5Ni–3Mo–0.15N) under so-called paraequilibrium conditions. A suite of state-of-the-art microchemical and structural characterization tools were employed following each treatment, and performance of the treated alloys assessed by chloride-based cyclic polarization and nano-indentation hardness measurements. Particular emphasis was placed on understanding the response of the ferritic phase, which has been a source of speculation and confusion since the development of such treatments. CALPHAD-based thermodynamic modeling was also used to predict phase stability in the 2205 system subjected to gas-phase paraequilibrium nitridation or carburization.

Analysis of the interstitially-hardened layer in the austenitic phase of 2205 provides results consistent with similar surface hardening treatments of single-phase austenitic stainless steels: a colossally supersaturated and precipitate-free hardened layer of expanded austenite is formed. The interstitial concentration, case depth, and concomitant mechanical properties can be tailored through control of the temperature, duration, and chemical activity with the gas-phase process.

Spatially-resolved chemical and structural analysis within the δ-ferrite of 2205 revealed two competitive transformation behaviors following nitridation, while carburization led to only one response. For both carburization and nitridation, carbon or nitrogen supersaturations in ferrite on the order of 20 at.% and 25 at.%, respectively, were observed—greater than $10^6$ times the equilibrium concentration at room temperature, yet remarkably with unmeasurable expansion or distortion of the bcc lattice. These supersaturated ferrite grains appear ‘featureless’ in the TEM, suggesting the presence of a high density of strain centers. High-resolution TEM revealed that, unlike austenite, ferrite may accommodate colossal concentrations of carbon or nitrogen through...
the formation of an ultra-high density dislocation network $\geq 10^{16}$ m$^{-2}$, as opposed to occupation of lattice-expanding interstitial sites. These linear defects, presumably formed during yielding under the large residual stresses of restricted lattice expansion, enhanced the kinetics of spinodal-like decomposition of the ferrite to nm-scale Fe-rich ($\alpha_{Fe}$) and Cr-rich ($\alpha'_{Cr}$) ferrite domains within the carburized or nitrided layer, and apparently provide lower-energy sites for carbon and nitrogen than in potential secondary phases.

Elsewhere in the case of nitrided 2205, an isothermal, nitrogen-induced ferrite-to-austenite phase transformation occurred due to the potent austenite-stabilizing nature of nitrogen. The austenite transformation product formed in a partitionless manner from the parent ferrite with a high-aspect-ratio plate-like morphology in Nishiyama–Wassermann orientation relationship. These, and other microstructural signatures lead to the conclusion that the austenite formed by a shear-like mechanism characteristic of martensitic reactions. The microstructural evolution of these phase transformations in $\delta$-ferrite accompanying low-temperature nitridation of 2205, and lack of carburization-induced transformation of ferrite to austenite, are discussed in light of the chemical and strain energies involved.
Chapter 1
Overview

1.1 Paraequilibrium and the Formation of Expanded Austenite

It is often the case that a material’s in-service performance is regulated by its surface properties and interaction with other media. Stainless steels—ferrous alloys with at least 12 wt.% Cr—are a superlative example, most often utilized for the adherent and chemically-inert chromium-rich oxide film present on the surface. It is this passive film that prevents the base metal from corroding, and is self-healing should the steel be scratched. Stainless steels however are not particularly suited for high-wear or abrasive environments, due in part to their relative softness compared to conventional carbon and alloy steels, thus limiting their more widespread use.

Thermochemical surface engineering treatments such as carburizing and nitriding are well-established industrial processes that have long been used to improve the mechanical and electrochemical performance of metallic materials via formation of a carbidic or nitridic surface layer. Certain technical barriers prevailed for many years in applying these treatments to stainless steels. Namely, the same surface oxide that imparts excellent corrosion resistance also impedes the inward diffusion of carbon or nitrogen atoms needed to create the hardened surface layer (the case). Furthermore, were the oxide to somehow be removed and the stainless steel treated by conventional thermochemical techniques, it would result in a dramatic decrease in corrosion resistance through sensitization of the alloy by precipitation of chromium nitride or carbide phases at grain boundaries\(^1\). This loss of chromium from solid solution precludes the alloy from passivation. It would therefore be futile in the eyes of the engineer to treat such an alloy and lose the primary property that it was likely chosen for in the first place. Yet to do so without compromise of the outstanding ductility and corrosion-resistance intrinsic to stainless steels would be certain to increase their utility and function in many demanding applications.

\(^1\)This is not to be confused with precipitation-hardening stainless steels (PHSS), whereby non-chromium intragranular precipitates are deliberately used to impart hardening.
1.1. PARAEQUIL. AND THE FORMATION OF EXPANDED AUSTENITE

Perhaps surprisingly, only in the last two or three decades have a variety of novel, low-temperature thermochemical processes been developed that have been shown to improve the surface hardness, wear-, and fatigue-resistance of austenitic stainless steels to unprecedented levels, without attenuation of corrosion resistance [1–5]. In fact, under optimal processing conditions such processes can remarkably lead to an improvement in corrosion resistance [6–9].

This rare feat of enhancing nearly all desirable properties of a material with no loss (save the additional processing costs) is achieved by diffusing immense concentrations of carbon and/or nitrogen into the surface of a workpiece under so-called paraequilibrium conditions, whereby precipitation of deleterious phases is kinetically suppressed, and the approach to (metastable) equilibrium determined only by the diffusion of interstitial species. At low temperatures typical of these processes (≤ 470 °C), the interstitial species can diffuse considerable distances while the substitutional solutes cannot. Such a ‘colossal’ supersaturation of interstitials—many orders of magnitude higher than the equilibrium concentration—is made possible by the high affinity of stainless steel alloying elements (e.g. Cr, Mo, Mn, etc.) for carbon and nitrogen.

The enhanced performance of stainless steels achievable through paraequilibrium surface modification has since emerged as a major research interest with great practical importance. It has opened the door for a range of applications not normally considered for stainless steels, improved those existing, and as is true of most engineered materials, allowed metastable states (extremely) far from equilibrium to be explored.

Despite how much is currently known about the nature and properties of this nitrogen- or carbon-supersaturated austenite (so-called expanded austenite\(^1\), S-phase, \(\gamma_N\), or \(\gamma_C\)), it is still very much an enigma. Most of the conventional wisdom stems from treatments of single-phase austenitic stainless steels (typically AISI 316L type) which represent only a small fraction of the total stainless steel market. This is in part due to the fact that face-centered cubic (fcc) matrices are able to accommodate much higher levels of carbon and nitrogen; that is, they possess a higher (metastable) paraequilibrium solubility limit for these interstitials than body-centered cubic (bcc) ferrite. Precipitation of pernicious secondary phases in ferrite (or martensite) at low temperatures is also generally more difficult to avoid due to more rapid transformation kinetics.

In short, the microstructural response of ferrite to paraequilibrium surface treatments in ferrite-containing stainless steels is largely unexplored.

\(^1\)This moniker is adopted throughout the remainder of this work.
1.2 Driving Force

Stainless steel is obviously not to be used where a lower-alloy, i.e. lower-cost, carbon steel will suffice. However, if strength and toughness are required where resistance to corrosion is imperative, stainless steels are the clear winner. The long-standing austenitic family, containing nominally 18 wt.% Cr and 8–12 wt.% Ni, are extensively used in chemical, nuclear, and food processing applications due to their ease of formability, excellent toughness at low or high temperatures, and overall good corrosion resistance. They are however also the most expensive grades due to their high nickel contents. Nickel, the primary alloying element in austenitic stainless steels next to chromium, is indeed one of the most expensive, as shown in Fig. 1.1.

![Figure 1.1: Global price fluctuations of the most common stainless steel constituents since 1970 [10].](image)

Fortunately, with advances in steelmaking technology came development and com-
mmercialization of new stainless steel varieties—the nitrogen-alloyed duplex grades (equal portion of austenite and δ-ferrite) being the newest, and those which are projected to grow most in the near future. The duplex stainless alloys, while containing much less nickel, offer improved strength and corrosion resistance over the austenitic variety at a fraction of the cost. Hence, from both a performance and economical perspective, a duplex grade may be more appealing in some applications than the more conventional austenitics. Unfortunately, less is known about how this class of stainless steels respond—in particular the ferritic phase—to paraequilibrium interstitial-hardening surface treatments that could otherwise be used to optimize their already outstanding performance.

It is of interest then to determine whether a similar improvement in performance is attainable in duplex stainless steels by low-temperature interstitial-hardening as has been demonstrated for austenitic grades. To that end, a more general understanding of the microstructural modifications giving rise to a change in properties is desirable for optimizing treatment of a given alloy.

In the few existing studies on surface-hardened duplex alloys, the data are scant and at times unreliable. Prior research in this area has led to many conflicting and sometimes confusing interpretations of the transformation behavior in the ferritic phase, which is mostly based on more global characterization techniques.

As 2205 (UNS no. S32205) is the most commonly used grade, it is the natural choice for further inquiry. Gas-phase interstitial-hardening processes are also preferred to plasma or ion-based techniques since they enable systematic study of the underlying thermodynamics and kinetics associated with the process. In addition to its attractive combination of mechanical and electrochemical properties, 2205 also provides an interesting method by which to study the individual response of austenitic and ferritic stainless steels simultaneously.

Perhaps the greatest certainty revealed by former studies on surface hardening of ferrite-containing stainless steels is that a fundamentally different response occurs. A detailed study of phase transformations and interstitial–matrix interactions in these steels at the atomistic scale would help fill a major gap in our understanding of this phenomena.

1.3 Scope of Research

Previous investigations at Case Western Reserve University (CWRU) on the paraequilibrium carburization of 2205 have been conducted with promising results [11]. Based on these, and similar paraequilibrium treatments at CWRU on austenitic, ferritic, and martensitic precipitation-hardening grades, the initial questions at the start of this investigation included:

- Can an improvement in desirable properties be obtained by low-temperature gas-
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phase nitriding of 2205?
○ What are the optimal processing parameters (time, temperature, nitrogen activity) for successful nitridation of this alloy?
○ How does each phase respond to a given treatment under these far-from-equilibrium conditions, from the micro- to atomistic-scale?
○ Can carbon or nitrogen be interstitially-dissolved in stainless ferrite to ‘colossal’ levels imposed via kinetic constraints?
○ How does the $bcc$ lattice accommodate large concentrations of interstitial species? Does it expand uniformly as observed for single-phase stainless austenite under a state of residual biaxial compression?
○ Does the ferrite remain ferromagnetic and/or how does its magnetic character change?
○ What secondary phases form within ferrite, under what conditions, and how do they affect physical properties?
○ Can an isothermal, nitrogen-induced allotropic phase transformation of ferrite to austenite take place upon low-temperature nitridation (or carburization), as previously postulated?
○ If so, what are the transformation mechanisms and structural evolution of this isothermal, compositionally-driven $\delta \rightarrow \gamma$ phase transformation?

The widely accepted CALPHAD-based approach to computational thermodynamics was first used to predict phase stability in the 2205 system subjected to nitridation or carburization treatment. The solubility limits of nitrogen and carbon in the ferritic and austenitic phases were determined (i) under constraints in which secondary phases are assumed to be kinetically suppressed and the approach to metastable paraequilibrium determined only by the chemical potential of interstitial species, and (ii) when secondary paraequilibrium carbide or nitride phases (i.e. those inheriting base metal chemistry) have formed. The plausibility of an isothermal nitrogen- or carbon-induced $\delta \rightarrow \gamma$ phase transformation in the 2205 system was also assessed.

It is worth mentioning here so as to prevent later confusion that the symbol $\delta$ is henceforth used to describe the ferritic phase of 2205 in lieu of the more common $\alpha$. This is to illustrate the fact that the ferrite in the alloy retained at room temperature is the high-temperature allotrope formed first during solidification of the melt and sustaining no further phase transformation upon cooling. The solid-state phase transformation of some $\delta$-ferrite to austenite occurs as the alloy is further cooled.

Following the established Swagelok® SAT12™ process for low-temperature carburization of AISI 316L ferrules, an experimental matrix using the treatment temperature and nitrogen activity as the primary processing parameters was devised. Nitridation, carburization, and nitrocarburization experiments were conducted at CWRU with use of a versatile furnace capable of variable atmosphere heat-treatments. This was then followed by
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mechanical, microstructural, and microchemical characterization of the diffusional layer within each phase.

With regard to the materials science and engineering axiom in which a material’s structure, controlled through processing, is related to its properties, culminating in its end performance (*function*), a more top-down approach is laid out in this work. The performance of the alloy following treatment is first evaluated, followed by structural and chemical characterization by more global techniques. After a general understanding of the ‘bulk’ material is made, the fine microstructure is studied with high spatial resolution in the electron microscope.
Chapter 2

Background

2.1 Stainless Steel

With the exception of concrete, ferrous alloys are the most ubiquitous engineered materials on Earth. Since iron smelting first began in Anatolia circa 1900 B.C. it has almost become synonymous with a prosperous nation. Steels, or alloys of iron and carbon, are found in thousands of applications ranging from the trite paper clip to critical components such as aerospace landing gear. World annual production of steel is over 2 billion metric tonnes—two orders of magnitude more than the next closest aluminum alloys, and more than all other metals combined [10]. Steel’s great success lies in its versatile range of properties, the relative abundance and ease of extraction of iron, and ease of production. By engineering the microstructure through proper alloying and heat-treatments, steels can be produced with strengths ranging from ~200 to 5000 MPa, while maintaining significant ductility.

Despite the staggering numbers of steel production, only a minor fraction falls under the class of stainless steels, i.e. iron–chromium alloys that do not rust in what are assumed to be fairly benign environments. Stainless steels are no exception; like most metallic materials (save gold, platinum, and palladium) they spontaneously react with oxygen in the atmosphere. The minimum concentration of 11–12 wt.% chromium (that required for Cr$_2$O$_3$ stability) ensures that it is the chromium which preferentially reacts at the surface, forming a molecularly-thin, transparent, chromium-rich oxide. This passive film, which is inert in most environments, does not spall from the surface due to the similarity of its molar volume with the metal matrix\textsuperscript{1}. Stainless steels possess good corrosion resistance in a variety of media, though no grade is universally applicable. In addition to resisting corrosion, stainless steels provide excellent combinations of strength and tough-

\textsuperscript{1}The Pilling–Bedworth (PB) ratio of iron oxides (FeO, Fe$_2$O$_3$, Fe$_3$O$_4$) is greater than 2, and thus the large intrinsic stresses present in iron oxides formed on steels often lead to their spallation. Chromium oxide (Cr$_2$O$_3$) on stainless steels has a PB ratio just less than 2, indicating that it forms with a robust interface, effectively passivating the surface.
ness, some even at cryogenic and near-melting-point temperatures. They are, however, also characterized by low hardness relative to conventional carbon and alloy steels, and therefore exhibit poorer tribological performance, impeding their more widespread use.

Stainless steels are produced through a two-step process. The melting of scrap and ferrous alloys is first conducted in an electric arc furnace (EAF), followed by a refining procedure to remove impurities and finely tune carbon and nitrogen contents. The refinement method has changed dramatically since the advent of the argon-oxygen decarburization (AOD) process in the 1970s [12].

Stainless steels are divided into five classes according to their microstructure: the ferritic (FSS), austenitic (ASS), martensitic (MSS), duplex (DSS), and precipitation-hardening (PH) grades (which are further subdivided into the austenitic or martensitic PHSS). The general characteristics of each class are described in Table 2.1. The major weakness of ASS is their susceptibility to chloride-based stress-corrosion cracking (SCC). The FSS are more immune to SCC, but have a lower hardness, and therefore poorer wear-resistance than the MSS and PHSS grades. Duplex grades have a higher strength than the austenitics and are tougher than the ferritics. Relative to the other classes, they also possess superior resistance to localized pitting, crevice corrosion, and SCC, especially in chloride-containing environments.

Despite their excellent mechanical properties, stainless steels are most often chosen in a particular application for their corrosion resistance, without which they would find little use as their mechanical properties can be equaled or exceeded by much less-expensive carbon steels. The majority tonnage is used in structural applications within the chemical and power engineering sectors [12], by virtue of their large production figures, but they are also chosen in many applications for more aesthetic purposes. A breakdown of typical stainless steel usage is presented in Table 2.2.

### 2.1.1 The Fe–Cr–Ni System

Stainless steels are best understood by analysis of the Fe–Cr–Ni ternary system. Next to chromium, nickel is the second most common alloying element in stainless steels, serving to stabilize the austenite at room temperature and delay the formation of brittle intermetallics. An isometric projection of the Fe–Cr–Ni phase diagram is shown in Fig. 2.1 revealing only three solid phases for nickel contents realistic of stainless steels: \(\alpha\)-ferrite, \(\gamma\)-austenite, and intermetallic \(\sigma\) phase. This ternary phase diagram alone accounts for three of the five stainless steel classes. A cross-section of the diagram at 70 wt.% Fe–30 wt.% Ni reveals how a dual or ‘duplex’ microstructure of ferrite and austenite can be achieved\(^1\). Other elements, e.g. molybdenum, manganese, silicon, cobalt, aluminum, copper, carbon,

\(^1\)Although not indicated in Fig. 2.1, the symbol \(\delta\) is henceforth used when describing the ferritic phase of a DSS, which first solidify as ferrite, to distinguish it from the lower-temperature \(\alpha\) form.
and/or nitrogen are added to improve particular properties, and from which a multitude of other stable and metastable phases can form, making the processing of stainless steels no trivial task. Molybdenum, for example, is commonly added to improve pitting and crevice corrosion resistance, but also increases the tendency for detrimental intermetallic phases to form, and is therefore usually limited to lower concentrations [15]. However useful equilibrium phase diagrams might be, they are rarely proficient in
2.1. STAINLESS STEEL

Table 2.2: Application field for stainless steels [12].

<table>
<thead>
<tr>
<th>Application</th>
<th>Percentage of Market</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Industrial Sectors</strong></td>
<td></td>
</tr>
<tr>
<td>Chemical and Power Engineering</td>
<td>34</td>
</tr>
<tr>
<td>Food and Beverage Industry</td>
<td>18</td>
</tr>
<tr>
<td>Transportation</td>
<td>9</td>
</tr>
<tr>
<td>Architecture</td>
<td>5</td>
</tr>
<tr>
<td><strong>Consumer Goods</strong></td>
<td></td>
</tr>
<tr>
<td>Domestic Appliances, Household Utensils</td>
<td>28</td>
</tr>
<tr>
<td>Small Electrical and Electronic Appliances</td>
<td>6</td>
</tr>
</tbody>
</table>

Figure 2.1: Ternary Fe–Cr–Ni phase diagram [14]. Note ‘S’ represents liquid.
predicting the microstructure following solidification of multi-constituent alloys. The
eponymous Schaeffler diagram [16] shown in Fig. 2.2 was developed as a more pragmatic
approach, which divides the primary stainless steel alloying elements into two groups:
the austenite and ferrite stabilizers. The stainless steel alloying elements are converted to

\[
\text{Cr}_{eq} = \%Cr + \%Mo + (1.5 \times \%Si) + (3 \times \%Ti) + (0.5 \times \%Nb) \\
\text{Ni}_{eq} = \%Ni + (30 \times \%C) + (20 \times \%N) + (0.5 \times \%Mn)
\]

Depending on the \( \text{Cr}_{eq} \) and \( \text{Ni}_{eq} \), the diagram is broken up into different regions representing ferritic, austenitic, martensitic, and duplex microstructures. Though the Schaeffler diagram is empirical and various expressions for the \( \text{Cr}_{eq} \) and \( \text{Ni}_{eq} \) have been proposed since its conception, it is still of practical importance when understanding how particular elements affect the microstructure of a stainless steel.

\(^1\)The \( \text{Cr}_{eq} \) and \( \text{Ni}_{eq} \) of 2205 are 26 and 9, respectively.
2.1.2 Duplex Stainless Steels

The duplex class of stainless steels are those metallurgically designed to contain roughly equal portions (by volume) of austenite and δ-ferrite at room temperature. The equal proportion of each phase leads to the optimal balance of strength and general/localized corrosion resistance [17]. This is achieved, as is apparent from the Schaeffler diagram in Fig. 2.2, by increasing the Cr/Ni equivalent ratio relative to the austenitic family. A pseudo-binary phase diagram (similar to the cross-section in Fig. 2.1) for 70 wt.% iron and varying chromium and nickel content is shown in Fig. 2.3, revealing four unique solidification modes. As most duplex grades are high in chromium and low in nickel, they will first solidify as δ-ferrite. As the δ-ferrite is further cooled, some fraction undergoes

![Figure 2.3: Pseudo-binary Fe–Cr–Ni phase diagram at 70 wt.% Fe [14]. Note ‘S’ represents liquid.](image-url)
solid-state transformation to austenite, the nucleation and growth of which produces a lamellar distribution of austenite within the δ-ferrite matrix.

The DSS take advantage of the best attributes of each phase, and are substantially lower in cost to produce due to the lower nickel content (see Fig. 1.1). Within the five families of stainless steels, the DSS represent but 1% of the total stainless steel market [18, 19]; their use however is projected to grow most in coming years, with an estimated annual increase in production of more than 10%.

The industrial sectors where DSS are most widely used include the chemical, petro-chemical, pulp and paper, food, nuclear, pharmaceutical, and automotive, where they are typically employed for heat exchangers, distillation columns, storage and transportation tanks, oil and gas pipelines, desalination plants, reinforcement, and structural purposes [18–20]. They have been gradually replacing the AISI 300 series in a variety of applications due to their lower cost, higher strength, and improved corrosion resistance, with many opportunities only starting to be explored. Several more-recent, large-scale applications where DSS have superseded their austenitic kin are shown in Fig. 2.4.

The DSS were first produced, by chance, as far back as the 1930s in Sweden and France as Cr–Ni–Mo alloys [18]. These first-generation duplex alloys exhibited excellent mechanical and electrochemical properties, but their use was limited to the as-cast condition. When welding, the heat-affected zone (HAZ) contained excess ferrite and/or secondary phases, imparting lower toughness and corrosion resistance than the base material. The application field for DSS remained limited until the 1970s when the advent of the AOD process made the deliberate addition of nitrogen as an alloying agent possible, greatly improving weld-toughness and corrosion resistance\(^1\). Thus began the commercial origins of second-generation DSS, characterized by their high nitrogen content. Nitrogen allowed the duplex alloys to readily be welded using standard processes without compromising their performance.

UNS S32205 (22Cr–5Ni–3Mo–0.15N) quickly became the workhorse grade, which today accounts for more than 80% of all DSS in use [19]. In addition to this alloy’s lower cost, its higher strength allows for reduced wall thicknesses, and therefore reduced weight, in a variety of platforms.

The austenitic phase of 2205 is typically 1–2 at.% higher in nickel and manganese than the nominal composition, while the δ-ferrite is enriched by 1–2 at.% in chromium and molybdenum, due to chemical partitioning taking place during solidification and later high-temperature processing. The nitrogen (and residual carbon) is almost entirely concentrated within the austenite due to the very limited solubility of these species in ferrite (see Figs. 2.8 and 2.9).

\(^1\)Controlled additions of nitrogen in stainless steels have since been encouraged, as it is known to improve the strength, fatigue-life, work-hardening rate, and localized pitting/crevice corrosion resistance [13, 20, 21]. As a potent austenite stabilizer, nitrogen can also be used as a substitute for nickel.
DSS offer a number of favorable characteristics including: a high resistance to nearly all forms of corrosion (uniform, pitting, crevice, intergranular, stress-corrosion cracking), excellent mechanical properties, low thermal expansion, and superplastic behavior. The combination of improved performance over the commonly used austenitics make the DSS an attractive alternative. Their main limitation is in high- and low-temperature applications, where over a dozen phase transformations can occur that are detrimental to these desired properties. They are typically recommended for use between $-50 \, ^\circ\text{C}$, due to a ductile-to-brittle transition (DBT) of the ferrite, and $300 \, ^\circ\text{C}$, above which long exposures can lead to formation of the embrittling $\alpha'_\text{Cr}$ phase through a spinodal decomposition process [18].
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The ratio of $\delta$-ferrite and austenite can also change dramatically with small heat-to-heat variations in chemistry and minor changes in thermal history. Within the specification limits of UNS S32205, microstructures containing 30–90 vol.% $\delta$-ferrite were found by Eckenrod and Pinnow [22] depending on the thermal history. Care must also be taken during forging or cold-work due to the varying stress-state between each phase.

Using the most recent thermodynamic database, the calculated equilibrium phase diagram for the 2205 system as a function of nitrogen content is shown in Fig. 2.5. From this diagram, the equilibrium volume fraction of each phase as a function of temperature can also be determined, as shown in Fig. 2.6. To achieve an equal portion of austenite and ferrite at room temperature, 2205 is normalized at $\approx 1135 \, ^\circ\text{C}$ and quenched. It is clear
Figure 2.6: Calculated equilibrium phase fraction (Thermo-Calc® Software) in the 2205 system as a function of temperature [24].

that this two-phase alloy, like many other stainless steels, is in a highly metastable state during use under ambient conditions.

A stainless steel’s resistance to pitting corrosion, i.e. localized breakdown of the native oxide without repassivation, is often measured by its pitting resistance equivalent number (PREN), presented in Eq. 2.2 for the alloy composition in wt.%.

\[
\text{PREN} = \%\text{Cr} + 3.3(\%\text{Mo} + 0.5 \times \%\text{W}) + 16 \times \%\text{N} \tag{2.2}
\]

Sustainability in chloride environments requires a PREN greater than 30. DSS 2205, with a PREN of 36, is well-suited for aqueous chloride environments. There are in general three subcategories of duplex grades, each designed for a specific corrosion media: the lean
### Table 2.3: Composition (in wt.%) and PREN of various duplex and austenitic grades [19].

<table>
<thead>
<tr>
<th>Grade</th>
<th>UNS</th>
<th>C</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>W</th>
<th>Cu</th>
<th>N</th>
<th>PREN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lean Duplex</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2101</td>
<td>S32101</td>
<td>0.03</td>
<td>21.5</td>
<td>1.5</td>
<td>0.3</td>
<td>–</td>
<td>–</td>
<td>0.22</td>
<td>25</td>
</tr>
<tr>
<td>2304</td>
<td>S32304</td>
<td>0.02</td>
<td>23</td>
<td>4</td>
<td>0.3</td>
<td>–</td>
<td>0.3</td>
<td>0.10</td>
<td>25</td>
</tr>
<tr>
<td>Standard Duplex</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1803</td>
<td>S31803</td>
<td>0.02</td>
<td>22</td>
<td>5.5</td>
<td>3.0</td>
<td>–</td>
<td>–</td>
<td>0.17</td>
<td>35</td>
</tr>
<tr>
<td>2205</td>
<td>S32205</td>
<td>0.03</td>
<td>22.5</td>
<td>5.8</td>
<td>3.2</td>
<td>–</td>
<td>–</td>
<td>0.17</td>
<td>36</td>
</tr>
<tr>
<td>Superduplex</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2750</td>
<td>S32750</td>
<td>0.02</td>
<td>25</td>
<td>7</td>
<td>4.0</td>
<td>–</td>
<td>0.5</td>
<td>0.27</td>
<td>43</td>
</tr>
<tr>
<td>2760</td>
<td>S32760</td>
<td>0.03</td>
<td>25</td>
<td>7</td>
<td>3.5</td>
<td>0.6</td>
<td>0.5</td>
<td>0.25</td>
<td>42</td>
</tr>
<tr>
<td>Superaustenitic</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
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</tr>
<tr>
<td>904L</td>
<td>N08904</td>
<td>0.02</td>
<td>20</td>
<td>24.5</td>
<td>4.2</td>
<td>–</td>
<td>1.5</td>
<td>0.05</td>
<td>35</td>
</tr>
<tr>
<td>254 SMO</td>
<td>S31254</td>
<td>0.02</td>
<td>20</td>
<td>18</td>
<td>6.1</td>
<td>–</td>
<td>0.7</td>
<td>0.20</td>
<td>43</td>
</tr>
<tr>
<td>Austenitic</td>
<td></td>
<td></td>
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<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>304L</td>
<td>S30400</td>
<td>0.02</td>
<td>18.2</td>
<td>8.1</td>
<td>0.3</td>
<td>–</td>
<td>–</td>
<td>0.07</td>
<td>20</td>
</tr>
<tr>
<td>316L</td>
<td>S21600</td>
<td>0.02</td>
<td>16.3</td>
<td>10.1</td>
<td>2.1</td>
<td>–</td>
<td>–</td>
<td>0.07</td>
<td>24</td>
</tr>
<tr>
<td>317L</td>
<td>S31703</td>
<td>0.02</td>
<td>18.4</td>
<td>12.4</td>
<td>3.2</td>
<td>–</td>
<td>–</td>
<td>0.07</td>
<td>30</td>
</tr>
</tbody>
</table>

duplex with PREN < 30, the standard duplex with 30 < PREN < 40, and superduplex with a PREN > 40. The chemistry and PREN of several DSS within these subcategories are presented in Table 2.3, along with a comparison to several austenitics.

A critical temperature for pitting corrosion (CPT) is usually defined for each grade, above which a pit could be expected to develop within roughly 24 hours, and below which pitting should not be expected for an indefinite length of time [15]. The CPT is environment-dependent, and is usually presented as a range of temperatures to account for the stochastic nature of pitting initiation. A similar critical temperature exists for crevice corrosion (CCT), which further depends on the geometry of the crevice. Typically, the CCT is 15–20 °C lower than the CPT for the same grade and environment. For comparison, the CPT and CCT of 316L in Cl⁻-solutions are −10 °C and 10 °C, while for 2205 the CPT and CCT are 15 °C and 33 °C, respectively [20].
2.1. STAINLESS STEEL

Stress-corrosion cracking is a specific type of corrosion that can occur in the presence of an applied or residual tensile stress. The duplex grades are typically superior in SCC resistance to the austenitics and ferritics in almost all corrosion media. A stress of 5% the yield strength will initiate a crack in 316L in Cl⁻-solutions at 120 °C, while 35% of the yield strength is required for 2205 to initiate a crack in the same solution. The standard AISI 300 series are typically susceptible to SCC above 60 °C, while the duplex grades are virtually immune below 150 °C [20].

Notable differences between the native oxide present on DSS relative to the other classes account for their improved corrosion resistance. In addition to the higher chromium content, a less-defective passive film was observed by Cheng et al. [25] on 2205 compared to 316L, thereby promoting slower diffusion kinetics. Despite this, and other known passive film properties, the synergy between each alloying element, as well as the addition of nitrogen on the stability of the passive film in DSS is an on-going investigation.

2.1.3 Phase Transformations in Duplex Stainless Steels

The study of phase transformations in DSS is worthy of a course in its own right. The family of DSS are subject to nearly every type of solid-state phase transformation including: eutectoid decomposition, precipitation reactions, martensitic reactions, spinodal decomposition, and combined reactions—most all of which compromise the mechanical properties and corrosion resistance of the alloy when they occur. Some of the more common phases observed in DSS are presented in Table 2.4. Most form only at higher temperatures, and can be avoided by carefully controlling the chemistry and heat-treatments.

Many of these deleterious phases precipitate within the δ-ferrite as a result of more rapid diffusion and transformation kinetics. The empirical time–temperature–transformation (TTT) diagram for 2205 is shown in Fig. 2.7. The other intermetallics not labeled on the TTT diagram form within the higher-temperature ‘C’-curve.

The \( \alpha \rightarrow \alpha_{Fe} + \alpha'_{Cr} \) phase separation\(^{1}\) into Fe-rich \( \alpha_{Fe} \) and Cr-rich \( \alpha'_{Cr} \) phases is the limiting factor for higher-temperature use, resulting in embrittlement and loss of toughness. The transformation can occur anywhere between 300 °C (thousands of hours) and 600 °C (a few minutes) [28]. It occurs rather quickly at a critical temperature of 475 °C and has been deemed in some circles as ‘475 °C embrittlement’.

In addition to embrittlement, the \( \alpha \rightarrow \alpha_{Fe} + \alpha'_{Cr} \) phase separation can also deteriorate the alloy’s resistance to corrosion [29–38]. The extent of deterioration is a strong function of alloy composition, aging time and temperature, and the corrosion media. In many studies, the passivating capability was only significantly affected when the aging at 400 °C lasted longer than 1,000 hours [30, 32, 35, 37], although embrittlement occurred much

\(^{1}\)This phase transformation can occur via conventional nucleation and growth or through a spinodal decomposition process, depending on the alloy composition and aging temperature.
2.1. STAINLESS STEEL

**Table 2.4: Secondary phases found in duplex stainless steels [17,21,26].**

<table>
<thead>
<tr>
<th>Phase</th>
<th>Unit cell</th>
<th>Atoms cell(^{-1})</th>
<th>Space Group</th>
<th>Lattice param. [nm]</th>
<th>Ideal composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intermetallic phases</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\sigma)</td>
<td>bct</td>
<td>30</td>
<td>(P4_2/mnm)</td>
<td>(a = 0.87–0.92)</td>
<td>(Fe,Ni)(_x)(Cr,Mo)(_y)</td>
</tr>
<tr>
<td>&amp;</td>
<td></td>
<td></td>
<td></td>
<td>(c = 0.4554–0.48)</td>
<td></td>
</tr>
<tr>
<td>(\chi)</td>
<td>bcc</td>
<td>58</td>
<td>(I\bar{4}3m)</td>
<td>(a = 0.881–0.895)</td>
<td>Fe(<em>{36})Cr(</em>{12})Mo(_{10})</td>
</tr>
<tr>
<td>&amp;</td>
<td></td>
<td></td>
<td></td>
<td>(Fe,Ni)(<em>{36})Cr(</em>{18})Mo(_4)</td>
<td></td>
</tr>
<tr>
<td>Laves</td>
<td>hcp</td>
<td>12</td>
<td>(P6_3/mmc)</td>
<td>(a = 0.473–0.483)</td>
<td>Fe(_2)Mo</td>
</tr>
<tr>
<td>((\eta))</td>
<td>rhomb.</td>
<td>13</td>
<td>(R3m)</td>
<td>(c = 0.772–0.786)</td>
<td></td>
</tr>
<tr>
<td>(\mu)</td>
<td>rhomb.</td>
<td>13</td>
<td>(R3m)</td>
<td>(a = 0.4762)</td>
<td>(Fe,Co)(_7)(Mo,W)(_6)</td>
</tr>
<tr>
<td>&amp;</td>
<td></td>
<td></td>
<td></td>
<td>(c = 2.5015)</td>
<td>(Cr,Fe)(_7)(Mo)(_2)(Cr,Fe,Mo)(_4)</td>
</tr>
<tr>
<td>Carbides</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{MC})</td>
<td>fcc</td>
<td>8</td>
<td>(Fm\overline{3}m)</td>
<td>(a = 0.4131–0.4698)</td>
<td>(Ti,Nb,V)C</td>
</tr>
<tr>
<td>(\text{M}_6\text{C})</td>
<td>fcc</td>
<td>112</td>
<td>(Fd\overline{3}m)</td>
<td>(a = 1.085–1.128)</td>
<td>(Fe,Mo,Nb,Cr)(_6)C</td>
</tr>
<tr>
<td>(\text{M}_7\text{C}_3)</td>
<td>ortho.</td>
<td>40</td>
<td>(Pnma)</td>
<td>(a = 1.3980)</td>
<td>(Cr,Fe)(_7)C(_3)</td>
</tr>
<tr>
<td>&amp;</td>
<td></td>
<td></td>
<td></td>
<td>(b = 0.6880)</td>
<td></td>
</tr>
<tr>
<td>&amp;</td>
<td></td>
<td></td>
<td></td>
<td>(c = 0.4523)</td>
<td></td>
</tr>
<tr>
<td>Nitrides</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{MN})</td>
<td>fcc</td>
<td>8</td>
<td>(Fm\overline{3}m)</td>
<td>(a = 0.4097–0.4577)</td>
<td>(Cr,Fe)N</td>
</tr>
<tr>
<td>(\text{M}_2\text{N})</td>
<td>trig.</td>
<td>9</td>
<td>(P\overline{3}1m)</td>
<td>(a = 0.478–0.480)</td>
<td>(Cr,Fe)(_2)N</td>
</tr>
<tr>
<td>&amp;</td>
<td></td>
<td></td>
<td></td>
<td>(c = 0.444–0.447)</td>
<td></td>
</tr>
</tbody>
</table>

earlier during aging. Tsuchiya et al. [39] observed pitting in the \(\delta\)-ferrite of a DSS after etching in a 10% HNO\(_3\) + 0.05% HF solution only when the \(\alpha_{Fe}\) decomposition product contained less than \(\approx 14\) at.% chromium—near the critical concentration required for passivation of a stainless steel (see Sec. 2.1).
2.2 Thermochemical Surface Engineering

The Fe–C system is perhaps the most well-known amongst any pupil of materials science and engineering. Lesser known, but still of technological significance, is the Fe–N system, both of which are here briefly reviewed for a proper understanding of any nitriding or carburizing case-hardening treatment of ferrous alloys. Special attention is made to the thermodynamically-controllable gas-phase nitriding process, where a high chemical activity of gaseous nitrogen, $a_{N_2}$, is used to realize significant concentrations of nitrogen in metals, but much of the discussion is applicable to gas-phase carburizing as well (utilizing CO or $C_2H_2$ gas, for example). Thermodynamically, the main difference between the two surface treatments is carbon’s stability as a solid at unit activity, which can precipitate in solid form within the metal if the chemical potential in solution reaches that of graphite. It is most commonly observed however that $\theta$-Fe$_3$C carbide (cementite) forms prior to graphite precipitation.

![TTT diagram of 2205 DSS](image-url)
2.2.1 The Fe–C System

The metastable\(^1\) Fe–Fe\(_3\)C phase diagram is shown in Fig. 2.8 for carbon concentrations up to 5 wt.% (\(\approx 20\) at.%). The vast majority of steels are hardened through various microstructural combinations of three primary phases: body-centered cubic (bcc) \(\alpha\)-ferrite, face-centered cubic (fcc) \(\gamma\)-austenite, orthorhombic Fe\(_3\)C-cementite, and a fourth, considering the metastable \(bct\) (body-centered tetragonal) \(\alpha'\) martensite phase that forms via a

\[
\begin{array}{c}
\text{Liquid} \\
\text{Liquid + Cementite} \\
\text{Austenite + Cementite (Fe}_3\text{C)} \\
\text{Austenite (}\gamma\text{-Fe)} \\
\text{A3} \\
\text{Fe} \\
\text{Ferrite (}\alpha\text{-Fe)} \\
\text{Ferrite + Cementite}
\end{array}
\]

\[
\begin{array}{c}
1538°C \\
1495°C \\
1394°C \\
1154°C \\
912°C \\
800°C \\
738°C (A\text{I}) \\
0°C
\end{array}
\]

\[
\begin{array}{c}
\text{Acm} \\
\text{A1} \\
\text{A3} \\
\text{A1} \\
\text{A3}
\end{array}
\]

Figure 2.8: The metastable Fe–Fe\(_3\)C (cementite) phase diagram calculated using the current CALPHAD parameters (Thermo-Calc\textsuperscript{\textregistered} Software).

The crystallographic information of stable and metastable phases found in the Fe–C

\(^{1}\)It should be remembered that \(\theta\)-Fe\(_3\)C is not thermodynamically stable with respect to graphite under STP (standard temperature and pressure) conditions. However, the kinetics of the cementite \(\rightarrow\) Fe + graphite decomposition are, for all practical purposes, too slow to be of concern in steels, and thus the metastable Fe–Fe\(_3\)C phase diagram is most common.
and Cr–C binary systems is presented in Table 2.5. Though of modest importance in the hardening of carbon steels, several paraequilibrium versions of these phases have been observed in 316L subjected to prolonged carburization, namely \( M_5C_2 \), \( M_7C_3 \), and \( M_{23}C_6 \), where \( M \) represents randomly distributed constituents on the metal sublattice with near base chemistry. Note that the \( Fe_7C_3 \) phase has been described by both trigonal and orthorhombic crystal systems. The important phase transitions within the Fe–C system are also given in Table 2.6.

### 2.2.2 The Fe–N System

Nitrogen was first noted to be dissolved in iron by Savart in 1828 [46] through the gas flow of ammonia over steel at high temperatures. It was not until later in the first half of the 20th century that a proper structural analysis of the nitride phases formed during these treatments was conducted by Hägg [47], and the thermodynamic description of ammonia gas-nitriding described shortly thereafter by Lehrer [48]. The first full determination of the metastable\(^1\) Fe–N phase diagram was conducted by Jack in the early 1950s [49], which is only marginally different from the currently accepted version of Wriedt et al. [50] shown in Fig. 2.9.

In Jack’s analysis, he found the interstitial solid solution phases \( \alpha \)-ferrite, \( \gamma \)-austenite, and \( \alpha'_M \)-martensite, along with compound phases \( \alpha''_M-Fe_{16}N_2 \), \( \gamma'-Fe_4N \), \( \varepsilon-Fe_2N_1-x \), and \( \zeta-Fe_2N \). The crystallographic information and stability range of each phase is presented in Table 2.7. Though most of the nitride phases are considered stable at STP, decomposition of \( \alpha'_M \)-martensite and \( \alpha''_M-Fe_{16}N_2 \) into \( \alpha \)-ferrite and \( \gamma'-Fe_4N \) given sufficient time and modest thermal energy has been observed [51]. Note that \( \gamma'-Fe_4N \) is normally treated as a stoichiometric compound, but does possess a narrow stability range as shown on the phase diagram, and is sometimes written more appropriately as \( Fe_4(N_1-x) \), where \( x \) represents the concentration of vacancies on the interstitial sublattice.

Several of the important phase transitions and reaction types within the Fe–N system are listed in Table 2.8.

#### 2.2.2.1 Crystal Structure of the \( \varepsilon \)-Phase

Some discussion is deserved concerning the \( \varepsilon \)-phase, or \( Fe_3N \) as it is most commonly written. The crystal structure is based on a hexagonal close-packed (hcp) arrangement of iron atoms with nitrogen occupation of the octahedral interstitial sublattice, and is isostructural with the stoichiometric trigonal \( Cr_2N \) phase found in the Cr–N system. The structure of the \( \varepsilon \)-phase—which has a wide stability range between 15–33 at.% nitrogen—has

---

\(^1\)Similar to the Fe–Fe\(_3\)C system, the phases present in the Fe–N phase diagram are not thermodynamically stable with respect to \( \alpha \)-ferrite and \( N_2 \) gas at STP, but decomposition kinetics are extraordinarily sluggish.
<table>
<thead>
<tr>
<th>Phase</th>
<th>Alias</th>
<th>Structure</th>
<th>Lattice Parameter</th>
<th>C&lt;sub&gt;c&lt;/sub&gt; [at. pct.]</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-Fe</td>
<td>ferrite</td>
<td>bcc (Im&lt;sub&gt;3&lt;/sub&gt;m)</td>
<td>0.28664</td>
<td>—</td>
</tr>
<tr>
<td>γ-Fe(C)</td>
<td>austenite</td>
<td>fcc (Fm&lt;sub&gt;3&lt;/sub&gt;m)</td>
<td>0.3572</td>
<td>—</td>
</tr>
<tr>
<td>α'ₘ-Fe(C)</td>
<td>martensite</td>
<td>bct (I&lt;sub&gt;4&lt;/sub&gt;/mm&lt;sub&gt;3&lt;/sub&gt;)</td>
<td>0.2859 0.2935 2.8</td>
<td>8.3</td>
</tr>
<tr>
<td>ε-Fe₂C₁₋ₓ</td>
<td>ε-phase</td>
<td>hcp (P&lt;sub&gt;6&lt;/sub&gt;&lt;sub&gt;3&lt;/sub&gt;22)</td>
<td>0.4767 0.4354</td>
<td>15.6–18.9</td>
</tr>
<tr>
<td>θ-Fe₃C</td>
<td>cementite</td>
<td>ortho. (Pnma)</td>
<td>0.45248 0.50896 0.67443</td>
<td>25</td>
</tr>
<tr>
<td>ε'-Fe₂₄C</td>
<td>ε'-carbide</td>
<td>hcp (P&lt;sub&gt;6&lt;/sub&gt;&lt;sub&gt;3&lt;/sub&gt;/mmc)</td>
<td>0.273 0.4313</td>
<td>29.4</td>
</tr>
<tr>
<td>Fe₇C₃</td>
<td>Eckström-Adcock carbide</td>
<td>hcp (P&lt;sub&gt;6&lt;/sub&gt;&lt;sub&gt;3&lt;/sub&gt;/mmc)</td>
<td>0.6882 0.4540</td>
<td>30</td>
</tr>
<tr>
<td>ω-Fe₇C₃</td>
<td>Fe₇C₃</td>
<td>ortho. (Pnma)</td>
<td>0.4537 0.6892 1.1913</td>
<td>30</td>
</tr>
<tr>
<td>τ-Cr₂₃C₆</td>
<td>τ</td>
<td>fcc (Fm&lt;sub&gt;3&lt;/sub&gt;m)</td>
<td>1.0659</td>
<td>20.7</td>
</tr>
<tr>
<td>Cr₇C₃</td>
<td>Cr₇C₃</td>
<td>ortho. (Pnma)</td>
<td>0.4532 0.7015 1.2153</td>
<td>30</td>
</tr>
<tr>
<td>Cr₃C₂</td>
<td>Cr₃C₂</td>
<td>ortho. (Pnma)</td>
<td>0.5540 0.2833 1.1494</td>
<td>40</td>
</tr>
</tbody>
</table>
### TABLE 2.6: Phase transitions in the Fe–C and metastable Fe–Fe₃C systems; G = gas and L = liquid [45].

<table>
<thead>
<tr>
<th>Reaction</th>
<th>C_C of each phase [at. pct.]</th>
<th>Temperature [°C]</th>
<th>Reaction Type</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Stable Fe–C (graphite) system</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>G ↔ L</td>
<td>0</td>
<td>2862</td>
<td>Boiling</td>
</tr>
<tr>
<td>L ↔ δ-Fe</td>
<td>0</td>
<td>1538</td>
<td>Melting</td>
</tr>
<tr>
<td>δ-Fe ↔ γ-Fe</td>
<td>0</td>
<td>1392</td>
<td>Allotropic</td>
</tr>
<tr>
<td>γ-Fe ↔ α-Fe</td>
<td>0</td>
<td>911</td>
<td>Allotropic</td>
</tr>
<tr>
<td>L + δ-Fe ↔ γ-Fe</td>
<td>2.34/0.40/0.74</td>
<td>1493</td>
<td>Peritectic</td>
</tr>
<tr>
<td>γ-Fe ↔ α-Fe + (C)</td>
<td>2.97/0.096/100</td>
<td>740</td>
<td>Eutectoid</td>
</tr>
<tr>
<td>L ↔ γ-Fe + (C)</td>
<td>17.1/9.06/100</td>
<td>1153</td>
<td>Eutectic</td>
</tr>
<tr>
<td>G ↔ graphite (C)</td>
<td>100</td>
<td>3826</td>
<td>Sublimation</td>
</tr>
<tr>
<td><strong>Metastable Fe–Fe₃C (cementite) system</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>γ-Fe ↔ α-Fe + Fe₃C</td>
<td>0.104</td>
<td>727</td>
<td>Eutectoid</td>
</tr>
<tr>
<td>L ↔ γ-Fe + Fe₃C</td>
<td>9.23</td>
<td>1147</td>
<td>Eutectic</td>
</tr>
<tr>
<td>L ↔ Fe₃C</td>
<td>25</td>
<td>1252</td>
<td>Congruent</td>
</tr>
</tbody>
</table>
Table 2.7: Crystallographic data of known phases present in the Fe–N and Cr–N systems [50].

<table>
<thead>
<tr>
<th>Phase</th>
<th>Alias</th>
<th>Structure</th>
<th>Lattice Parameter</th>
<th>$C_N$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>$a$ [nm]</td>
<td>$b$ [nm]</td>
</tr>
<tr>
<td>$\alpha$-Fe</td>
<td>ferrite</td>
<td>bcc $(I\bar{m}3m)$</td>
<td>0.28664</td>
<td>—</td>
</tr>
<tr>
<td>$\gamma$-Fe(N)</td>
<td>austenite</td>
<td>fcc $(Fm\bar{3}m)$</td>
<td>0.3572</td>
<td>—</td>
</tr>
<tr>
<td>$\alpha'_M$-Fe(N)</td>
<td>martensite</td>
<td>bct $(I4/mmm)$</td>
<td>0.2861 0.2936 2.8</td>
<td>0.2848 0.3120 9.5</td>
</tr>
<tr>
<td>$\alpha''$-Fe$_{16}$N$_2$</td>
<td>$\alpha''$</td>
<td>bct $(I4/mmm)$</td>
<td>0.572 0.629 11.1</td>
<td></td>
</tr>
<tr>
<td>$\gamma'$-Fe$_4$N</td>
<td>$\gamma'$</td>
<td>cubic $(Pm\bar{3}m)$</td>
<td>0.3798</td>
<td>19.3–20.0</td>
</tr>
<tr>
<td>$\epsilon$-Fe$<em>2$N$</em>{1-x}$</td>
<td>$\epsilon$</td>
<td>hcp $(P6_3/mmc)$†</td>
<td>0.2705 0.4376</td>
<td>≈15–33</td>
</tr>
<tr>
<td>$\zeta$-FeN</td>
<td>$\zeta$</td>
<td>ortho. $(P\bar{2}22)$</td>
<td>0.5525 0.4827 0.4422</td>
<td>33.3</td>
</tr>
<tr>
<td>$\gamma''$-FeN</td>
<td>$\gamma''$</td>
<td>fcc $(F\bar{4}3m)$</td>
<td>0.43</td>
<td>50.0</td>
</tr>
<tr>
<td>$\gamma'''$-FeN</td>
<td>$\gamma'''$</td>
<td>fcc $(Fm\bar{3}m)$</td>
<td>0.45</td>
<td>50.0</td>
</tr>
<tr>
<td>CrN</td>
<td>CrN</td>
<td>fcc $(Fm\bar{3}m)$</td>
<td>0.4148</td>
<td>50.0</td>
</tr>
<tr>
<td>Cr$_2$N</td>
<td>$\epsilon$</td>
<td>trig. $(P\bar{3}1m)$</td>
<td>0.4796 0.4470</td>
<td>30–33.3</td>
</tr>
</tbody>
</table>

† See Sec. 2.2.2.1
### Table 2.8: Phase transitions in the Fe–N system [50].

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$C_N$ of each phase [at. pct.]</th>
<th>Temperature [$^\circ$C]</th>
<th>Reaction Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_{\text{para.}} \leftrightarrow a_{\text{ferro.}}$</td>
<td>0</td>
<td>770</td>
<td>Curie point</td>
</tr>
<tr>
<td>$\gamma \leftrightarrow \alpha$</td>
<td>0</td>
<td>912</td>
<td>Allotropic</td>
</tr>
<tr>
<td>$\gamma \leftrightarrow \delta$</td>
<td>0</td>
<td>1394</td>
<td>Allotropic</td>
</tr>
<tr>
<td>$L \leftrightarrow \delta$</td>
<td>0</td>
<td>1538</td>
<td>Melting</td>
</tr>
<tr>
<td>$\varepsilon \leftrightarrow \gamma'$</td>
<td>19.5</td>
<td>680</td>
<td>Congruent</td>
</tr>
<tr>
<td>$\varepsilon \leftrightarrow \zeta$</td>
<td>33.3</td>
<td>$\geq$ 480</td>
<td>Congruent</td>
</tr>
<tr>
<td>$\gamma \leftrightarrow \alpha + \gamma'$</td>
<td>8.8/0.4/19.3</td>
<td>592</td>
<td>Eutectoid</td>
</tr>
<tr>
<td>$\varepsilon \leftrightarrow \gamma + \gamma'$</td>
<td>15.9/10.3/19.3</td>
<td>650</td>
<td>Eutectoid</td>
</tr>
<tr>
<td>$\gamma \leftrightarrow \alpha + \alpha''$ $^+$</td>
<td>...</td>
<td>...</td>
<td>Probably eutectoid</td>
</tr>
<tr>
<td>$L + \delta \leftrightarrow \gamma$ $^+$</td>
<td>11/3.5/6</td>
<td>1495</td>
<td>Probably peritectic</td>
</tr>
<tr>
<td>$L + \gamma + \varepsilon$ $^+$</td>
<td>...</td>
<td>...</td>
<td>Peritectic or eutectic</td>
</tr>
</tbody>
</table>

$^+$ Not observed, though conceptually possible
2.2. THERMOCHEMICAL SURFACE ENGINEERING

Figure 2.9: The metastable Fe–N phase diagram (after Wriedt et al. [50]). Note that $\gamma''$-$\text{Fe}_{16}\text{N}_2$ is unstable above $\approx 300 \degree C$.

been studied more than any other in the Fe–N system (cf. [52–63]). The structure has been described in terms of a (i) disordered trigonal $P\overline{3}12$ lattice, (ii) ordered trigonal supercell $P\overline{3}1m$ (ideal Fe$_2$N), (iii) ordered hexagonal supercell $P\overline{6}m2$ (ideal Fe$_3$N), and (iv) a disordered hexagonal $P\overline{6}3/mmc$ (Fe$_2$N$_{1-x}$) lattice. The arrangement of iron and nitrogen atoms within these proposed structures is depicted in Fig. 2.10.

Lee et al. attempted to unambiguously determine the long-range order of nitrogen in this ‘$M_2N$’ phase occurring in austenitic stainless steels by electron [65] and neutron [66] diffraction techniques. They concluded that nitrogen ordered such that the structure is best described by a trigonal supercell with $P\overline{3}1m$ symmetry, Fig. 2.10(d). Lee et al. [67] later determined by convergent beam electron diffraction (CBED) that electron irradiation induced disordering of nitrogen in the trigonal $P\overline{3}1m$ $M_2N$ supercell to a random distribution of nitrogen on octahedral interstices, as shown in Fig. 2.10(a) and described by
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Figure 2.10: Crystal structures describing the $\varepsilon$-phase in the Fe–N system [64]. (a) an hcp arrangement of iron atoms with ABAB stacking where octahedral interstitial sites (o.s.) are indicated, described by space group $P6_3/mmc$. (b) View of octahedral interstices in (a) whose sites are uniquely label as A1, A2, ..., C2. (c) Long-range nitrogen order (black sites) for an ideal Fe$_3$N structure ($P6_3m2$), (d) nitrogen occupation in ideal Fe$_2$N ($P\overline{3}1m$), and (e) structure compatible with $P6_322$ symmetry, but with random occupation of additional nitrogen (hatched sites), i.e. Fe$_3$N$_{1+x}$.

$\text{hcp } P6_3/mmc$ symmetry. Notably however, no mention of the metal or nitrogen composition of this phase was made in any of these analyses (stoichiometric M$_2$N being implicitly assumed).

A concurrent study by Liu et al. [64] was perhaps the most thorough structural analysis of the $\varepsilon$-phase by electron diffraction of homogenous Fe$_3$N$_{1+x}$ powders with nitrogen
2.2. THERMOCHEMICAL SURFACE ENGINEERING

contents varying from $0.00 \leq x \leq 0.39^1$. In their interpretation of diffraction patterns, they considered the possibility of double diffraction (performed by careful tilting experiments), which Lee et al. [67] did not, possibly leading to an erroneous conclusion. They determined that powders of Fe$_3$N$_{1.00}$, Fe$_3$N$_{1.30}$, and Fe$_3$N$_{1.39}$ possessed nitrogen order best described by a hexagonal supercell with $P6_322$ symmetry, Fig. 2.10(c), while a lower symmetry $P312$ form was observed in Fe$_3$N$_{1.22}$ and in some particles of Fe$_3$N$_{1.30}$. There is apparently no monotonous increase in occupational order of nitrogen between Fe$_3$N$_{1\pm x}$ and an ideal Fe$_2$N$_{0.99}$. The structure of the $\varepsilon$-phase is complex, to say the least.

Considering the unknown long-range order and/or stability range of nitrogen that may occur in paraequilibrium versions of the $\varepsilon$-nitride in stainless steel, the $\varepsilon$-Fe$_2$N$_{1-x}$ convention is adopted throughout the remainder of this work to describe this unique phase. When simulating electron diffraction and Kikuchi patterns for comparison with TEM and EBSD data, both the ordered and disordered versions of this phase were considered.

Lastly, when the nitrogen content of the Fe$_2$N$_{1-x}$ phase increases from 33.0 at.% to 33.2 at.% an anisotropic distortion of the $hcp$ lattice occurs, forming the stoichiometric and orthorhombic $\zeta$-Fe$_2$N phase [49, 68]. The FeN phase has not been observed during ammonia gas nitriding treatments, but has been produced through sputtering techniques [69, 70]. The structure was determined to be either that of ZnS$^2$ ($\gamma''$) or rock-salt NaCl ($\gamma'''$)—isostructural with CrN found in the Cr–N system.

2.2.3 Gas-phase Nitriding

Nitriding, in its various forms, is a routinely used thermochemical case-hardening process applied to low-alloy steels. The common techniques employed for nitriding include: gas (NH$_3$), salt-bath (cyanide- and cyanate-based), plasma, pulsed laser deposition, reactive magnetron sputtering, nitrogen implantation, and plasma immersion ion implantation (PIII) [71], each with their own inherent strengths and weaknesses. For instance, gas-phase nitriding, though it uses a hazardous gas, is a conformal, thermodynamically-controllable, and ambient pressure process, whereas plasma nitriding is faster and more environmentally sound, but requires vacuum and is ‘line-of-site’, and thus not suited for complex or internal geometries. Temperature and temperature uniformity are also more difficult to control with plasma-based processes.

The first industrial applications of gas-phase nitriding date back to the early 1900s with a patent by Machlet [72] and later Fry in 1921 [73] in a process that is essentially the same today. It is still the most common and versatile form of the various nitriding treatments.

---

1The maximum nitrogen content of Fe$_3$N$_{1+x}$ occurs at $x \approx 0.48$, i.e. Fe$_2$N$_{0.99}$, at which point a transformation to $\zeta$-Fe$_2$N occurs.

2It is unusual that nitrogen should be found in the tetrahedral interstices in the $fcc$ iron lattice, which are smaller and presumably higher-energy sites than octahedral interstices, but the evidence provided by the investigators is strong, and may occur during some preparation methods due to magnetic effects.
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The process permits simultaneous nitriding and carburizing if a carbon-containing source, e.g. CO or C\(_2\)H\(_2\), is also used. When performed in the austenitic regime, this treatment is referred to as carbonitriding (750 °C < \(T\) < 900 °C) or nitrocarburizing if in the ferritic regime (500 °C < \(T\) < 580 °C) [71]. Conventional gas-phase nitriding is conducted within the ferritic regime at temperatures between 500–600 °C, much lower than those involved in traditional carburizing, resulting in lower distortion and deformation of the workpiece. Carburization of ferrous alloys is typically conducted at temperatures ≥ 950 °C within the austenitic regime.

Gaseous nitriding involves the dissociation of ammonia, NH\(_3\), to liberate nascent (atomic) nitrogen for diffusion into the workpiece by complex physical and chemical means. The resulting hardened layer ranges from a few to tens of micrometers in thickness. The dissociation of ammonia allows high chemical potentials of nitrogen to be realized—otherwise difficult or impossible to achieve with pure N\(_2\) gas. A schematic illustration of the gas nitriding process is shown in Fig. 2.11. Within the topmost compound or so-called ‘white layer’ the \(\varepsilon\)-Fe\(_2\)N\(_{1-x}\) phase forms, followed by a \(\gamma'\)-Fe\(_4\)N layer that extends into a diffusional zone containing very fine nitride precipitates and/or nitrogen interstitially dissolved in ferrite. Increasing the carbon content of the alloy serves to increase the \(\varepsilon\) layer thickness, \(d_{\varepsilon}\), while decreasing the carbon increases the \(\gamma'\) layer thickness, \(d_{\gamma'}\) [71].

The underlying physical mechanisms behind the process are complex and not yet fully understood, being controlled by catalysis, dissociation, absorption, desorption, mass-transport, etc. However, compared to the other methods, gaseous nitriding is the most well-understood from a thermodynamic perspective.

The main processing parameters involved during gaseous nitriding include the chemical activity of nitrogen \(a_{N_2}\) (sometimes referred to as the nitriding potential), treatment duration \(t_N\), nitriding temperature \(T_N\), alloy composition, surface roughness, and surface pre-treatment\(^1\). The effect of surface cleanliness on the successful nitridation of any alloy cannot be overemphasized. The presence of any surface contamination can fully hinder the process or result in a non-uniform hardened layer.

2.2.3.1 Thermodynamics of Gas-phase Nitriding

Ammonia will dissociate into gaseous hydrogen and nitrogen according to the following chemical equilibrium reaction:

\[
\text{NH}_3(\text{g}) \rightleftharpoons \frac{3}{2}\text{H}_2(\text{g}) + \frac{1}{2}\text{N}_2(\text{g})
\]

\(^1\)Other important processing parameters may include the total gas flow (TGF) into the furnace and flow characteristics around the component.
2.2. THERMOCHEMICAL SURFACE ENGINEERING

\[ \Delta G = G_{\text{NH}_3} - \frac{1}{2} G_{\text{N}_2} - \frac{3}{2} G_{\text{H}_2} = 0 \]  

Figure 2.11: Schematic illustration of decomposition, adsorption, and diffusional processes involved during gas-phase nitriding. The topmost compound or ‘white’ layer consists of \( \varepsilon - \text{Fe}_2\text{N}_{1-x} \) nitride, followed by a layer of \( \gamma' - \text{Fe}_4\text{N} \) nitride, and lastly a diffusional zone containing nitrogen in solution and/or nano-precipitates.
2.2. THERMOCHEMICAL SURFACE ENGINEERING

The $G$ of each gas phase, for example $N_2$, is given by:

$$G_{N_2} = \circ G_{N_2} + RT \ln(p_{N_2})$$

where $\circ G_i$ is the standard Gibbs free energy (measured at 1 atm and 298.15 K), $p_{N_2}$ the partial pressure of nitrogen, $R$ the universal gas constant, and $T$ the absolute temperature. Inserting the standard Gibbs free energy $\circ G_i$ and partial pressures $p_i$ into Eq 2.6 yields:

$$\Delta \circ G = \circ G_{NH_3} - \frac{1}{2}\circ G_{N_2} - \frac{3}{2}\circ G_{H_2} = -RT \ln \left( \frac{p_{NH_3}}{p_{N_2}^{1/2} \cdot p_{H_2}^{3/2}} \right)$$

where the empirical value for the standard Gibbs energy of the reaction $\Delta \circ G$ in Eq. 2.3 is given by [74]:

$$\Delta \circ G = 43515 - 12.9T \ln(T) - 15.85T \quad [\text{J mol}^{-1}]$$

At a given temperature, the equilibrium condition can also be described by the equilibrium constant, $K_{eq}$, through Eq. 2.8:

$$K_{eq} = \frac{p_{NH_3}}{p_{H_2}^{3/2} \cdot p_{N_2}^{1/2}} = \exp \left( \frac{-\Delta \circ G}{RT} \right)$$

or to refer to the nitriding potential in terms of nitrogen gas activity $a_{N_2}$, Eq. 2.8 can be simplified to:

$$a_{N_2} = \left( \frac{K_{eq} \cdot p_{NH_3}}{p_{H_2}^{3/2}} \right)^{1/2}$$

The chemical potential of one nitrogen atom in the gas phase is therefore defined according to Eq. 2.10:

$$\mu_{N_2}^{\text{gas}} = \frac{1}{2} \circ G_{N_2}^{\text{gas}} + \frac{RT}{2} \ln \left( a_{N_2} \right)$$

Equilibrium between the various phases in the Fe–N system can be calculated as a function of temperature and nitrogen activity (expressed as the partial pressure of nitrogen gas) as shown in Fig. 2.12, or similarly, according to the thermodynamics of ammonia decomposition as a function of temperature and the ammonia-to-hydrogen ratio $p_{NH_3}/p_{H_2}^{3/2}$ (the ‘nitriding potential’) on the Lehrer diagram.

---

1 More correctly, the fugacity $f_i$ of each gas phase, which is equal to the fugacity coefficient $\phi$ times the ideal gas pressure $P_i$, should be used in place of partial pressure $p_i$. Usually the gas is considered to be ideal, i.e. fugacity coefficient equal to unity, and the partial pressure can be used instead. For the remainder of this work, the unitless nitrogen activity $a_{N_2}$, which is simply the fugacity divided by some reference pressure (typically 1 atm), is used when describing the nitriding potential, and can be thought of as the virtual partial pressure of nitrogen $p_{N_2}$ surrounding the workpiece.
Figure 2.12: (a) $T$–$p_{N_2}$ and (b) Lehrer diagram representing stability between various phases in the Fe–N system [75].
2.3 Expanded Austenite: The Conventional Wisdom

A summary of what is currently known about expanded austenite formation in austenitic stainless steels is presented here, along with information gathered from previous investigations on the low-temperature nitridation and carburization of duplex alloys.

2.3.1 History

Unlike carbon and low-alloy steels, austenitic stainless steels cannot be hardened through allotropic phase transformations, nor can they be case-hardened by conventional means due to loss of passivating capability. The first successful and deliberate attempt at case-hardening an austenitic stainless steel without loss of corrosion resistance dates back to 1983 in the experiments of Kolster [76], in which he observed a hard and corrosion-resistant surface layer after (suspected) liquid salt-bath treatment.

Two years later, Zhang and Bell [77], and concurrently Ichii et al. [78], published similar improvements in surface hardness and corrosion resistance following low-temperature plasma nitridation of 316L at 400 °C. In the post-treatment X-ray diffractograms, Ichii et al. noted five peaks not listed in the ASTM index in addition to the primary γ-austenite substrate peaks, and arbitrarily labeled them as S1–S5 (‘satellite’ peaks). Hence the nickname S-phase, which is still sometimes used in the literature to describe carbon- or nitrogen-supersaturated austenite.

Since these seminal experiments and through the large number of future works in the area of low-temperature surface hardening of austenitic stainless steels, it is now understood that the S-phase produced by these treatments is not truly a new phase in the thermodynamic sense, but rather a metastable state of austenite containing a truly colossal supersaturation of interstitial species. Thus it seems most appropriate to refer to this interesting phenomena as expanded austenite, the term adhered to in this work.

2.3.2 Formation Mechanisms

The process of expanded austenite formation in stainless steels is best understood by examination of the time–temperature–transformation (TTT) diagram in Fig. 2.13 for 316 austenitic stainless steel (17Cr–12Ni–2.5Mo) with two levels of carbon concentration. Within the ‘C’-curve, precipitation of M23C6 (M = randomly distributed Fe, Cr, Ni) carbide occurs. The relatively rapid formation of M23C6 at temperatures above ≈ 450 °C, even with such modest carbon concentrations, limits the interstitial-hardening effect that could otherwise be achieved in this alloy. It is apparent however that at lower temperatures, appreciable time is required for nucleation and growth of this deleterious secondary phase (primarily dependent upon the diffusivities of substitutional species) during isothermal aging, thereby allowing a processing window for carburization (or nitridation) in which
2.3. EXPANDED AUSTENITE: THE CONVENTIONAL WISDOM

SECONDARY PHASES CAN BE KINETICALLY SUPPRESSED\(^1\). BY SUBJECTING THE STAINLESS STEEL TO A CARBON- OR NITROGEN-RICH AMBIENT BELOW THIS CURVE, SUBSTANTIAL QUANTITIES OF INTERSTITIAL SOLUTES CAN BE DISSOLVED INTO THE SURFACE GENERATING A PRECIPITATE-FREE CASE (HARDENED SURFACE LAYER) WITH A COLOSSAL SUPERSATURATION OF THESE SOLUTES.

A PREREQUISITE FOR DISSOLUTION OF COLOSSAL CONCENTRATIONS OF INTERSTITIAL CARBON AND NITROGEN IS THE PRESENCE OF CARBIDE AND NITRIDE FORMERS (E.G. CR, MO, MN, V, ETC.) IN STAINLESS STEELS, WHICH HAVE A HIGH AFFINITY FOR CARBON AND NITROGEN AND SERVE TO REDUCE THE ACTIVITY COEFFICIENT, \(\gamma_i = a_i/X_i\), OF CARBON OR NITROGEN IN SOLUTION [82]. IT IS THE HIGH CONCENTRATION OF THESE ELEMENTS IN STAINLESS STEELS WHICH ENABLES LARGE \(\textit{paraequilibrium}\) SUPERSATURATIONS TO BE REALIZED WHEN SECONDARY PHASES ARE KINETICALLY SUPPRESSED.

\(^1\)IT IS NOTED HERE THAT AFTER SUFFICIENTLY LONG TREATMENT TIMES OR ISOTHERMAL HOLDS AT TEMPERATURES NEAR 400–450 °C, PRECIPITATION OF SECONDARY PHASES CAN OCCUR IN LOW-TEMPERATURE CARBURIZED OR NITRIDED 316L [1,80]. OF THE MORE DETAILED ANALYSES PERFORMED, THE NEW PHASES HAD FORMED IN A NEARLY PARTITIONLESS MANNER [81].

\(T(K)
\[
\begin{align*}
X_C = 0.0031 \\
X_C = 0.0010
\end{align*}
\]

**FIGURE 2.13:** Time–temperature–transformation (TTT) diagram for the precipitation of \(M_{23}C_6\) in 316 alloys of two carbon contents (0.10 at.% and 0.31 at.%) revealing how kinetic suppression of secondary phases is achieved at lower temperatures [79].
The term paraequilibrium [83, 84] is used in describing these treatments to indicate a state of metastability, whereby equilibration of only certain chemical species in the system occurs. In the case of nitriding or carburizing at low temperatures, this applies to equilibration of the chemical potentials of carbon or nitrogen in solution with the atmosphere, but not those of metal constituents, which are effectively immobile. Fig. 2.14 demonstrates the dramatic difference in diffusivity between interstitial and substitutional species in both fcc austenite and bcc ferrite matrices. Below 450 °C, the diffusional distance of sub-

![Figure 2.14: Interstitial and substitutional diffusion of common stainless steel alloying elements in α-ferrite and γ-austenite matrices at infinite dilution [85].](image)

stitutional elements may be no more than a few atomic spacings, while interstitial carbon and nitrogen can diffuse appreciable distances (tens of micrometers) in reasonably short times (≈ 20 hours). The thermodynamic origins of this metastable supersaturation have been previously discussed within the context of the CALPHAD-based multi-sublattice
2.3. EXPANDED AUSTENITE: THE CONVENTIONAL WISDOM

The most common method for synthesizing expanded austenite in stainless steels has been through use of plasma nitriding or carburizing techniques with several variants: dc, pulsed dc, rf, high-pressure plasma, or low-pressure plasma [1]. The plasma-based techniques have the benefit of enabling an *in situ* ‘surface activation’, or removal of native oxide (de-passivation) that is first needed for mass-transport of interstitial species into the workpiece surface. As described earlier, plasma techniques do suffer from being line-of-sight, limiting them to treatment of simple geometries, and lack precise thermodynamic or temperature control. Ion-implantation processes likewise provide an *in situ* de-passivation of the surface through simultaneous sputtering of native oxide and implantation of carbon and nitrogen with use of high energy carbon or nitrogen ions (higher energy than plasma-based techniques) leading to the formation of expanded austenite. The variants of ion-implantation techniques include: beam ion implantation (BII), plasma ion implantation (PII), and plasma immersed ion implantation (PIII).

Conformal and thermodynamically-controllable gas-phase carburizing and nitriding were more recently enabled through novel methods of de-passivating the surface of a workpiece [86,87] prior to exposure to a carbon- or nitrogen-rich atmosphere. The current state-of-the-art in surface hardening of stainless steels is through use of gases which both de-passivate the surface and provide nascent carbon and nitrogen for inward diffusion into the workpiece [88]. Still used industrially (see Table 2.10), but less common in practice is expanded austenite formation via cyanide- or cyanate-based salt-bath treatments (cf. [89–92]).

A flowchart summarizing the general approach to synthesis and characterization of expanded austenite observed throughout the literature is shown in Fig. 2.15.

2.3.3 Structure

X-ray diffraction (XRD) is the most commonly used technique for structural characterization of the surface region following nitridation or carburization of stainless steels. In austenitic stainless steels, it is observed that the austenite peaks shift to lower $2\theta$ (larger $d_{hkl}$) as a direct result of the dilation of the *fcc* lattice induced by carbon or nitrogen interstitials, which are larger than the octahedral interstices in austenite. Residual stresses and stacking faults also play a role in the observed peak-shifts [93]. Peak broadening is also a common feature in X-ray diffractograms as a consequence of the gradient in nitrogen or carbon concentration and a very high density of planar or linear defects.

An example of the austenite peak-shifting and broadening following gas-phase nitridation of bulk 316L samples is shown in Fig. 2.16(a) as a function of the nitriding activity. The higher activity leads to larger non-equilibrium supersaturation of nitrogen and hence larger lattice expansion. If assumed that the structure in various grains remains *fcc*, the
SYNTHESIS OF EXPANDED AUSTENITE | S-PHASE | $\gamma_N$ | $\gamma_C$

Fe + Nitride/Carbide Forming Element

Cr | Mo | Mn | Al | V | Ti

Surface Pretreatment

Surface Finish | Pre-cleaning

Surface Activation

Halogen-based Gas | Ni or Fe coating | N.A. for Plasma or Ion Implantation Processes

Low-temperature Treatment

Interstitial Element

Gas

Ion Implantation

Plasma

Characterization

C

C + N

N

Mechanical (hardness, strength, fatigue, wear)

Corrosion Resistance

Microstructure (XRD, SEM, EBSD, TEM, MFM)

Chemistry (XEDS, AES, XPS, APT)

Biocompatibility

Figure 2.15: Flow chart describing the general approach to synthesis and characterization of expanded austenite in stainless steels.

The lattice parameter corresponding to each peak in the diffractograms can be determined as shown in Fig. 2.16(b), and is apparently highly anisotropic. The nature of this anomalous, though systematic orientation-dependent expansion will be discussed in further detail later.

Lattice parameter expansions of up to 10–11% have been reported for nitrogen-expanded austenite [94,95], while carbon-expanded austenite is typically around 3% expanded [96]. The larger lattice expansion attainable by nitridation results from nitrogen’s higher paraequilibrium solubility limit (≈ 38 at.%) compared to that of carbon (≈ 15 at.%), though both are equally strong dilators [97].

While there has been some debate in the literature throughout the years regarding the crystal structure of expanded austenite, the experiments of Christiansen and Somers [95,98,99] were able to unequivocally prove for the first time that expanded austenite re-
2.3. EXPANDED AUSTENITE: THE CONVENTIONAL WISDOM

Figure 2.16: (a) X-ray diffractograms (Cu-K\(_x\) source) obtained from bulk 316L samples nitrided at 440 °C for 20 h with varying nitrogen activity. (b) Lattice parameter of austenite as measured from X-ray diffractograms in (a) as a function of surface normal grain orientation. The large variation in lattice expansion between individual sets of grains is not due to non-cubic symmetry, but results from orientation-dependent supersaturations and magnetic effects [94].
mains just that—an fcc solid solution with random occupation of nitrogen or carbon, presumably on the octahedral interstitial sublattice. In their structural analysis, they nitrided or carburized thin 316L foils (≈ 20 µm thick) such that stress-free and homogeneous powders of expanded austenite were produced\(^1\). By overcoming the experimental difficulties that thwarted previous structural analyses on bulk samples, they were able to determine from XRD that the homogeneous powders clearly fit a (faulted) fcc crystal structure. They also observed a linear relationship between the degree of expansion and the concentration of interstitial species.

Fewell and Priest [100] conducted a synchrotron-based structural analysis of nitrogen-expanded austenite on bulk samples in which they attempted to fit the high-order diffraction data against an array of candidate structures. Their conclusion that expanded austenite did not conform to a simple structure was plagued by the fact that they did not consider (i) the orientation-dependent variations in lattice expansion between individual grains (rooted in the material’s elastic anisotropy) or (ii) the effect of incidence angle in their analysis of the data. When the effect of biaxial residual stress and incident angle are accounted for, the experimental results of Fewell and Priest can also be explained by a strained fcc structural model.

The dilation per atom of carbon or nitrogen determined by Christiansen and Somers [97] in the stress-free and homogeneous expanded austenite powders is shown in Fig. 2.17. Note that the concept of site fraction, \(Y_i\), is used instead of the conventional mole fraction, \(X_i\), to indicate the concentration of nitrogen or carbon on the interstitial sublattice. The two conventions are directly related through:
\[
X_{\text{fcc}}^{N,C} = \frac{Y_{N,C}}{(Y_{N,C} + 1)}.
\]
In an fcc lattice, the site fraction, \(Y_{N,C} = 1\) when each octahedral site is fully occupied by interstitials, corresponding to a mole fraction of interstitials, \(X_{N,C} = 0.5\) (see [101]).

A similar relationship between the lattice parameter and interstitial nitrogen concentration was determined by Wu et al. [94] as shown in Fig. 2.18 after treatment of bulk 316L samples with varying nitrogen activity. The nitrogen concentration represents that measured at the free surface by calibrated Auger electron spectroscopy (AES) depth-profiling. The Poisson expansion resulting from compressive biaxial residual stresses [102], as well as the orientational dependencies on nitrogen concentration, were corrected for in the analysis. Unlike the high-nitrogen thin foil data of Christiansen and Somers, the plot reveals two linear regions: one at low and high nitrogen concentrations of approximately the same slope, with a step occurring near 16–18 at.% nitrogen. The additional expansion (≈ 0.017 nm) near 16–18 at.% nitrogen is attributed to a para-to-ferromagnetic transition that occurs in austenite when its lattice expands by a critical amount of ≈ 5% [94,103]. The data of Christiansen and Somers in Fig. 2.17 all occur within this higher-nitrogen regime,

\(^1\)A powder was all that remained of the thin foils after treatment as a result of the brittle nature of expanded austenite and large biaxial stresses that developed during the initial stages of nitridation/carburization.
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![Graph showing lattice parameter vs. interstitial site fraction.]

\[ a_{\gamma_N} = 0.36395 + (0.05987 \pm 0.00164)Y_N \]
\[ a_{\gamma_C} = 0.35965 + (0.06029 \pm 0.00189)Y_C \]

**Figure 2.17:** The lattice parameter of homogeneous carbon- or nitrogen-expanded austenite (\(\gamma_C\) or \(\gamma_N\)) as a function of interstitial concentration [97]. The concentration is varied by adjusting the ambient nitriding or carburizing potential during treatment.

i.e. after the para-to-ferromagnetic transition.

To summarize these observations, the level of supersaturation in individual grains—and thus the degree of expansion—strongly depends on crystallographic orientation. This phenomena is attributed to the elastic anisotropy of austenite (\(C_{11} \neq C_{44}\)), and exacerbated by a nitrogen-induced para-to-ferromagnetic transition. The intrinsic elastic anisotropy of austenite is at the root of the anomalous orientational-dependent lattice expansion observed in Fig. 2.16. This scenario is summarized schematically in Fig. 2.19. Furthermore, this likely explains why a linear regression through the data of homogenous powders in Fig. 2.17 at the high-end of the nitrogen spectrum did not pass through the nominal lattice parameter of austenite. The nitrogen-supersaturated powder was in each case ferromagnetic. Carburization does not induce the para-to-ferromagnetic transition in austenite due to its maximum lattice dilation of \(\approx 3\%\).

The lattice expansion associated with colossal dissolution of carbon and/or nitrogen...
2.3. EXPANDED AUSTENITE: THE CONVENTIONAL WISDOM

Figure 2.18: The lattice parameter of carbon- or nitrogen-expanded austenite ($\gamma_C$ or $\gamma_N$) as a function of interstitial concentration [94].

also leads to an impressive increase in their respective concentration-dependent diffusion coefficients [104–107] in fcc stainless steels. How this lattice expansion affects the diffusivity of substitutional constituents is largely unknown.

Transmission electron microscopy (TEM) has further demonstrated expanded austenite to be a precipitate-free fcc solid solution [108], though precipitation of nitrides can occur when nitriding at very high activities [109]. TEM investigations of expanded austenite consistently reveal deformation micro-twinning, slip bands, stacking-faults, and high dislocation densities—all indicative of plastic flow during growth of the case, and formed primarily as a means of stress-relaxation under the restricted in-plane expansion.

2.3.4 Properties and Characteristics

Interestingly, near-surface hardness values of carbon- or nitrogen-expanded austenite can exceed that of even the hardest carbon or nitrogen martensites [1] (1,300–1,500 HV for nitrogen-expanded and 700–1,000 HV for carbon-expanded austenite) as a result of a large
### Figure 2.19: The interstitial concentration and lattice parameter of carbon- or nitrogen-expanded austenite ($\gamma_C$ or $\gamma_N$) as a function of surface normal orientation in polycrystalline austenitic stainless steel.

<table>
<thead>
<tr>
<th>Surface Normal</th>
<th>Surface Conc.</th>
<th>Case Depth</th>
</tr>
</thead>
<tbody>
<tr>
<td>001</td>
<td>Highest</td>
<td>Deepest</td>
</tr>
<tr>
<td>113</td>
<td>Medium</td>
<td>Medium</td>
</tr>
<tr>
<td>111</td>
<td>Lowest</td>
<td>Shallowest</td>
</tr>
</tbody>
</table>

The interstitial-hardening effect\(^1\). Furthermore, this impressive increase in hardness is not accompanied by a significant loss of component ductility.

Typical concentration- and hardness-depth profiles through a series of plasma carburized, nitried, and nitrocarburized samples of 316 are shown in Fig. 2.20. The concave shape of the concentration profile, and thus the hardness profile, is characteristic of all interstitially-hardened stainless steels. The surface concentration of nitrogen is typically higher than carbon for treatment of a given alloy, and the nitrogen profile shallower and more plateau-like, whereas carbon extends deeper and the profile more gradual. The concentration of nitrogen at the surface typically ranges between 20–35 at.%, and carbon between 5–12 at.% (the reason for this large difference is described in Chapter 4).

A hybrid low-temperature nitrocarburization treatment generates a concentration profile also shown in Fig. 2.20, where the majority of carbon is found deeper than a nitrogen-enriched surface layer. Gu [111] demonstrated that this effect is a direct result of the lowering of the carbon activity coefficient in solution by the introduction of nitrogen. This is the chemical driving force behind the inward ‘push’ of carbon. Wu [109] observed this

\(^1\)The exceptional hardness in expanded austenite may further be attributed to ‘strain ellipsoids’ from the clustering of point defects, whose symmetry is lower than that of the matrix [110]
2.3. EXPANDED AUSTENITE: THE CONVENTIONAL WISDOM

Figure 2.20: (a) Concentration- and (b) hardness-depth profiles through low-temperature plasma carburization [$C$], nitridation [$N$], and (simultaneous) nitrocarburization [NC] treatments of 316L [1].
2.3. EXPANDED AUSTENITE: THE CONVENTIONAL WISDOM

effect regardless of whether the nitrocarburization was conducted simultaneously, carburization was followed by nitridation, or nitridation was followed by carburization.

Due to the thicker case, higher surface hardness, and more gradual hardness profile achievable with a hybrid nitrocarburization treatment, it has received significant attention in recent years as an optimization of both aspects of carbon- and nitrogen-expanded austenites. Although the two interstitial solutes differ by only one electron and proton, their effect on the end performance of expanded austenite is distinct\(^1\).

The origin of the concave concentration profile with a rapidly decreasing tail unique to expanded austenite has also been the subject of great debate since it was first discovered. It has been explained by both a concentration-dependent diffusivity and a trapping-detrapping model (or a combination of the two). As a good fit of the experimental data on 316L can be achieved by both models [94], it is inconclusive at present which model aptly describes the observed phenomena. Experiments aimed at resolving which is the correct or dominate mechanism are on-going [112].

As mentioned earlier, a state of equibiaxial compressive stress (\(\sigma_b\) where \(\sigma_{ij} = 0\) for \(i \neq j\) and \(\sigma_{11} = \sigma_{22} = \sigma_b\) while \(\sigma_{33} = 0\)) is generated in monolithic specimens as a result of the restricted in-plane lattice expansion. Such large residual compressive stresses are highly desirable, greatly improving the high-cycle fatigue and stress-corrosion cracking resistance. The exceptional ductility of austenitic stainless steels is retained after paraequilibrium treatments, and despite the extremely high surface hardness, ductility within the carburized or nitried layer has been evidenced by global and high-resolution techniques [96, 108]. In samples where the cross-sectional area of the hardened layer approaches that of bulk material, e.g. a stainless steel wire, the tensile strength is improved with only minor loss of ductility [113].

A residual stress profile measured by X-ray techniques in nitrided and nitrocarburized 316L is shown in Fig. 2.21. The large biaxial compressive stresses upwards of \(-9\) GPa are significantly higher than attainable by shot peening, which typically result in residual compressive stresses no greater than \(-1\) GPa. Carburization usually leads to compressive stresses on the order of \(-2\) GPa [110], from the lower paraequilibrium solubility limit of carbon and hence the smaller lattice expansion. It should be noted however that these measurements, which are destructive in nature, are made with several critical assumptions. First, they assume that the polishing of successive layers of material does not relieve or induce any stress. Second, they assume that the residual stress in all grains is the same. Based on the aforementioned observations in X-ray diffractograms this is an unlikely scenario, though the extent of stress or strain partitioning (measured according to the so-called Reuss, iso-stress, and Voigt, iso-strain, limits) between contiguous grains has yet to be worked out. Lastly, they assume that the elastic constants of expanded austen-

\(^1\)As one of the the central tenets of this work, carbon and nitrogen also lead to profound differences when dissolved in stainless ferrite.
2.3. EXPANDED AUSTENITE: THE CONVENTIONAL WISDOM

![Stress-depth profiles](image)

**Figure 2.21:** Stress-depth profiles measured by destructive means in (a) nitrided and (b) nitrocarburized 316L bulk samples [4].

...ite remain unchanged. The large expansion of interatomic distances will undoubtedly change the nature of the interatomic potential well. The effect of this change on the elastic properties also remains an unanswered question. While conventional X-ray techniques preclude strain measurement in individual grains, the synchrotron-based technique of micro-Laue diffraction does permit such measurements to be made. These experiments are ongoing and will be discussed in more detail in Appendix 8.1.

The electrochemical performance is unattenuated under most conditions, and with optimal processing can result in an improvement in corrosion resistances [7]. The remarkable electrochemical stability of expanded austenite can be qualitatively observed by its response to chemical etching, as typified in an etched cross-section of a carburized 316L sample in Fig. 2.22. The micrograph reveals a surface layer \( \approx 20 \, \mu m \) thick that is virtually immune to attack compared to the bulk. Presumably, the line running parallel to the surface represents the region where the carbon or nitrogen profile drops off, but may not directly indicate the penetration depth of interstitials. Microchemical analytical techniques such as glow-discharge optical emission spectroscopy (GDOES), Auger electron spectroscopy AES, Rutherford back-scattering spectrometry (RBS), or nuclear reaction analysis (NRA) can be used for accurate measure of case thickness. Quantitative anal-
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![Etched cross-section of low-temperature carburized (9 h at 460 °C) 316L revealing a featureless, hardened, and chemically-resistant layer of expanded austenite [114].](image)

Figure 2.22: Etched cross-section of low-temperature carburized (9 h at 460 °C) 316L revealing a featureless, hardened, and chemically-resistant layer of expanded austenite [114].

Analysis of light elements such as carbon or nitrogen is a persistent challenge; while GDOES, RBS, or NRA can provide accurate standardless quantification of these interstitials (the latter two only in expanded austenite layers of modest thickness), the spatial resolution afforded by techniques such as AES is essential when characterizing the diffusional layer in multi-phase alloys.

Expanded austenite is metastable. Given sufficient annealing time it will decompose into equilibrium nitride or carbide phases (CrN, Cr$_2$N, M$_5$C$_2$, M$_7$C$_3$ have been reported), austenite, and ferrite. The metastability of carbon- or nitrogen-supersaturated expanded austenite in 304 and 316L is shown in an empirical TTT diagram in Fig. 2.23 for decomposition into carbides and nitrides after isothermal holds. Work by Ernst et al. [116] has indicated that the presence of nickel may actually suppress the formation of equilibrium phases in expanded austenite. Though nickel serves to decrease the attainable non-equilibrium supersaturation of both carbon and nitrogen, its presence in some quantity may be vital to the formation of stable expanded austenite.
While it is generally assumed that precipitation of nitrides or carbides hinders the electrochemical performance of the interstitially-hardened stainless steel, more recent work has suggested that formation of paraequilibrium versions of these secondary phases (which is most often the case) can preserve enough chromium in solution so as to allow passivation of the surface.

To paraphrase, the range of novel thermochemical surface engineering techniques used to interstitially-harden stainless steels via formation of a metastable, supersaturated, expanded austenite are relatively low-cost, industrially viable, and represent one of few value-added processes of a material that result in all gain at no loss. These paraequilibrium treatments lead to miniscule dimensional changes, they are conformal (as are most gas-phase techniques), and involve essentially the retrofitting of existing operations.
2.3.5 Paraequilibrium Surface Hardening of Duplex Stainless Steels

The microstructural response of low-temperature paraequilibrium treatments applied to bcc-based stainless steels is largely unknown. Of the limited number of investigations on paraequilibrium treatments of ferritic, martensitic, or duplex stainless steels, several general conclusions can be made: kinetic suppression of secondary phases (carbides and nitrides) in ferrite is difficult, the corrosion resistance is highly varied, and in some cases, that a ferrite-to-austenite phase transformation occurs due to the stabilizing nature of carbon and nitrogen for austenite. Most of these investigations involved only basic metallographic analyses or global characterization techniques such as XRD, and were focused more on the efficacy of the treatment (e.g. hardness, wear, corrosion) than investigation of the underlying transformation mechanisms.

Of all previous surface hardening studies in ferrite-containing stainless steels, perhaps the fewest have been conducted on expanded austenite formation in duplex grades. A summary of these previous investigations is presented in Table 2.9, along with the observed response within the surface layer of (former) δ-ferrite grains.

In most of these studies, the duplex alloy was treated in addition to other stainless steels and the performance evaluated. All suggest that the austenitic phase of the DSS responds in a similar manner to treatments of single-phase ASS: a precipitate-free, carbon- or nitrogen-supersaturated layer of expanded austenite is produced. It is most widely reported that the near-surface δ-ferrite transformed to expanded austenite upon low-temperature nitridation and carburization. There is also strong evidence that secondary phases in the δ-ferrite phase are difficult to avoid, and the structure is apparently sensitive to the process and temperature.

Most of the studies also report that the diffusion layer in former δ-ferrite grains is thicker than the austenite grains, as a result of the difference in diffusivity between carbon and nitrogen in ferrite and austenite matrices. From these observations, it is concluded that the nitrogen front through δ-ferrite extends some distance ahead of the austenite grains, before the δ-ferrite is transformed to (expanded) austenite or some other phase. Several investigators further claim that untransformed δ-ferrite remained within the case.

An etched cross-section of plasma nitrided 2205 from a study of Spies et al. [114] is shown in Fig. 2.24. The case depth in each phase can be qualitatively estimated from the response to chemical etching. The austenite phase shows the usual response, whereby a fairly linear feature separates the supersaturated austenite and bulk material. The nitrogen-enriched layer in former δ-ferrite grains reveals ‘plates’ that protrude into the bulk δ-ferrite, which were attributed to some unspecified nitride. The corrosion resistance of this alloy was notably improved by the treatment.

Most of the claims that the ferritic phase transformed to austenite were based on XRD evidence alone, from the (debatable) disappearance or decrease in intensity of the ferrite
Table 2.9: Survey of prior investigations on the low-temperature surface hardening of duplex stainless steels, and the observed response of δ-ferrite.

<table>
<thead>
<tr>
<th>Material</th>
<th>Technique</th>
<th>Observations</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>2205</td>
<td>Gas nitridation</td>
<td>δ → γ → γ_N + “expanded martensite” (+ CrN &gt; 475 °C)</td>
<td>[117]</td>
</tr>
<tr>
<td>2205</td>
<td>PIII</td>
<td>δ → γ → γ_N → α + CrN</td>
<td>[118, 119]</td>
</tr>
<tr>
<td>2205</td>
<td>Plasma nitridation</td>
<td>&lt; 350 °C: δ → γ → γ_N, &gt; 400 °C: δ → γ’ + CrN</td>
<td>[120]</td>
</tr>
<tr>
<td>2205</td>
<td>Plasma carburization, nitridation, nitrocarburization, 380–500 °C, 9–32 h</td>
<td>δ → nitrides</td>
<td>[114]</td>
</tr>
<tr>
<td>2205</td>
<td>Plasma nitridation</td>
<td>350 °C: δ → γ’ + α’’ + ζ</td>
<td>[121–123]</td>
</tr>
<tr>
<td>2205</td>
<td>Plasma nitridation</td>
<td>350 °C, 40 h; 400 °C, 20 h</td>
<td>[121–123]</td>
</tr>
<tr>
<td>AISI 329</td>
<td>Gas nitridation (pure NH_3)</td>
<td>400 °C: δ → γ → γ_N, 450 °C: δ → ε + CrN + Cr_N_2</td>
<td>[124]</td>
</tr>
<tr>
<td>AISI 329</td>
<td>Plasma nitridation</td>
<td>δ → γ’ + α’ + CrN</td>
<td>[125]</td>
</tr>
<tr>
<td>AISI F51</td>
<td>DC-Plasma carburization</td>
<td>δ → γ → γ_C</td>
<td>[126]</td>
</tr>
<tr>
<td>Unknown</td>
<td>Salt-bath carburization (Kolsterizing®)</td>
<td>δ → γ → γ_N</td>
<td>[127]</td>
</tr>
</tbody>
</table>
2.3. EXPANDED Austenite: The Conventional Wisdom

Figure 2.24: Etched cross-section of 2205 DSS following plasma nitridation at 380 °C for 12 h [114].

peaks. Thus far, neither direct evidence nor an atomistic mechanism for this transformation has been provided or proposed.

Recent TEM work of Dong [1] on an unspecified treatment of a DSS was said to indicate a highly-defective δ-ferrite within the case, by the high degree of streaking and blurring of each reflection in the selected-area electron diffraction (SAED) pattern shown in Fig. 2.25. No mention is made of the interstitial specie nor its concentration in this region, or if any expansion of the ferrite lattice could be detected. Interestingly, the indexing of the SAED pattern from this δ-ferrite grain was not given, but upon further analysis most closely conforms to an fcc ⟨011⟩ viewing direction, as demonstrated by the superimposed ⟨011⟩\textsubscript{fcc} and ⟨111⟩\textsubscript{bcc} simulated diffraction patterns. The ⟨011⟩\textsubscript{fcc} better fits the geometry of intensity maxima in the primary reflections than the next closest ⟨111⟩\textsubscript{bcc} viewing di-
2.3. EXPANDED AUSTENITE: THE CONVENTIONAL WISDOM

Figure 2.25: SAED pattern from δ-ferrite grain following interstitial-hardening of an unspecified DSS. Note that the indexing was not indicated in the original publication, but is found to most closely conform to an $f_{cc}$ ⟨011⟩ viewing direction [1].

It is further noted that there do not appear to be any sharp, separate reflections in the diffuse tails of the primary reflections; however, if there were, the orientation relationship between the δ-ferrite and primary austenite reflections would follow the well-known Kurdjumov-Sachs (K-S) orientation relationship, albeit with an expanded austenite lattice:

\[
\begin{align*}
(111)_{fcc} & \parallel (110)_{bcc} \\
[\bar{1}10]_{fcc} & \parallel [\bar{1}11]_{bcc}
\end{align*}
\]  \hspace{1cm} (2.11)

Perhaps the most convincing evidence of a carburization-induced $\delta \rightarrow \gamma$ transformation...
tion in a ferrite-containing stainless steel was provided in a study by Michal et al. [128] on AISI 301. Though the stainless steel is considered an austenitic, it can contain large fractions of martensite or ferrite depending on its thermal and mechanical history. The particular sample of 301 was said to contain 40 vol. pct. ferrite in the as-received condition from XRD analysis, but whether the peaks in the diffractogram corresponded to ferrite or martensite was not addressed. Following low-temperature carburization, the ferrite peaks were fully absent from the X-ray diffractogram, and magnetic force microscopy (MFM) on the cross-section revealed a uniform, paramagnetic, supposed expanded austenite layer.

The distinction of whether the initial microstructure contained ferrite or martensite is important. Chen [129] observed by TEM and EBSD analyses that the martensitic phase (≈ 25 vol. pct. in the as-received condition) of 17-7 PHSS (condition A heat-treated) was fully converted to expanded austenite following low-temperature carburization, while the small volume fraction of residual δ-ferrite (≈ 5 vol. pct.) in the initial microstructure did not.

Bielowski et al. [130] applied a low-temperature nitriding treatment to 2205 in pure NH$_3$ after a novel surface activation involving in situ ion-sputtering with N$_2$ and H$_2$ gas$^1$. Electropolished samples were treated between 350–550 °C for 10.8 ks (3 h). XRD confirmed broadening, a lowering of intensity, and perhaps some expansion of the ferritic phase, but was not further elaborated upon. A thicker diffusional layer occurred in the initial ferrite grains. Cross-sectional EBSD (Fig. 2.26) confirmed the austenitic phase remained fcc, while the ferritic phase was non-indexable as bcc, fcc, or any of the known iron or chromium nitrides. No further mention was made of the plausible structure. The low-quality Kikuchi back-scatter patterns obtained from this region that could not be indexed were (correctly) stated to be indicative of a highly-defective and/or highly-stressed structure. In a later study, Bielowski and Baranowska [117] treated 2205 between 400–550 °C for 10.8–42.3 ks (3–12 h) and at various nitriding activities. From XRD they concluded an expanded austenite and ‘expanded martensite’ structure exists in samples treated below 475 °C, while at higher temperatures, clearly identifiable CrN-like peaks appeared in the diffractograms.

The structural response and transformation mechanisms in the δ-ferrite of DSS subjected to low-temperature interstitial-hardening treatment remains ambiguous due to these varied observations and interpretations of several investigators. There is thus need for a detailed analysis to reconcile these observations in this fundamentally important family of materials. It is most clear that the response of the ferrite phase in a DSS (as well as other ferrite-containing stainless steels) to low-temperature surface treatments is less straightforward than in single-phase austenitics.

$^1$H$_2$ was found to result in better activation than N$_2$ alone due to its reducing character.
2.3. EXPANDED AUSTENITE: THE CONVENTIONAL WISDOM

FIGURE 2.26: Cross-sectional EBSD phase mapping in an unspecified DSS following gaseous nitridation in pure NH$_3$ at 450 °C. (a) SEM micrograph, (b) EBSD phase map for austenite, (c) EBSD phase map for ferrite. Austenite is indexable within the nitrided layer, while the case in prior δ-ferrite grains is non-indexable as bcc, fcc, or any known nitride structure [130].

2.3.6 Industrial Relevance

Despite the remarkable performance improvements noted in interstitially-hardened stainless steels throughout laboratories worldwide in the past 30 years, only a handful of industries have since emerged due to the technological, economical, and environmental constraints inherent of the process. A list of the current industrial suppliers of interstitially-hardened stainless steel components is shown in Table 2.10. Though the generic process
2.3. EXPANDED AUSTENITE: THE CONVENTIONAL WISDOM

of each is known, the details are often proprietary. Based on the aforementioned characteristics of interstitially-hardened stainless steels, it is clear that the full potential of this enabling technology is far from being exhausted.
### Table 2.10: Commercial vendors of interstitial-hardening surface treatments of stainless steels.

<table>
<thead>
<tr>
<th>Company Name</th>
<th>Trade Name</th>
<th>Process</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bodycote PLC (U.K.)</td>
<td>Kolsterizing&lt;sup&gt;®&lt;/sup&gt;</td>
<td>Salt-bath † carburization</td>
</tr>
<tr>
<td>Nitruvid S.A. (France) ††</td>
<td>Nivox&lt;sup&gt;2™&lt;/sup&gt;</td>
<td>Plasma nitridation</td>
</tr>
<tr>
<td></td>
<td>Nivox&lt;sup&gt;4™&lt;/sup&gt;</td>
<td>Plasma carburization</td>
</tr>
<tr>
<td></td>
<td>Nivox LH&lt;sup&gt;™&lt;/sup&gt;</td>
<td>Plasma carburization</td>
</tr>
<tr>
<td>Air Water Ltd. (Japan)</td>
<td>NV Pionite</td>
<td>Gas carburization</td>
</tr>
<tr>
<td></td>
<td>NV Super Nitriding</td>
<td>Gas nitridation</td>
</tr>
<tr>
<td>Swagelok Company&lt;sup&gt;®&lt;/sup&gt; (U.S.A.)</td>
<td>SAT12&lt;sup&gt;™&lt;/sup&gt;</td>
<td>Gas carburization</td>
</tr>
<tr>
<td>Nihon Parkerizing Co. Ltd. (Japan)</td>
<td>Palsonite</td>
<td>Salt-bath nitrocarburization</td>
</tr>
<tr>
<td>Expanite A/S (Denmark)</td>
<td>Expanite&lt;sup&gt;®&lt;/sup&gt;</td>
<td>Gas nitrocarburization</td>
</tr>
<tr>
<td></td>
<td>Expanite HT&lt;sup&gt;®&lt;/sup&gt;</td>
<td>Solution nitridation</td>
</tr>
<tr>
<td></td>
<td>Super Expanite&lt;sup&gt;®&lt;/sup&gt;</td>
<td>Expanite HT&lt;sup&gt;®&lt;/sup&gt; + Expanite&lt;sup&gt;®&lt;/sup&gt;</td>
</tr>
<tr>
<td>Nitrex Metal Inc. (Canada)</td>
<td>Nano-S&lt;sup&gt;®&lt;/sup&gt;</td>
<td>Plasma nitridation</td>
</tr>
<tr>
<td></td>
<td>Nitreg-S&lt;sup&gt;®&lt;/sup&gt;</td>
<td>Gas nitridation</td>
</tr>
<tr>
<td>Heat &amp; Surface Treatment B.V. (Netherlands)</td>
<td>Stainhard&lt;sup&gt;®&lt;/sup&gt; NC</td>
<td>Gas nitrocarburization</td>
</tr>
<tr>
<td>Gerster Technologie AG (Switzerland)</td>
<td>HARD-INOX&lt;sup&gt;®&lt;/sup&gt;-P</td>
<td>Solution nitriding</td>
</tr>
<tr>
<td></td>
<td>HARD-INOX&lt;sup&gt;®&lt;/sup&gt;-S</td>
<td>Gas nitrocarburization</td>
</tr>
</tbody>
</table>

† Speculative

†† Acquired by Bodycote in 2010
Chapter 3

Experimental Methods and Procedures

3.1 Gas-phase Nitriding and Carburizing Treatment

3.1.1 Material

Duplex stainless steel is most often used in wrought form, but to better study the responses of the ferritic and austenitic phases individually, both cast and wrought material were treated. Raw material was supplied by the U.S. Naval Research Laboratory (NRL) in the form of 20 mm \times 20 mm \times 3 mm coupons. The typical microstructure of cast and wrought forms of 2205 is shown in Fig. 3.1, from which the austenitic phase (light contrast) is observed to precipitate within the \(\delta\)-ferrite matrix (dark contrast).

The nominal and certified compositions of the as-received material are presented in Table 3.1. Note that the cast material is slightly below the specification limits for chromium and molybdenum, which is the usual circumstance for casting of this alloy [131]. ASTM specifications require 2205 to meet a 0.2\% yield strength \(\sigma_y\) of 450 MPa and ultimate tensile strength \(\sigma_{\text{uts}}\) of 655 MPa with a minimum strain to failure \(\epsilon_f\) of 0.25. The Young’s modulus \(E\) of 2205 is nominally 200 GPa.

The volume fraction of austenite \(V_\gamma\) and ferrite \(V_\delta\) and their respective lattice parameters in the non-treated (NT) material were measured by XRD (see Sec. 3.3.1), the results of which are shown in Table 3.2. The nominal grain size in cast and wrought (viewed in the short-transverse direction) material determined from optical micrographs is also presented. The higher volume fraction of austenite in the cast material is a result of its higher concentration of austenite-stabilizing nickel and nitrogen, and lower concentration of chromium relative to the wrought material.

---

\[1\]Three treatments—(i) \(t_N = 440^\circ\text{C}\) and \(a_{N_2} = 1.8 \times 10^2\), (ii) \(t_N = 440^\circ\text{C}\) and \(a_{N_2} = 4.0 \times 10^9\), (iii) \(t_N = 350^\circ\text{C}\) and \(a_{N_2} = 5.8 \times 10^4\)—contained only wrought material.
3.1. GAS-PHASE NITRIDING AND CARBURIZING TREATMENT

3.1.2 Furnace and Processing

All nitriding and nitrocarburizing treatments were performed at CWRU using a custom CVD Equipment Corporation (Ronkonkoma, NY) furnace designed for the purposes of low-temperature gas-phase carburizing and nitriding, and is shown in Fig. 3.2. One carburization run was performed at CWRU, while two carburized samples were treated by the Swagelok Company®. The furnace is equipped with multiple gas cabinets, housing NH₃, HCl, H₂, N₂, CO, and C₂H₂. Though the system is capable of operating under vacuum, all treatments were conducted at ambient pressure. Samples were housed in a nickel basket which was then sealed in a fused silica retort containing an upper, lower,
3.1. GAS-PHASE NITRIDING AND CARBURIZING TREATMENT

Table 3.1: Nominal and certified composition of starting 2205 material (UNS no. S32205).

<table>
<thead>
<tr>
<th>Element</th>
<th>Symbol</th>
<th>Nominal Comp. [wt. pct.]</th>
<th>Cast Cert. [wt. pct.]</th>
<th>Wrought Cert. [wt. pct.]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron</td>
<td>Fe</td>
<td>63.72–70.36</td>
<td>67.807</td>
<td>66.403</td>
</tr>
<tr>
<td>Chromium</td>
<td>Cr</td>
<td>22.00–23.00</td>
<td>21.590</td>
<td>22.37</td>
</tr>
<tr>
<td>Nickel</td>
<td>Ni</td>
<td>4.50–6.50</td>
<td>5.910</td>
<td>5.750</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>Mo</td>
<td>3.00–3.50</td>
<td>2.560</td>
<td>3.230</td>
</tr>
<tr>
<td>Manganese</td>
<td>Mn</td>
<td>2.00 max.</td>
<td>0.750</td>
<td>1.500</td>
</tr>
<tr>
<td>Silicon</td>
<td>Si</td>
<td>1.00 max.</td>
<td>0.935</td>
<td>0.390</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>N</td>
<td>0.14–0.20</td>
<td>0.180</td>
<td>0.177</td>
</tr>
<tr>
<td>Carbon</td>
<td>C</td>
<td>0.03 max.</td>
<td>0.020</td>
<td>0.018</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>P</td>
<td>0.03 max.</td>
<td>0.016</td>
<td>0.021</td>
</tr>
<tr>
<td>Sulfur</td>
<td>S</td>
<td>0.02 max.</td>
<td>0.002</td>
<td>0.001</td>
</tr>
<tr>
<td>Copper</td>
<td>Cu</td>
<td>—</td>
<td>0.230</td>
<td>0.140</td>
</tr>
</tbody>
</table>

Table 3.2: Phase fraction and lattice parameter of as-received material.

<table>
<thead>
<tr>
<th></th>
<th>Cast</th>
<th>Wrought</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_δ$ [vol. pct.]</td>
<td>37.2 ± 0.3</td>
<td>56.9 ± 0.3</td>
</tr>
<tr>
<td>$V_γ$ [vol. pct.]</td>
<td>62.8 ± 0.3</td>
<td>43.1 ± 0.3</td>
</tr>
<tr>
<td>$a_δ$ [nm]</td>
<td>0.28823 ± 0.00001</td>
<td>0.28824 ± 0.00066</td>
</tr>
<tr>
<td>$a_γ$ [nm]</td>
<td>0.36050 ± 0.00039</td>
<td>0.36082 ± 0.00066</td>
</tr>
</tbody>
</table>

Nominal grain size [µm] $\sim$75–100 $\sim$5–10

and mid-range thermocouple device to ensure adequate thermal stability within ±1 °C.

The many processing parameters ultimately play a synergistic role in determining the efficacy of a particular paraequilibrium nitriding/carburizing treatment. However, because the experimental space for 2205 was limited, the nitriding temperature $T_N$ and the ambient nitrogen activity $a_{N_2}$ were chosen as the primary processing variables for systematic study. The experimental matrix using these processing parameters (devised rather arbitrarily to include low, medium, and high $T_N$ and $a_{N_2}$) is given in Table 3.3. The last
3.1. GAS-PHASE NITRIDING AND CARBURIZING TREATMENT

![CVD Equipment Corporation furnace](image)

**Figure 3.2:** CVD Equipment Corporation furnace used for low-temperature gas-phase carburizing, nitriding, and nitrocarburizing treatments.

Sample identifier ‘WC’ indicates whether the treatment contained wrought and/or cast material. The highest activity of $4.0 \times 10^9$ corresponded to treatment in pure NH$_3$ and N$_2$ where it was assumed that 1% H$_2$ was produced from the dissociation of ammonia, sometimes referred to in the literature as ‘infinite’ nitriding potential. Three carburization
3.1. GAS-PHASE NITRIDING AND CARBURIZING TREATMENT

and two nitrocarburization runs were also performed, with treatment time, \( t_C \) or \( t_{NC} \), and temperature, \( T_C \) or \( T_{NC} \), also given in Table 3.3.

Table 3.3: Processing space for low-temperature gas-phase nitriding, carburizing, and nitrocarburizing of 2205 following the Swagelok® SAT12™ process. W and C identifiers indicate treatment of wrought and/or cast material.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>( T_N ) [K] / [°C]</th>
<th>( t_N ) [ks] / [h]</th>
<th>( a_{N_2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>N2205-07WC</td>
<td>598 / 325</td>
<td>72 / 20</td>
<td>3.0 ( \times ) 10^3</td>
</tr>
<tr>
<td>N2205-06WC</td>
<td>623 / 350</td>
<td>72 / 20</td>
<td>1.8 ( \times ) 10^2</td>
</tr>
<tr>
<td>N2205-05WC</td>
<td>623 / 350</td>
<td>72 / 20</td>
<td>3.0 ( \times ) 10^3</td>
</tr>
<tr>
<td>N2205-03W</td>
<td>623 / 350</td>
<td>72 / 20</td>
<td>5.8 ( \times ) 10^4</td>
</tr>
<tr>
<td>N2205-10WC</td>
<td>623 / 350</td>
<td>72 / 20</td>
<td>1.4 ( \times ) 10^5</td>
</tr>
<tr>
<td>N2205-08WC</td>
<td>653 / 380</td>
<td>72 / 20</td>
<td>3.0 ( \times ) 10^3</td>
</tr>
<tr>
<td>N2205-04WC</td>
<td>653 / 380</td>
<td>72 / 20</td>
<td>1.4 ( \times ) 10^5</td>
</tr>
<tr>
<td>N2205-09WC</td>
<td>673 / 400</td>
<td>72 / 20</td>
<td>3.0 ( \times ) 10^3</td>
</tr>
<tr>
<td>N2205-11WC</td>
<td>673 / 400</td>
<td>72 / 20</td>
<td>4.0 ( \times ) 10^9</td>
</tr>
<tr>
<td>N2205-01W</td>
<td>713 / 440</td>
<td>72 / 20</td>
<td>1.8 ( \times ) 10^2</td>
</tr>
<tr>
<td>N2205-02W</td>
<td>713 / 440</td>
<td>72 / 20</td>
<td>4.0 ( \times ) 10^9</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>( T_C ) [K] / [°C]</th>
<th>( t_C ) [ks] / [h]</th>
<th>treated</th>
</tr>
</thead>
<tbody>
<tr>
<td>C2205-01C</td>
<td>653 / 380</td>
<td>288 / 80</td>
<td>CWRU</td>
</tr>
<tr>
<td>C2205-02W</td>
<td>653 / 380</td>
<td>540 / 150</td>
<td>Swagelok</td>
</tr>
<tr>
<td>C2205-03C</td>
<td>693 / 420</td>
<td>540 / 150</td>
<td>Swagelok</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>( T_{NC} ) [K] / [°C]</th>
<th>( t_{NC} ) [ks] / [h]</th>
<th>treated</th>
</tr>
</thead>
<tbody>
<tr>
<td>NC2205-01WC</td>
<td>713 / 440</td>
<td>72 / 20</td>
<td>CWRU</td>
</tr>
<tr>
<td>NC2205-02WC</td>
<td>653 / 380</td>
<td>144 / 40</td>
<td>CWRU</td>
</tr>
</tbody>
</table>

The total gas flow (TGF) for all experiments (conducted at CWRU) was maintained at 16.7 mL s\(^{-1}\) (1 L min\(^{-1}\)) by calibrated mass-flow controllers, whereby the flow rates of
3.1. GAS-PHASE NITRIDING AND CARBURIZING TREATMENT

NH₃, H₂ (ultra-high purity), and N₂ were adjusted accordingly to achieve the desired nitrogen activity, i.e. virtual partial pressure of nitrogen. For carburization, gas flow of CO, H₂, and N₂ was used, and for nitrocarburization all four gas were simultaneously used. During the pre-treatment activation (de-passivation) step, flow rates of 3.3 mL s⁻¹ HCl (0.2 L min⁻¹) and 30 mL s⁻¹ N₂ (1.8 L min⁻¹) were used. It is true that the actual nitrogen activity within the retort or in contact with the surface of the sample may not be known, but the calculated equilibrium value still provides a feasible metric for comparison.

Each gas-phase nitriding, carburizing, and nitrocarburizing treatment followed the established Swagelok® SAT12™ process [86] for carburization of AISI 316L ferrules, but using a shorter nitridation time of 72 ks (20 h) than standard carburization times (150 h). The process begins with an activation of the stainless steel surface to remove its native oxide by reaction with HCl gas for 10.8 ks (2 h). This is followed by an isothermal nitriding, carburizing, or nitrocarburizing intermediate step for 10.8 ks (2 h). The sample is then re-activated with HCl for 10.8 ks, followed by exposure to a longer isothermal treatment (18 h for nitrided samples). Following treatment, the samples were furnace cooled to room temperature using a gas mixture of H₂ and N₂. The standard time–temperature diagram of the process is shown in Fig. 3.3. The double two-hour activation procedure was empirically found to produce a thicker and more uniform case than a single activation step during carburization. A constant activation temperature $T_A$ of 598 K (325 °C) was used for all treatments. Between each activation and nitriding step, the gas lines were purged with N₂ for 30 minutes to ensure adequate removal of all caustic species. The 20 h nitriding duration conveniently permitted case depths that could be comprehensively studied in the electron microscope, but could have been extended to allow for any desirable case depth.

3.1.3 Material Preparation

Prior to treatment, the cast and wrought coupons were wet-ground and polished using SiC emery papers on at least one side through the following sequence: P400, P800, P1200, P1500, P2400, P4000 with a final 1 μm diamond suspension polishing step. Each coupon was ultrasonically cleaned in acetone, and again in ethanol for a minimum of 300 s directly before introduction into the furnace to ensure adequate removal of any surface residue. It should be noted that the surface preparation and surface roughness is as important a step as the treatment itself. Several studies [132,133] have confirmed the importance of surface finish to the successful plasma nitridation of 316L.

Following removal from the furnace, the samples displayed a dull and mottled finish, an example of which is shown in Fig. 3.4, and were sometimes covered in a thin layer of soot. The white powder which sometimes appeared on the surface was identified by XRD as ammonia chloride (NH₄Cl). The furnace was also routinely used for carburization
3.1. GAS-PHASE NITRIDING AND CARBURIZING TREATMENT

![Time-Temperature Diagram]

**Figure 3.3:** Schematic time–temperature diagram for low-temperature gas-phase nitriding (similar for carburizing and nitrocarburizing).

...and the inside surfaces of the retort and nickel basket were often heavily sooted, some of which may have fallen or deposited on the surface during treatment. Despite this visible surface contamination following nitriding, no ingress of carbon was detectable by Auger line-scans. Most of the post-treatment surface contaminants could be removed through light scrubbing and cleaning with acetone.

To prepare cross-sectional samples for metallographic and chemical analyses, the treated coupons were cut using a low-speed saw and SiC wafering blade and mounted in Buehler® EpoMet® F thermoset epoxy so as to yield the best edge-retention. The samples were ground and polished in the same pre-treatment procedure with an additional 0.25 µm diamond and 0.05 µm Al₂O₃ final polishing step. To reveal the nitrogen- or carbon-enriched case, the samples were swab-etched (≈ 30 s) in a modified aqua regia solution (1 HNO₃ : 2 HCl : 1 H₂O) for metallographic analyses. Samples prepared for concentration-depth profiling were left in the as-polished condition prior to introduction into the ultra-high vac-
uum chamber. The initial $\sim 50 \text{ nm}$ of material removed by the $\text{Ar}^+$ plasma sputtering process (used to remove hydrocarbon contaminants and native oxide) effectively etched the surface well enough to allow for optical distinction between the case and core in austenite and ferrite.

3.2 Performance Assessment

3.2.1 Corrosion Resistance

Perhaps the single greatest metric for measuring the efficacy of surface hardening treatment of 2205 is whether the corrosion resistance was maintained, improved, or degraded as a result of the process. Corrosion, or chemical attack and deterioration of the base metal, is nature’s method for bringing engineered materials back to their ground state. Corrosion can lead to perforations resulting in leakage, loss of strength or fracture toughness from the reduced cross-sections, and ultimately premature failure of a component. The various forms of corrosion include uniform corrosion or dissolution of the passive layer, pitting corrosion involving local breakdown and dissolution of the passive film, crevice corrosion (similar to pitting but resulting from a deposit, gasket, or some other crevice in contact with the surface), stress-corrosion cracking, and intergranular corro-
3.2. PERFORMANCE ASSESSMENT

Polarization techniques are widely used in assessing the general corrosion resistance of stainless steels and other corrosion-resistant alloys [15]. To gauge how nitridation affected the pitting corrosion resistance and passivating capability of 2205, potentiodynamic cyclic polarization in a chloride-environment was conducted by the Naval Research Laboratory (Washington, D.C.). Several of the nitrided samples were sectioned into 1.5 cm \times 1.5 cm pieces, after which the surfaces were thoroughly cleaned with a cotton swab and acetone. Cyclic polarization curves were then obtained using a PAR flat-cell (Ametek Instruments, Oak Ridge, TN) in a 0.6 M NaCl solution at room temperature, prepared from high-purity NaCl and water. A 1 cm\textsuperscript{2} area was exposed to the solution using a polytetrafluoroethylene (PTFE) O-ring. The open-circuit potential was first established for 43.2 ks (12 h) prior to the start of each scan, which began at 20 mV below the open-circuit potential. The scan rate was 0.17 mV s\textsuperscript{-1} (10 mV min\textsuperscript{-1}), and was reversed when the current exceeded 1 mA cm\textsuperscript{-2}. Ag/AgCl immersed in the same 0.6 M NaCl solution was used as the reference electrode, while the counter electrodes were pure platinum wire.

3.2.2 Nano-indentation Hardness Measurement

Though it is ideal to measure the adequacy of nitriding in improving the surface hardness by depth profiling, the task was largely hindered by case depths on the order of 1–5 µm following 20 h nitridation. Accurate measurement of hardness even with the most precise instruments should occur at least 1–2 µm from the sample edge. Therefore, to estimate with some statistical certainty the hardness increase within former ferrite and austenite grains, plan-view nano-hardness measurements were obtained using an Agilent Technologies (Chandler, AZ) G200 Nano-indenter equipped with a Berkovich-type tip using an applied load of 1.0 gF. Plan-view hardness measurements were obtained on a cast sample with case depths in δ-ferrite and austenite of \( \approx 5 \) µm (N2205-04C) as determined from AES composition-depth profiling. The surface was left in the as-treated condition, which did not impart a significant increase in surface roughness. Discernment between the former ferrite regions and austenite ‘islands’ within the ferrite matrix was made possible by the slight color variation in native oxide formed on each phase following treatment (see Fig. 3.5). The indentation depth in the former ferrite and austenite grains was \( \approx 1 \) µm, and thus did not reach the core material.

Hardness-depth profiling was performed on several commercially-treated samples (of unknown processing conditions) with much thicker cases in wrought and cast 2205, using the same instrument and 1.0 gF applied load. Polished cross-sections were prepared to 0.05 µm surface finish and lightly swab-etched (5 s) using the modified aqua regia recipe described earlier for optical estimation of the case depth. An array of indents with a minimum separation of 7 µm was made through the etch-resistant case and core mate-
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Figure 3.5: Optical plan-view micrograph of nitrided 2205.

rial. The distance of each indent from the free surface was then determined using optical micrographs of the indent array. Nomarski differential interference contrast (DIC) micrographs were obtained for this purpose using an Olympus® (Center Valley, PA) FluoView™ FV1000 confocal microscope.

3.3 Chemical and Microstructural Characterization

3.3.1 X-ray Diffractometry

X-ray diffraction (XRD) was used to (i) quantify the initial volume fraction and lattice parameters of austenitic and ferritic phases in the NT material, (ii) determine phases present in the surface layer, and (iii) estimate the lattice parameter expansion following treatment. A Scintag (Cupertino, CA) X-1 X-ray diffractometer equipped with a monochromated copper source (incident wavelength $\lambda_{\text{Cu-K}} = 0.1541838$ nm) and digital iron-fluorescence
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filter was used in the Bragg-Brentano (θ–θ) and glancing-incidence (GI-XRD) geometries for all obtained diffractograms. The tube voltage and current were 45 kV and 39.5 mA, respectively. Peaks were digitally fit using a Pearson VII equation and DMSNT software package. The diffractograms were indexed according to the Power-Diffraction Files (PDF) in the Joint Committee for Powder Diffraction Standards (JCPDS) database.

3.3.1.1 Direct Comparison Method

To accurately quantify the initial volume fraction of austenite, \( V_\gamma \), and \( \delta \)-ferrite, \( V_\delta \) where \( V_\gamma + V_\delta = 1 \), the direct comparison technique [134] was used assuming a randomly-oriented, uniformly-sized aggregate mixture of each phase in the as-received material. The volume fraction of each phase can be determined through:

\[
\frac{I_{\gamma}^{hkl}}{I_{\delta}^{hkl}} = \frac{R_{\gamma}^{hkl} \cdot V_\gamma}{R_{\delta}^{hkl} \cdot V_\delta}
\]

(3.1)

where \( I_{\gamma}^{hkl} \) and \( I_{\delta}^{hkl} \) represent the integrated diffracted intensity of peak \( hkl \) (\( i \) may or may not equal \( j \)) and \( R_{hkl}^{\gamma} \) is a substance- and peak-dependent parameter that can be determined empirically or calculated through:

\[
R_{hkl}^{\gamma} = \left( \frac{1}{v^2} \right) \left[ |F_{hkl}|^2 p \left( \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta} \right) \right] e^{-2M}
\]

(3.2)

where \( v \) is the volume of the unit cell, \( F \) is the structure factor for the particular reflection \( hkl \), \( p \) is the multiplicity factor, and \( e^{-2M} \) is the Debye-Waller temperature factor. It is vital to use non-overlapping or adjacent peaks when using the direct comparison technique so as to reduce uncertainty in the integrated intensity. The \( \gamma(002), \gamma(022), \delta(002), \) and \( \delta(112) \) peaks are well-suited for this purpose, whose absolutes values for \( R_{hkl}^{\gamma} \) are [135]:

\[
\frac{R_{\delta}^{002}}{R_{\gamma}^{002}} = 0.4174 \quad \frac{R_{\delta}^{112}}{R_{\gamma}^{002}} = 0.8027
\]

\[
\frac{R_{\delta}^{002}}{R_{\gamma}^{022}} = 0.7821 \quad \frac{R_{\delta}^{112}}{R_{\gamma}^{022}} = 1.5039
\]

3.3.1.2 Bragg-Brentano Geometry

Following treatment and thorough cleaning of the surface, the samples were scanned in the conventional \( \theta–\theta \) Bragg-Brentano geometry for phase identification and lattice parameter measurement. Bragg-Brentano XRD scans were recorded between 35–100° to include
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the unit cell, whose crystallographic planes are defined by Miller indices \((hkl)\) and separated by distance \(d_{hkl}\), will diffract, or constructively scatter photons when Bragg’s Law, given in Eq. 3.3, is satisfied:

\[
\begin{align*}
n\lambda &= 2d_{hkl} \sin \theta \\
\lambda &= 2d_n(hkl) \sin \theta
\end{align*}
\] (3.3)

where \(\lambda\) is the incidence wavelength and \(n\) an integer multiple relating the order of the reflection. In cubic materials, the \(d\)-spacing between a family of planes is related to the lattice parameter \(a\) through:

\[
d^2_{hkl} = \frac{a^2}{k^2 + l^2 + t^2}
\] (3.4)

All crystalline materials then with a unique structure can be identified according to their reciprocal lattice “fingerprint”.

When measuring the lattice parameter \(a_0\) of a material, the instrumental errors associated with measuring \(a_{hkl}\) from each peak can be minimized through use of the Nelson-
Riley extrapolation function:

\[ a_{hkl} = a_0 \left(1 - C \left[ \frac{\cos^2 \theta}{\sin \theta} + \frac{\cos^2 \theta}{\theta} \right] \right) \]  \hspace{1cm} (3.5)

where \( C \) is some constant. By plotting the lattice parameter according to each peak versus \( \cos \theta \cot \theta \), the “true” lattice parameter will be given where a linear extrapolation intersects the ordinate at \( \cos \theta \cot \theta = 0 \). The Nelson-Riley extrapolation was used for determination of the austenite and ferrite lattice parameters in the as-received material.

### 3.3.1.3 Glancing-incidence Geometry

The relatively low temperatures and short treatment times imparted case depths of \( \sim 5 \) µm or less in most of the nitrided samples, and consequently, due to the penetration depth of X-ray photons, the diffractograms obtained in the \( \theta-\theta \) geometry included some contribution from the core material. To better determine the structure of phases present only within the case, a fixed low-incidence angle geometry was used such that a majority of the signal came from the topmost few micrometers. The penetration depth \( x \) of a photon with an angle of incidence \( \theta \) to the surface is determined by [134]:

\[ x = \ln \left( \frac{1}{1 - G_x} \right) \left( \frac{\sin \theta}{2 \mu_\phi} \right) \]  \hspace{1cm} (3.6)

where \( G_x \) represents the fraction of the total integrated intensity at depth \( x \) and \( \mu_\phi \) is the linear absorption coefficient of the material. For the multi-constituent 2205 alloy, \( \mu \) is determined through:

\[
\left( \frac{\mu}{\rho} \right)_{2205} = W_{Fe} \left( \frac{\mu}{\rho} \right)_{Fe} + W_{Cr} \left( \frac{\mu}{\rho} \right)_{Cr} + W_{Ni} \left( \frac{\mu}{\rho} \right)_{Ni} \\
+ W_{Mo} \left( \frac{\mu}{\rho} \right)_{Mo} + W_{Mn} \left( \frac{\mu}{\rho} \right)_{Mn}
\]  \hspace{1cm} (3.7)

where \( W_i \) is the weight fraction of constituent \( i \) in the alloy and \( \rho \) the mass density. Using the nominal 2205 composition and density (7.805 g cm\(^{-3}\)), and the absorption coefficients of each constituent with Cu-\( K_\alpha \) radiation [134], the linear absorption coefficient \( \mu_{2205} \) is roughly 2140 cm\(^{-1}\). The penetration depth of Cu-\( K_\alpha \) radiation in 2205 as a function of incident angle is shown in Fig. 3.7. Considering a 95% contribution to the total signal intensity, the penetration depth of Cu-\( K_\alpha \) radiation at a fixed incidence angle of \( 3^\circ \) is approximately 400 nm. Even with the shallowest case produced in any of the treatments of \( \sim 1 \) µm, the diffracted signal at \( 3^\circ \) incidence occurs almost entirely within the case. This glancing-incidence geometry was conducted between 35–52° to include the major
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Figure 3.7: Penetration depth of Cu-K$_\alpha$ radiation in 2205 as a function of incident angle and signal contribution. The inset shows the same penetration depth at higher incident angles.

Ferrite/austenite peaks as well as those of possible nitrides/carbides. The step size was 0.04° with a dwell time of 4 s for all XRD and GI-XRD scans.

3.3.2 Auger Electron Spectroscopy

The various interactions that can result between high-energy electrons and a material are shown schematically in Fig. 3.8. Auger electron spectroscopy (AES) involves the three-electron (or four, if considering the incident, inelastically scattered electron) process of Auger emission, in direct competition with X-ray fluorescence following an inner-shell
ionization event. A schematic of these two competitive processes is shown in Fig. 3.9. By measuring the energy of Auger electrons emitted from within the topmost 1–3 nm of material, AES can provide similar quantitative elemental and chemical information to that provided by other extremely surface-sensitive techniques such as X-ray photo-electron spectroscopy (XPS), but with greatly improved spatial resolution. The technique is also well-suited for quantitative analysis of light elements such as carbon and nitrogen.

The sum of probabilities of Auger emission $\omega_A$ and X-ray fluorescence $\omega_F$ is unity following any ionization event, shown in Fig. 3.10 for various levels of competitive Auger and fluorescence processes. The nomenclature for Auger emission uses the principle quantum shell letters, e.g. ABC, where A represents the level from which the ionization event occurred, B the level from which an electron degenerates and fills the vacancy, and C the level of Auger emission. X-ray fluorescence follows the nomenclature that letters in-
A Physical Electronics, Inc. (Chanhassen, MN) PHI-680 Scanning Auger Nanoprobe™ equipped with a field-emission gun and cylindrical mirror analyzer was used for cross-sectional line-scans across the nitrided or carburized layer. The samples were ultrasonically cleaned in ethanol prior to introduction into the ultra-high vacuum chamber ($\approx 10^{-9}$ Pa). The cross-sectional surface was sputter-cleaned with a PHI 650 Ar$^+$ gun for 300 s to remove the native oxide and any hydrocarbon contaminants present on the surface. Using the maximum ion flux, the estimated removal rate in stainless steels is $\approx 10$ nm per minute. The instrument’s fine electron probe is able to provide spatial resolution on the order of 10 nm allowing compositional depth-profiling to be conducted through very shallow cases, as well as through individual ferrite and austenite grains in cast material.

From the Auger spectra obtained after each line-scan, a standardless quantification procedure was performed within the PHI MultiPak software, following software derivation of the raw data for background removal and peak accentuation. All peak identifications were compared against known peaks within The Handbook for Auger Electron Spectroscopy (PHI) to determine if any chemical shift (i.e. change in bonding state) had occurred.
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Line-scans were performed at 10 kV and 20 nA (probe diameter ≈ 30 nm) so as to yield the best signal-to-noise ratio, and were positioned orthogonal to the treated surface such that the last few acquisitions were well within the matrix (as determined optically from the varying sputtering rates between the case and core material). Line-scans through individual austenite and δ-ferrite grains in cast material were also permissible by the varying removal rate of each phase, and further verified by the Cr/Ni ratio.

3.3.2.1 Calibration

The software is able to quantitatively estimate the composition by using an internal algorithm that includes “sensitivity factors” acquired from standard samples. Because the behavior, and therefore the elemental sensitivity factors, of the treated alloy in question may be different from samples reported in the software, the quantification must first be taken cautiously as standardless AES quantification procedures may be more challenging than XPS, due the nature of quantification routines and difficulty in separating the slightly broader peaks. A calibration procedure for high-carbon stainless steels was previously performed on this instrument [128, 136]. Two standard nitrogen-containing steel specimens (B.S.81N and MBH NSC4) were analyzed in a similar fashion with good agreement. Based on these calibrations, the analytical uncertainty in absolute nitrogen and carbon concentration measured in the AES system is estimated to be ±1 at.%.

3.3.2.2 Dynamic Sputtering

All solid materials, regardless of how well-cleaned, will always contain some degree of surface contamination, mostly in the form of hydrocarbons, or so-called adventitious carbon. When a high-energy electron beam interacts with a material’s surface, the bonds between the hydrocarbons may break and a thin layer of graphitic carbon can be deposited. During AES spectral acquisition on carburized samples, a dynamic sputtering procedure was performed using a minimal flux of Ar⁺ ions to mitigate this effect, which would otherwise hinder accurate quantification of the underlying base metal chemistry. The electron beam is therefore continuously exposed to the “cleanest” surface to interact with. Furthermore, dynamic sputtering during spectral acquisition on stainless steels is imperative so as to prevent repassivation of the surface from residual oxygen in the chamber, where the overlap between primary oxygen and chromium peaks would further degrade accurate quantification.

To determine this effect during depth-profiling of nitrogen, line-scans through individual austenite and δ-ferrite grains were conducted with and without dynamic sputtering on the same specimen. Both procedures yielded identical results (within the analytical un-

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1 In the SEM, this is commonly referred to as “raster-burn”.

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certainty). Regardless, all nitrogen and carbon depth-profiling was performed with use of dynamic sputtering, considering sample-to-sample variations in surface cleanliness or future contamination within the specimen chamber.

3.3.3 Atom Probe Tomography

Atom probe tomography (APT) was used to further investigate the local nitrogen concentration and its distribution within \( \delta \)-ferrite grains. The APT technique allows three-dimensional (3D) chemical imaging of a material with atomic-scale resolution: \( \approx 0.1-0.3 \) nm in depth resolution and 0.3–0.5 nm laterally. The destructive technique is performed on a very sharp “tip”, whose radius of curvature does not exceed 40–50 nm, which is cooled and biased at high voltage (2–20 kV). The high DC voltage generates a very large electrostatic field at the surface of the tip, just below the point of atomic evaporation (10–50 V nm\(^{-1}\)). The micro-tip is then either pulsed with a higher voltage or UV laser (\( \leq 100 \) pJ), thereby evaporating atoms at the surface which are projected onto a position sensitive detector (PSD) consisting of a micro-channel plate (MCP) and delay-line detector. The delay-line detector measures the \((x, y)\) position of each ion impact, while the MCP measures the time of flight (ToF) of each ion between the pulse and impact event on the detector, thereby allowing the mass-to-charge ratio to be determined. The combination of mass-to-charge and spatial information of single evaporation events allows 3D reconstructions of the micro-tip to be performed. The local electrode atom probe (LEAP) is a newer advancement in the field of APT (cf. [137–142]), in which a local electrode is positioned near the micro-tip (\( \approx 30 \) µm away), allowing lower voltages to be used for evaporation, and thus larger data sets to be acquired before eventual fracture of the tip. A schematic illustration of the LEAP technique is shown in Fig. 3.11.

LEAP provides detection sensitivity down to a few ppm, regardless of elemental mass. However, some of its pitfalls are a detection efficiency \( \leq 60\%\), resulting from the open area of the MCP, and the inability of the delay-line detector to differentiate between single and multi-ion impact events. The laser-pulsed mode allows for larger data sets to be acquired, due to the lower electrically-induced stresses in the micro-tip than in voltage-pulse mode, which can prematurely fracture the tip. Laser-pulse mode also affords better mass resolution, as each atomic evaporation event is more discrete. It does however provide lower spatial resolution than voltage-pulse mode due to potential atomic migration at the micro-tip surface before evaporation. A typical LEAP tomograph in laser-pulse mode may consist of a volume approx. \( 50 \times 50 \times 100 \) nm containing tens of millions of atoms.

APT was performed using a CAMECA (Gennevilliers, France) LEAP 4000X HR™ instrument. Atom-probe samples were prepared from plan-view cast and wrought 2205 samples by the FIB technique using an FEI™ Helios NanoLab™ 650 DualBeam™ SEM/-
FIB. A protective Pt strip 15 µm × 3 µm was first deposited on the surface, and a wedge-shape extending approximately 5 µm below the surface was extracted using an Oxford Instruments OmniProbe 200 nano-manipulator after Ga⁺-ion milling. Slices from the ∼15 µm × 3 µm × 5 µm wedge were then milled to a width of ∼2 µm and Pt-welded to a prefabricated Si micro-tip array. Thinning of the sample was performed using successive annular Ga⁺ ion milling steps until a very sharp tip whose radius of curvature did not exceed 50 nm was obtained. Approximately 100–150 nm below the tip surface, the diameter was around 150 nm (the optimal geometry for preventing premature sample fracture). Final annular milling was performed at 1 kV to remove the damaged and/or Ga-implanted surface layer. An illustration of the process from welding of the wedge to the Si micro-tip array to final thinning of an ideal LEAP sample is shown in the SEM micrographs of Fig. 3.12.

APT data was acquired at a temperature of 50 K in pulsed-UV laser mode with 20 pJ laser power and pulse rate of 250 kHz. Due to peak overlap of ¹⁴N⁺ and ²⁸Si²⁺, the peaks at all nitrogen positions were assigned to nitrogen in the mass-to-charge-ratio spectrum. The actual Si concentration was calculated based on the known natural abundances of its isotopes (²⁹Si and ³⁰Si) and subtracted from measured nitrogen concentration.
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Figure 3.12: SEM micrographs showing (a) the initial welding of a FIB lift-out wedge to the Si micro-tip array and successive annular Ga\(^+\)-ion milling until (h) the ideal LEAP sample geometry is achieved.
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3.3.4 Scanning Electron Microscopy

The scanning electron microscope (SEM) is perhaps the most widely used technique for imaging, structural, and chemical characterization, due in part to its excellent spatial resolution, relative ease of sample preparation, image interpretation, versatility, and overall user-friendliness. The SEM can quite easily provide complementary information simply by changing the detected interaction signal. The SEM was used in this investigation for imaging of the treated layer, preparation of site-specific TEM foils using the focused ion beam (FIB) technique, XEDS chemical identification of grains, electron back-scatter diffraction (EBSD), and transmission Kikuchi diffraction (TKD)—a variation of EBSD performed on TEM foils—for microstructural analysis.

Etched cross-sections of treated samples were imaged using an FEI™ (Hillsboro, OR) Nova NanoLab™ DualBeam™ 200 SEM/FIB equipped with a Schottky thermal field-emission gun. All micrographs were obtained using a secondary electron (SE) signal at an accelerating voltage of 5 kV or 10 kV. The back-scattered electron (BSE) signal was used for identification of austenite and ferrite grains in cast material prior to FIB extraction. XEDS and EBSD analyses were conducted with an accelerating voltage of 20 kV and current of 17 nA to provide the optimal signal-to-noise ratio.

3.3.5 Electron Back-scatter Diffraction

The electron back-scatter diffraction (EBSD) technique was used in addition to XRD to investigate structural transformations following carburization or nitridation. Cross-sectional samples were prepared in the usual fashion to a 0.1 µm diamond suspension finish, and were subsequently placed in a Beuhler (Lake Bluff, IL) VibroMet® chemo-mechanical polishing system with a 0.05 µm colloidal silica slurry for approximately 7.2 ks (2 h). The final chemo-mechanical polishing step is used not necessarily to achieve the smoothest, but most deformation-free surface as possible, greatly enhancing the quality of the EBSD pattern.

The Nova NanoLab™ 200 instrument equipped with an Oxford Instruments (Abingdon, UK) Nordyls II EBSD detector was used for recording of back-scattered Kikuchi patterns. Polished samples were removed from the mount material and fixed to a special stud such that the sample surface is inclined 70° to the incidence electron beam (the optimal geometry for EBSD analysis). This setup is shown schematically in Fig. 3.13. A region of interest (ROI) approximately 100 µm × 25 µm extending from the free-surface to the core was selected for two-dimensional (2D) phase and orientation mapping with a step size of 0.5–1.0 µm. The Orientation Image Microscopy (OIM) software package was used for indexing raw Kikuchi patterns by measuring the interplanar angles of the pattern at each step and comparing against candidate structures.

Despite the quality of polishing and sharpness of the edge, achieving a high indexing
rate within a few µm of the sample edge is troublesome. To get a better idea of what, if any, phase transformations had occurred following treatment, plan-view EBSD specimens were prepared as follows: cut using a slow-speed saw from the treated coupon, mounted to a flat polishing surface with Crystalbond™ 509 adhesive, and polished using the VibroMet® and 0.5 µm colloidal silica solution for a few minutes so as not to remove a significant amount of material. Precision micrometer measurement indicated the amount of material removal to be less than 1 µm. The plan-view samples were mounted to the 70°stud and analyzed in a similar fashion as the cross-sectional samples, with a ROI of approximately 60 µm × 60 µm and step size of 0.5–1.0 µm.

### 3.3.5.1 Transmission Kikuchi Diffraction

Transmission Kikuchi diffraction (TKD), also referred to as transmission EBSD (t-EBSD), is a rapidly emerging and powerful technique for structural characterization at the nm-length scale [144–147] within the SEM. This versatile technique allows for combined sample preparation, imaging, crystallographic, and chemical information all to be obtained.
in the SEM with a spatial resolution of 5–10 nm, filling the gap between what was once possible only in the TEM.

With this technique, TEM lift-out foils are analyzed in the SEM using a specialized holder, whereby the EBSD detector images the Kikuchi pattern after transmission of electrons through the foil, rather than in the conventional back-scattered mode. This allows for better spatial resolution than can normally be achieved with EBSD (forward-scattered electrons scatter through smaller angles). The geometry of this setup is shown in Fig. 3.14. A TEM lift-out sample is positioned between 10–20° relative to the incident electron beam, and the detector records the Kikuchi pattern generated by electrons scattered within the back 10–20 nm of the foil.

![Figure 3.14](image-url) (a) Schematic illustration of the geometry involved in TKD and (b) CCD image [148] of the setup in the Nova NanoLab™ instrument with STEM FIB lift-out sample holder.

Several FIB lift-out lamellae of nitrided and carburized material were analyzed by TKD in the FEI™ Nova NanoLab™ 200 instrument using a custom 38° pre-tilt STEM sample holder provided by FEI™. The system was upgraded to an Oxford Instruments NordlyNano EBSD detector with AZtecSynergy EBSD and EDS analysis software. 2D orientation and phase maps were acquired at 30 kV accelerating voltage and 17 nA beam current with step sizes ranging from 0.01–0.05 µm. Post-processing of the EBSD/TKD data was performed using the HKL CHANNEL5 software module.

### 3.3.6 Magnetic Force Microscopy

Magnetic force microscopy (MFM) was used to investigate if the δ → γ transformation had occurred, or if newly formed phases in the case exhibited different magnetic behavior than the parent phase from which it formed. It is known [103, 149] that a paramagnetic to
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Ferromagnetic transition can occur within nitrided 316L austenitic stainless steel when a critical nitrogen concentration in the expanded austenite of approximately 14–15 at. pct. is achieved, corresponding to a lattice expansion of nearly 5%\(^1\). Although the ferrite is itself ferromagnetic, ferromagnetic domains of any austenite transformation product within the former ferrite may be distinguished by different magnetic characteristics. A calibrated Veeco Instruments (Plainview, NY) Dimension 3100 AFM/MFM with Co-coated Si tip was employed in non-contact MFM mode on both the as-treated plan-view surface and polished cross-sections of several samples. The force, as measured by the deflection of the cantilever, between the tip and sample surface provided topographic information, while the phase oscillation of the tip induced by magnetic domains in the sample provided phase contrast.

3.3.7 Transmission Electron Microscopy

Transmission electron microscopy (TEM) was used to investigate the fine microstructure and local chemistry of the carburized and nitrided layer. Site-specific cross-sectional TEM samples were prepared using the FIB technique in two FEI™ DualBeam™ SEM/FIB instruments: a Nova NanoLab™ 200 and Helios NanoLab™ 650. Prior to FIB foil extraction, plan-view samples were sputter-coated with a thin (\(\approx 200\) nm) layer of Pd to protect the surface from ion damage during the initial stages of imaging. A Bruker™ (Madison, WI) XFlash™ detector 4010 XEDS system was used to distinguish the \(\delta\)-ferrite and \(\gamma\)-austenite phases in wrought material by their respective Cr/Ni ratio and determine the rolling (LT) direction. Back-scattered electron images allowed distinction of each phase in cast material with a much larger grain size. A 2–3 \(\mu\)m protective layer of Pt was deposited on the ROI using a focused low-energy \(\text{Ga}^+\) ion beam (30 kV/0.3 nA) across \(\delta\) and \(\gamma\) grains in wrought material, perpendicular to the rolling direction, while foils in cast material were extracted from single \(\delta\)-ferrite grains. The Pt-layer serves to preserve the surface and promote uniform milling. The characteristic dimensions of the Pt strip were 15–20 \(\mu\)m \(\times\) 3 \(\mu\)m to allow for a relatively large transparent area in the final cross-sectional foil. A composite Cr/Ni XEDS map and corresponding SE-SEM micrograph revealing deposition of the Pt layer in the LT direction of wrought material are shown in Fig. 3.15.

Milling was conducted with the \(\text{Ga}^+\) ion beam for removing a slice of material from the bulk. The slice of material was welded to an Oxford Instruments OmniProbe 200 nano-manipulator, and subsequently top- or side-mounted to a 3 mm copper grid with the Pt source. A SE-SEM micrograph of a cross-section foil in a \(\delta\)-ferrite grain of cast material before final extraction and mounting to the copper grid is shown in Fig. 3.16. Samples were then further thinned using successively lower accelerating voltages and

\(^1\)The lattice parameter expansion accompanying low-temperature carburization has not been observed to exceed 3%, and hence the lack of ferromagnetic behavior in carburized austenitic stainless steels.
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Figure 3.15: (a) Superimposed Cr/Ni XEDS maps revealing the δ-ferrite and austenite phases and LT direction in wrought material. (b) SE-SEM micrograph revealing deposition of a protective Pt layer over the ROI prior to foil extraction.

Figure 3.16: SEM micrograph showing the FIB lift-out process of a cross-sectional TEM foil from a single δ-ferrite grain in cast 2205 ($T_N = 400 \, ^\circ C$ and $a_{N_2} = 4.0 \times 10^9$). The sample is tilted 25° relative to electron column.
beam currents until the foil appeared sufficiently bright in a SE-SEM micrograph at 5 kV. The final thinning/cleaning of the foil was conducted with a 1 kV/50 pA Ga\(^{+}\) ion beam on the Helios NanoLab\textsuperscript{™} 650 to reduce the extent of the damaged layer.

The FIB lamellae underwent a final cleaning procedure using a Fischione (Export, PA) NanoMill\textsuperscript{™} 1040. The system uses a very low-energy Ar\(^{+}\) source (50–2000 eV) to lightly polish both surfaces of the foil, thereby reducing the thickness of the amorphized zone induced on the foil surfaces by higher-energy milling with the FIB. Under optimal conditions, the amorphous layer can almost entirely be removed. The samples were first exposed to an ion beam at 900 eV for approximately 300 s on each side at ±10° tilt, and subsequently at 500 eV for 300 s at ±10°. After analysis in the TEM, the samples may have undergone a second round of cleaning in the NanoMill\textsuperscript{™}.

Due to the large residual compressive stress gradients present within the case region, samples often began to “warp” prematurely during thinning, preventing further uniform milling. To circumvent this difficulty in TEM sample preparation by mitigating the effect of the near-surface residual compressive stress, several samples were compressed to the extent that a few percent plastic flow occurred within the softer matrix. A schematic illustration of this procedure is shown in Fig. 3.17. Using a sample sectioned from the bulk and an INSTRON\textsuperscript{®} 1125 machine, several specimens were compressed until a plastic strain of \(\approx 3–4\%\) had been achieved. The sample dimensions were first measured, and the nominal yield strength \(\sigma_y\) of 2205 (450 MPa) was used to estimate the required load. The surface of the sample was covered with Teflon\textsuperscript{®} tape to lower the frictional force. After application of a set load (loading rate of 445 N s\(^{-1}\)), the thickness of the sample was measured and further loaded until the samples had strained by 3–4%. It is noted that the plastic flow of the matrix does not return the sample to a stress-free state, but would lower the magnitude of the residual compressive stress, ideal for thin foil production. A compressive test was initially performed on an as-received sample to determine if the nominal yield strength of 2205 was applicable. It was determined that the yield strength of wrought material was closer to 470 MPa. Following 3–4% plastic deformation of the as-received sample, the surface displayed prolific formation of slip bands. Following compression of the nitried samples, the surface did not show evidence of slip bands, indicating that the 3–4% plastic flow likely occurred within the weaker matrix. Minimal dislocation movement within the case following the compressive test could be expected.

The conventional “sandwich method” for preparation of cross-sectional TEM foils was used following compression of the specimens, but was unsuccessful. The samples fell apart in the final dimpling stages, perhaps due to remnant residual stresses. Samples prepared by the FIB technique following compression did not warp as severely as the as-treated samples, indicating some of the stress may have been relieved.

Comparing the integrated intensities of the total and zero-loss peak in the the electron energy-loss spectra (EELS) allowed for an estimation of the (absolute) local foil thickness,
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FIGURE 3.17: Schematic representation of the compression test used to minimize the near-surface biaxial compressive stress in bulk samples for later TEM sample preparation.
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assuming the inelastic mean-free path length for electrons in 2205 is similar to 316L, i.e. \( \lambda_{2205} \approx 100 \text{ nm} \) \[150\].

Two TEMs at CWRU were utilized for microstructural and chemical analyses. A ZEISS (Jena, Germany) Libra\( ^\text{®} \) 200FE S/TEM (scanning TEM) with aberration-corrected in-column OMEGA energy filter, Schottky field-emission electron gun (FEG), and Köhler illumination system operating at 200 kV was used for conventional and STEM imaging, selected area electron diffraction (SAED), XEDS (Thermo Scientific NORAN\( ^\text{™} \) detector), and EELS chemical analysis. An FEI\( ^\text{™} \) Tecnai\( ^\text{™} \) G2 F30 S/TEM with a Schottky FEG and post-column energy filter (Gatan GIF 2002) operating at 300 kV was also used for zero-loss and high-resolution (HR) imaging, SAED, and nano-diffraction, i.e. convergent beam electron diffraction (CBED) patterns acquired using a shallow convergence angle\(^1\). All bright-field (BF)/dark-field (DF) micrographs (as well as SAED patterns from the in-column filtered Libra\( ^\text{®} \) 200FE instrument) were acquired by filtering of the zero-loss beam (energy spread \( \approx \) 30 eV). Such zero-loss images and diffraction patterns acquired using only the elastically-scattered portion of the beam offer improved clarity over those formed with the additional contribution of inelastically-scattered electrons. The STEM camera length for imaging and chemical analysis was set to 1.44 m and STEM micrographs were recorded using the high-angle annular dark-field detector (HAADF). All Libra\( ^\text{®} \) 200EF SAED patterns were recorded with a calibrated camera length of 0.9 m, while Tecnai\( ^\text{™} \) patterns were acquired at a calibrated camera length of 1.0 m. Simulation and indexing of diffraction patterns against the various phases in the (Fe,Cr)–C and (Fe,Cr)–N systems was performed using the JEMS 2.0 software package. SAED patterns acquired from the bulk material below the case (under identical imaging conditions) were used as an internal calibration for accurate measurement of lattice parameter within the nitrided or carburized zone.

To supplement structural identification by electron diffraction, high-resolution (HR) XEDS elemental maps were acquired by an FEI\( ^\text{™} \) Image-corrected Titan\( ^\text{™} \) G2 300 kV S/TEM equipped with quad-silicon drift detectors (Super-X / ChemiSTEM). HR-STEM images were acquired using an FEI\( ^\text{™} \) Probe-corrected Titan\( ^\text{™} \) G2 300 kV S/TEM at a camera length of 60 mm (i.e. images predominately show Z contrast).

\(^1\)Also known as a Kossel-Möllenstedt pattern.
Chapter 4
Thermodynamics of Paraequilibrium Carburization and Nitridation

A brief treatise on the underlying principles of the CALPHAD method is presented here, along with its specific application to modeling phase paraequilibria upon carburization or nitridation of 2205. A routine including the most recent thermodynamic assessments within the (Fe,Cr,Ni,Mo,Mn)–(N,C) systems written in Wolfram Mathematica® 10.0.2 was used for all of the following simulations. A more thorough discussion on the application of CALPHAD modeling to paraequilibrium surface treatments of stainless steels can be found in Ref. [101], which contains the source code and parameters used in the analysis.

From a review of the (Fe,Cr,Ni,Mo,Mn)–(N,C) thermodynamic database, a nearly complete description of the 2205 system is available. All of the solid solution and relevant carbide/nitride phases can be described for each of the primary alloy constituents, with the exception of Mo₄N and (Cr,Ni,Mo)₅C₂. Of the dozen or so phase transformations that can occur within the 2205 system (see Fig. 2.4), many are intermetallics formed only at higher temperatures (see Fig. 2.7), and were thus ruled out as potential secondary phases during low-temperature paraequilibrium treatments.

The potential nitrides included: MN, ε-M₂N₁₋ₓ, M₂N, and γ’-M₄N. Within the Cr–N system, only two equilibrium nitride phases exist: stoichiometric hcp Cr₂N and rock-salt structured CrN. Though the Cr₂N phase is experimentally observed to have a narrow stability range (i.e. nearly a linear compound on the Cr–N phase diagram), it is considered within the CALPHAD structural framework to be isomorphic with the nitrogen-deficient ε-Fe₂N₁₋ₓ phase. Thermodynamic data of other nitride phases found especially in the Fe–N system, e.g. ζ-Fe₂N, α’-martensite, and α”-Fe₁₆N₂ are lacking, but their propensity to form in stainless steels during low-temperature nitriding has not been widely reported.

A full description is also available for the τ-M₂₃C₆, θ-M₃C, and ω-M₇C₃ carbides, while for Hägg χ-M₅C₂ carbide only Fe₅C₂ and Mn₅C₂ have been assessed. This carbide, though rarely observed in conventional steels, can form during low-temperature carbur-
4.1. COMPUTATIONAL THERMODYNAMICS: THE CALPHAD FORMALISM

ization of stainless steels, but was excluded in this analysis due to a lack of data. The $\omega$-M$_7$C$_3$ and $\tau$-M$_{23}$C$_6$ carbides have also been observed in 316L subjected to prolonged carburization or isothermal annealing [80,81,113], while $\theta$-M$_3$C has been observed in carburized martensitic 15-5 PH stainless steel [151].

4.1 Computational Thermodynamics: The CALPHAD Formalism

To circumvent the experimental difficulties in determining equilibrium phase diagrams for multi-component systems, a computational technique colloquially referred to as the CALPHAD (CALculation of PHase Diagrams) method was developed in the mid-1970s. Sundman and Ågren, in their seminal 1981 paper [152], summarized a general, multi-sublattice and multi-component thermodynamic model, which laid the foundation for most of the CALPHAD assessments made today. The expression ‘computational thermodynamics’ is more often used in place of ‘calculations of phase diagrams’ to reflect the fact that a phase diagram is only one piece of information that be obtained from thermodynamic calculations. The beauty of the CALPHAD method is that it allows for thermodynamic predictions in higher-order systems with data extrapolated from binary or ternary systems, and can describe phases that are normally unstable within the binary system. It also has the advantage of allowing predictions of metastable phase equilibria and determination of other thermodynamic factors, e.g. chemical potential, activity, heat capacity, etc., not present on a phase diagram. Quantification of changes in phase stability with a change in chemistry is then relatively straightforward. The CALPHAD formalism is behind the well-known Thermo-Calc® Software, for which many of the assessments used in the following calculations were originally conducted.

With regard to the paraequilibrium carburization and nitridation of 2205 DSS in this work, CALPHAD-based thermodynamic modeling allows for a prediction of the following:

- The solubility limit of carbon or nitrogen in the $\delta$-ferrite and $\gamma$-austenite solid solution phases of 2205 under paraequilibrium assumptions whereby secondary phases are kinetically inhibited from forming.

- The solubility limit of carbon or nitrogen in thermodynamic equilibrium with a paraequilibrium carbide or nitride, i.e. one which has nucleated and grown in a partitionless manner.

- The heterogeneous equilibrium boundaries between $\delta$-ferrite and $\gamma$-austenite as a function of temperature and interstitial content, the paraequilibrium eutectoid temperature, and thus the driving force for an isothermal, carbon- or nitrogen-induced $\delta \rightarrow \gamma$ phase transformation.
The CALPHAD method is built on describing the Gibbs free energy, \( G(\equiv H - TS) \), representing the energetic state of a closed system in equilibrium at fixed composition, temperature, and pressure, from which many other important thermodynamic variables are also derived. The choice of the Gibbs free energy as a minimizing function is due to the fact that the Gibbs energy is a function of temperature and pressure—properties that are conveniently controlled in experiments. The CALPHAD description for the Gibbs free energy is based on the crystal structure of the phase.

Because of the importance in maintaining a self-consistent description of lower-order systems, the temperature-dependence of \( G = f(T) \) relative to the standard-state enthalpy for pure elements and compounds is described empirically by Eq. 4.1 using the convention established by the Scientific Group Thermodata Europe (SGTE):

\[
G - H_{\text{SER}}^0 = a + bT + cT \ln(T) + dT^2 + eT^3 + fT^{-1} + ... \tag{4.1}
\]

where \( H_{\text{SER}}^0 \) represents the standard element reference (SER) enthalpy of the stable state as measured at 298.15 K and 1 atm. The coefficients \( a, b, c, d, \text{etc.} \) represent the model parameters. For simplicity, the pressure-dependence and magnetic contribution to the Gibbs free energy are handled separately. The pressure-dependence of \( G = f(P) \) is mostly known for only the pure elements, and consequentially most of the published data are valid only at 1 atm. The SGTE data for the elements have been compiled by Dinsdale [153]. Unfortunately, there is at present no universal criterion for the precision required of each CALPHAD parameter, which varies greatly between individual assessments.

In its most generic form, the molar Gibbs free energy of a solid solution, \( G_m \), is described by Eq. 4.2:

\[
G_m = G_{\text{mech}} + \Delta G_{\text{mix}} \tag{4.2}
\]

where

\[
\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T\Delta S_{\text{mix}} \tag{4.3}
\]

\( G_{\text{mech}} \) represents the mechanical mixture of the pure components and \( \Delta G_{\text{mix}} \) the additional free energy associated with the interaction between atoms upon mixing, which can further be reduced to the enthalpic \( \Delta H_{\text{mix}} \) and entropic \( \Delta S_{\text{mix}} \) contributions.

In the CALPHAD-based multiple sublattice description of solid solutions, \( G_\phi^\Phi \) represents the free energy of one mole of formula units of phase \( \phi \), and is comprised of five independent contributions according to Eq. 4.4:

\[
G_\phi^\Phi = \text{mech}G_{m}^{h\phi} + \text{ideal}G_{m}^{\Phi} + \text{excess}G_{m}^{\Phi} + \text{mag}G_{m}^{\Phi} + \text{pres}G_{m}^{\Phi} \tag{4.4}
\]

where \( \text{mech}G_{m}^{h\phi} \) represents the mechanical mixture of end members, \( \text{ideal}G_{m}^{\Phi} \) the ideal (configurational) entropic contribution, \( \text{excess}G_{m}^{\Phi} \) the additional free energy arising from non-
ideal interactions between constituents on separate sublattices, \( \text{mag} G_m^\phi \) the magnetic contribution, and \( \text{pres} G_m^\phi \) the change in free energy with pressure. Note that the superscript \( h\phi \) represents a hypothetical non-magnetic state of the pure elements and compounds as the magnetic contribution is handled separately.

The partial molar Gibbs free energy, henceforth referred to as the chemical potential, \( \mu_i \), is an important concept in the realm of thermodynamics, and can be thought of as physically representing the change in the free energy of a system when changing the composition by one atom or particle. Based on whether the constituent has a high or low chemical potential indicates its willingness to enter, leave, or react within the system. From the above CALPHAD description of \( G_m^\phi \), the chemical potential \( \mu_i \) of each constituent can be derived according to Eq. 4.5:

\[
\mu_i = \left( \frac{\partial G}{\partial n_i} \right)_{T,P,n_{j\neq i}}
\]  

where \( n \) is the number of moles of constituent \( i \). For example, the chemical potential of a metal constituent \( M \), \( \mu_M^{f\text{cc}} \), in 2205 austenite with nitrogen\(^1\) described by (Fe,Cr,Ni,Mo,Mn):\( (N,Va)_1 \) (the subscript indicating the number of sublattice sites per unit cell) is given in Eq. 4.6:

\[
\mu_M^{f\text{cc}} = G_m^{f\text{cc}} + \left( \frac{\partial G_m^{f\text{cc}}}{\partial Y_M} \right) - Y_{Fe} \left( \frac{\partial G_m^{f\text{cc}}}{\partial Y_{Fe}} \right) - Y_{Cr} \left( \frac{\partial G_m^{f\text{cc}}}{\partial Y_{Cr}} \right) - Y_{Ni} \left( \frac{\partial G_m^{f\text{cc}}}{\partial Y_{Ni}} \right) - Y_{Mo} \left( \frac{\partial G_m^{f\text{cc}}}{\partial Y_{Mo}} \right) - Y_{Mn} \left( \frac{\partial G_m^{f\text{cc}}}{\partial Y_{Mn}} \right) - Y_N \left( \frac{\partial G_m^{f\text{cc}}}{\partial Y_N} \right) - Y_{Va} \left( \frac{\partial G_m^{f\text{cc}}}{\partial Y_{Va}} \right)
\]  

The chemical potential of interstitial species, e.g. nitrogen in an \( f\text{cc} \) or \( b\text{cc} \) solution depends on the site occupancy between interstitial and substitutional sublattices, and is de-

\(^1\)The \( f\text{cc} \) lattice is treated as having two interpenetrating sublattices—one substitutional and one interstitial—where vacancies, \( Va \), are also treated as a constituent. In \( f\text{cc} \) solutions with a 1:1 site occupancy between substitutional and octahedral interstitial sublattices, the nitrogen concentration when each interstitial site is occupied is \( X_N = 0.5 \) (an ‘\( MN \)’ nitride), and similarly for \( b\text{cc} \) solutions with a site occupancy of 1:3, the maximum nitrogen concentration is \( X_N = 0.75 \) when each octahedral site is occupied (an ‘\( MN_3 \)’ nitride).
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termined according to Eq. 4.1:

\[
\mu_{N}^{\text{fcc}} = \left( \frac{\partial G_{m}^{\text{fcc}}}{\partial Y_{N}} \right) - \left( \frac{\partial G_{m}^{\text{fcc}}}{\partial Y_{Va}} \right)
\]

\[
\mu_{N}^{\text{bcc}} = \frac{1}{3} \left[ \left( \frac{\partial G_{m}^{\text{bcc}}}{\partial Y_{N}} \right) - \left( \frac{\partial G_{m}^{\text{bcc}}}{\partial Y_{Va}} \right) \right]
\]

Atomic nitrogen diffuses into an activated surface of stainless steel only because it can lower its chemical potential in solution relative to the gas phase. When the chemical potential of nitrogen, for example, in solution equals that in the gas phase, a balance of chemical forces exists, and there is no longer a driving force for further dissolution. Given sufficient time, the chemical potential of nitrogen at the gas–solid interface will equilibrate, establishing the metastable paraequilibrium solubility limit for the ambient nitrogen activity in the open system. Under the paraequilibrium kinetic constraints where only interstitial species are equilibrated (due to the limited diffusion of substitutional solutes), this paraequilibrium nitrogen solubility limit, \( X_{N}^{\text{max}} \), in both the bcc and fcc phases is established according to Eq. 4.7:

\[
\mu_{N}^{\text{fcc}} = \mu_{N}^{\text{gas}}
\]

\[
\mu_{N}^{\text{bcc}} = \mu_{N}^{\text{gas}}
\]

where the chemical potential of nitrogen in the gas is controllable through the ratio of NH\(_{3}\) and H\(_{2}\) according to Eqs. 2.9 and 2.10. The paraequilibrium solubility limit of nitrogen in solution thus increases as the chemical activity of nitrogen in the atmosphere increases. This situation is shown schematically in Fig. 4.1, where the chemical potential is defined by the common tangent to the molar Gibbs free energy\(^1\), \( G_{m} \), curve at a particular composition and temperature. As the chemical potential in the gas phase is increased, the tangents intersect the ordinate at higher values, and the solubility limit in bcc and fcc solutions increases. Though the chemical activity of carbon in a gas can be increased well above unity, it is useful to consider the paraequilibrium solubility limit of carbon in stainless steel with respect to graphite (i.e. \( a_{C}^{\text{gra}} = 1 \)). When the chemical potential of carbon in solution reaches that in graphite, a solid, there is a driving force for its precipitation in the steel, unlike nitrogen, which is a gas at unit activity.

Next, the solubility limit of nitrogen and carbon when a partitionless nitride or carbide has formed is considered. This situation does not represent one of true equilibrium because it is assumed that the carbide or nitride formed in a partitionless manner, adopting the parent phase chemistry. If the equilibrium phase were considered, metal atoms

\(^1\)There is a straightforward relationship between the description of \( G_{m} \) per mole of formula units used in the CALPHAD methodology and \( G'_{m} \) on a mole of atoms basis in the elementary thermodynamic model: \( G_{m} = (1 - X_{N})G_{m} \) [82].
on the substitutional sublattice would need to partition such that the lowest energy composition of the phase at the particular temperature was achieved. However, where secondary phases have been observed in low-temperature treatments of stainless steels, they are most often found to form in a (nearly) partitionless manner [81], due to the sluggish diffusion of metal constituents at treatment temperatures (see Fig. 2.14). In the case of forming a $\text{M}_x\text{N}_y$ nitride, M is equivalent to the matrix composition. With this constraint, the nitrogen solubility in ferrite or austenite is established by the molar free energy of the nitride phase, $G_{m}^{\text{M}_x\text{N}_y}$ (assuming the compound has unit activity), according to Eq. 4.8:

$$G_{m}^{\text{M}_x\text{N}_y} = x\mu_{\text{M}} + y\mu_{\text{N}}$$  \hspace{1cm} (4.8)
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The solubility limit in the presence of a nitride is determined by the nitrogen content that satisfies \( \Delta G = 0 \) associated with the \( \gamma \to M_xN_y \) or \( \delta \to M_xN_y \) reaction, i.e. \( \Delta G^{\gamma \to M_xN_y} = 0 \).

Lastly, the common tangent construction of the molar Gibbs free energy curves can be used to determine the heterogeneous equilibrium between \( \delta \)-ferrite and austenite in 2205 as function of interstitial nitrogen or carbon. The conditions satisfying this heterogeneous equilibrium in a closed system, i.e. the equilibrium boundaries between \( bcc \) and \( fcc \) solid solutions with nitrogen, dictate that the chemical potentials of the metal atoms and nitrogen atoms be equal in both phases (Eq. 4.9):

\[
\begin{align*}
\mu^{bcc}_M &= \mu^{fcc}_M \\
\mu^{bcc}_N &= \mu^{fcc}_N
\end{align*}
\]  

This equilibrium condition between the two phases is represented schematically on the molar Gibbs free energy curves in Fig. 4.2, where the equilibrium concentrations of nitrogen \( X_N({eq.}) \) in each phase establish the two-phase boundaries of coexisting ferrite and austenite at a particular temperature.

Note that an additional increase in supersaturation of the ferrite above \( X_N^{bcc}({eq.}) \) is required to provide the necessary compositionally-induced driving force for sustained growth of an austenite nuclei in a ferrite matrix (shown schematically in Fig. 4.3). Assuming there is no partitioning of metal constituents, a nuclei of austenite can only grow when \( \mu^{\gamma}_M < \mu^{\delta}_M \). If this critical supersaturation in ferrite is (i) less than the paraequilibrium limit established by Eq. 4.7 and (ii) above the eutectoid temperature \( T_e \) defined by the intersection of these phase boundaries, an isothermal carbon- or nitrogen-induced \( \delta \to \gamma \) phase transformation can occur.

4.1.1 Stress Effects

It was noted in Sec. 2.3 that low-temperature surface-hardening of bulk 316L can impart significant residual biaxial compressive stresses, as large as 3 GPa for the most carbon-enriched [154, 155] and 9 GPa for the most nitrogen-enriched [95, 156] expanded austenites. Wu [94] measured the surface residual biaxial stress in nitrided 316L using the XRD \( \sin^2 \psi \) sample-tilting method as a function of nitriding time, temperature, and activity. For the higher activity, and subsequently larger nitrogen supersaturation treatments, anomalous splitting of the [311] peak was observed at higher tilts. Of the two peaks, one corresponded to a tensile stress of 0.1 GPa and the other a compressive stress of 13 GPa. The \( \sin^2 \psi \) technique for stress measurement in expanded austenite samples may not be practical as it assumes all grains in a particular sample have the same lattice parameter, which is far from the case, at least in the most nitrogen-expanded austenite (Fig. 2.16). The resid-
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\[ G'_{m} \text{ [J mol}^{-1}\text{]} \]

\[ X_N \text{ (eq.) given by} \]

\[ \mu_N^{fcc} = \mu_N^{bcc} \]

\[ \mu_M^{fcc} = \mu_M^{bcc} \]

**Figure 4.2:** Schematic representation of \( G'_{m} \) for bcc and fcc solutions as a function of nitrogen concentration \( X_N \). The common tangent to the two curves establishes the composition \( X_N \text{ (eq.)} \) of the equilibrium phase boundaries between coexisting ferrite and austenite as a function of temperature.

Material stress measurements listed above are further complicated by the fact that they assume expanded austenite inherits the same elastic constants as the 316L from which it formed. Given that significant lattice expansions can be realized in expanded austenite, it seems reasonable that the nature of the interatomic potential will change, though it is not yet known what effect this may have on expanded austenite’s elastic anisotropy.

Despite the experimental challenges with measuring stress in expanded austenite, the results indicate that significant residual stresses can be realized\(^1\), especially innitrided

\(^1\)For comparison, shot peening, which is used to impart residual compressive stresses at the surface of metallic components, typically provides compressive stresses \(\leq 1 \text{ GPa}.\)
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open system $\rightarrow$ dissolve C or N

$T > T_{eut}$

$\delta \rightarrow \gamma$

$X_c = X_c(eq)$

$\gamma$ nuclei stable

$\mu_C = \mu_C$

$\mu_M = \mu_M$

$\mu_C > \mu_C$

$\mu_M > \mu_M$

$X_c(eq) < X_c < X_c(max)$

$\gamma$ nuclei grow

FIGURE 4.3: Schematic representation of nitrogen- or carbon-induced $\delta \rightarrow \gamma$ phase transformation above the eutectoid temperature. Critical supersaturation of $\delta$-ferrite required for sustained growth of austenite nuclei.

samples. Such large residual compressive stresses will affect the paraequilibrium solubility in accordance with Le Chatelier’s principle: in response to a biaxial compressive stress, the maximum metastable solubility limit will decrease. Furthermore, the importance of GPa-order stresses in the synthesis of expanded austenite is noted by the experiments of Christiansen et al. [97], in which they observed a substantial increase in maximum carbon and nitrogen supersaturations over those in bulk samples following treatment of 316L thin foils, which were converted to stress-free powders of homogeneous expanded austenite.

The contribution of a hydrostatic pressure $P$ to the Gibbs free energy of a phase, $\phi^{\text{pres}}G^\phi$, is described within the CALPHAD framework by Eq. 4.10:

$$
\text{pres}G^\phi_m = \frac{A \exp\left(a_0 T + a_1 T^2 + a_2 T^3 + a_3 T^{-1}\right)}{(K_0 + K_1 T + K_2 T^2)(n - 1)} \left[\left(1 + nP \left(K_0 + K_1 T + K_2 T^2\right)\right)^{1 - \frac{n}{2}} - 1\right]
$$

(4.10)

where $A, a_i, K_i,$ and $n$ are fitting parameters and $T$ the absolute temperature. Using the elemental data$^1$ for iron (bcc and fcc), chromium (bcc), nickel (fcc), and molybdenum (bcc) of Dinsdale [153], the change in Gibbs free energy $G_i$ of the elements with increasing hydrostatic pressure at 723 K (450 $^\circ$C) is shown in Fig. 4.4. Apparently, pressures on the order of several GPa significantly increases the free energy of these elements, all by roughly the same extent. This change in energy is comparable, if not larger than the contributions from the mechanical mixture and/or non-ideal interactions ($^{\text{mech}}G^\phi_m + ^{\text{excess}}G^\phi_m$) in stainless steels, and will therefore have a measurable effect on the paraequilibrium solubility limit.

To incorporate this stress-effect into the free energy description of 2205 $\delta$-ferrite and

---

$^1$The pressure-dependence on the free energy of manganese is not tabulated.
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![Graph showing change in Gibbs free energy with hydrostatic pressure of 2205 alloying elements relative to their respective standard states at 723 K (450 °C).]

**Figure 4.4:** Change in Gibbs free energy with hydrostatic pressure of 2205 alloying elements relative to their respective standard states at 723 K (450 °C).

austenite, a straightforward rule-of-mixtures was applied, despite the fact that the pressure-dependencies of the free energy of Cr, Ni, and Mo are known only for their standard states:

\[
\begin{align*}
\text{pres}_{G_{\text{m}^{2205-\gamma}}} &= X_{\text{Fe}} \text{pres}_{G_{\text{Fe}^{\text{bcc}}}} + X_{\text{Cr}} \text{pres}_{G_{\text{Cr}^{\text{bcc}}}} + X_{\text{Ni}} \text{pres}_{G_{\text{Ni}^{\text{fcc}}}} + X_{\text{Mo}} \text{pres}_{G_{\text{Mo}^{\text{bcc}}}} \\
\text{pres}_{G_{\text{m}^{2205-\delta}}} &= X_{\text{Fe}} \text{pres}_{G_{\text{Fe}^{\text{bcc}}}} + X_{\text{Cr}} \text{pres}_{G_{\text{Cr}^{\text{bcc}}}} + X_{\text{Ni}} \text{pres}_{G_{\text{Ni}^{\text{fcc}}}} + X_{\text{Mo}} \text{pres}_{G_{\text{Mo}^{\text{bcc}}}}
\end{align*}
\] (4.11)

A factor of \( \frac{2}{3} \sigma_b \) is used in Eq. 4.10 in place of \( P \) to represent the biaxial stress state that is induced by the restricted in-plane expansion of colossally-supersaturated austenite (balanced by lower tensile stresses in the core).

\(^1\)The small amount of manganese unaccounted for in the pressure-dependency was added to iron.
4.2 Predicted Stability in the 2205 System

When performing the calculations described above to determine the paraequilibrium solubility limit of carbon or nitrogen, etc., the compositions of the $\delta$-ferrite and austenite phases in 2205 listed in Table 4.1 were used. These compositions represent the average partitioning that was experimentally measured during AES line-scans of NT material. The ferritic 2205 phase is enriched several percent in chromium and molybdenum, and the austenite enriched in nickel and manganese.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Fe</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta$-ferrite</td>
<td>66.8</td>
<td>23.5</td>
<td>4.0</td>
<td>4.2</td>
<td>1.5</td>
</tr>
<tr>
<td>$\gamma$-austenite</td>
<td>69.2</td>
<td>20.0</td>
<td>6.3</td>
<td>2.0</td>
<td>2.5</td>
</tr>
</tbody>
</table>

4.2.1 Low-temperature Nitridation

The predicted paraequilibrium solubility limit for nitrogen in austenitic and ferritic 2205 is shown in Fig. 4.5 as a function of temperature, nitrogen activity, and biaxial compressive stress. The solubility as a function of temperature shown in Fig. 4.5(a) and (c) was determined for an iso-activity treatment of $a_{N_2} = 1.0 \times 10^5$. Similarly, the solubility as a function of nitrogen activity shown in Fig. 4.5(b) and (d) was calculated at an isothermal nitriding temperature of $T_N = 673$ K (400 °C). The solubility limits in 2205 austenite were plotted for residual stresses up to 12 GPa, which is an overestimate of what has experimentally been measured, but does give predictions in line with solubilities measured in nitrided austenitic stainless steels. The predicted solubility in 2205 ferrite was plotted for more modest stresses, due to the fact that a highly expanded ferrite has yet to be observed in treatment of ferrite-containing stainless steels. It is clear that both ferrite and austenite phases of 2205 are predicted to show retrograde nitrogen solubility. In the absence of residual stress, very large supersaturations are predicted in both phases, even with a modest activity of $a = 1.0 \times 10^5$—near the maximum of 38 at.% nitrogen achievable.
4.2. PREDICTED STABILITY IN THE 2205 SYSTEM

**Figure 4.5**: CALPHAD-determined paraequilibrium solubility of nitrogen in austenitic and ferritic 2205 as a function of temperature, activity, and biaxial stress state. Paraequilibrium solubility limit in (a) $\gamma$-austenite for an iso-activity treatment $a_{N_2} = 1.0 \times 10^5$, (b) $\gamma$-austenite for an isothermal treatment $T_N = 673$ K (400 °C), (c) $\delta$-ferrite for an iso-activity treatment $a_{N_2} = 1.0 \times 10^5$, and (d) $\delta$-ferrite for an isothermal treatment $T_N = 673$ K (400 °C).
4.2. PREDICTED STABILITY IN THE 2205 SYSTEM

in stress-free expanded austenite in 316L [157]. The effect of residual stress on paraequilibrium nitrogen solubility is much more pronounced in δ-ferrite. Likewise, the nitrogen activity has much stronger effect on the paraequilibrium solubility in δ-ferrite, i.e. for a given increase in nitrogen activity, the solubility in δ-ferrite should increase to a larger extent than austenite. Although the nitrogen solubility in 2205 δ-ferrite is lower than austenite at low activities, it is predicted to surpass the solubility in austenite when the activity reaches \( \approx 1.0 \times 10^4 \) in the absence of stress.

Ignoring any kinetic constraints, the solubility limit for nitrogen in austenitic and ferritic phases of 2205 when a partitionless nitride has formed is shown in Fig. 4.6. Due to the lack of experimental data on the pressure-dependence of \( G_m^\phi \) for the nitrides, it seems reasonable as a first approximation to assume that the addition of a hydrostatic or biaxial stress changes the free energy of the nitride or carbide by roughly the same extent as the solution. Therefore, according to the equilibrium condition given in Eq. 4.8 between a solid solution of metal and nitrogen atoms and an ordered nitride compound, the pressure terms drop out. It is noted however that the volume expansion associated with any δ-ferrite/austenite \( \rightarrow \) nitride/carbide phase transformation will further suppress such a transformation from occurring in the presence of a compressive stress.

With reference to the vertical lines at 20 at. pct. and 50 at. pct. in Fig. 4.6(a) representing M\(_4\)N and MN respectively, it is apparent that paraequilibrium versions of these nitrides are unstable in 2205 γ-austenite, and would not form unless significant partitioning of metal species occurred. The isomorphic M\(_2\)N and M\(_2\)N\(_{1-x}\) nitrides are stable in 2205 γ-austenite, and a driving force to nucleate this hcp phase exists near 10–15 at. pct. nitrogen at temperatures typical of low-temperature nitriding. The M\(_2\)N\(_{1-x}\) phase is plotted for \( x = 0.75 \), i.e. the interstitial sublattice is 75% vacant. Decreasing the nitrogen concentration of this paraequilibrium phase only further increases its stability, such that it is stable at even a 5–10 at. pct. nitrogen. The most nitrogen-deficient version of the \( \varepsilon \)-Fe\(_2\)N\(_{1-x}\) phase in the Fe–N system occurs at 15 at. pct. near 700 °C (Fig. 2.9). According to the CALPHAD prediction, if a partitionless nitride were to form in 2205 γ-austenite, it is most likely to be a nitrogen-deficient hcp M\(_2\)N\(_{1-x}\) phase, which has been reported in higher-temperature treatments of 316L.

The ferritic phase of 2205 is much less stable with respect to nitride phases, noted by the lower solubility limits in Fig. 4.6(b). With the exception of paraequilibrium MN, the other nitrides can form at negligible nitrogen concentrations below 750 K. Nitrogen-deficiency of the M\(_2\)N\(_{1-x}\) phase is also more stable in ferrite than the stoichiometric nitride. From these thermodynamic predictions, a nitrogen-supersaturated δ-ferrite in 2205 would be much less stable compared to supersaturated γ-austenite. As substitutional species in the non-close-packed hcc lattice diffuse more rapidly than in fcc by several orders of magnitude (Fig. 2.14), kinetic suppression of secondary phases in 2205 ferrite may be more sensitive to temperature and time.
Figure 4.6: Calculated solubility limit of nitrogen in (a) austenitic and (b) ferritic 2205 when a partitionless MN, M$_2$N, M$_2$N$_{1-x}$, or M$_4$N nitride forms. The M$_2$N$_{1-x}$ nitride solubility limit is plotted for a nitrogen concentration of 25% on the interstitial sublattice, i.e. M$_2$N$_{0.25}$.
4.2. PREDICTED STABILITY IN THE 2205 SYSTEM

4.2.2 Low-temperature Carburization

Considering now the predicted response of 2205 to carburization, the paraequilibrium solubility limit of carbon is shown in Fig. 4.7 as a function of temperature and biaxial stress. These lines represent the carbon concentration at which point the chemical potential of carbon in solution is equal to that of graphite, and thus there is a driving force for precipitation of graphite. The biaxial stresses incorporated into the calculation represent the limit of those that have been measured in carburized 316L.

The action of compressive stress has a greater effect on the predicted solubility of carbon than nitrogen in both phases. Disregarding the effect compressive stress, carbon solubility is moderately exothermic in austenite, but as the stress increases above 1 GPa, the solubility is predicted to become endothermic, and is nearly independent of temperature in the presence of a 1 GPa biaxial compressive stress. The paraequilibrium solubility limit for carbon in 2205 δ-ferrite is substantially low ($\approx 1$ at.%) at typical processing temperatures $\leq 713K$ (440 °C), even in the absence of stress. It is noted here the Cr–C CALPHAD parameters for austenite were insufficiently exothermic at low temperatures, three of which were revised through an optimization procedure to yield better agreement with experimental carbon supersaturations in 316L [128] (the effect of stress was not considered in this revision). It is possible that a similar optimization procedure is required for the Cr–C or Fe–C interaction parameters in ferrite.

The solubility limit for carbon in 2205 in equilibrium with a partitionless carbide is shown in Fig. 4.8 as a function of temperature. Like the nitrides, it is assumed that the pressure-dependence of $G^p_{m}$ for the solution and carbide phases is roughly identical, and the predicted solubility thus independent of stress-state.

In 2205 γ-austenite, the partitionless $\tau$-M$_{23}$C$_{6}$ is unstable, as shown by the vertical line at 20.7 at. pct. carbon. The $\theta$-M$_{3}$C carbide is not stable below $\approx 700$ K, and apparently the most stable of these carbides in 2205, $\omega$-M$_{7}$C$_{3}$, can only form when the carbon concentration in austenite reaches 18–20 at. pct. (at temperatures typical for carburizing of stainless steel). These rather fortunate results point to the great success in paraequilibrium carburization treatments of austenitic stainless steels. However, the thermodynamic data are not currently available to gauge the stability of a paraequilibrium $\chi$-M$_{5}$C$_{2}$—the most commonly observed carbide to form in carburized 316L after long or higher-temperature exposures.

Similar to the stability of nitrides, there is a much lower tolerance for carbon in δ-ferrite than austenite with respect to the carbides. Ignoring kinetic or stain-energy considerations, above $\approx 700$ K, $\theta$-M$_{3}$C appears the most stable carbide to form within δ-ferrite, while at temperatures between 650–700 K, $\omega$-M$_{7}$C$_{3}$ and $\theta$-M$_{3}$C are similarly stable. Around 625 K, there is an equal driving force for formation of the three paraequilibrium carbides when the nitrogen concentration in ferrite reaches $\approx 1$ at. pct.
Figure 4.7: Calculated paraequilibrium solubility limit of carbon (with respect to graphite at unit activity) in (a) austenitic and (b) ferritic 2205 as function of temperature and biaxial compressive stress.
Figure 4.8: Calculated solubility of carbon in (a) austenitic and (b) ferritic 2205 when a partitionless \( \tau\)-M\(_{23}\)C\(_6\), \( \theta\)-M\(_3\)C, or \( \omega\)-M\(_7\)C\(_3\) carbide forms.
4.2.3 Isothermal Nitrogen- or Carbon-induced Ferrite-to-Austenite Transformation

A pseudo-phase diagram showing the equilibrium phase boundaries between 2205 δ-ferrite and γ-austenite, and the paraequilibrium solubility for carbon and nitrogen in each phase at unit activity is shown in Fig. 4.9. Such paraequilibrium diagrams can be used to determine whether the nitrogen- or carbon-induced δ → γ phase transformation could occur during treatment of a ferrite-containing stainless steel. Intersection of the maximum and equilibrium boundaries define the paraequilibrium eutectoid temperature, $T_{eut}$. If the treatment is conducted above this temperature, the transformation can occur. With reference to Fig. 4.9, the equilibrium boundary for ferrite is lower than the paraequilibrium solubility at unit activity for both nitrogen and carbon, at all temperatures. The eutectoid reaction (between precipitation of graphite or nitrogen gas at unit activity) is entirely suppressed in this alloy, and an isothermal δ → γ phase transformation could occur at any realistic temperature. It is observed that nitrogen in 2205 δ-ferrite is highly unstable, due to its potent stabilizing nature for austenite, even as low as several parts per million (ppm) at typical treatment temperatures. This confirms that essentially all nitrogen in the 2205 alloy is segregated within the austenite phase. Though carbon also destabilizes 2205 δ-ferrite with respect to austenite, it can accommodate three orders of magnitude more carbon than nitrogen.

With this thermodynamic information, it would be expected that the first and most likely structural transformation to occur in 2205 δ-ferrite following colossal dissolution of interstitials would be transformation to austenite, ignoring any kinetic barriers. It is of interest to determine the processing parameters (nitriding temperature, time, and activity) that provide the kinetics needed for the reaction to take place, yet before precipitation of nitrides or carbides occur. To date, no direct evidence has been presented of an isothermal nitrogen- or carbon-induced δ → γ transformation occurring in DSS.
4.2. PREDICTED STABILITY IN THE 2205 SYSTEM

![Diagram of pseudo-phase diagram in the 2205 system for nitrogen and carbon.]

**Figure 4.9**: Pseudo-phase diagram in the 2205 system for (a) nitrogen and (b) carbon, showing the heterogeneous equilibrium boundaries (Eq.) between δ-ferrite and γ-austenite, and paraequilibrium solubility limit (Max.) in each phase at unit nitrogen and carbon activity.
5.1 Pitting Corrosion Resistance: Cyclic Potentiodynamic Polarization

The passivating capability of nitrided 2205—arguably the most important metric for determining the success or failure of a given surface hardening treatment of stainless steel—was measured by the resistance to pitting corrosion (i.e. passive film breakdown) in cyclic potentiodynamic polarization tests. The potentiodynamic polarization curves of as-received material and several nitrided 2205 samples during anodic oxidation in a 0.6 M NaCl solution are shown in Fig. 5.1. The 0.6 M NaCl solution is used to simulate seawater. The polarization curves show that the pitting resistance of samples treated at or below 380 °C is on par with the as-received material. The breakdown observed at higher potentials is not due to pitting, but results from transpassive dissolution—oxygen evolution at the surface, beyond which cyclic polarization hysteresis is followed and the sample repassivated. As the applied potential increases, simultaneous growth and dissolution of the passive oxide occurs until some instability is reached.

While no further surface analysis of the films present on these samples was conducted, it is worth mentioning that in interstitially-hardened 316L, growth and dissolution of the passive film occurred without the ingress of Cl\textsuperscript{−} ions in similar anodic oxidation experiments [7]. Instead, breakdown of the passive film was attributed to mechanical failure, which was improved in carburized 316L samples over non-treated material by a decreased growth rate and/or increased dissolution rate during anodic oxidation. As only one polarization test was conducted for each sample, it is not immediately clear whether the minor differences in open circuit potential, breakdown potential, or passive current density for each of the nitrided samples represent the stochastic nature of pitting initiation and re-passivation, or are indicative of meaningful changes in the passive oxide growth mechanisms.
5.1. PITTING CORROSION RESISTANCE

Despite these minor differences between various treatments, the results are promising and show that (at least) the passivating capability of 2205 can be maintained following nitridation at or below 380 °C. It is of further interest to know how the passive film performs in other types of corrosion, e.g. in the presence of a crevice, following the same treatments.

Low-temperature carburized 2205 likewise showed a comparable response as the non-treated material during anodic polarization, while the crevice corrosion resistance was dramatically improved [11]. In a week-long crevice corrosion experiment, carburized and non-treated samples were held in natural seawater in a specially designed holder main-
5.2 NANO-INDENTATION HARDNESS MEASUREMENT

tained at high potential (+300 mV). The non-treated cast and wrought 2205 material each displayed crevice initiation after only 1.44 ks (0.4 h) and 15.8 ks (4.4 h), respectively, while no crevice was initiated in carburized samples after the week-long exposure. Perhaps the most remarkable aspect of this improved electrochemical performance was that it occurred despite formation of a paraequilibrium carbide in the near-surface austenite grains (Sec. 6.2). Paraequilibrium secondary phases were observed in some of the near-surface δ-ferrite grains following nitridation (described later), which likewise do not appear to adversely affect the passivating capability of 2205.

The polarization behavior of the two wrought samples treated at 440 °C is interesting. Both samples were the only shown by XRD (Sec. 5.6) to contain significant concentrations of surface nitrides, albeit of two different types or chemistries. The sample treated at $a_{\text{N}_2} = 4.0 \times 10^9$ exhibited poorer pitting resistance than the samples treated below 380 °C, yet still showed some passivating characteristics despite prolific $\text{M}_2\text{N}_{1-x}$ formation at the surface. The sample treated with a nitriding activity $a_{\text{N}_2} = 1.8 \times 10^2$ contained a similar surface nitrogen concentration and a different nitride, yet showed no passivating capability, instead behaving like a conventional carbon steel.

Evidently, not all paraequilibrium nitrides are created equal, some greatly impairing the corrosion resistance and others only marginally so. The nature of these nitrides formed at higher treatment temperatures (440 °C) and their effect on passive oxide formation would be worth further investigation. Additionally, the nitride(s) in the sample treated at $a_{\text{N}_2} = 1.8 \times 10^2$ appears to be sub-surface and only within the austenite grains, whereas the sample treated at $a_{\text{N}_2} = 4.0 \times 10^9$ contained a fully nitridic surface layer. Metallographic and XRD structural analysis of the near-surface region of the $a_{\text{N}_2} = 1.8 \times 10^2$ sample (Sec. 5.6) indicate the nitride to be below 1 µm of the surface and most likely within the austenite phase. This nitride was observed in conventional ($\theta$–$\theta$) XRD, though not in a glancing-incidence geometry probing only the topmost several hundred nanometers of material. Furthermore, this sample did not exhibit extensive surface cracking like the sample treated at $a_{\text{N}_2} = 4.0 \times 10^9$, in which both δ-ferrite and austenite at the surface appeared to transform into $\text{M}_2\text{N}_{1-x}$.

In conclusion, similar to carburization, it appears that nitridation of 2205 is optimally performed at or below 380 °C, regardless of the nitriding activity. The two samples treated at 400 °C were not tested by cyclic polarization, but may show a similar response as the samples treated at 380 °C, as detailed structural analyses indicated the near-surface microstructure of these samples to be essentially identical.

5.2 Nano-indentation Hardness Measurement

The primary goal of nitriding or carburizing treatment is to increase the surface hardness of a material. In stainless steels, this is achieved by an interstitial-hardening effect, lead-
5.2. NANO-INDENTATION HARDNESS MEASUREMENT

The hardness of austenite and δ-ferrite in the as-received cast material was ≈ 5 GPa in both phases. The hardness of wrought material was nominally 6 GPa. The increased hardness over cast material is likely the result of work-hardening that occurs during rolling. It is noted here that these bulk hardness values were maintained in the core material following each treatment.

By producing 100 plan-view indents (with 1 gF) in each phase of cast 2205 nitrided at 380 °C and nitriding activity of $1.4 \times 10^5$, the surface hardness of austenite and δ-ferrite were $(6.3 \pm 0.3)$ GPa and $(7.0 \pm 0.2)$ GPa, respectively. The case-depth in the austenite and δ-ferrite grains of this sample were determined by AES depth-profiling to be 3.0 µm and 4.5 µm, respectively. With the 1.0 gF applied load, the indentation depth in each phase was ≈ 1 µm, indicating that the indent had not reached the core material, and some measurable increase in surface hardness of both phases was achieved by nitridation.

Apparently, the nitrided δ-ferrite is harder than the austenite. This measurable difference could result from the larger nitrogen supersaturation in the δ-ferrite (23 at.%) than the austenite (20 at.%) of this sample. As will be discussed later, the δ-ferrite showed two competitive responses to nitridation, either undergoing a transformation to (expanded) austenite, or spinodal-like decomposition into nanometer-scale Fe-rich and Cr-rich ferrite domains. It is not clear whether the indents made in former δ-ferrite grains occurred within the austenite transformation product or within regions that had decomposed. However, considering (i) the increased nitrogen supersaturation in former δ-ferrite (from its higher chromium/lower nickel concentration) as well as (ii) the nanometer-scale microstructure of both the austenite transformation and decomposition products, it seems reasonable that the former δ-ferrite would possess an increased resistance to dislocation motion over the larger austenite grains.

Several commercially-treated samples of wrought and cast 2205 were provided by the NRL that included the various gas-, salt-, and plasma-based carburizing, nitriding, and nitrocarburizing techniques listed in Table 2.10. Though the details of each production cycle are unknown, the samples, in general, possessed larger case-depths (10–20 µm) than the samples which were treated in this work, and were thus amenable to hardness-depth profiling. It is noted that these commercially-treated samples contained similar microstructures (from optical metallography/XRD) to the nitrided 2205 samples produced in this work—an expanded austenite and remnant ferrite were the only phases observed in each case.

An array of nano-indents was made on cross-sections of these samples, an example of which is shown in an optical micrograph in Fig. 5.2. The samples were lightly swab-etched for ≈ 5 s so as to not significantly increase the surface roughness following mechanical polishing, yet allowing for optical estimation of the case depth prior to making the indent array. The displaced volume of each indent is directly related to the hardness, which is generally less nearer the free surface where interstitial concentrations are highest.
5.2. NANO-INDENTATION HARDNESS MEASUREMENT

By relating the distance from the free surface of each indent in the array, hardness-depth profiles were produced, as shown for the various commercial samples in Fig. 5.3. The general shape of the hardness profiles is similar to that obtained following interstitial hardening of austenitic stainless steels, and is related to the shape of the nitrogen and/or carbon profiles. Overall, the near-surface hardness of these 2205 samples was increased 3- to 4-fold over bulk values (unchanged by the treatment). The fine-grained microstructure of wrought samples precludes hardness measurement in individual $\delta$-ferrite or austenite grains. In cast samples where individual indents in $\delta$-ferrite or austenite grains could be discerned, the hardness at a given depth was generally higher in $\delta$-ferrite, a potential explanation of which was discussed above. Further microstructural and microchemical analysis would be needed to determine the origin of the increased $\delta$-ferrite hardness over that achieved in the prior austenite grains.

The near-surface hardness values above 15 GPa are greater than even the hardest expanded austenite produced in single-phase austenitic stainless steels [1]. It is possible that these high hardness values correspond to small carbides or nitride precipitates near the surface that were not detectable by XRD or optical metallography. Most of these high hardness measurements were obtained within former $\delta$-ferrite grains, which, as will be described later, undergo transformation to austenite or decomposition to nitrogen-supersaturated domains of Fe-rich and Cr-rich ferrite. The natures of these phase trans-
FIGURE 5.3: Nano-hardness-depth profiles through commercially-treated (gas, salt, or plasma carburized, nitrided, or nitrocarburized) samples of 2205. Each color corresponds to a different (unspecified) treatment.

Formations in δ-ferrite most likely contribute to these exceptionally high hardness values. Whatever structural alterations occur in the near-surface grains, it is clear that 2205 can achieve a similar, if not greater increase in surface hardness over austenitic stainless steels by a colossal supersaturation interstitial hardening effect, and can be achieved without compromise of the corrosion resistance.\(^1\)

\(^1\)Though not shown, the pitting and/or crevice corrosion resistance of the commercially-treated samples was improved relative to non-treated material.
5.3 Metallography of Nitrided Samples

The surface of several cast and wrought 2205 samples following nitridation is shown in Fig. 5.4. Each surface was lightly swab-etched (∼ 5 s) in the modified aqua regia solution following cleaning and removal of any surface contaminants. The ‘islands’ of austenite in cast material are clearly distinguished from the matrix of δ-ferrite by the surface topography and minor variations in oxide thickness atop each phase. The rolling direction and former δ-ferrite and austenite grains are also discernible in the wrought sample. The contrast in native oxide that forms on δ-ferrite and austenite grains may be attributed to differences in base metal chemistry or nitrogen-supersaturation, and/or how the surface reacts with this particular reagent. Pristine surfaces can be achieved after surface hardening treatment by electrochemical techniques, which is indeed the usual circumstance for commercial providers of this technology. With the exception of a few etching pits and ‘browning’ of the austenite in the nitrocarburized sample, the surfaces appear similar to non-treated material when etched in the same fashion. Furthermore, secondary nitrides, if present in sufficient quantities, would likely be revealed by the etchant.

Plan-view DIC micrographs of a cast sample treated at 400 °C in pure ammonia (aN2 = 4.0 × 109) are shown in Fig. 5.5. This sample contained the largest surface concentration of nitrogen in both phases. The DIC micrographs highlight the difference in topography between former δ-ferrite and austenite grains following treatment. Later structural analyses revealed the δ-ferrite at the surface of this particular sample either transformed to austenite martensitically or spinodally decomposed into nitrogen-supersaturated Fe-rich and Cr-rich ferrite. The surface uplift and linear features that are observed in these micrographs result from the heavily-twinned, expanded austenite structure, also observed in the most nitrogen-supersaturated 316L stainless steel.

The improved electrochemical performance of the nitrogen-enriched layer relative to the bulk material can be qualitatively estimated by its response to chemical etching, as typified in the cross-section of carburized 316L. A cross-sectional SE-SEM micrograph1 of the wrought sample nitrided at 440 °C and aN2 = 1.8 × 102 is shown in Fig. 5.6. With the wrought microstructure, a majority of the phase in this particular cross-section (viewed in the ST direction) in contact with the free surface was δ-ferrite. The penetration depth of nitrogen can be estimated by the linear feature halfway through the austenite grains about 5 µm below the free surface, later confirmed by AES depth-profiling (Fig. 5.14). The ferrite grains in contact with the free surface contain ≈ 22 at.% nitrogen. The features in these grains may either be cracks formed under the large residual biaxial stresses or possibly secondary phases. This sample was shown by XRD (Fig. 5.26) to contain M2N1−x-like nitride, which could be representative of the dark contrast features arrowed within the

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1 All further SEM micrographs were recorded using the secondary electron (SE) Everhart-Thornley detector (ETD), unless otherwise noted.
5.3. METALLOGRAPHY OF NITRIDED SAMPLES

FIGURE 5.4: Optical plan-view micrographs of (a) cast nitrided, (b) nitrocarburized, (c) nitrocarburized and nitrided, and (d) wrought nitrided 2205.
5.3. METALLOGRAPHY OF NITRIDE SAMPLES

Figure 5.5: DIC plan-view micrographs of cast 2205 nitrided at 400 °C in pure ammonia \( (a_{N_2} = 4.0 \times 10^9) \).
5.3. METALLOGRAPHY OF NITRIDED SAMPLES

FIGURE 5.6: Cross-sectional SEM micrograph of wrought sample treated at 440 °C and \( a_{N_2} = 1.8 \times 10^2 \). The dark contrast features arrowed in the near-surface austenite grains are presumably paraequilibrium nitrides.

near-surface austenite. It was further noted by GI-XRD (Fig. 5.30) that this nitride was primarily sub-surface, i.e. below several hundred nanometers of the free surface. GI-XRD also revealed that a non-expanded, remnant \( \delta \)-ferrite phase also existed at the surface.

An etched cross-section of the sample treated at 440 °C in pure ammonia (\( a_{N_2} = 4.0 \times 10^9 \)) is shown in Fig. 5.7. XRD and GI-XRD (Figs. 5.26 and 5.30) indicated this sample contained a large volume fraction of \( hcp \) \( M_2N_{1-x} \) nitride at its surface. By AES compositional depth-profilng, the surface contained approximately 20 at.% nitrogen and extended at least 27 µm into the sample. There are several distinct layers apparent within the etched cross-section. The surface of the sample shows a darker contrast and is highly embrittled as evidenced by a prolific crack network (presumably due to the formation of nitrides in both phases). The case depth ranges from 27–32 µm below the free surface whereby a
transition between a smooth and course etching response of the bulk material is observed. Both the δ-ferrite and austenite grains in the lower-nitrogen region of the case are more etch-resistant than the bulk. The austenite grains below the brittle surface layer display linear features, likely slip bands or micro-twins formed as a means of stress relaxation during the restricted in-plane expansion. Similar features are found in interstitially-hardened austenitic stainless steels, and have been shown by TEM to be micro-twins and/or stacking faults and not necessarily secondary phases. The presence of such features is indicative of retained ductility in the expanded austenite.

It is interesting that this sample outperformed the sample treated at the same temperature with an activity of $1.8 \times 10^2$ during anodic polarization (Fig. 5.1). Due to the
extensive crack network at the surface of this sample, the Cl\textsuperscript{−}-containing solution may have penetrated to regions of precipitate-free expanded austenite, for which the passivating characteristics were actually gauged during the cyclic polarization experiment. The sample treated at 440 °C and \(a_{\text{N}_2} = 1.8 \times 10^2\) did not show as extensive a crack network, and from metallography/XRD appeared that nitrides had formed only in the near-surface austenite grains. The sensitization of near-surface austenite grains in this sample may have hindered its ability to form a protective oxide.

The electrochemical response of former δ-ferrite and austenite grains in samples which did not reveal secondary nitrides by metallographic or XRD analyses is indicated in Fig. 5.8 for samples nitrided between 325 °C and 400 °C with nitriding activities between \(1.8 \times 10^2\) and \(4.0 \times 10^9\). The surface layer within each sample was shown by GI-XRD to contain only expanded austenite and some volume fraction of non-expanded ferrite. The case depths, with the exception of the sample treated at 400 °C and \(a_{\text{N}_2} = 4.0 \times 10^9\), are quite shallow (≤ 6 µm) following 7.2 ks (20 h) nitridation. In each of the micrographs there is contrast between the etching response of the nitrogen-supersaturated δ-ferrite and austenite relative to the bulk material. A more distinct boundary exists between the nitrogen-supersaturated and bulk austenite, as is observed in 316L, where the surface layer appears elevated relative to the core. Linear features are observed in the near-surface austenite grains, later confirmed by TEM to be micro-twins. The difference in electrochemical attack is more gradual in the δ-ferrite grains, where the removal rate appears similar in both the case and core, though the nitrogen-enriched δ-ferrite appears smoother and also shows linear features not observed in the bulk δ-ferrite.

The network of plate-like features in the δ-ferrite case was most prevalent in the etched cross-section of the sample treated at 380 °C and \(a_{\text{N}_2} = 1.4 \times 10^5\). Several micrographs of this sample are shown in Fig. 5.9. This network of features in former δ-ferrite grains was identified as transformed austenite. The nature of this transformation product will be described in further detail later.

The differing response between the near-surface and bulk δ-ferrite/austenite to chemical etching was confirmed by AES line-scans (Fig. 5.16) to correspond to the penetration depth of nitrogen in each phase. The line running parallel to the surface in each phase is within ±1 µm of the measured nitrogen profile. For each nitridation treatment, the nitrogen profile extends deeper within the δ-ferrite grains. There is also evidence of enhanced diffusion resulting in an extension of the austenite case near the δ-ferrite–austenite inter-phase boundary. Nitrogen could have diffused along the short-circuit δ-ferrite–austenite interface at an increased rate, or nitrogen from the adjacent δ-ferrite grain could have also diffused laterally into the austenite. The diffusivity of nitrogen, at least at infinite dilution, is 3–5 orders of magnitude higher in ferrite than austenite (Fig. 2.14) at the nitriding temperatures used in this investigation. With reference to the micrograph in Fig. 5.8(g), it seems most likely that the extension of the austenite case near the δ-ferrite–austenite
FIGURE 5.8: Cross-sectional SEM micrographs of cast 2205 (with the exception of (d), which is wrought) nitrided at (a) 325 °C and $a_{\text{N}_2} = 3.0 \times 10^3$, (b) 350 °C and $a_{\text{N}_2} = 1.8 \times 10^2$, (c) 350 °C and $a_{\text{N}_2} = 3.0 \times 10^3$, (d) 350 °C and $a_{\text{N}_2} = 5.8 \times 10^4$, (e) 350 °C and $a_{\text{N}_2} = 1.4 \times 10^5$, (f) 380 °C and $a_{\text{N}_2} = 3.0 \times 10^3$, (g) 400 °C and $a_{\text{N}_2} = 3.0 \times 10^3$, (h) 400 °C and $a_{\text{N}_2} = 4.0 \times 10^3$. 

5.3. METALLOGRAPHY OF NITRIDED SAMPLES
5.3. METALLOGRAPHY OF NITRIDED SAMPLES

Figure 5.9: Cross-sectional micrographs obtained from a cast sample treated at 380 °C and $a_{\text{N}_2} = 1.4 \times 10^5$, revealing a high density of plate-like features in former $\delta$-ferrite grains. These features were later identified as an austenite transformation product that grew isothermally during nitrogen dissolution in the $\delta$-ferrite.
interface occurred as a result of the more rapid diffusion of nitrogen through δ-ferrite. That is, ignoring any concentration-dependent or in-plane diffusion, the nitrogen profile in austenite extends deeper near the interphase boundary only where there exists an oblique angle between the free-surface austenite and δ-ferrite grains, as shown schematically in Fig. 5.10.

![Figure 5.10: Schematic representation of extended nitrogen profile near δ-ferrite–austenite interface resulting from the increased diffusivity of nitrogen in δ-ferrite.](image)

It was mentioned in Sec. 2.3 that an orientation dependence on the surface concentration, and therefore penetration depth of nitrogen, is observed during nitridation of 316L as a result of the elastic anisotropy of the material. For example, after nitridation of 316L at 440 °C for 288 ks (80 h), the surface concentration and case depth for ⟨111⟩-oriented grains were 18 at.% and 10 µm, and 19 at.% and 17 µm in ⟨100⟩-oriented grains. Such an exaggerated difference in case depth with minor differences in surface concentration between individual δ-ferrite and austenite grains was not observed in any of the nitrided 2205 samples, although longer treatments, and hence thicker cases, may be required to determine if a similar orientational-dependent case depth occurs in 2205.

### 5.4 Concentration Depth-Profiling by AES

Cross-sectional Auger line-scans were conducted on cast material to measure the case depth and surface concentration of nitrogen and carbon in the δ-ferrite and austenite phases of 2205. A representative SEM micrograph acquired in the AES system after Ar⁺ sputtering with superimposed cross-sectional line-scans through each phase is shown in Fig. 5.11. The varying sputter-rates between the two phases, as well as that between the
5.4. CONCENTRATION DEPTH-PROFILING BY AES

nitrogen-enriched layer and core material, effectively etches the surface and allows each region of the microstructure to be optically distinguished. Whether the line-scan was performed through a ferritic or austenitic grain was verified by the respective chromium, nickel, and molybdenum concentrations.

Figure 5.11: SEM micrograph revealing cross-sectional Auger line-scans through ferritic and austenitic grains of nitrided 2205 (cast) following Ar$^+$ sputter-cleaning of the surface.

Line-scans were also conducted on the three wrought specimens. A cross-sectional SEM micrograph of wrought 2205 after Ar$^+$-sputtering in the AES system is shown in Fig. 5.12. The $\delta$-ferrite and austenite grains within the case are again discerned by their different sputtering rates. Cross-sectional line-scans through the case traversed multiple grains of each phase.

The nitrogen concentration plotted as function of depth through the wrought sample treated at $T_N = 440$ °C in pure ammonia ($a_{N_2} = 4.0 \times 10^9$) is shown in Fig. 5.13. The normalized chromium, nickel, and molybdenum concentrations are included in the concentration-depth profile for discernment of the nitrogen content through $\delta$-ferrite and austenite grains. The concentration of nitrogen in $\delta$-ferrite grains is consistently higher than adjacent austenite grains.
Interestingly, even with the metallic elements normalized, the iron (not shown) and chromium composition measured in the case are slightly higher and lower, respectively, than in the bulk material (also observed in line-scans of cast material). The same phenomena was observed during AES depth-profiling of nitrided 316L \[109\]. The quantification routine of AES spectra performed by the software uses internal sensitivity factors for each element in the analysis. Even with the exclusion of nitrogen from the quantification, these sensitivity factors yield a slight over- and under-estimation of iron and chromium concentrations in the case, though the bulk $\delta$-ferrite and austenite compositions agree with other spatially-resolved measurements (e.g. XEDS). This relationship between the measured nitrogen and chromium concentration indicates that the yield of Auger electrons from chromium atoms is somehow affected by the presence of large concentrations of interstitial nitrogen, otherwise known in AES as a 'matrix effect'. The possibility of chromium evolution (highly volatile at higher temperatures) at the activated gas–metal interface during treatment can be ruled out by the fact that substitutional diffusion of chromium at the temperatures of interest is no more than a few atomic spacings after 7.2 ks (20 h) (see
5.4. CONCENTRATION DEPTH-PROFILING BY AES

![Graph showing concentration-depth profile](image)

**Figure 5.13:** Auger concentration-depth profile through wrought sample nitrided at $T_N = 440 \, ^\circ C$ and $a_{N_2} = 4.0 \times 10^9$. The metal composition is normalized.

This matrix effect was not observed during quantification of AES spectra in carburized samples. Despite the modest underestimation of chromium in the nitrogen-enriched layer, the general trend between ferrite and austenite is observed allowing the nitrogen content through each phase to be determined.

The nitrogen depth-profiles measured by several line-scans on the wrought sample treated at $T_N = 440 \, ^\circ C$ and $a_{N_2} = 1.8 \times 10^2$ are shown in Fig. 5.14, and similarly for the wrought sample treated at $T_N = 350 \, ^\circ C$ and $a_{N_2} = 5.8 \times 10^4$ in Fig. 5.15. The matrix composition used to distinguish between each phase is not shown. The nitrogen concentration is similar at a given depth for each line-scan through the same phase, and again a strong discontinuity between the $\delta$-ferrite and austenite nitrogen concentrations is observed. The two nitrogen profiles in the samples treated at $T_N = 350 \, ^\circ C$ and $a_{N_2} = 5.8 \times 10^4$ were conducted mainly through $\delta$-ferrite, and both through roughly the same thickness.
5.4. CONCENTRATION DEPTH-PROFILING BY AES

Figure 5.14: Auger concentration-depth profiles through wrought sample nitrided at $T_N = 440 \, ^\circ C$ and $a_{N_2} = 1.8 \times 10^2$.

of austenite. Though each line-scan showed approximately the same nitrogen concentration at the surface of austenite and ferrite grains, the penetration depth of nitrogen was greater for the profile which contained an austenitic surface grain than the line-scan with a sub-surface austenite grain. Although the diffusivity of nitrogen at low concentrations is higher in ferrite, the diffusivity of interstitial nitrogen in austenite is strongly concentration-dependent, increasing with increasing supersaturation. Nitrogen may have initially extended deeper in the region with a ferritic surface, but the supersaturation of nitrogen, and hence the diffusivity of nitrogen, is ultimately greater in the surface austenite grain, permitting more nitrogen to be supplied to the underlying ferrite.

The surface concentration of nitrogen was higher in the sample treated at $T_N = 440 \, ^\circ C$ and $a_{N_2} = 1.8 \times 10^2$ than that treated at $T_N = 440 \, ^\circ C$ with a much higher activity of $4.0 \times 10^9$ where $\delta$-ferrite was in contact with the surface; however, the case depth was
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**Figure 5.15**: Auger concentration-depth profiles through wrought sample nitrided at $T_N = 350 \, ^\circ\text{C}$ and $a_{N_2} = 5.8 \times 10^4$.

significantly less (5 µm vs. 30 µm). One explanation is that the extensive surface cracking exhibited by the sample treated with $a_{N_2} = 4.0 \times 10^9$ interfered with the yield of Auger electrons during lateral translation of the electron beam near the free surface. Another possibility is that the $M_2N_{1-x}$ nitrides, once formed at the surface of the $a_{N_2} = 4.0 \times 10^9$ sample prevented further supersaturation of interstitials in these grains. Although these observations in higher temperature treatments are worthy of further inquiry, they were ultimately deemed less virtuous in this work due to the impaired corrosion resistance of 2205 when nitrided at a temperature of 440 °C.

The nitrogen concentration-depth profiles measured through individual $\delta$-ferrite and austenite grains of cast material showing no evidence of nitride precipitation are plotted in Fig. 5.16 as a function of nitriding temperature and activity. The surface concentration, $C_{N_\delta}^{\delta}$, and penetration depth, $x_{N_\delta}^{\delta}$, of nitrogen measured to within ±0.5 at.% and ±0.5 µm

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5.4. CONCENTRATION DEPTH-PROFILING BY AES

in each of these samples is also presented in tabular form in Table 5.1.

The effects of nitriding temperature and activity as they relate to surface concentration and diffusion depth are observed for each phase. The concave shape of the nitrogen profiles through both 2205 δ-ferrite and austenite grains are similar to those observed after nitridation of 316L austenitic stainless steel [1, 94]. Increasing the nitrogen activity at a fixed nitriding temperature increases the surface concentration and case depth in each phase of 2205, the effect of which is more pronounced in the δ-ferrite, especially at lower temperatures. At 350 °C for example, increasing the nitriding activity from $1.8 \times 10^2$ to $1.4 \times 10^5$ increases the surface concentration of nitrogen in δ-ferrite from 15.5 at.% to 21 at.%, respectively, while the increase in austenite is from 14.5 at.% to 15 at.%. This effect is lessened for the higher nitriding temperatures of 380 °C and 400 °C, where the increase in activity yielded roughly similar increases in surface concentration for both phases. This strong temperature dependence may be explained by the catalysis of ammonia decomposition and nitrogen adsorption at the surface of ferrite and austenite at higher temperatures. Furthermore, the δ-ferrite showed the most prolific transformation to austenite for nitriding temperatures of $T_N = 380$ °C and 400 °C, although some transformation was observed when treated at 325 °C and 350 °C.

Unlike the effect observed in 316L [94], lowering the nitriding temperature at a fixed nitrogen activity (observed for $a_{N_2} = 3.0 \times 10^3$ but not $a_{N_2} = 1.4 \times 10^5$) serves to increase the surface concentration of nitrogen in both austenite and ferrite. This is in line with the CALPHAD-based thermodynamic calculations, which predict exothermicity of nitrogen dissolution in ferritic and austenitic 2205 (see Fig. 4.5). Retrograde nitrogen solubility in 316L is also predicted by CALPHAD. This difference in the effect of nitriding temperature on surface concentration between the two stainless steels could be attributed to the higher nickel content of 316L compared to 2205, and the fact that the CALPHAD interaction parameters used to predict the paraequilibrium nitrogen solubility may not be accurate at lower temperatures. Similar to the effect of activity on surface concentration, the temperature dependence on surface concentration is also strongest in δ-ferrite.

The highest supersaturation of nitrogen in δ-ferrite was 28 at.%, although the near-surface δ-ferrite of this sample had completely transformed to austenite (discussed later). The highest nitrogen concentration measured in bulk 316L nitrided at 440 °C in pure ammonia was 25 at.% [94], identical to the highest measured concentration in the austenitic phase of 2205 (treated at $T_N = 400$ °C in pure ammonia). The highest nitrogen concentration in which bcc ferrite was identified at the surface by TEM was 23 at.% in the sample treated at 380 °C and $1.4 \times 10^5$ nitriding activity. This concentration of nitrogen in ferrite solid solution is orders of magnitude higher than the equilibrium solubility ($\sim 10^{-3}$ at.%) from Fig. 4.9) at the nitriding temperature, although is significantly less than the paraequilibrium solubility predicted by CALPHAD in Fig. 4.5 using the current interaction parameters. In the absence of residual stress, CALPHAD predicts the paraequilibrium
Figure 5.16: Nitrogen concentration-depth profiles measured by AES through (a) austenite and (b) δ-ferrite grains of cast 2205 nitrided at various temperatures and activities. The analytical uncertainty in nitrogen concentration is ±1 at.-%.
Table 5.1: Surface concentration, $C^\delta_N$, and penetration depth, $x^\delta_N$, of nitrogen as a function of nitriding temperature and activity, measured to within ±0.5 at.% and ±0.5 µm in each of the cast nitrided samples.

<table>
<thead>
<tr>
<th>$T_N$ [°C]</th>
<th>$a_{N_2}$</th>
<th>325</th>
<th>350</th>
<th>380</th>
<th>400</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C^\delta_N$ [at.%]</td>
<td>3.0 x 10^3</td>
<td>1.8 x 10^2</td>
<td>3.0 x 10^3</td>
<td>1.4 x 10^5</td>
<td>3.0 x 10^3</td>
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<tr>
<td>325</td>
<td>21.0</td>
<td>15.5</td>
<td>19.0</td>
<td>21.0</td>
<td>16.0</td>
</tr>
<tr>
<td>350</td>
<td>19.0</td>
<td>14.5</td>
<td>13.5</td>
<td>15.0</td>
<td>13.5</td>
</tr>
<tr>
<td>$x^\delta_N$ [µm]</td>
<td>1.5</td>
<td>1.5</td>
<td>3.5</td>
<td>4.0</td>
<td>5.0</td>
</tr>
<tr>
<td>325</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>2.0</td>
<td>3.0</td>
</tr>
</tbody>
</table>
solubility limit of nitrogen in ferrite at 380 °C and $1.4 \times 10^5$ nitriding activity to be nearly 36 at.%. For each phase in each of the treatments, the predicted paraequilibrium solubility is significantly higher than the experimental value. The origin of this discrepancy could lie in (i) inaccurate interaction parameters for the temperatures of interest (as previously shown for paraequilibrium carbon solubility in austenite [128]), (ii) the existence of a large residual biaxial stress state which serves to lower the paraequilibrium solubility (Fig. 4.5, or (iii) the fact that a true paraequilibrium condition was not reached at the gas–metal interface after 72 ks (20 h) treatment. It was shown in 316L [94] that the surface concentration of nitrogen increased from 17 at.% to 19 at.% when the nitriding duration increased from 72 ks (20 h) to 288 ks (80 h). Even if kinetic processes prevent a true paraequilibrium condition (i.e. the activity of nitrogen in solution equaling that in the gas) from being established at the gas–metal interface, the discrepancy is significant and most probably caused by inaccurate interaction parameters or the effect of stress on the calculation.

AES line-scans through a carburized sample of 2205 (cast) are shown in Fig. 5.17 following Ar$^+$ sputtering. The overall case-depth in each phase can, like chemical etching, be qualitatively estimated by the differing sputtering rates between the nitrogen-enriched and core material. The concentration-depth profiles through the three carburized samples (Table 3.3) are shown in Fig. 5.18, from which several key observations can be made. For each carburization temperature $T_C$, the carbon supersaturation at the surface is higher in $\delta$-ferrite (also true of nitridation). The solubility of carbon in both 2205 $\delta$-ferrite and austenite is also found to be exothermic, though CALPHAD predicts endothermic solubility in $\delta$-ferrite, and exothermic solubility in austenite only in the absence of residual stress. The profile also drops off more quickly in the $\delta$-ferrite grains, unlike nitrogen which is always found to extend deeper in $\delta$-ferrite. These observations can be explained on the following basis. It was mentioned that nitridation led some, if not a majority of the near-surface $\delta$-ferrite to transform to austenite; elsewhere in the case, a spinodal reaction occurred. Carburization did not lead to any $\delta \rightarrow \gamma$ transformation, and instead the spinodal decomposition was the only structure response within the carbon-enriched zone. Although nitrogen and carbon diffuse more rapidly through ferrite, the high-dislocation density associated with the spinodal decomposition may have provided sufficiently stable sinks for interstitial carbon that prevent any further ingress. Following transformation to austenite during nitridation, the nitrogen atoms continued to diffuse through the austenite and supersaturated $\delta$-ferrite allowing for a deeper, more gradual profile to be achieved. This point will be returned to in a later discussion.

Lastly, the nitrogen and carbon depth-profiles through a commercially-nitrocarburized sample of 2205 are shown in Fig. 5.19, along with the SEM image and superimposed line-scans used to form them in Fig. 5.20. The general trend of each individual nitriding or carburizing treatments is observed in both phases. The nitrogen (and maximum carbon) concentration is higher in $\delta$-ferrite. The penetration depth of nitrogen is roughly
the same in both phases, while the carbon profile extends deeper in austenite. The inner carbon profile is a general feature of nitrocarburizing treatment of stainless steels, and as discussed earlier results from the lowering of the carbon activity coefficient in solution in the presence of nitrogen. It is hypothesized, based on the aforementioned results, that the nitrogen-enriched layer in δ-ferrite transformed to austenite, while the carbon-enriched zone underwent spinodal decomposition to Fe-rich and Cr-rich ferrite.
Figure 5.18: Carbon concentration-depth profiles through 2205 (a) austenite and (b) δ-ferrite grains following gas-phase carburization.
Figure 5.19: Nitrogen and carbon concentration-depth profiles through 2205 (a) austenite and (b) δ-ferrite grains following a commercial nitrocarburizing treatment.
5.5 MICROCHEMICAL ANALYSIS: APT

Inasmuch as AES composition profiling provided a spatial resolution on the order of 30 nm (the size of the electron probe used in the analysis), microstructural features in the $\delta$-ferrite phase were shown to be even smaller by TEM. To better determine the composition of nitrogen and its distribution within the $\delta$-ferrite grains at an even finer scale, the APT technique was used on several nitrided samples. APT micro-tips were prepared by the FIB technique from individual grains of $\delta$-ferrite in wrought and cast material treated at $T_N = 380^\circ C$ and $a_{N_2} = 1.4 \times 10^5$. Micro-tips from the wrought sample was extracted from the plan-view surface (i.e. where the nitrogen concentration was highest), while the cast micro-tips were prepared from a cross-section of the sample. As shown in the micrographs in Fig. 5.9, the cast sample revealed a high-density of new plate-like features (later verified by TEM to be an austenite transformation product) within the former $\delta$-ferrite grains. The goal in APT micro-tip preparation from this cast sample was to capture an interface between the plates and the adjacent matrix somewhere near the middle of the

![SEM micrograph revealing cross-sectional Auger line-scans through a nitrocarburized sample of cast 2205 following Ar$^+$ sputter-cleaning of the surface.](image-url)
5.5. MICROCHEMICAL ANALYSIS: APT

nitrogen profile where the density of plates was lower. The near-surface δ-ferrite grains in the wrought sample also contained similar features.

The 3D reconstructions of a micro-tip obtained from a wrought and cast sample are shown in Fig. 5.21. Each point (a “voxel”) in the 3D reconstruction represents an individual atom detected by the LEAP instrument. These reconstructions were produced using only the nitrogen (yellow) and chromium (pink) atoms for clarity. The overall metal composition of each tip was identical to that measured by AES in bulk 2205 δ-ferrite (Table 4.1).

The bulk nitrogen concentration in the wrought and cast samples was 16.0 at.% and 10.9 at.%, respectively. The software is able to construct a so-called iso-concentration surface, whereby the surface connects regions of a fixed, predefined concentration. The iso-concentration surface for the wrought micro-tip in Fig. 5.21(a) was constructed for 19.0 at.% nitrogen, and in the cast micro-tip in Fig. 5.21(b) for 14.2 at.% nitrogen. By performing a “cluster analysis” with the aid of the Cameca IVAS software package, the nitrogen atoms (as well as all metal atoms) were determined to be randomly distributed throughout each of these micro-tips. That is, at least in these samples, the nitrogen and metal atoms were homogeneously distributed and no preferential ordering had occurred. The same was true for all wrought and cast APT micro-tips (10 in total) with the exception of one wrought sample. The nitrogen and chromium 3D reconstruction of this sample is shown in Fig. 5.22.

The bulk nitrogen concentration of this micro-tip was identical to that measured in the other wrought samples, 16.0 at.%. This concentration of nitrogen, although high, was less than that measured at the surface by AES in the cast sample treated under the same condition, 23 at.%. Considering that the chromium and nickel concentrations in the wrought material were slightly higher and lower than in cast material, the surface concentration of nitrogen would presumably be similar if not higher in the wrought δ-ferrite. Although the wrought micro-tips were prepared from a plan-view surface, final ion thinning of the sample produced a volume of material for analysis approximately 1–2 µm below the free surface. Still, according to the AES depth profile, the nitrogen concentration at this depth should be closer to 20 at.%. It is known that the detection efficiency of carbon in bainitic steels by LEAP tomography can be lessened by an analytical artifact [158, 159], which might also account for an underestimate of the high-nitrogen content within these samples.

This sample was the only shown by a cluster analysis to possess a statistically non-random distribution of nitrogen. An iso-concentration surface at 22.5 at.% is shown in Fig. 5.22(a). This surface appears in the general form of a plate near the surface of the micro-tip. The nitrogen content of the high-nitrogen “plate” is itself not uniform. A composition profile through the cylindrical region of interest in Fig. 5.22(b) is plotted in Fig. 5.23 from near the surface of the micro-tip extending into the bulk. The metal atoms
5.5. MICROCHEMICAL ANALYSIS: APT

Figure 5.21: 3D APT reconstructions of a δ-ferrite micro-tip from (a) wrought and (b) cast 2205 nitrided at 380 °C with an activity of $1.4 \times 10^5$. Each voxel represents an individual atom detected by the LEAP instrument. Each reconstruction was produced using only the nitrogen (yellow) and chromium (pink) atoms. The bulk nitrogen concentration of the wrought and cast micro-tips was measured to be 16.0 at.% and 10.9 at.%, respectively. The iso-concentration surface of nitrogen in the wrought sample is shown for 19.0 at.% and in the cast sample for 14.2 at.%. The concentration of nitrogen and metal atoms in each of the samples was shown to be homogeneously distributed.

have been normalized to the bulk concentration. The composition in and around this iso-concentration surface can also be plotted in a so-called proximity histogram or “proxigram” as shown in Fig. 5.24. Within the proxigram, the software determines the composition in the vicinity of the iso-concentration surface (negative distances from the iso-concentration surface represented at 0 nm) which is plotted into the center of the surface (positive distances). The region within and around the plate according to the composition profile is enriched in nitrogen, chromium, and manganese, and depleted in iron. Within
the plate itself, the nitrogen concentration approaches nearly 30 at.%, and interestingly, the chromium concentration is maximum near the surface and further reduced within it. Inside the surface, molybdenum is highly enriched and manganese is depleted. There appears to be a slight enrichment of nickel as well. Were this high-nitrogen plate-like region to represent an $M_4N$ nitride, a nearly stoichiometric compound according to the Fe–N phase diagram, the nitrogen content would be expected to be uniform. The other possibility is that it represents an $M_2N_{1-x}$ nitride, whose nitrogen content can widely vary, although it is strange that any chromium depletion or molybdenum enrichment should occur within this phase. The hexagonal $M_2N_{1-x}$ nitride was observed to form on occasion by TEM near the free surface $\delta$-ferrite grains in several wrought samples.
Insofar as APT provides “chemical” and not structural contrast, it is inconclusive as to what this nitrogen-enriched feature within the already-high nitrogen δ-ferrite phase represents. Current LEAP technologies permit analysis of micro-tips welded to 3 mm copper grids conventionally used for TEM analysis of FIB lamellae. Although this method is not as efficient as analyzing micro-tips welded to a silicon array as performed in this work, it is strongly suggested that future APT analyses of interstitially hardened 2205 (and other stainless steels) be performed on samples prepared on copper grids for initial TEM investigation. By this means, better comparison between the chemistry determined by APT and the local microstructure can be made.

It was clear that in all of the APT samples analyzed in this work, only one contained some form of “interface” within the δ-ferrite microstructure, the rest representing only a homogenous region of the grain. The volume of material, approximately 60 nm × 60 nm × 150 nm, analyzed in a typical APT micro-tip is quite small, and compared to the fea-
Fig. 5.24: Compositional proxigram around the 22.5 at.\% iso-concentration surface (0 nm distance) shown in Fig. 5.22(a). Metal composition is normalized to 100 at.\%.

Trends of interest in these samples (20–40 nm in width, separated by up to several hundred nm) observable by metallography, it seems there is a bit of “luck” involved whether or not such interfaces were captured in the final thinned micro-tip. TEM imaging of all micro-tips would at the very least provide knowledge of which samples are suitable for further APT analysis. On the other hand, imaging of APT samples in the TEM is not trivial, as the usual volume of “sacrificial” material that exists in conventional FIB lamellae is not available for alignment of the instrument and setting up of the imaging conditions. Prolonged exposure of the higher-energy electron beam in the TEM has been shown to alter or damage the micro-tip [160]. This proposed method for future chemical and structural analysis of interstitially hardened stainless steels is at the cutting-edge of what is currently being performed in the field of APT, and it seems likely that new advancements will be made that better permit structural determination by TEM of APT samples.
5.6 Structural Analysis: XRD

5.6.1 Bragg-Brentano Geometry

X-ray techniques were utilized as an initial means of structural analysis following interstitial-hardenning. The X-ray diffractograms of as-received wrought and cast material used for δ-ferrite/austenite lattice parameter and volume fraction determination are shown in Fig. 5.25. Note that the absence of the δ (200) peak in cast material is not due to texturing, but results from the fact that the δ-ferrite grain size in cast material is on the order of several mm. With the characteristic sample dimensions of 20 mm × 20 mm × 3 mm, no (200) surface normal grains of δ-ferrite happen to be present in this sample. As mentioned earlier, the volume fraction of austenite in the cast material is higher than in the wrought material, due to its slightly higher nickel and lower chromium content.

The conventional θ–θ X-ray diffractograms following nitridation are shown in Fig. 5.26 for wrought and in Fig. 5.27 for cast material. The standard XRD peaks of ferrite, austenite, and nitride phases with a Cu-Kα source according to the JCPDF database are also

![X-ray diffractograms of as-received wrought and cast 2205. The inset shows the lattice parameter of each phase determined by a Nelson-Riley correction factor. The volume fractions of δ-ferrite and austenite were estimated by a direct comparison method.](image-url)

**Figure 5.25:** X-ray diffractograms of as-received wrought and cast 2205. The inset shows the lattice parameter of each phase determined by a Nelson-Riley correction factor. The volume fractions of δ-ferrite and austenite were estimated by a direct comparison method.
5.6. STRUCTURAL ANALYSIS: XRD

plotted in Fig. 5.28 for comparison. The strong peaks of ferrite, austenite, CrN, Cr$_2$N, and Fe$_4$N all occur between 41–45° 2θ.

Apart from the sample treated at 440 °C in pure ammonia with an ‘infinite’ nitrogen activity, the maximum case depth achieved in any of the samples was approximately 6 µm as determined from AES line-scans, and consequently the diffractogram for each sample includes some contribution from the underlying matrix. The signal from the matrix δ-ferrite and austenite generally decreases with increasing temperature and nitrogen activity, i.e. with increasing case depth. Both the wrought and cast samples treated at $T_N = 380$ °C and $a_{N_2} = 3.0 \times 10^3$ showed a pronounced $\delta_{(110)}$ peak compared to others treated at the same temperature and/or activity. Considering that these samples were determined by AES to have a similar surface concentration and penetration depth of nitrogen, this anomaly may have resulted from incomplete activation during gas flow of HCl, though the temperature and gas flow readouts for the particular run were as prescribed. Non-uniform activation of the surface may also have occurred by contamination of a small region of the surface after introduction into the furnace.

The two wrought samples treated at $T_N = 440$ °C were the only to show evidence of secondary nitride precipitation by XRD. The additional peaks indicated in the diffractogram for the pure ammonia treatment are clearly identified as Cr$_2$N (presumably M$_2$N where M = matrix composition) while the three additional peaks for the $a_{N_2} = 1.8 \times 10^2$ treatment did not match any of the known nitrides. These peaks may be associated with a paraequilibrium M$_2$N$_{1-x}$ nitride whose exact chemistry and stoichiometry is not known. Metallography revealed both the δ-ferrite and austenite at the surface of the infinite activity sample to have transformed to a nitride, whereas the $a_{N_2} = 1.8 \times 10^2$ sample showed evidence of precipitation only within the near-surface austenite. It may be that the paraequilibrium nitride formed in the austenite of the $a_{N_2} = 1.8 \times 10^2$ sample possessed lattice parameters inconsistent with Cr$_2$N, while those apparently formed at the higher activity in δ-ferrite and/or austenite did. Complete transformation of δ-ferrite in the infinite activity sample was further verified by GI-XRD, whereas the $a_{N_2} = 1.8 \times 10^2$ sample showed a non-expanded, remnant δ-ferrite at the surface.

With the exception of these nitride peaks, each peak in the diffractograms can be accounted for as either expanded austenite, or bulk δ-ferrite and austenite. For nearly all of the samples, the only pronounced expanded austenite peak was the $\gamma_{N(111)}$ peak, which shifted to lower angles with increasing activity for a fixed temperature, indicating a larger expansion of the fcc lattice. The $\gamma_{N(200)}$ peak can be distinguished in the wrought samples, but was much weaker or absent in most of the cast samples.

While most of the matrix, and some of the expanded austenite peaks are visible for the wrought samples, interestingly the intensity of nearly all peaks is diminished in cast material. This is exceptional for the $T_N = 325$ °C, $a_{N_2} = 3.0 \times 10^3$ sample (shallowest case depth) whose matrix peaks are almost entirely muted except for the $\delta_{(211)}$ peak, which
5.6. STRUCTURAL ANALYSIS: XRD

**Figure 5.26:** X-ray diffractograms of wrought 2205 following nitridation at various temperatures and nitrogen activities.
5.6. STRUCTURAL ANALYSIS: XRD

![XRD Diffractograms](image)

**Figure 5.27:** X-ray diffractograms of cast 2205 following nitridation at various temperatures and nitrogen activities.
Figure 5.28: Relative intensity of ferrite, austenite, and nitride XRD peaks with a Cu-K$_\alpha$ source according to the JCPDF database.
5.6. STRUCTURAL ANALYSIS: XRD

is highly pronounced relative to even the expanded $\gamma_{N(111)}$ peak. Similar behavior was found when analyzing the surface structure of the treated cast material by EBSD (described later). The structure of expanded austenite is known to be highly defective, and high concentrations of structural defects present in the $\delta$-ferrite and austenite following treatment may account for such a lack of diffraction information. It is unclear from conventional XRD what contributes to the lower intensity of ferrite peaks, and for that matter why a stronger signal from expanded austenite peaks is absent. A similar phenomena was observed in the diffractograms of nitrided 316L shown in Fig. 2.16. Furthermore, the differences between the initial and post-treatment defect structure (i.e. dislocation density) in the large-grained cast and fine-grained wrought material is not known, and would be worthy of further characterization.

Although a better estimate of the (average) lattice parameter expansion of austenite in the nitrided layer was precluded by the absence of multiple expanded austenite peaks, the effect of nitriding temperature and activity on the lattice parameter expansion of austenite as measured from the $\gamma_{N(111)}$ peak in cast and wrought material is shown in Fig. 5.29. The treatments containing wrought and cast material display an identical shift of the $\gamma_{N(111)}$ peak, with the exception of samples treated at $T_N = 350$ °C and $a_{N_2} = 1.4 \times 10^5$ for which the wrought sample exhibited a larger expansion. Both samples had the same surface finish of 1 µm prior to treatment, were positioned adjacent to one another in the nickel basket, and appeared visibly identical after removal from the furnace. Most likely, the difference in the measured expansion between the wrought and cast samples of this treatment was the result of incomplete activation of the cast sample due to insufficient pre-cleaning. Still, the similar lattice expansion of austenite between wrought and cast material indicates the surface concentration of nitrogen to have been nearly identical for each treatment, despite the minor differences in chemistry.

In contrast to the AES data in Fig. 5.16, an increase in nitriding temperature results in a slightly larger expansion of the $\gamma_{(111)}$ peak. Although the samples treated at a higher temperature have a lower nitrogen concentration for a given activity, the nitrogen profile extends deeper. As the peaks measured by XRD correspond to some “average” lattice parameter within the nitrogen profile, it is plausible that the expanded austenite lattice parameter determined in the higher temperature samples corresponds to an averaging over regions where interstitial nitrogen concentrations are higher.

5.6.2 Glancing-Incidence Geometry

To better determine the structure of phases present within only the nitrogen-enriched layer, a fixed glancing-incidence geometry of 3° was used, having a 95% integrated intensity penetration depth of 0.37 µm. The GI-XRD results of nitrided samples are shown in Fig. 5.30 for wrought and in Fig. 5.31 for cast material.
It is clear that some ferrite signal remains in all of the samples, and is highest for the $T_N = 380 \, ^\circ C$, and $T_N = 440 \, ^\circ C$ with $a_{N_2} = 1.8 \times 10^2$ treatments. Only the wrought sample treated at $T_N = 440 \, ^\circ C$ in pure ammonia (and possibly the $T_N = 350 \, ^\circ C$, $a_{N_2} = 5.8 \times 10^4$ sample) shows an absence of ferrite in the case following treatment, which presumably transformed to Cr$_2$N. Only one of the three additional unidentified peaks for the $T_N = 440 \, ^\circ C$ and $a_{N_2} = 1.8 \times 10^2$ treatment is marginally visible in the glancing incidence diffractogram, which further verifies this nitride to have formed in sub-surface grains.

The ferrite signal is however far lower in intensity relative to the expanded austenite peak in most of the samples when compared to the non-treated material. This could indicate some $\delta \rightarrow \gamma$ transformation. The $\gamma_{N(111)}$ and remaining $\delta_{(110)}$ peaks are also highly broadened relative to the non-treated material due to either a high density of structural
5.6. STRUCTURAL ANALYSIS: XRD

Figure 5.30: Glancing-incidence X-ray diffractograms of wrought 2205 following nitridation at various temperatures and nitrogen activities.
5.6. STRUCTURAL ANALYSIS: XRD

![Graph showing X-ray diffractograms](image)

**Figure 5.31:** Glancing-incidence X-ray diffractograms of cast 2205 following nitridation at various temperatures and nitrogen activities.
defects or a nano-crystalline substructure within each of the grains. Several of the samples also reveal a very broad and low intensity peak attributed to \( \gamma_{N(200)} \). The \( \delta_{(110)} \) peak in several of the samples shifted slightly to higher diffracting angles, indicating that some partitioning of the substitutional metal constituents may have occurred (which was indeed later verified by TEM).

Based on the XRD and GI-XRD analyses of the nitrided samples, the following conclusions can be made: (i) a high density of secondary nitrides formed only at the treatment temperature of 440 °C, (ii) some volume fraction of non-expanded \( \delta \)-ferrite remains in the case, (iii) and some of the \( \delta \)-ferrite may have transformed to austenite. Where nitrides were observed in \( \delta \)-ferrite grains by TEM, their size and volume fraction was sufficiently low to prevent them from contributing to the diffracted X-ray signal. The high-nitrogen content and lack of expansion in \( \delta \)-ferrite grains will be the topic of later discussion.

For reference, conventional and glancing-incidence X-ray diffractograms taken from an earlier publication [11] on carburized 2205 are shown in Fig. 5.32. For all carburization treatments, the austenite peaks shift to lower 2\( \theta \) indicating expansion of the austenite lattice (\( \approx 3\% \)) by carbon interstitials. Furthermore, the lattice expansion is larger at lower treatment temperatures, in agreement with the depth profiles in Fig. 5.18 revealing the carbon solubility to be exothermic in austenite. With reference to the GI-XRD scans in Fig. 5.32(b), again some \( \delta \)-ferrite signal remains which is heavily broadened and lower in intensity relative to the non-treated material.
Figure 5.32: (a) Conventional and (b) glancing-incidence X-ray diffractograms of wrought 2205 following carburization at various temperatures [11].
5.7 Magnetic Force Microscopy

MFM was used to investigate the magnetic characteristics of δ-ferrite and austenite grains following nitridation. Had some \( \delta \rightarrow \gamma \) phase transformation occurred, as suggested by XRD/GI-XRD, the austenite transformation product within the δ-ferrite could exhibit a different magnetic character than the ferromagnetic matrix from which it formed. MFM phase contrast images of non-treated cast and wrought material are shown in Fig. 5.33 for comparison. The regions of uniform contrast represent paramagnetic austenite grains, while the regions of alternating light and dark contrast represent ferromagnetic Weiss domains within δ-ferrite.

![MFM phase contrast image of non-treated cast and wrought 2205](image)

**Figure 5.33:** MFM phase contrast image of non-treated (a) cast and (b) wrought 2205. Regions of uniform contrast represent paramagnetic austenitic while alternating light and dark contrast represent ferromagnetic δ-ferrite.

The sample treated at \( T_N = 400 \, ^\circ C \) and \( a_{N_2} = 4.0 \times 10^9 \) showed the highest concentration of nitrogen (Fig. 5.16), the deepest case, and the most extensive transformation of near-surface δ-ferrite to austenite by TEM and TKD structural analyses. The magnetic character of this sample was investigated on the plan-view surface, shown in Fig. 5.34, and in cross-section, shown in Fig. 5.35.

Optical micrographs of this sample were shown in Fig. 5.5, revealing surface uplift and slip band formation in the austenite and former δ-ferrite grains. As discussed in Sec. 2.3, expanded austenite can undergo a para-to-ferromagnetic transition when the nitrogen concentration reaches a critical supersaturation of approximately 14–15 at.%. According
to the depth profiles in Fig. 5.16, the surface concentration of nitrogen in the former δ-ferrite and austenite grains of this sample was 28 at.% and 25 at.%, respectively, indicating that a para-to-ferromagnetic transformation of the austenite should have occurred. It is clear from the plan-view MFM image in Fig. 5.34 that the surface austenite grains are
indeed ferromagnetic, and are distinct from the former $\delta$-ferrite grains in their magnetic character. The blurring and streaking observed in the AFM and MFM images is an artifact of the technique.

The magnetic domains within the former $\delta$-ferrite are not as sharp as in the expanded austenite, and represent a magnetic structure more commonly observed in martensite. From TEM analysis, the austenite formed at the surface of $\delta$-ferrite grains did transform in a manner similar to a martensitic reaction, yielding plates or laths of austenite typically 20–40 nm in thickness and containing a high-density of internal sub-structure. The interface between former $\delta$-ferrite and austenite also shows a unique MFM contrast unlike that observed in the bulk of each phase.

The prior austenite and $\delta$-ferrite grains can be distinguished in the cross-sectional MFM image of the sample in Fig. 5.35(b). From the MFM image of the austenite grain in Fig. 5.35(d), ferromagnetic austenite is observed up to a depth of 4 µm below the surface. From Fig. 5.16, this corresponds to a nitrogen concentration of 15 at.%—the critical supersaturation (i.e. critical lattice expansion) required for ferromagnetism in austenite. A magnetic character different from the bulk $\delta$-ferrite is observed in Fig. 5.35(f) to a depth 9–10 µm, which also corresponds from AES depth-profiling to 15 at.% nitrogen.

This is further strong evidence of a $\delta \to \gamma$ transformation with the isothermal dissolution of nitrogen at low-temperatures. If the network of new features observed in $\delta$-ferrite grains were a nitride phase (and furthermore, one which was not detected by XRD), it seems unlikely that its magnetic character would differ from bulk $\delta$-ferrite to a depth that corresponds to the critical supersaturation required for attaining a ferromagnetic austenite. Although the nitrogen profile in the $\delta$-ferrite of this sample extended 2–3 µm beyond this transition point, the density of austenite laths is far lower than near the surface, which extend into the supersaturated $\delta$-ferrite whose ferromagnetic domains dominate the MFM contrast at this depth.
5.7. MAGNETIC FORCE MICROSCOPY

Figure 5.35: Low-magnification cross-sectional (a) AFM and (b) MFM images of cast 2205 sample nitrided at 400 °C and $a_{N_2} = 4.0 \times 10^9$. Higher-magnification (c) AFM and (d) MFM images of austenite grain, and (e) AFM, (f) MFM images of δ-ferrite grain (both regions indicated in (b) the lower-magnification MFM image). Arrows in the AFM images indicate the free surface.
5.8 Microstructural Analysis: EBSD

The technique of electron back-scatter diffraction was used for structural analysis at a finer length-scale than can be provided by XRD. The Kikuchi bands recorded during each EBSD analysis were indexed according to either ferrite, austenite, and all known nitride (or in the case of carburization, carbide) phases. Crystal files for each of the phases were constructed using the Oxford Instruments Twist software package according to the symmetry listed in Tables 2.5 and 2.7. The Wyckoff positions of the atoms in each phase were often found in the references listed earlier. Note that ordered and disordered versions of Fe$_2$N$_{1-x}$ were constructed and used in all analyses. Both contain an hcp unit cell with nitrogen concentrations between $\approx 15–32$ at.%. In the ordered version of this compound, long-range nitrogen order contributes to the total diffraction intensity giving rise to additional superlattice reflections in the diffraction pattern. In all analyses, the Kikuchi patterns were recorded for post-processing. The lattice parameter of a phase, e.g. austenite, was later optimized so as to yield the lowest mean angular deviation (MAD) number between the experimental and simulated diffraction pattern. In situations where the software identified multiple solutions to a given diffraction pattern, the goodness of fit was again gauged by the MAD number.

The most critical aspect of any EBSD experiment is achieving a high quality surface. The quality of the back-scattered pattern, which is generated in the top 10–50 nm of material, is heavily affected by lattice strain or contamination. Therefore, great care was taken during sample preparation to ensure a clean and deformation-free surface. Cross-sectional samples were initially analyzed after careful sectioning, mounting, and polishing. Fig. 5.36 shows the cross-sectional phase and orientation mapping of the sample treated at $T_N = 440$ °C and $d_{N_2} = 1.8 \times 10^2$. Blue regions represent fcc austenite, red bcc $\delta$-ferrite, and black non-indexable pixels. All EBSD phase and orientation maps shown represent that determined by the software during indexing of each pixel; that is, no non-indexable regions were later extrapolated by the software to represent the nearby phase(s). The black regions were either non-indexable due to an insufficient pattern quality or because the phase did not conform to an fcc, bcc, or a known nitride structure. In most instances, the Kikuchi patterns of black pixels appeared to conform to the nearby indexable patterns, but the quality was such that bands could not be digitally assigned, and thus were left unsolved. The free surface, i.e. the top edge of the cross-sectional sample, is represented by the top of each map, and the case depth of the sample measured by AES was $\approx 5$ µm. The indexing rate of the matrix below this depth is high, nearly 85%, indicating that a relatively smooth and damage-free layer had been achieved from the sample preparation.

Within the case and near the top edge however, the indexing rate is much lower. Also, it is clear that where the EBSD pattern was indexable within the case, austenite was the
Figure 5.36: Cross-sectional EBSD phase and orientation maps of wrought sample treated at $T_N = 440 \, ^\circ C$ and $a_{N_2} = 1.8 \times 10^2$. The free surface is represented by the top edge in each map. (a) Austenite orientation, (b) ferrite orientation, (c) combined austenite/ferrite phase map. In phase map, blue indicates $fcc$ austenite, red $bcc$ $\delta$-ferrite, and black a non-indexed pixel. The orientation of each grain can be determined from the inverse pole figure in Fig. 5.39 in which 001, 101, and 111 are surface normal planes/directions in the cubic crystal reference frame.
only phase identified. Due to the wrought nature of the sample it is difficult to ascertain which part of the case in this cross-section along the longitudinal direction was originally austenite or ferrite, but following the pattern of the bulk microstructure, it appears the majority of near-surface grains were formerly $\delta$-ferrite. Inspection of the sub-surface $\delta$-ferrite grain to the left reveals a linear feature, about 5 $\mu$m below the surface, above which the indexing rate is low and below which is high. As this corresponds to the penetration depth of nitrogen in the sample, it seems that the nitrogen has somehow affected the crystal quality of the ferrite, which was not indexable as a nitride. Furthermore, adjustment of the $\delta$-ferrite lattice parameter did not yield any improved indexing rate within this, or the near surface region, which agrees with the XRD results showing a non-expanded ferrite at the surface. Interestingly, the nitride observed within austenite by XRD and metallography was not detected by EBSD. As the density of this secondary phase was low, it may have been lacking in this region of interest or was too small to be resolved with the prescribed probe diameter and step size. Or, the lattice parameters of this presumably paraequilibrium phase may have deviated to such a degree (as suggested by XRD) from the candidate structures that its back-scattered patterns were not indexable. Tweaking of the $\text{Fe}_2\text{N}_{1-x}$ unit cell did not yield any better results.

A cross-sectional EBSD phase map of the wrought sample treated at $T_N = 350$ °C and $a_{N_2} = 5.8 \times 10^4$ is shown in Fig. 5.37, acquired along the short-transverse direction. The case depth of this sample was $\approx 2.5–3.5$ $\mu$m. The indexing rate up to this depth below the surface is low, and again, no nitrides were detectable within the case. Similar to the line observed in Fig. 5.36, there is a distinct line in a $\delta$-ferrite grain corresponding to the penetration depth of nitrogen above which the indexing is practically nil. Several Kikuchi patterns acquired within this region are shown in Fig. 5.37 highlighting the degraded pattern quality. Although bands are observed, the number or quality of such bands hindered the software from solving the pattern. The quality of this and all other patterns from formerly ferritic regions is degraded heavily relative to the core ferrite. Whatever its structure, it appears that it is highly defective and/or stressed.

Even with optimal sample preparation, achieving high indexing rates near the edge of a mechanically polished specimen is encumbered by the fact that rounding of the specimen edge occurs regardless of the mounting material, due to the dissimilar wear rates at the interface. Cross-sectional EBSD is therefore not ideal for structural characterization of the shallow cases produced in this work. Plan-view EBSD was conducted on several wrought samples whose surface was polished to 1 $\mu$m prior to nitridation. Sections from the nitrided coupon were made, and the surface lightly chemo-mechanically polished in a colloidal silica slurry so as to minimize the surface roughness and contamination without removal of the nitrided layer.

The results following EBSD analysis of as-received and several nitrided samples are shown throughout Figs. 5.38 (band contrast maps), 5.39 (orientation maps), and 5.40
5.8. MICROSTRUCTURAL ANALYSIS: EBSD

Figure 5.37: Cross-sectional EBSD phase map of sample treated at $T_N = 350$ °C and $a_{N_2} = 5.8 \times 10^4$. In phase map, blue indicates fcc austenite, red bcc δ-ferrite, and black a non-indexed pixel. Several Kikuchi back-scatter patterns obtained from a near-surface δ-ferrite grain are shown.

(Phase maps). The band contrast is a pattern quality parameter: the higher (brighter) the band contrast, the sharper the bands in the back-scattered pattern. A similar approach was conducted on cast samples (Fig. 5.41), but with less promising results. The indexing rate of treated cast material following the same sample preparation was far lower, even for the austenitic phase. Based on this and XRD information, there may be differences in the defect structure or stress-state within treated cast and wrought material.

The major difficulty with a plan-view analysis of the treated specimens, apart from achieving a smooth, damage-free surface without removal of the thin nitrided layer, is the high defect density, i.e. dislocations, stacking faults, microtwins, point defects, etc. associated with dissolving immense concentrations of interstitials, that contribute to degrade the quality of the back-scattered diffraction pattern. Indeed, many of the Kikuchi patterns acquired from the treated samples were not of sufficient quality for the software to interpret, even after relaxing the indexing constraints. Still, the results are enlightening and confirm much of what was gathered from XRD.

The measured phase fraction of δ-ferrite and austenite in the as-received wrought ma-
5.8. MICROSTRUCTURAL ANALYSIS: EBSD

**Figure 5.38:** Plan-view EBSD band contrast images of non-treated and wrought samples following low-temperature nitriding.
5.8. MICROSTRUCTURAL ANALYSIS: EBSD

Figure 5.39: Plan-view EBSD inverse pole mapping of non-treated and wrought samples following low-temperature nitriding. The orientation of each grain can be determined from the color key in which 001, 101, and 111 are surface normal planes/directions in the cubic crystal reference frame.
5.8. MICROSTRUCTURAL ANALYSIS: EBSD

Figure 5.40: Plan-view EBSD phase mapping of non-treated and wrought samples following low-temperature nitriding. Blue indicates fcc austenite, red bcc δ-ferrite, and black a non-indexed pixel.
5.8. MICROSTRUCTURAL ANALYSIS: EBSD

Figure 5.41: Plan-view EBSD band contrast, orientation, and phase mapping of cast sample treated at $T_N = 380 \, ^\circ C$ and $a_{N_2} = 1.4 \times 10^5$. Inverse pole figure shown in Fig. 5.39. In phase map, blue indicates $fcc$ austenite, red $bcc$ $\delta$-ferrite, and black a non-indexed pixel.

Material is consistent with XRD, and from the phase map in Fig. 5.40 the rolling direction can be observed. Despite the lower indexing of nitrided samples, new information can be gleaned from the plan-view analysis, particularly from the band contrast and phase mapping results. First, the only phase detectable at the surface is austenite, and the volume fraction of austenite is increased relative to the non-treated material, suggesting that some $\delta \rightarrow \gamma$ transformation was induced by each treatment. The rolling direction can still be interpreted by the high indexing rate of the $fcc$ phase, and interestingly there are regions within the former $\delta$-ferrite that were indexed as $fcc$. Regions within the apparent former $\delta$-ferrite that were not indexed as austenite, $\delta$-ferrite, or a nitride phase showed Kikuchi patterns similar to those shown for the near-surface $\delta$-ferrite in Fig. 5.37. Rather than sharp bands, the patterns were almost entirely dominated by noise, indicating the occurrence of a highly disturbed lattice. The band contrast images of the treated samples are the most telling: where austenite is indexed, the pattern quality is high, while regions in the larger-grained former $\delta$-ferrite provide degraded diffraction information. The quality within these $\delta$-ferrite grains is also not uniform, as shown in the higher-magnification band contrast image for the $T_N = 350, a_{N_2} = 5.8 \times 10^4$ sample, instead showing a speckled contrast.

Although it cannot be stated with certainty that all of the austenite grains identified in the treated samples were not originally present, based on the fact that all samples were obtained from the lot and the phase fraction of austenite increased after nitridation, it is highly suggested that some of the small equiaxed austenite grains must have grown within regions of former $\delta$-ferrite. From the orientation maps in Fig. 5.39, no texturing of the austenite grains observed.
The cast sample, containing a higher concentration of nitrogen in each phase than the wrought samples in Figs. 5.38—5.40, showed the lowest indexing rate of the plan-view analyses. The marked difference could have resulted from a different density or distribution of structural defects, which may be higher in the cast sample with its higher supersaturation of nitrogen. No regions within the $\delta$-ferrite matrix were indexable as either $\delta$-ferrite, austenite, or a nitride. Taken as a whole, the plan-view EBSD analyses further corroborate earlier XRD results in that some transformation of $\delta$-ferrite to austenite took place, nitrides—if present—are small enough so as to be imperceivable by both techniques, and that a highly disturbed, non-expanded residual $\delta$-ferrite exists following nitridation.
Chapter 6

Structural Investigation of the Hardened Layer by Electron Microscopy

In the preceding chapter, an overview was given of the interstitially-hardened 2205 forest. In this chapter, a look at the trees will be presented. The TEM as a powerful characterization tool was used to reconcile the inconclusive XRD, EBSD, and MFM. TEM specimens were also structurally probed with high spatial resolution in the SEM by the TKD technique. The low temperatures and shorter nitridation treatment (7.2 ks) conveniently allowed for comparison between the interstitially-hardened case and bulk material within a single cross-sectional TEM foil.

Many samples running the gamut of processing space were ultimately analyzed in the TEM; this chapter presents some of the more notable observations made across the range of samples with no particular attention to the processing parameters involved. It was ultimately determined that the same microstructural response occurred irrespective of the nitriding activity or temperature for $T_N \leq 400 \, ^\circ C$. That is, the effect of nitrogen activity and/or temperature served only to modify the case depth and surface concentration in each phase, as described in Chapter 5. Additional TEM micrographs and diffraction patterns substantiating these findings can be found in Appendix 8.1.

6.1 General Microstructural Observations in Ferrite and Austenite Grains by TEM

The first and most general statement to be made about the microstructure—particularly within the ferritic phase—following low-temperature nitridation or carburization is that it is complex. To give a flavor for the kind of microstructure present within the nitrogen-enriched surface layer, several cross-sectional TEM/STEM overview micrographs of wrought samples nitrided between $325 \, ^\circ C$ and $380 \, ^\circ C$ are shown in Figs. 6.1–6.4, along with the
XEDS nickel maps used for identification of prior austenite and δ-ferrite grains\(^1\). The high-angle annular dark-field (HAADF) STEM camera length was in each case 1.44 m, and therefore diffraction contributes most heavily to the observed contrast.

The maximum case depth in any of these samples was 5 µm (Fig. 6.4) as determined by AES depth-profiling. Similar to chemical etching, the penetration depth of nitrogen in the TEM foils can be estimated by the observed change in near-surface microstructure relative to the bulk material \(\geq 5\) µm below the free surface (indicated by the protective Pt layer). These microstructures are representative of all nitrided cast and wrought samples investigated by TEM\(^2\), with one central exception that will be the subject of separate discussion. This exception—a spinodal-like phase separation into nanometer-sized Fe-rich (\(\alpha_{Fe}\)) and Cr-rich (\(\alpha'_{Cr}\)) ferrite supersaturated with nitrogen—was the only structural response observed in δ-ferrite following low-temperature carburization.

From the diffraction contrast most prevalent in these micrographs, the near-surface austenite grains appear to closely resemble those in the core, containing characteristic linear features confirmed by electron diffraction to be micro-twins. It is not clear if these features represent deformation micro-twins formed as a means of stress relaxation during growth of the interstitially-hardened layer, or were deformation/annealing twins present in the as-received material. Plastic flow of austenite grains during interstitial hardening of austenitic stainless steels is widely observed, and thus it seems reasonable that most of these near-surface deformation twins in austenite were generated during growth of the case.

The microstructural features observed within (former) δ-ferrite grains are markedly different from those in the core, the nature of which is the primary focus of this chapter. Where nitrogen diffused, the δ-ferrite grains are almost entirely consumed by plates or laths extending from the free surface into the bulk material. Such features in near-surface δ-ferrite grains are observed after treatments as low as \(T_N = 325\) °C, and appear to form regardless of the nitriding activity, at the low, medium, and high end of the nitrogen activity spectrum.

To summarize what is ultimately gathered from additional BF/DF imaging, microchemical analysis, and electron diffraction, these high-aspect-ratio plate-like features represent a heavily-twinned—and expanded—austenite transformation product that formed from the nitrogen-supersaturated δ-ferrite. Given the microstructural signatures and partitionless manner in which these new austenite plates formed, it is inferred that they grew

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\(^1\)As previously mentioned, the diffusion of metal constituents in ferrite and austenite at temperatures and times typical of low-temperature interstitial hardening is no more than a few atomic distances. Therefore, the δ-ferrite and austenite grains retain their respective chemistries inherited from higher temperature processing.

\(^2\)Because of the significant decrease in corrosion resistance following nitridation at 440 °C and macroscopic evidence of nitride formation, which have been extensively studied in stainless steels, these particular samples were not further characterized by TEM.
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FIGURE 6.1: Cross-sectional STEM micrograph of a wrought sample (in ST direction) treated at $T_N = 325^\circ C$ and $n_{N_2} = 3.0 \times 10^5$. 

$\delta_{form}$
FIGURE 6.2: Cross-sectional BF micrograph of a wrought sample (in ST direction) treated at $T_N = 350 \, ^\circ\text{C}$ and $a_{N_2} = 1.8 \times 10^2$. The XEDS nickel map used to distinguish $\delta$-ferrite and austenite grains is shown in the lower left.
6.1. GENERAL MICROSTRUCTURAL OBSERVATIONS BY TEM

FIGURE 6.3: Cross-sectional STEM micrograph of a wrought sample (in ST direction) treated at $T_N = 350^\circ C$ and $\alpha_v = 5.8 \times 10^4$. The XEDS nickel map used to distinguish $\delta$-ferrite and austenite grains is shown in the lower left.
6.1. GENERAL MICROSTRUCTURAL OBSERVATIONS BY TEM

Figure 6.4: Cross-sectional STEM micrograph of a wrought sample (in ST direction) treated at $T_N = 380 \, ^\circ C$ and $a_{\delta}/a_{\gamma} = 1.4 \times 10^5$. The XEDS nickel map used to distinguish $\delta$-ferrite and austenite grains is shown in the lower left.
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in a diffusionless, martensitic (i.e. shear or displacive) fashion.

This finding, and the lack thereof for any carbon-induced transformation of $\delta \rightarrow \gamma$, is not surprising considering the implications of the CALPHAD calculations in Chapter 4, which suggest nitrogen in 2205 is a far more potent austenite stabilizer than carbon, and a very large driving force for a $\delta \rightarrow \gamma$ phase transformation exists with even minute concentrations of nitrogen in $\delta$-ferrite.

6.2 The Response of Austenite in 2205 to Interstitial Hardening

6.2.1 TEM Imaging and Electron Diffraction

Before delving into the more complicated diffraction patterns acquired from within the nitrided layer, several selected-area electron diffraction (SAED) patterns from the core $\delta$-ferrite and austenite grains are presented in Fig. 6.5 for comparison.

These single crystal zone-axis patterns match well with the simulated diffraction patterns of single bcc and fcc crystals, and provide a satisfactory internal calibration of camera length for comparison with patterns obtained from within the nitrided/carburized layer. The lattice plane spacings, $d_{hkl}$, measured according to the peak-to-peak distance in an intensity profile across the largest reciprocal lattice diffraction vectors, $\bar{g}$, where $|\bar{g}| = 1/d_{hkl}$, are within $\leq 2\%$ of those accurately measured by XRD in non-treated material, and the interplanar angles within $\pm 1^\circ$. The reciprocal lattice reflections show a uniform intensity and absence of artifacts, and are indicative of a ‘good’ crystal. This was generally untrue of diffraction patterns acquired from within the interstitially-hardened layer.

Various zone-axes with minimal excitation errors could be reached in the core material with the aid of Kikuchi lines. This was precluded in most of the near-surface grains by the high defect concentrations induced by the treatment. Zone-axes within the surface layer were reached by a more trial-and-error approach. Or, when analyzing TEM specimens extracted from single grains in cast material, by first bringing the core region into zone and then slightly adjusting the tilt within the near-surface region to account for any bending.

In each of the nitrided samples studied by TEM for treatments $T_N \leq 400^\circ C$ and nitriding potentials as high as achieved with pure NH$_3$, the austenite grains within the nitried layer retain their single-phase, though measurably expanded, fcc structure, along with deformation micro-twins and a high dislocation density generated during restricted expansion of the lattice. This agrees with most previous TEM structural analyses of interstitially-hardened austenitic stainless steels. Only after nitriding at $440^\circ C$ for 7.2 ks (20 h) in pure NH$_3$ did 316L show evidence of nitrogen ordering consistent with an M$_4$N nitride [109]. For all lower nitriding activities or temperatures in this study, the nitrogen-supersaturated austenite grains likewise remained $fcc$ solid solutions with random occupation of nitrogen with interstitial concentrations remarkably approaching 20 at.%.
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Figure 6.5: SAED zone-axis patterns obtained from core $\delta$-ferrite and austenite grains in wrought TEM specimens.
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Unlike 316L, XRD on nitrided 2205 revealed M$_2$N-like nitride formation after 20 h treatment at 440 °C at both low and high nitriding activities. From metallography and the chemical etching response in these samples, the secondary phases presumably formed within the austenite grains (Fig. 5.6). This difference in transformation behavior between the duplex and austenitic alloys despite similar treatment may result from the higher chromium and lower nickel content of 2205 relative to 316L. Interstitial concentrations were consistently and considerably higher in the austenite of 2205 compared to 316L for a given treatment, as predicted by thermodynamic modeling. Therefore, the critical concentration needed for precipitation of paraequilibrium nitrides could be reached in 2205 with lower nitriding potentials. If biaxial compressive stresses play a role in the observed transformation behavior or lack thereof, it would also indicate a difference in stress-state between supersaturated austenite grains in 316L and the islands of austenite in 2205 dispersed within a sea of (transforming) δ-ferrite.

Several representative diffraction patterns acquired from nitrogen-supersaturated austenite grains are shown in Figs. 6.6–6.8, along with an indication of the location from which they were acquired. Streaking of the reflections was common, as shown in Fig. 6.7 along a [011]$_{fcc}$ viewing direction. These artifacts can be attributed to the presence of micro- or nano-twins/stacking faults in a direction orthogonal to the streaks. Discernible twin reflections of the dominant {111} ⟨110⟩-type in fcc metals were also common depending on the size and location of the area-selecting aperture. A set of these fcc twin reflections are shown in Fig. 6.8 along a [011]$_{fcc}$ viewing direction.

Insofar as lattice plane spacings can be measured by SAED, all diffraction patterns recorded from austenite grains in the case showed a measurable expansion of the lattice on the order of several percent relative to austenite grains in the core recorded under identical imaging conditions. Such measurements are admittedly unreliable, due to relaxation of the Laue condition in thin TEM specimens, and are of little use for comparison with the measured nitrogen concentration—and therefore the expected dilation of the lattice at a given depth—with the data presented in Fig. 2.18. The more accurate technique of convergent-beam electron diffraction (CBED) for lattice parameter measurement by TEM was inhibited, like many other techniques, by the high concentration of planar and linear defects. Where attempted, the transmitted CBED disk showed diffuse contrast and lacked higher-order Laue zone (HOLZ) lines, despite the relative thickness of the specimens and efforts to remove ion beam-induced surface damage by low-energy Ar$^+$ polishing.

1The size of the superimposed circle roughly corresponds to the size of the area-selecting aperture used to record each pattern.
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Figure 6.6: SAED pattern along a \([111]\)\(_{fcc}\) viewing direction acquired from an expanded austenite grain in wrought 2205 nitrided at \(T_N = 350\) °C and \(N_2 = 5.8 \times 10^4\).
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6.2.2 Observation of Anomalous Reflections

In one particular diffraction pattern along a \([013]_{\text{fcc}}\) direction (Fig. 6.9) obtained from the austenite grain in Fig. 6.7 in contact with the free surface, additional reflections appeared that were initially thought to originate from a secondary phase. Though not shown, dark-field (DF) imaging from one such reflection indicated that they originated from planar features commensurate within all expanded austenite grains. Upon further analysis, these reflections along half of the \(\frac{1}{2}\tilde{g}_{113}\) and \(\frac{1}{2}\tilde{g}_{133}\) vectors, were inconsistent with any nitride structure, assuming that they, along with \(\tilde{g}_{200}\), constitute the three primary vectors of the reciprocal lattice.

These peculiar reflections are forbidden in an fcc lattice on structure factor grounds, and cannot be explained by simple twinning or by double diffraction. The observation of these reflections in the austenitic phase of 2205 was isolated to that particularly-thick near-surface austenite grain.

Interestingly, the same forbidden \(\frac{1}{2}\tilde{g}_{113}\) vectors appeared in several diffraction patterns (along \([114]_{\text{fcc}}, [112]_{\text{fcc}},\) and \([013]_{\text{fcc}}\) zone-axes) acquired from expanded austenite in 17-7 PHSS (condition A heat-treated) after similar low-temperature nitridation [161]. These anomalous reflections were likewise shown by dark-field imaging to originate from within banded features of the austenite grain. The forbidden reflections in this study were attributed to local nitrogen ordering within an austenite superlattice consisting of eight unit cells (32 atoms) with 4 nitrogen atoms occupying opposing body-centered octahedral sites as shown in Fig. 6.10. This proposed superlattice is distinct from the metastable Fe\textsubscript{16}N\textsubscript{2} phase (distorted 2 × 2 × 2 α-ferrite superlattice) found in the Fe–N system, and could account for the observed superlattice reflections in some, but not all viewing directions.

This unique nitrogen ordering was initially accepted as the probable cause without any further inquiry. Characterization of the former δ-ferrite grains revealed the same forbidden \(\tilde{g}\) vectors in some of the diffraction patterns acquired from the martensitic austenite transformation product. A more thorough discussion of this result, which was ultimately attributed to complex twinning and double diffraction mechanisms, is deferred until the presentation of additional data.

6.2.3 Structural Characterization by TKD

It was concluded that at least for \(T_N \leq 400 \, ^\circ\text{C}\), nitride formation can be suppressed in 2205 after a 20 h gas-phase treatment regardless of the nitriding activity. Suppressing carbide formation was also possible during carburization treatments of 2205 less than 80 h at 380 \(^\circ\text{C}\). After 150 h carburization at 380 \(^\circ\text{C}\), a mixture of Hägg M\textsubscript{5}C\textsubscript{2} and M\textsubscript{7}C\textsubscript{3} carbide had formed within near-surface austenite grains. This is shown in the TKD phase map of a
wrought sample in Fig. 6.11. The core δ-ferrite and austenite grains indicate the short-transverse direction from which the TEM foil was extracted.

The Hägg carbide, forming at a greater depth and stabilized by lower carbon concentrations, presumably formed first and was later followed by precipitation of M$_7$C$_3$ near the surface. The same structural evolution was observed following carburization of 316L at 465 °C and 470 °C [80]. The lower volume fraction of M$_7$C$_3$ near the surface is consistent with the hypothesis that M$_5$C$_2$ is a precursor to its formation. These carbides however did not consume the grain and regions of untransformed expanded austenite still exist. The TKD indexing rate of the austenite grains near the surface is low, due to either FIB-induced damage, a high concentration of carburization-induced defects, or a combination of the two.

Most strikingly, this 150 h treatment performed well during cyclic polarization and crevice corrosion testing [11] despite the presence of these secondary phases$^1$. This finding further highlights the notion that secondary phases, though generally assumed as undesirable, may not fully compromise the passivating capability of a stainless steel when formed under the far-from-equilibrium conditions of paraequilibrium interstitial surface hardening. That is, with a paraequilibrium carbide (or nitride) of near parent chemistry, a sufficient concentration of chromium could remain in (austenite) solid solution to allow for growth of a passivating chromium-rich scale.

Still, an understanding of the long term effects or later structural modifications at these elevated temperatures is incomplete. The unexpected formation of a carbide in 2205 austenite (given what is known of carburization of single-phase austenitics) at this temperature underscores the importance of treatment duration when interstitially-hardening non-austenitic stainless steels$^2$. Temperatures and/or times assumed to be benign for surface hardening of austenitics grades may not be ideal for bcc-based stainless steels.

Further investigation of the transformation products in the austenite of 2205 after prolonged carburization was beyond the scope of this work, as was exploration of the structural modifications following prolonged (> 20 h) nitridation in the lower temperature regime (≤ 400 °C). It is ultimately of interest to determine at what temperatures and times nitrides do form in 2205, within each phase, and how they affect the performance of the alloy. The optimized temperature$^3$ of 380 °C determined for carburization of 2205 may not apply to nitridation where thicker (≥ 5 µm) cases are desired, and hence treatments lasting longer than 20 h required.

$^1$The carbides were initially misidentified as having formed within δ-ferrite grains prior to application of the TKD technique.
$^2$316L austenitic stainless steel is industrially carburized at 470 °C for 20–30 h leading to carbide-free expanded austenite.
$^3$The corrosion resistance decreased when treated above 380 °C.
The sub-surface $\delta$-ferrite grain in Fig. 6.11 with a very low indexing rate\(^1\) results from the nm-scale phase separation that occurs in supersaturated $\delta$-ferrite during carburization at low temperatures. The most noteworthy observation here is that where the software was able to index the Kikuchi patterns in this grain, ferrite was the only phase identified with any reliability. The random pixels identified as a carbide can be considered ‘noise’. The mean angular deviation (MAD) parameter measuring the quality of fit between the experimental pattern and candidate structure in these few regions is too high to be reliable. The same applies to the few yellow regions identified as Fe\(_3\)C cementite in the near-surface austenite grains. At each of these pixels, the goodness-of-fit indicated by the MAD number is only modestly less for other candidate structures (e.g. MAD = 1.19 for Fe\(_3\)C and MAD = 1.22 for M\(_5\)C\(_2\)), though the software will choose that with the lowest MAD as an initial solution based on the predefined constraints. This emphasizes why great care must be taken in any automated analysis, especially in highly defective and far-from-equilibrium samples where deviations from ideal behavior are the norm.

Generally, a MAD number less than 1 is assumed to be a ‘good’ fit (though less is always preferred); provided the MAD number is not similar for other candidate structures, the solution is reliable. This was indeed the case for the other regions in this carburized 2205 sample properly identified as ferrite, austenite, M\(_5\)C\(_2\), and M\(_7\)C\(_3\). This methodology was applied to all other TKD analyses.

\(^{1}\)The low quality of Kikuchi patterns obtained from this grain are indicated by its dark contrast in the band-contrast image.
6.2. RESPONSE OF AUSTENITE TO INTERSTITIAL HARDENING

Figure 6.7: SAED patterns along a [011]_fcc viewing direction acquired from expanded austenite grains at two different depths in wrought 2205 nitrided at $T_N = 380 \degree$C and $a_{N_2} = 1.4 \times 10^5$. 
6.2. RESPONSE OF AUSTENITE TO INTERSTITIAL HARDENING

**Figure 6.8:** SAED pattern along a $[011]_{fcc}$ viewing direction acquired from an expanded austenite grain in wrought 2205 nitrided at $T_N = 350 \, ^\circ$C and $a_{N_2} = 1.8 \times 10^2$. Faint reflections near primary 002 and 111 reflections are $fcc$ twins.
6.2. RESPONSE OF AUSTENITE TO INTERSTITIAL HARDENING

Figure 6.9: SAED pattern obtained from the upper-right austenite grain in Fig. 6.7 along a [013]_{fcc} direction showing faint superlattice reflections at \( \frac{1}{2} \bar{g}_{113} \) and \( \frac{1}{2} \bar{g}_{133} \) of the austenite.
FIGURE 6.10: Proposed austenite superlattice to account for $\frac{1}{2}\mathbf{g}_{113}$ vectors in diffraction patterns obtained from the nitrogen-supersaturated austenite grains of 17-7 PHSS and 2205 DSS.
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FIGURE 6.11: TKD band-contrast (left) and phase maps (right) of a TEM specimen obtained from wrought 2205 carburized at 380 °C for 150 h.
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6.3 The Response of Ferrite in 2205 to Interstitial Hardening

6.3.1 Comments Concerning the Application of TEM to Surface Hardened Ferrite-containing Stainless Steels

A few comments are deserved concerning the applicability of the TEM in structural analysis of surface-hardened ferrite- or martensite-containing stainless steels. The microstructural response of the ferritic phase in 2205 to low-temperature interstitial hardening, one of the primary objectives of this work, proved also to be the source of greatest confusion. This was exacerbated by the fact that no detailed or reliable TEM investigations in this area had previously been performed (or published) for comparison with the present results. As mentioned in Sec. 2.3.5, the handful of prior structural investigations relied mostly upon XRD information alone, which was already shown earlier (Sec. 5.6) to be potentially misleading. Furthermore, where previous TEM data was available, the interpretation was open to debate.

In the early stages of this investigation, the TEM data were at times misinterpreted or uninterpretable, and could not fully be reconciled with the fact that the more global structural characterization methods hinted at an isothermal, nitrogen-induced $\delta \rightarrow \gamma$ phase transformation, while at the same time seemed to rule out extensive nitride or carbide precipitation. By later application of modern advances in electron microscopy—namely the TKD technique and spatially-resolved imaging/chemical analysis afforded by state-of-the-art TEM systems—a new understanding was eventually reached.

To say that the structural or mechanistic description of the isothermal, nitrogen-induced martensitic phase transformation of $\delta$-ferrite to austenite is complete would be a gross understatement. It is hoped that the analysis herein will promote more work in this fundamentally and practically important area of phase transformations in ferrous alloys. Many of the conclusions drawn from electron diffraction will be open to interpretation, and in some sense the limits of conventional microscopy exhausted. For example, discernment between a ferritic (or martensitic) and austenitic microstructure by conventional electron diffraction, though the geometry of their zero-order Laue zones (ZOLZ) appear similar along certain crystallographic directions, is often easily made with even a rough calibration of camera length and an a priori knowledge of the microstructure; indeed, this discernment has caused little grief for metallurgists since development of the TEM. However, in the interstitially-hardened stainless steel where lattice parameter expansions up to $\approx 11\%$ (!) have been reported, with defect concentrations contributing to diffraction artifacts on par with the most severely deformed metals, this distinction becomes less obvious. A diffraction pattern along a $[001]_{f.c.c}$ direction in austenite with a lattice parameter expansion of 10% differs only by $\approx 3\%$ for a diffraction pattern of non-expanded ferrite in the same direction. The high defect concentration further serves to reduce the accu-
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Accuracy in determining reciprocal lattice vector intensity maxima, which is poor even in the most pristine crystals, and precludes other spatially-resolved techniques such as CBED that could otherwise be used for more accurate crystallographic characterization. Fine features such as nano-twins, stacking faults, or anti-phase boundaries (APB) can also lead to artifacts in electron diffraction patterns that make for arduous interpretation in even well-behaved systems.

To exacerbate the situation, the extremely large residual stresses in interstitially-hardened stainless steels\(^1\) lead to challenges in preparation of ideally-thin TEM samples\(^2\), which is arguably the most difficult and important aspect of any TEM study.

In short, the interpretation of TEM data from interstitially-hardened \(bcc\)-based stainless steels must be met with special care and attention to detail. In spite of these challenges, a new understanding of the response of \(\delta\)-ferrite was ultimately reached through application of the TEM. The more general observations through the range of processing conditions are provided below.

6.3.2 Conventional TEM Imaging and Electron Diffraction in Former Ferrite Grains

A BF micrograph of a wrought \(\delta\)-ferrite grain after nitridation at 380 °C and \(a_{N_2} = 1.4 \times 10^5\) is shown in Fig. 6.12. The grain is several micrometers below the free surface, but still within the nitrogen diffusion zone. The lenticular, plate-like transformation product appears to have nucleated at the adjacent austenite grain in a direction pointing toward the free surface. The plates, viewed primarily edge-on and in the most strongly diffracting condition, are not purely flat but exhibit an interface with strong curvature. Several variants of the transformation product appear in well-defined relation to one another.

Growth of the plates by a shearing mechanism is clear from the uppermost variants running parallel to the surface. The plates terminate at a very sharp interface somewhere near the depth of the measured nitrogen profile. This atomically-sharp tapering of the plates is further characteristic of a martensitic transformation. It is noted that an abrupt change in contrast exists in the regions between the plates and the bending contours/dislocation debris characteristic of the nominal \(\delta\)-ferrite somewhere near the middle of the grain. The uniform contrast observed between plates in the upper region also extends to a depth corresponding to the penetration depth of nitrogen measured by AES. This weak contrast is most likely indicative of significant internal lattice strain.

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\(^1\) Recent work [151] on the interstitial-hardening of PHSS has demonstrated that in the absence of residual stresses, e.g. in treatment of fine powders, the phase transformations can differ from those in a bulk sample where internal stresses presumably play a role.

\(^2\) As mentioned in Sec. 3.3.7, plastically deforming a treated sample by several pct. in compression can reduce the magnitude of the residual compressive stress in the hardened layer, and thereby allow preparation of thinner TEM foils. This approach is recommended for future TEM studies of surface-hardened stainless steels.
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FIGURE 6.12: Composite BF micrograph of a δ-ferrite grain in wrought 2205 nitrided at 380 °C and $n_{N_2} = 1.4 \times 10^5$. 

free surface

δ-form
Additional BF micrographs of the martensitic austenite transformation product in this sample under different diffracting conditions are provided in Fig. 6.13 to further illustrate these prominent microstructural features. The plates are typically 20–40 nm wide when viewed edge-on, and contain significant sub-structure. These internal planar defects represent deformation nano-twins occurring within the martensitic austenite and presumably form, like many of the microstructural features, to counter the pre-existing stain energy in the material generated during the transformation. Closer to the free surface, the lamellae originate from the ferrite–austenite interphase boundary and are surrounded by regions of uniform weak contrast. Near the terminating end, they are surrounded by regions with contrast typical of heavily dislocated material (determined by electron diffraction to be δ-ferrite). For some tilting conditions, the plates appear uniform in contrast (plates and interior regions are in-zone), but it was more common to observe different regions within the plates excited at different tilts.

Several XEDS line-scans acquired through and across the transformation product are shown in Fig. 6.14. The plates and neighboring regions of uniform contrast clearly inherit the nominal δ-ferrite composition, and the transformation thus occurred in fully partitionless fashion. Whether the transformation was diffusion-controlled (massive) or diffusionless (martensitic) will be touched upon in the next chapter. Within the limits provided by the technique for standardless quantification (∼ 5 at.%), the concentration of nitrogen within, between, and across the two regions is both high and uniform, i.e. the plates and adjacent regions locally possess the same composition.

The quantification of nitrogen by XEDS without standards is suspect, however it is noted that in regions near the terminating end of the plates further from the surface where conventional contrast was observed, only a modest nitrogen signal existed\(^1\). Hence, though the error may be high, a measurable and significant concentration of nitrogen exists within the transformed regions. Furthermore, the concentration of nitrogen in the transformation product is not fixed, but varies widely. The transformation product is stabilized in regions with both high (10–20 at.%) and low (a few at.%) nitrogen. If this transformation product were truly an ordered nitride phase, the only possibility is that of \(\varepsilon\)-M\(_2\)N\(_{1-x}\) based on composition alone within the experimental error of nitrogen content.

It would be most useful to know the nitrogen concentration of the plates at the terminating end, which by XEDS was unmeasurable, using electron energy-loss spectroscopy (EELS), the preferred technique for light element analysis. However, for all the reasons mentioned earlier, most specimens were relatively thick (∼ 30–70 nm) and not well-suited for EELS.

STEM micrographs in a different specimen from the same treatment are shown in Fig. 6.15. The features in the micrograph running orthogonal to the free surface represent

\(^1\)Quantified as a few at.% nitrogen, which is lower than the experimental error.
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Figure 6.13: Several BF micrographs obtained from the nitrogen-induced transformation product in δ-ferrite under various diffracting conditions and depths from the surface.
6.3. RESPONSE OF FERRITE TO INTERSTITIAL HARDENING

Figure 6.14: XEDS line-scans performed within the transformed region of a former $\delta$-ferrite grain.
so-called *curtaining*—an artifact of the FIB preparation method. A SAED pattern and corresponding BF and DF images acquired from the triangular δ-ferrite grain near the surface are shown in Fig. 6.16. These two micrographs most strongly indicate the nanometer-scale internal twins.

The same plate-like transformation product appears, in this case nearly consuming all δ-ferrite grains in contact with the surface. The phase appears to form in multiple variants at the surface where nitrogen is highest. The density of the transformation product is higher than in the sub-surface δ-ferrite grain shown in Fig. 6.13 due to the grain’s higher nitrogen content. In regions where the plates were not sectioned edge-on, a fairly uniform diffraction contrast is again observed. However, thicker bands with internal substructure appear, as though these regions represent the same plate-like variants sectioned along a thicker dimension.

The SAED pattern in Fig. 6.16 obtained from the former δ-ferrite grain, like most, contains numerous artifacts (e.g. streaking, diffuse intensity, additional reflections), but reflections consistent with a twinned [011]_{fcc} viewing direction can be distinguished. The additional reflections observed at g’s slightly larger than primary and twin reflections likely result from microstructural features (whether nano-twins/stacking faults and/or double diffraction is not fully clear) as they could not be indexed according to the known nitrides. Again, within the accuracy provided by the technique, the austenite lattice is measurably expanded by a few pct. relative to the nominal material. The \{200\}_T reflection used to form the DF image is circled in the diffraction pattern. A DF image from the primary reflection (not shown) complements the DF image and confirms the twin relationship.

The very high density of planar defects within the martensitic austenite lamellae is shown by both BF and DF imaging techniques. These internal features closely resemble those found in ferrous martensites. Without verification by higher-resolution imaging, they are most likely nanometer-scale deformation twins resulting from the transformation. The upper left-hand corner of the BF image in particular shows how these internal features may be related in adjacent twins.

Without too much confusion, it is shown that the new features appearing in 2205 δ-ferrite following nitridation represent a highly twinned, plate-like austenite transformation product that apparently grew by a diffusionless, shear-based mechanism. This fully corroborates the XRD, EBSD, and MFM results. This martensitic austenite transformation product is henceforth described by the following nomenclature: γ′<sub>M</sub>.

To return to the regions between and near the terminating end of the plates of austenite in Fig. 6.13, two single-crystal SAED patterns are shown in Fig. 6.17 obtained from the uniform and conventional contrast zones. Each can be indexed according to: a [114]_{fcc}
6.3. RESPONSE OF FERRITE TO INTERSTITIAL HARDENING

Figure 6.15: HAADF STEM micrographs in wrought 2205 nitrided at 380 °C and $a_{\text{N}_2} = 1.4 \times 10^5$. 
6.3. RESPONSE OF FERRITE TO INTERSTITIAL HARDENING

Figure 6.16: BF and DF images obtained from the triangular surface δ-ferrite grain in Fig. 6.15. The SAED pattern (inset) is indexed as twinned (expanded) austenite in a [011]_fcc viewing direction. The reflection used to form the DF is circled in the SAED pattern.
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Figure 6.17: (a) BF image and (c) SAED pattern obtained from the matrix surrounding the end of austenite plates identified as a $[111]_{bcc}$ zone-axis, (b) BF image and (d) SAED pattern obtained from the uniform contrast region between the plates in Fig. 6.13 identified as a $[114]_{fcc}$ zone-axis.
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zone-axis in the upper uniform region, and a \([111]_{bcc}\) zone-axis near the end of the plates. With this understanding in mind, the following conclusions concerning the transformation can be made:

- It occurs within the nitrogen-enriched layer of former \(\delta\)-ferrite grains through a diffusionless, shear-based mechanism.
- The plate-like \(\gamma'_M\) lamellae and adjacent regions represent measurably-expanded \(fcc\) austenite in twinning relation with one another.
- The lamellae contain a high density of internal planar defects.
- The number of a given variant to nucleate and grow may be proportional to the local nitrogen enrichment.
- The morphology is deduced from the consistent features observed across a range of wrought and cast TEM specimens.
- The regions within the case of \(\delta\)-ferrite where the plates of austenite were not sectioned edge-on can be understood as variants of the austenite transformation product that run orthogonal to the edge-on variants.

Such a microstructure described here is well-known in ferrous \(a'_M\) martensites.

The following series of diffraction patterns and BF/DF images were what initially led to some confusion in interpretation. A SAED pattern and corresponding BF/DF images are shown in Fig. 6.18 along a \([013]_{fcc}\) zone-axis, and in Fig. 6.19 along a \([114]_{fcc}\) zone-axis. Both were acquired from the same far-left \(\delta\)-ferrite grain in the Fig. 6.15 specimen treated at 380 °C and \(aN_2 = 1.4 \times 10^5\).

When indexing the diffraction pattern in Fig. 6.18, it was initially assumed that the two or three shortest \(\bar{g}\) vectors were the primary reflections belonging to some unidentifiable nitride phase. The shortest \(\bar{g}\) vectors in Fig 6.18(a) show six-fold symmetry (though not of equal intensity) and do not belong to a primary \(bcc\) or \(fcc\) zone-axis. From the measured plane-spacing, these reflections could correspond to the basal plane of an \(hcp\) structure, i.e. a \([001]_{hcp}\) zone-axis. The next closest to the six-fold reflections (circled in green), if considered primary reflections, have a low symmetry with lattice plane spacings and interplanar angles inconsistent with known iron and chromium nitrides. A common feature observed in many of the diffraction patterns were spots with a diffuse intensity, and often with diffuse emanating ‘tails’. These diffuse spots fit a slightly expanded \(fcc\) structure along a \([013]_{fcc}\) zone-axis. If the reflections circled by blue and red belong to a separate zone-axis with twinning, with a clearer diffraction pattern.
6.3. RESPONSE OF FERRITE TO INTERSTITIAL HARDENING

**Figure 6.18:** (a) SAED pattern and (b) BF image from a former δ-ferrite grain along a [013]$_{fcc}$ zone-axis. (c)–(f) DF images formed using the circled $\vec{g}$ vectors in (a). The circle in each of the micrographs is the area-selecting aperture.
6.3. RESPONSE OF FERRITE TO INTERSTITIAL HARDENING

Figure 6.19: (a) SAED pattern and (b) BF image from a former δ-ferrite grain along a [114]_{fcc} zone-axis. (c)–(f) DF images formed using the circled \( \bar{g} \) vectors in (a). The circle in each of the micrographs is the area-selecting aperture.
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hcp phase, it would share the following orientation relationship with the austenite:

\[
\begin{align*}
(\overline{131})_{fcc} & \parallel (110)_{hcp} \\
[013]_{fcc} & \parallel [001]_{hcp}
\end{align*}
\]  

(6.1)

When indexing the outer diffuse reflections as a [013]_{fcc} zone, it is noted that the additional reflections are identical to the forbidden \(\frac{1}{2}\overline{g}113\) appearing in the diffraction pattern in Fig. 6.9 acquired from an austenite grain. The DF images from a diffuse tail and a \(\frac{1}{2}\overline{g}113\) indicate both originate from the same region between the strongly diffracting plates in the BF image of Fig. 6.18(b). The DF images obtained from two of the six-fold \(\overline{g}\) vectors indicate that these reflections originate from different regions of the microstructure (apparently two of the plate variants), thus ruling out that they belong to the basal plane of an hcp structure. It is further noted that some of the microstructural features may overlap with one another in projection because of the relative thickness of the sample.

To compare this information with the other diffraction patterns obtained from the same specimen (Figs. 6.16 and 6.17(d)) clearly indexable as austenite, it is possible that the [013]_{fcc} pattern consists of three phases—austenite, an hcp structure, and a low-symmetry structure whose lattice has not fully been described—each in a well-defined orientation relationship with the austenite. It is also possible that another twinning-related austenite zone-axis exists in the pattern that has not yet been identified. A third possibility exists in which all of the addition reflections normally forbidden in the [013]_{fcc} ZOLZ can be attributed to combined contributions arising from micro-twins, nano-twins, and double diffraction. A discussion of this latter possibility is to follow in the next chapter.

The SAED pattern in Fig. 6.19 acquired from the same grain along a [114]_{fcc} zone-axis is less ambiguous, where the inner reflections are identified as [011]_{fcc} twins arising from the dominant fcc {111} \{110\} twinning system. The pattern still shows diffuse reflections and their associated ‘tails’. There is an additional \(\overline{g}\) vector observed near \(200\)_{fcc} appearing as a distinct and diffuse reflection. This particular \(\overline{g}\) vector, though it could be a separate phase, according to the DF image in Fig. 6.19(c) appears in the same microstructural variants already identified as austenite. It was realized that these \(\overline{g}\) vectors, tripling the period normal to common \{111\}_{fcc} planes, can arise from overlap of first generation twins in the [011]_{fcc} viewing direction by a double diffraction mechanism. This is most consistent with the microstructural observations. It is interesting that the DF image from the \{200\} and \{111\} \(\overline{g}\) vector in the [011]_{fcc} pattern do not necessarily excite equivalent regions within the plates. Comparing Fig. 6.19(d) and (f), Fig. 6.19(f) includes some intensity from the second variant in the field of view, likely due to some overlap of the objective aperture with the diffuse intensity of the twin-related reflection circled in red.

A BF image and SAED pattern from the sub-surface \(\delta\)-ferrite grain on the far left in Fig. 6.4 is shown in Fig. 6.20. This diffraction pattern was unique, and could not be
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FIGURE 6.20: BF (left) and SAED pattern (right) from former δ-ferrite grain. Indexing of some reflections as [112]_fcc is indicated.
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indexed until it was realized that the indicated reflections fit a [112]_fcc zone axis. The remaining reflections do not confirm to a known nitride. In other [112]_fcc zone axis patterns acquired from δ-ferrite grains (see Appendix 8.1), the recurring 1/2\(\bar{g}\)113 vector was observed. The [112]_fcc SAED pattern in Fig. 6.20 did not include 1/2\(\bar{g}\)113, but shows two reflections opposite of where they would appear. Without claiming a complete understanding of such a diffraction pattern, based on the aforementioned results and the fact that they could not be attributed to a secondary nitride, these peculiar reflections were ultimately attributed to complex twinning and double diffraction mechanisms within the relatively thick specimen. The BF micrograph of the grain is also unique from many other δ-ferrite grains, lacking perceivable twins with internal structure. It is possible that such features are present, but multiple overlaps within the thickness of the foil could prevent them from being resolved in projection.

An additional series of BF/DF micrographs and corresponding SAED pattern are shown in Fig. 6.21, obtained from a single δ-ferrite grain in cast material after nitridation at 400 °C and \(\delta_{N_2} = 3.0 \times 10^3\). The microstructure within this partially-transformed δ-ferrite grain again consists of thin lamellae, separated by a region showing lower contrast, but also with some evidence of planar defects. The diffuse spots in the diffraction pattern, indexed in Fig. 6.22, do not conform well to any bcc or fcc zone-axes. The diffuse intensity, along with the measured lattice plane spacings most closely fits an expanded [112]_fcc zone-axis pattern. A [213]_fcc zone-axis may also contribute to the perceived intensity, though two distinct \(\bar{g}\) vectors within the diffuse intensity are not observed. Sharp reflections appear at small \(\bar{g}\) vectors and do not coincide with the [112]_fcc zone-axis pattern as 1/2\(\bar{g}\)113 reflections. This is confirmed by DF imaging from the circled \(\bar{g}\) vectors. The sharp reflections originate from the edge-on plates and the diffuse reflections from the interior regions. The innermost sharp \(\bar{g}\) vectors lack any symmetry, and taken as primaries do not fit a bcc, fcc, or known nitride structure.

It was later realized that these reflections are in good agreement with a twinned [123]_fcc zone-axis pattern as shown in Fig. 6.21. One set of the additional reflections lie along the twin plane at 1/3\(\bar{g}\)422, and taken as a whole account for most of the observed reflections in the pattern. The twinned [123]_fcc pattern with anomalous 1/3\(\bar{g}\)422 is confirmed by the angular relationship measured between the plate-like variants of austenite in Fig. 6.22. Both \(\gamma'_M\) variants and twinned [123]_fcc with superlattice reflections are rotated by 56°.

Additional SAED patterns from the case along different zone-axes are shown in Fig. 6.22. Near the surface the patterns were indexed as (expanded) austenite, with twins if the area-selecting aperture included multiple variants. The SAED pattern in Fig. 6.22(c) was acquired at a depth from the surface near the edge of the nitrogen diffusion zone, and shows both [112]_fcc and [112]_bcc zone-axes in Nishiyama-Wasserman (N-W) orientation.
FIGURE 6.21: (a) SAED pattern, (b) BF, (c) and (d) DF images obtained from a single cast \( \delta \)-ferrite grain following nitridation at 400 \textdegree C and \( a_{N_2} = 3.0 \times 10^3 \).
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Figure 6.22: SAED patterns obtained from single cast δ-ferrite specimen in Fig. 6.21. (a) Aperture including only region between plates indexed as \([013]_{fcc}\) zone-axis, (b) Aperture includes plate-like features indexed as twinning-related \([114]_{fcc}\) and \([011]_{fcc}\) zone-axes, (c) Aperture near edge of nitrogen diffusion layer including \(bcc\) core and austenite transformation product indexed as \([112]_{fcc}\) and \([112]_{bcc}\) zone-axes close to N-W orientation relationship, (d) Indexing of pattern in Fig. 6.21(a).
6.3. RESPONSE OF FERRITE TO INTERSTITIAL HARDENING

relationship:

\[
\begin{align*}
(111)_{\text{fcc}} & \parallel (110)_{\text{bcc}} \\
[\overline{1}01]_{\text{fcc}} & \parallel [001]_{\text{bcc}}
\end{align*}
\] 

(6.2)

The reflections appear diffuse regardless of tilt, which like many other features are thought to arise from the very large concentration of defects. It is not surprising to find the N-W orientation relationship between parent ferrite and product austenite following a shear transformation, where closest-packed planes and directions in both crystals lie parallel so as to minimize strain energy contributions. It is commonly observed between austenite and ferrous martensites.

6.3.3 Structural Characterization Using TKD

A cross-sectional TEM foil produced from a single $\delta$-ferrite grain of 2205 nitrided at 400 $^\circ$C and $4.0 \times 10^9$ nitrogen activity was investigated by TKD. Phase mapping against all known iron and chromium nitrides is shown in Fig. 6.23, along with a forward-scatter detector (FSD) image\(^1\) of the foil. The nitrogen penetration depth in the $\delta$-ferrite of this sample extends 10–13 $\mu$m.

Most notably, no nitrides were identified through the entire depth of the case. A high density of $\gamma'$-M plates is observed in the FSD image, which extend from the free surface to the depth of the nitrogen profile. Furthermore, all regions between the edge-on austenite variants are indexed as austenite. From the concave shape of the interface between the transformed and bulk $\delta$-ferrite, the austenite plates may assume a narrower width near their terminating edge. The orientation relationship between the product austenite and parent ferrite at this interface is again in good agreement with the N-W relationship given in Eq. 6.2.

Indexing against bcc, fcc, and nitride phases of regions near the free surface was practically zero, as shown in Fig. 6.24, due to the highly defective nature of the lattice in these regions with highest nitrogen concentration. Kikuchi bands were almost non-existent. Where indexable however, it is noted that austenite was the most likely structure. The average MAD number for the regions indexable as austenite was 0.84, while greater than 1 for a $M_2N_{1-x}$ (ordered and disordered) and $M_4N$ nitride. Finely tuning the lattice parameters in each candidate structure did not lead to an increase in indexing rate or decrease in MAD number.

Diffraction patterns from this sample can be found in Appendix 8.1, each indexable as

\(^1\)The mechanisms contributing to contrast in an FSD image are complex, and consist primarily of orientation, atomic density, and/or topographic contrast. The orientation of the diode to the phosphor screen, the number of diodes, their orientation to the sample, beam properties, etc. can all lead to strong changes in perceived contrast. This useful method for generating unique contrast on bulk or thin samples in the SEM is an on-going subject of active research.
Figure 6.23: Cross-sectional TKD phase analysis on a TEM foil extracted from a δ-ferrite grain in cast 2205 nitrided at 400 °C and $4.0 \times 10^9$ nitrogen activity. FSD image of the foil on the left, with the free surface 1–2 µm above the top of the image. On right, band-contrast (top), orientation (middle), and phase map (bottom).
In one such SAED pattern, very faint, diffuse tails can be indexed as a $bcc\ [011]_{bcc}$ zone-axis if assumed that the diffuse intensity corresponds to a specific set of lattice planes. If regions of $bcc$ $\delta$-ferrite still exist within the nitrogen-rich layer, the SAED pattern in this region suggests the K-S orientation relationship (Eq. 2.11) with the $\gamma'_M$ expanded austenite transformation product.

### 6.4 Featureless Ferrite Containing Colossal Supersaturation

In addition to the martensitic transformation of nitrogen-supersaturated $\delta$-ferrite to austenite at low temperatures, a second, albeit rarer during nitridation, microstructural response was observed by TEM. This was also the exclusive response of $\delta$-ferrite following carburization of 2205 in any of the TEM specimens, i.e. no carbon-induced transformation of $\delta \rightarrow \gamma$ was directly observed.

An overview BF micrograph of a TEM specimen extracted from a single $\delta$-ferrite grain in cast 2205 following nitridation at 380 °C and $a_{N_2} = 1.4 \times 10^5$ is shown in Fig. 6.25. The micrograph, unlike the others, shows no obvious sign of transformation products, but instead a region of uniform contrast void of any features extending $\approx 5 \mu m$ below the free surface. This ‘featureless’ region corresponds precisely to the penetration depth of nitrogen as determined by AES depth profiling in this sample. Below the apparent
Figure 6.25: Overview BF micrograph of a TEM sample extracted from a single δ-ferrite grain in cast 2205 following nitridation at 380 °C and $a_{N_2} = 1.4 \times 10^5$. Featureless zone extending $\approx 5$ below the free surface corresponds to the penetration depth of nitrogen in this sample.
6.4. FEATURELESS FERRITE CONTAINING COLOSSAL SUPERSATURATION

interface, conventional contrast arising from bending contours is observed. Note that the linear features orthogonal to the surface of the foil represent curtaining from the FIB foil extraction. An example of such uniform, featureless contrast observed in δ-ferrite grains following low-temperature carburization is shown in Fig. 6.26.

FIGURE 6.26: Overview STEM micrograph acquired from a wrought 2205 specimen following carburization at 380 °C for 150 h.
6.4. FEATURELESS FERRITE CONTAINING COLOSSAL SUPERSATURATION

A nano-diffraction profile along a \([001]_{\text{bcc}}\) zone-axis through the weak-contrast \(\delta\)-ferrite is shown in Fig. 6.27. These nano-diffraction patterns were obtained using a converged beam \(\approx 5\) nm in diameter, the high intensity of which conveniently created carbon de- posits on the foil surface (confirmed by tilting) where each pattern was acquired. The diffuse spots (diameter related to the small C2 aperture used) conform to a \(\text{bcc}\) \(\delta\)-ferrite lattice, and show no signs of distortion or secondary phases extending from the surface into the core material.

To further investigate the structural or chemical origin of this peculiar result, high- resolution imaging and chemical analysis of the foil in Fig. 6.25 was performed. HR-XEDS elemental Fe and Cr maps obtained near the free surface (nitrogen concentration of region \(\approx 15–20\) at.\%) of the foil are shown in Fig. 6.28, along with a lower magnification HAADF STEM image near the apparent interface along a \([001]_{\text{bcc}}\) viewing direction.

The elemental mapping reveals nanometer-scale Fe and Cr modulations akin to spinodal decomposition in the Fe–Cr system. The bright contrast in the HR-STEM images corresponds to Fe-rich regions and the dark contrast to Cr-rich regions. The brightness of the Fe-rich ‘islands’ is attributed to a diffraction contribution to the STEM HAADF detector. Higher-magnification STEM images of this region are also shown in Fig. 6.29 in the \([001]_{\text{bcc}}\) viewing direction.

Good crystallinity is observed within the Fe-rich regions, while atom columns within Cr-rich regions are heavily distorted and/or ‘blurred’ so as to be nearly indistinguishable. From XEDS, the Cr content is estimated at 40 at.\% and 10 at.\% within the Cr-rich and Fe-rich regions, respectively. A Burgers circuit analysis of such images for locating (pure edge) dislocations was made difficult by the inability to clearly distinguish atom columns within the Cr-rich domains. It is suggested that the dislocation density within this region of nitrided \(\delta\)-ferrite is at the very least \(10^{16}\) m\(^{-2}\) as estimated from similar supersaturated \(\delta\)-ferrite grains in 17-7 PHSS after low-temperature carburization [162]. The thickness of the foil in these regions was not measured. Based on the \(\approx 3–5\) nm characteristic wavelength (normal to the surface) of the phase separation, the foil must contain some overlap of both decomposition products through its thickness. The modulations are apparently smallest in the direction of inward nitrogen diffusion and longer parallel to the free surface. This would imply longer chemical modulations within the thickness of the foil, and thus a local foil thickness near 15–20 nm could contain Fe-rich and Cr-rich ferrite without such overlap, thus permitting atom columns through each region to be imaged.

From the APT results on the same treatment, nitrogen presumably segregates to these Cr-rich regions, due to the higher affinity between the two species. It is noted that high-resolution imaging and chemical mapping within the core regions of \(\delta\)-ferrite (as shown in Fig. 6.28) did not show the same decomposition, thereby confirming that the nanometer-scale phase separation is somehow related with the colossal supersaturation of interstitials and not a result of the heat-treatment by itself. A mechanism by which the ferrite lattice
6.4. FEATURELESS FERRITE CONTAINING COLOSSAL SUPERSATURATION

Figure 6.27: Nano-diffraction profile along a [001] zone-axis through a weak-contrast region of a 2205 δ-ferrite grain following nitridation. The dark spots running orthogonal to the free surface in the BF image represent adventitious carbon build-up from the high intensity of the focused electron probe.
Figure 6.28: HR-XEDS elemental Fe, Cr, and composite maps and HAADF STEM image from weak-contrast $\delta$-ferrite grain. Bright contrast in the STEM image corresponds to Fe-rich and dark contrast to Cr-rich regions. Lower-magnification STEM image near the apparent interface also shown in the upper-right.
6.4. FEATURELESS FERRITE CONTAINING COLOSSAL SUPERSATURATION

Figure 6.29: HR-STEM images along [001]$_{bcc}$ in δ-ferrite of 2205 following nitridation at 380 °C and $1.4 \times 10^5$ nitrogen activity. Bright contrast corresponds to Fe-rich and dark contrast to Cr-rich regions.
is able to accommodate such colossal concentrations of interstitials with imperceivable lattice expansion or distortion is proposed in the following chapter after some discussion on the effect of stress on the observed transformation behavior.

The characteristic wavelength of the spinodal reaction, $\lambda_{SD}$, at least normal to the surface is estimated at 4–5 nm$^1$. The phase separation in $\delta$-ferrite through a spinodal reaction is almost certain, as these compositional modulations are too small to result from conventional nucleation and growth.

At first glance, it seems remarkable that atom columns, at least in the Fe-rich domains, could be imaged at all given such small composition fluctuations. At 4–5 nm, it could be expected that some overlap of Fe-rich and Cr-rich domains exists within the thickness of the foil. Considering the highly defective nature of Cr-rich ferrite implied from the HR-STEM images, such overlap would lead to interference in projection thereby rendering the image uniformly diffuse. Though the local foil thickness in the regions ($\approx 20 \times 20$ nm) from which HR-STEM images were acquired was not directly measured, these images, which are not trivial to obtain, represent the very thinnest regions of the foil. Based on the contrast of the foil imaged in the SEM-FIB system at low accelerating voltage (3 kV), the average foil thickness was estimated to be 40–50 nm$^2$. Subsequent low-energy $Ar^+$ ion milling used to clean the foil after FIB extraction further removed an estimated $\approx 5$ nm of material from both sides of the foil. It is important to note that decomposition appears highly directionally-dependent, i.e. it is preferentially elongated in elastically soft $\langle 001 \rangle_{bcc}$ directions. Therefore, the composition modulations in the plane of the foil are larger than the vertical wavelength, thereby allowing uniform regions of $\alpha_{Fe}$ and $\alpha'_{Cr}$ to be imaged in some locations.

$^1$The interdiffusion coefficient of the spinodal reaction, $D_{SD}$, can be approximated through $\lambda_{SD} \approx \sqrt{D_{SD} t}$ where $\lambda_{SD}$ is the characteristic wavelength and $t$ the time. Estimating the wavelength normal to the surface at $\approx 4$ nm yields $D_{SD}(653K) \approx 10^{-22}$ m$^2$ s$^{-1}$. This crude estimate is far from the extrapolation of known Fe and Cr interdiffusion data in ferrite, though it is admittedly difficult to accurately measure substitution coefficients at these low temperatures.

$^2$The fact that this single-crystal foil extracted from a decomposed $\delta$-ferrite grain was able to be thinned without much warping gives some insight into the local stress-state of these regions. Relative to foils extracted from regions with martensitic austenite, which began to warp around 100 nm, the decomposed regions may therefore accommodate the stress through the ultra-high dislocation density.
Chapter 7

Stress Effects on Paraequilibrium Solubility and Transformation Behavior

It was demonstrated in Chapter 6 that there are essentially only two microstructural responses of δ-ferrite in the 2205 alloy to paraequilibrium nitridation or carburization\(^1\): nitridation (primarily) induces martensitic formation of austenite, while carburization (and to a lesser extent, nitridation) induces spinodal decomposition to nm-scale Fe-rich and Cr-rich ferrite. Both the martensitic austenite and decomposition products contain nitrogen or carbon supersaturations orders of magnitude higher than predicted equilibrium values.

The following chapter presents a model to explain this transformation behavior. Chapter 4 considered the chemical driving force; this chapter focuses particularly on the implications of strain energy to the total driving force, which is pertinent to all chemical and structural aspects of the diffusion layer covered in Chapters 5 and 6. This phenomenological model, built upon the combined contributions of chemistry and stress, is more speculative in nature, but nevertheless able to describe much of the transformation behavior observed in stainless steels of all types when subjected to interstitial hardening treatments.

7.1 The Predicted Paraequilibrium Solubility Limit in Austenite

It was mentioned in Chapter 4 that there was previously an assessment [128] of the CALPHAD database with regard to metastable carbon supersaturation in 316-type austenitic stainless steel following paraequilibrium carburization. That work led to the revision of several Cr-C interaction parameters (which were found to be insufficiently exothermic for austenitic matrices) for better low-temperature agreement with experimental supersaturation limits.

\(^1\)At least for temperatures \(\leq 400\) °C whereby desirable improvements in both surface hardness and corrosion resistance are achieved.
7.1. THE PREDICTED PARAEQUILIBRIUM SOLUBILITY LIMIT IN AUSTENITE

reration data. The data obtained in this work permits a similar assessment of the current CALPHAD database as concerns metastable nitrogen supersaturation in \( \text{fcc} \) and \( \text{bcc} \) stainless steels.

The CALPHAD-predicted paraequilibrium nitrogen solubility in 2205 austenite and \( \delta \)-ferrite is shown in Fig. 7.1 against the accumulated data. The predicted solubility and measured surface concentration following paraequilibrium nitridation of 316L grade is shown in Fig. 7.2 for comparison. Retrograde solubility of nitrogen is generally observed in both the austenite and (former) ferrite, as suggested by CALPHAD. However, the measured surface concentration is consistently lower in each sample than the model prediction when neglecting the contribution of compressive stress on the chemical potential of nitrogen in solid solution.

It is recalled that a large, albeit of unknown magnitude, residual biaxial compressive stress exists near the surface of interstitially hardened material (balanced by smaller tensile stresses in the core). It is also reminded that numerous experimental challenges pervade accurate residual stress measurement in interstitially hardened stainless steels, especially in multi-phase alloys. The largest reported value of average\(^1\) residual compressive stress in the literature currently stands at 9 GPa\(^2\) in surface hardened 316L-type austenitic stainless steel (Fig 2.21). Stresses of this magnitude do have a sizable contribution to the total free energy of the solution, as demonstrated within the CALPHAD framework (Fig. 4.4).

It is proposed that the large residual compressive stresses present in these samples contribute most strongly to the discrepancy between experimental and model prediction of paraequilibrium nitrogen supersaturation. As demonstrated in Figs. 7.1 and 7.2, suitable agreement exists in both 2205 austenite and 316L with incorporation of GPa-order biaxial compressive stresses. The discrepancy at lower temperatures is most likely explained on the basis of the rate-limiting kinetics of ammonia decomposition and nitrogen adsorption. That is, a true state of paraequilibrium, \( \mu_{\text{gas}} = \mu_{\text{fcc}} \), was likely not achieved at the gas–metal interface in these samples within the relatively short processing cycle.

Perhaps the strongest support of this stress-induced decrease in paraequilibrium supersaturation concerns the thin foil datum\(^3\) of Christiansen and Somers [95] included in Fig. 7.2. CALPHAD does accurately predict (within 1–2 at.\%) the paraequilibrium nitrogen supersaturation in homogenous, stress-free expanded austenite powder.

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\(^1\)The data overwhelmingly suggest that there is significant stress-partitioning between individual grains in polycrystalline material (Sec 2.3.4).

\(^2\)To put the magnitude of such residual stress into perspective, significant effort often goes into shot-peening critical metallic components for improved fatigue life by imparting residual compressive stresses \( \leq 1 \) GPa. The hydrostatic pressure at the bottom of the Mariana Trench, the deepest known part of the ocean, is 0.11 GPa. Were the ocean to be filled with mercury, the hydrostatic pressure at its greatest depth would be 1.5 GPa.

\(^3\)Nitrogen concentration from a thin 316L foil nitrided at 440 °C in pure NH\(_3\).
7.1. THE PREDICTED PARAEQUILIBRIUM SOLUBILITY LIMIT IN AUSTENITE

**Figure 7.1:** Paraequilibrium solubility limit of nitrogen in austenitic and ferritic 2205 as a function of temperature, nitrogen activity, and biaxial stress-state. Paraequilibrium solubility limit with temperature in (a) $\gamma$-austenite and (c) $\delta$-ferrite in an atmosphere with $a_{N_2} = 3.0 \times 10^3$). Predicted solubility limit with activity in (b) $\gamma$-austenite and (d) $\delta$-ferrite during nitridation at 350 °C. Data points in each plot represent AES-determined surface concentrations with an analytical uncertainty of ±1 at.%. 

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[Image of the graphs showing the solubility limits]
### Figure 7.2: Paraequilibrium solubility limit of nitrogen in austenitic 316L as a function of temperature, nitrogen activity, and biaxial stress-state. Paraequilibrium solubility limit in $\gamma$-austenite (a) with temperature in atmosphere with $a_{N_2} = 7.4 \times 10^3$) and (b) with changing activity during nitridation at 440 °C. Black data points in each plot represent AES-determined surface concentrations following 20 h gas-phase nitridation of 316L [94] with an analytical uncertainty of ±1 at.%; red datum from 316L thin foil [95].

Future work to refine and improve this approach to modeling metastable supersaturation of interstitial solutes in stainless steels should be aimed at addressing how increasing the nitridation duration affects the surface concentration, particularly at lower temperatures (e.g. 325–350 °C). That is, how does the surface concentration within each phase vary when time is the independent variable (cf. [94])? Most importantly, there is strong need for a sound estimate of residual stress in 2205, in both the austenite and former $\delta$-ferrite grains. Considering the experimental challenges mentioned earlier, this will likely require synchrotron-based or theoretical means (e.g. finite element analysis).

Overall, the current CALPHAD database is deemed satisfactory for prediction of paraequilibrium nitrogen supersaturation in austenite with consideration of residual stress. The CALPHAD-predicted supersaturation of carbon in 2205 austenite however yields poor agreement with the data shown in Fig. 7.3. Incorporation of reasonable residual stress in this case (1–3 GPa—typical values reported in carbon-supersaturated austenite) does not lead to much improvement. However, this conclusion is drawn from only two mea-

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1Making use of the revised interaction parameters [128].
FIGURE 7.3: Predicted paraequilibrium solubility limit for carbon in (a) austenitic and (b) ferritic 2205 at 380 °C as function of biaxial stress state. Data points represent AES-measured surface concentration of carbon for samples carburized at 380 °C (20 at.% in fcc, 20–21 at.% in bcc) and 420 °C (15 at.% in fcc, 19 at.% in bcc).
7.2. THE PREDICTED PARAEQUILIBRIUM SOLUBILITY LIMIT IN FERRITE

Measurements of carbon in austenite. There is thus need for more supersaturation data in carburized 2205 before any conclusion is drawn. Moreover, it is recalled that carbides had formed within near-surface austenite grains in at least one of the carburized samples. Therefore, the $\approx 50$ nm AES electron probe locally averaged the carbon concentration of the carbide(s) and carbon-supersaturated austenite in cross-sectional line-scans. This would lead to an erroneous overestimate of carbon supersaturation, which is indeed the case. Accordingly, no comment is to be made concerning the applicability of the revised CALPHAD parameters to paraequilibrium carburization of 2205 without additional data. Such data must also include verification that no carbides are present in the austenite.

7.2 The Predicted Paraequilibrium Solubility Limit in Ferrite

Given that the near-surface $\delta$-ferrite under all processing conditions assuredly transformed, it follows that there is little utility for CALPHAD in predicting paraequilibrium nitrogen (or carbon) supersaturation in ferrite. Use of the AES-determined nitrogen supersaturation in former ferrite grains (the austenite transformation product) does however yield suitable agreement to the predicted paraequilibrium solubility in an fcc matrix of nominal $\delta$-ferrite composition, with incorporation of GPa-order residual stresses.

CALPHAD prediction of carbon supersaturation in carbide-free, decomposed ferrite on the other hand is an order of magnitude too low (Fig. 7.3(b)). As concluded from extensive microstructural and microchemical analysis, carburization always led to a dislocation-enhanced spinodal decomposition of the $\delta$-ferrite. Dislocations—not lattice expanding interstitial sites—were the mechanism by which 2205 $\delta$-ferrite became supersaturated with carbon. These non-equilibrium lattice defects are incompatible within the CALPHAD framework. Solution thermodynamics for predicting paraequilibrium carbon solubility are therefore of no relevance when such defects are involved.

There was recently an attempt [163] to incorporate non-equilibrium defects such as dislocations into the CALPHAD framework. In the solid solution model, dislocations were treated as a separate sublattice with a unique thermodynamic description (as are the conventional substitutional and interstitial lattices). The Gibbs free energy functions describing the dislocation sublattice were obtained through an optimization procedure of experimental data as pertains to strong carbon–dislocation interactions and the trapping of carbon at dislocations in tempered martensite. At least in carbon steels, the model can accurately predict the fraction of carbon atoms pinned by dislocations and the amount of ‘free’ carbon available in martensite for carbide formation. For an alloy steel, the model suggests that the dislocation density—and hence the available carbon pinning sites—has an even stronger influence on retarding cementite formation during tempering of martensite. Such a model is still in its infancy and not yet applicable to the present considerations of carburization of stainless steels. Nevertheless, data acquired from interstitial hardening...
of bcc-based stainless steels may very well aid future development of such models.

### 7.3 Strain Energy Implications on the Inhibition of Secondary Phases

In addition to the chemical driving forces implied by CALPHAD calculations, the phase transformations, or lack thereof, associated with interstitial hardening of fcc- or bcc-based stainless steels can be understood with even rudimentary consideration of the strain energies involved. Table 7.1 presents the lattice strain\(^1\) associated with a ferrite, austenite, or expanded austenite lattice undergoing solid-state transformation to each conceivable nitride or carbide. The expanded austenite assumes a 5% increase in nominal lattice parameter. This analysis also makes the basic assumption that the volumetric thermal expansion coefficients of parent and product phases are roughly equal, such that the treatment-induced lattice strain is proportional to that at room temperature. Further, it assumes that the (largely unknown) lattice parameters of partitionless nitrides or carbides are not sufficiently different from equilibrium versions of these phases. The latter assumption is arguably a stretch \([80,81,116]\), but nevertheless provides a useful frame of reference.

This simple analysis can help explain, at least semi-quantitatively, much of the observed transformation behavior accompanying interstitial hardening treatments of 2205, and other stainless steels for that matter. The lattice strain associated with either ferrite or austenite transforming to each secondary phase is substantial, \(\geq 10\%\). The forward reaction is thus energetically unfavorable with application of compressive stress. That is, the transformation of ferrite/austenite \(\rightarrow\) carbide/nitride can proceed only when the chemical driving force exceeds the opposing (intrinsic) strain energy. A much lower stress-state invariably exists during conventional thermal and thermochemical processing of steels where these transformations are common, and thus the lattice can more easily overcome the opposing strain energy.

With reference to Figs. 4.6 and 4.8, nitrogen and carbon supersaturations of \(\approx 10\) at.\% and \(\approx 18\) at.\%, respectively, at typical treatment temperatures are necessary in austenite before any driving force exists to form partitionless nitride or carbide phases\(^2\). Large GPa-order compressive stresses opposing nitride or carbide formation will have developed within the case prior to these supersaturation levels. Concerning the critical supersaturation in \(\delta\)-ferrite, it is noted that transformation to either austenite or spinodal decomposition products will have occurred prior to the requisite supersaturation for partitionless carbide/nitride formation. Finally, the critical supersaturation of 18 at.% carbon

\[\Delta V_{\text{trans}} = (V_f - V_i)/V_i\] where \(V_i\) and \(V_f\) are the initial and final volumes of the two unit cells with equivalent number of atoms.

\(^2\)These critical supersaturations are obviously much less when considering an equilibrium phase, but it is assumed that substitutional solutes (Fe, Cr, Ni, etc.) are immobile at interstitial hardening temperatures and hence secondary phases inherit base metal chemistry.
Table 7.1: Lattice strain associated with potential carburization- or nitridation-induced phase transformations in 2205.

<table>
<thead>
<tr>
<th>Parent Product</th>
<th>M atoms cell(^{-1})</th>
<th>(a) [nm]</th>
<th>(b) [nm]</th>
<th>(c) [nm]</th>
<th>(\Delta V_{\text{trans}}) [pct.]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\delta \to \gamma)</td>
<td>4</td>
<td>0.3605</td>
<td></td>
<td></td>
<td>-3.2</td>
</tr>
<tr>
<td>M(_3)C</td>
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<td>0.5090</td>
<td>0.6744</td>
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<td>M(_5)C(_2)</td>
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<td>0.4573</td>
<td>0.5060</td>
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<tr>
<td>M(_7)C(_3)</td>
<td>28</td>
<td>1.1913</td>
<td>0.6892</td>
<td>0.4537</td>
<td>11.4</td>
</tr>
<tr>
<td>M(_2)3C(_6)</td>
<td>92</td>
<td>1.0630</td>
<td></td>
<td></td>
<td>9.3</td>
</tr>
<tr>
<td>M(_4)N</td>
<td>4</td>
<td>0.3798</td>
<td></td>
<td></td>
<td>14.7</td>
</tr>
<tr>
<td>M(<em>2)N(</em>{1-x})</td>
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<td>0.4796</td>
<td>0.4470</td>
<td></td>
<td>24.3</td>
</tr>
<tr>
<td>M(_3)N</td>
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<td>0.4697</td>
<td>0.4377</td>
<td></td>
<td>16.7</td>
</tr>
<tr>
<td>MN</td>
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<td>0.4148</td>
<td></td>
<td></td>
<td>49.4</td>
</tr>
<tr>
<td>(\gamma \to \delta)</td>
<td>2</td>
<td>0.2882</td>
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<td>M(_3)C</td>
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<td>M(_7)C(_3)</td>
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<tr>
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<td></td>
<td>12.9</td>
</tr>
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<td>0.4377</td>
<td></td>
<td>20.5</td>
</tr>
<tr>
<td>MN</td>
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<td>0.4148</td>
<td></td>
<td></td>
<td>54.3</td>
</tr>
<tr>
<td>(\gamma_N (5%) \to \delta)</td>
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<td>0.2882</td>
<td></td>
<td></td>
<td>-10.8</td>
</tr>
<tr>
<td>M(_3)C</td>
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<td>0.4525</td>
<td>0.5090</td>
<td>0.6744</td>
<td>-3.4</td>
</tr>
<tr>
<td>M(_5)C(_2)</td>
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<td>0.4573</td>
<td>0.5060</td>
<td>-0.2</td>
</tr>
<tr>
<td>M(_7)C(_3)</td>
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<td>1.1913</td>
<td>0.6892</td>
<td>0.4537</td>
<td>-0.7</td>
</tr>
<tr>
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<td>92</td>
<td>1.0630</td>
<td></td>
<td></td>
<td>-2.5</td>
</tr>
<tr>
<td>M(_4)N</td>
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<td>0.3798</td>
<td></td>
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</tr>
<tr>
<td>M(<em>2)N(</em>{1-x})</td>
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<td>0.4470</td>
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</tr>
<tr>
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<td>0.4377</td>
<td></td>
<td>4.0</td>
</tr>
<tr>
<td>MN</td>
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<td>0.4148</td>
<td></td>
<td></td>
<td>33.2</td>
</tr>
</tbody>
</table>
7.3. STRAIN ENERGY ON THE INHIBITION OF SECONDARY PHASES

in 2205 austenite is near the maximum paraequilibrium supersaturation ever reported in austenitic 316-type alloys.

In short, concomitant with the kinetic constraints imposed on substitutional diffusion which inhibit carbide/nitride formation, these favorable ‘stress effects’ add to the explanation for how homogeneous expanded austenite can be realized via low-temperature interstitial hardening, at least in reasonable processing times, though a large chemical driving force for structural transformation exists.

It is also interesting to note that where observed, nitrides or carbides in 2205 formed only within prior austenite grains, and not the $\gamma'$ transformation product. This would suggest either (i) a large difference in stress partitioning between the parent $\gamma$ and $\gamma'$ grains, or (ii) that the defect structure of $\gamma'$ more strongly suppresses further transformation, as the chemical driving force in both parent and product austenite is roughly equal.

7.3.1 Carburization-induced Structural Evolution in Austenite

The strain energy contribution is next considered to explain the structural evolution observed in 2205 austenite during prolonged carburization treatment. It is interesting that the decomposition of austenite is identical in both 316L [164, 165] and 2205: $\gamma \rightarrow \gamma_C \rightarrow M_5C_2 \rightarrow M_7C_3$. However, this sequence in 2205 can apparently occur at lower temperatures and/or shorter times than in 316L grade. This would imply either a higher driving force (larger supersaturation, due to higher Cr content) or reduced compressive stress in the austenite of 2205. It is furthermore surprising that this sequence does not include $M_3C$ cementite, being the densest carbide and that with the lowest carbon concentration.

The structural evolution in austenite during carburization may be explained as follows. The lattice parameters of partitionless carbides occurring in stainless steels are predominantly unknown. It is plausible that partitionless $M_3C$ may not in fact be denser than $M_5C_2$ or $M_7C_3$. The lack of a complete thermodynamic description for $M_5C_2$ also precludes quantification of the chemical driving force for its formation in stainless steels. It is also possible that $M_5C_2$ is stabilized at lower carbon content in austenitic stainless steels than either $M_3C$ or $M_7C_3$.

Barring quantitative support, partitionless $M_5C_2$ must be the most thermodynamically stable and/or densest phase. It forms only after prolonged ($>100$ hr) treatments. This observation suggests that $M_5C_2$ nucleates and grows only after a critical expansion of the austenite lattice is achieved, such that little-to-no volume change occurs during the transformation. At 5% lattice expansion of the austenite, there is negligible lattice strain associated with $\gamma_C \rightarrow M_5C_2$ (Table 7.1). By analogy, $M_4N$ is observed in 316L grade subjected to high activity, prolonged nitriding treatments [109], although CALPHAD implies a much higher chemical driving force for $M_2N_{1-3}$ formation. In contrast to the other
nitrides\(^1\), \(M_4N\) alone can form with negligible volume change from a \(\approx 5\%\) expanded austenite lattice.

The fact that the decomposition in 2205 austenite occurs at a lower temperature than has been observed in 316L may be indicative of meaningful changes in residual stress build-up between duplex 2205 and singe-phase 316L. Because the \(\delta\)-ferrite in 2205 decomposes during carburization rather than expand, it accommodates the stress imposed by surrounding austenite through work-hardening, thereby ‘relaxing’ the in-plane lattice expansion of the austenite. It follows that the reduced compressive stress in carbon-supersaturated austenite of 2205 relative to 316L could more easily enable carbide formation.

### 7.4 Strain Energy Implications on the Ferrite-to-Austenite Phase Transformation

The CALPHAD-generated paraequilibrium phase diagrams (Fig. 4.9) reveal that the paraequilibrium eutectoid temperatures for 2205 are well below that of any feasible nitridation or carburization. It is thus thermodynamically permissible for isothermal, compositionally-driven allotropic phase transformation of ferrite to austenite to occur in an open system via dissolution of either solute. The central point is that the \(\delta \rightarrow \gamma\) reaction is the *only* potential phase transformation to occur with a decrease in volume; there is no need for the lattice to overcome volume-misfit stress. In fact, it is energetically favored with application of compressive stress.

The CALPHAD implications of an extremely large driving force for \(\delta \rightarrow \gamma\) phase transformation with miniscule (ppm-level) nitrogen supersaturation give further credence to the observed behavior. In short, considering (a) the large chemical driving force and (b) favorable strain energy contributions, it is not surprising that (c) the \(\delta \rightarrow \gamma\) reaction occurred during low-temperature nitridation\(^2\).

Three possibilities may explain why carburization of 2205 did not induce the \(\delta \rightarrow \gamma\) transformation. First, it is recalled that in order for the \(\delta \rightarrow \gamma\) reaction to proceed spontaneously, an additional increase in supersaturation of \(\delta\)-ferrite above \(X_{\text{bcc}}^{\text{eq}}\) (eq) is required to provide the necessary compositionally-induced driving force for sustained growth of an austenite nuclei in a ferritic matrix (Fig. 4.3). This is analogous to undercooling in any thermally-driven transformation. From the paraequilibrium phase diagrams, both nitrogen and carbon destabilize ferrite with respect to austenite at minute concentrations, though the potency of nitrogen as an austenite stabilizer in 2205 is remarkably stronger. Moreover, the concentration of nitrogen in austenite in equilibrium with ferrite is \(\approx 2\) at.\%

\(^1\)The stoichiometric \(\zeta\)-\(M_3N\) phase is not expected as it has never been observed in nitrided stainless steel.

\(^2\)It could also have been predicted that this transformation would occur via either a massive or martensitic transformation type given the low temperatures.
7.4. STRAIN ENERGY ON THE FERRITE-TO-AUSTENITE TRANSFORMATION

at 400 °C. This is compared to the carbon concentration of \( \approx 11 \) at.% in austenite in equilibrium with ferrite at the same temperature. Therefore, a stable carbon-supersaturated austenite nucleus would by necessity form with a much higher intrinsic lattice strain than a nitrogen-stabilized nucleus. Sustained growth of the austenite would also occur against a large, and in this case retarding extrinsic stress in 2205 during carburization. That is, by the time critical supersaturation of the ferrite is achieved, a large compressive stress will have developed in prior austenite grains. This is compared to a nitrogen-stabilized austenite nuclei, which at \( \approx 2 \) at.% interstitial nitrogen is still favored by compressive stress (see Table 7.1). In short, though the chemical driving force for ferrite to reconfigure as austenite exists when supersaturated with carbon, the opposing intrinsic and extrinsic stresses may be sufficiently large so as to inhibit the forward reaction.

A second explanation for lack of carburization-induced \( \delta \to \gamma \) transformation may actually reside in the response of the parent austenite grains. This argument more directly supports why such a high propensity for nitrogen-induced transformation was observed, but the converse is also true. As demonstrated, the \( \delta \to \gamma \) reaction is the only potential phase transformation favored by application of compressive stress. Disregarding for the moment what happens within \( \delta \)-ferrite grains during the early stages of treatment, the austenite grains will gradually build in biaxial compressive stress. The magnitude of this compressive stress increases as supersaturation increases. In 2205, the paraequilibrium supersaturation of nitrogen in austenite is always greater than the feasible supersaturation of carbon. This is indeed verified by all experimental data. Therefore, larger compressive stresses develop (and perhaps earlier) in the nitrided austenite grains than occur during carburization. Further, the nitrogen profiles are more plateau-like, suggesting a more rapid accumulation of compressive stress in austenite. In other words, the larger and more rapidly developing compressive stress attainable via nitridation than carburization could have provided the necessary stress to adjacent \( \delta \)-ferrite grains to facilitate the \( \delta \to \gamma \) reaction (at some point early during treatment).

Lastly, as a corollary to the above considerations, carbon-induced \( \delta \to \gamma \) transformation was likely inhibited by the dislocation-enhanced spinodal decomposition of the \( \delta \)-ferrite that either preceded (i) the critical supersaturation requirement or (ii) development of the necessary compressive stress in carbon-supersaturated austenite grains to initiate the reaction. From the earlier remarks, the smaller and slower build-up of compressive stress in parent austenite would lead to lower work-hardening of contiguous \( \delta \)-ferrite grains. The reduced work-hardening of ferrite imposed by carburization would imply fewer heterogeneous nucleation sites (dislocations) for austenite nucleation, and hence the spinodal reaction, with no such barrier to nucleation, would have kinetically dominated. Due to the very strong binding energy between carbon and dislocation cores, the spinodally decomposed ferrite sustained no further transformation. The observation that some \( \delta \)-ferrite also spinodally decomposed during nitridation gives credence to the no-
tion that the $\delta \rightarrow \gamma$ reaction is kinetically dictated by nucleation at dislocations. The fact that the $\gamma_M'$ austenite product formed martensitically—rather than through massive-like growth at austenite–ferrite interphase boundaries—also supports the notion that dislocations are intimately tied to the transformation.

The question remains: why do most $\delta$-ferrite grains transform completely to austenite and others spinodally decompose during nitridation? Plan-view EBSD analyses suggest that wrought material contained more $\gamma_M'$ than the cast samples. This was indeed supported by comprehensive TEM study of both materials. It is unclear at present which local microstructural features within the starting material govern the transformation behavior. The complexity of the developing stress-state in the two-phase alloy makes prediction of the dominant transformation mode in various regions of the microstructure difficult. It seems reasonable to suggest that the much larger $\delta$-ferrite grains in cast 2205 (> 300 µm) would exhibit different work-hardening characteristics imposed by (far-field) austenite grains, relative to the fine-grain ferrite in wrought material (5–10 µm). This would imply a lower dislocation density and hence lower probability for heterogeneous $\gamma_M'$ nucleation in cast $\delta$-ferrite.

With this description in mind, it would be most useful to deduce whether the chemical driving force (supersaturation) or mechanical driving force imposed by the parent austenite grains is the strongest contributor to the observed behavior, or if a combination of both stimuli is required (a chemomechanical effect). As will be discussed in a later section, preparation and time-variant interstitial hardening of a duplex stainless alloy thermally processed to contain a (metastable) fully ferritic microstructure would be most useful in this regard.

### 7.5 Phase Transformations in Other Stainless Steels

This framework in which stress, in tandem with the chemical driving force, governs the transformation behavior in the ferrite and austenite of 2205 following paraequilibrium nitridation or carburization can also explain the structural evolution observed in other bcc-based stainless steels. There is a strong indication from the literature on interstitial hardening of single-phase ferritic or martensitic stainless steels that carbide or nitride formation is difficult to avoid [128,166–168]. Without delving into the details of each individual study, the data overwhelmingly support that secondary phases form regardless of the technique employed or the processing parameters involved. It follows then from the aforementioned arguments that some austenite in the base material is required to impose the necessary stress to surrounding ferrite or martensite to either (i) inhibit carbide/nitride formation or facilitate the (ii) $\delta \rightarrow \gamma$ or (iii) spinodal reaction. What critical volume fraction of austenite is required to inhibit formation of secondary phases is unknown. Most often, it is observed that these surface carbides or nitrides do compromise the passi-
7.5. PHASE TRANSFORMATIONS IN OTHER STAINLESS STEELS

Varying characteristics of the stainless steel, although they do improve the hardness. Once formed, the uniform carbide or nitride surface layer also acts as a diffusion barrier, and will thereby prevent development of thicker case depths.

Commensurate with these remarks concerning the importance of strain energy on the transformation behavior, preliminary results on paraequilibrium carburization and nitriding of PH martensitic stainless steels indicate marked differences in transformation behavior between bulk and powder samples of the same alloy. Fig. 7.4 presents X-ray diffractograms acquired from carburized/nitrided bulk and powder samples of 17-7 PH and 15-5 PH. The fine, presumably stress-free powders are clearly more prone to secondary phase formation.

![X-ray diffractograms following nitridation and carburization of bulk and powder samples of 17-7 PH and 15-5 PH stainless steels](image)

**Figure 7.4:** X-ray diffractograms following nitridation and carburization of bulk and powder samples of 17-7 PH and 15-5 PH stainless steels [151].

A marked difference in structural response was also observed in treatment of bulk 17-7 PH samples with modified base microstructures [161]. 17-7 PH is considered a semi-austenitic stainless with residual δ-ferrite, aged hardened with intragranular NiAl precipitates. 17-7 PH samples in both the ‘A’ and ‘T’ heat-treated condition were subjected to the same gas-phase nitriding and carburizing processes employed in this work. The distinction that the initial 17-7 PH material was condition A (primarily austenitic) or condition T (primarily martensitic) heat-treated is important. Condition A heat-treating yields a microstructure containing nominally 70% austenite, 25% martensite, and 5% residual δ-
7.5. PHASE TRANSFORMATIONS IN OTHER STAINLESS STEELS

ferrite by volume, and condition T a microstructure with 70% martensite, 25% austenite, and 5% δ-ferrite. Structural characterization revealed that nitridation or carburization of condition A material induced the martensite-to-austenite transformation within the case. The resulting uniform surface layer of austenite (save the residual δ-ferrite stringers) contained large, equiaxed grains of austenite, presumably the same ‘prior austenite’ morphology from which the 25% martensite had formed during prior heat-treatment. This carburization- or nitridation-induced ‘reverse martensite’ transformation is contrasted with a martensitic austenite transformation product that appeared after nitridation of the condition T material. Evidently, only some martensite within the case of condition T material transformed to γM. The residual αM martensite in the case showed signs of possible expansion of the bct lattice in electron diffraction suggesting that it too was supersaturated with interstitial solutes.

As an addendum to the implications of compressive stress, a recent study by Li et al. [169] corroborates the earlier remarks. In this work, an in situ tensile stress (up to 80 MPa) was applied—in an effort to reduce the effect of compressive stress—to 316L samples during plasma carburization. The influence of tensile stress led to the following:

- increased case depth with increasing tensile stress (interpreted as a lowering of the activation energy for diffusion when the compressive stress was mitigated)
- promoted precipitation of fine carbides and α-ferrite near the surface
- reduced stability of expanded austenite at elevated temperature, i.e. increased propensity for carbide formation

Interestingly, although the case depth (determined only by metallographic analysis) increased with increasing tensile stress, the resulting surface hardness was unchanged. The surface concentration of carbon as a function of applied stress was not measured, but the consistent surface hardness could suggest that the supersaturation in each case was independent of tensile stress. This observation stands opposed to the remarks in Sec. 7.1 in which it was postulated that a smaller biaxial compressive stress should lead to a increase in paraequilibrium supersaturation. On the other hand, surface carbides formed in the stressed samples, which would have halted further supersaturation.

The most surprising discovery of these experiments is perhaps that an in situ tensile stress \( \leq 80 \) MPa led to any measurable difference at all. A tensile stress of this magnitude is insignificant compared to the GPa-order compressive stresses present near the surface of carburized 316L. The tensile stress was measured according to the cross-sectional area of the samples. The results may perhaps be explained if it is assumed that a majority of the load was supported by the superficial layer of ‘expanding’ austenite at the surface, thereby generating a more comparable tensile stress. Whatever the underlying mechanism, the study nevertheless confirms that residual stress is an important aspect to the interstitial hardening of stainless steels.
7.6. PHENOMENOLOGICAL THEORY OF COLOSSAL INTERSTITIAL SUPERSATURATION IN FERRITE

To summarize, the synergy between chemical and strain energies play a decisive role in the transformation behavior, or lack thereof, accompanying interstitial hardening of all stainless steel families. This perspective underscores the importance for thoroughly understanding the initial microstructure of an alloy prior to application of such treatments, where the success or failure, at least in non-austenitic grades, may be sensitive to seemingly subtle changes in base microstructure.

The benefit of GPa-order residual compressive stress accompanying colossal supersaturation of interstitials is two fold: it significantly improves high-cycle fatigue life while suppressing formation of secondary phases, thereby allowing precipitate-free colossal interstitial supersaturation to be realized. Moreover, the implications of residual stress give credence to the notion that some fraction of austenite in the parent material is a prerequisite to successful interstitial hardening. That is, without a sufficient amount of austenite in the base alloy, there is less chance for development of advantageous compressive stress, and hence a higher propensity for secondary phases. This hypothesis is substantiated by most pre-existing interstitial hardening studies on single-phase ferritic or martensitic alloys.

7.6 Phenomenological Theory of Colossal Interstitial Supersaturation in Ferrite

It was shown in Sec. 6.4 that the near-surface δ-ferrite grains following carburization, and in some cases nitridation, displayed a uniform, weak-contrast in conventional TEM. This ‘featureless’ appearance was ultimately attributed to a high density of overlapping strain centers accompanying a spinodal decomposition of the ferrite. Such weak-contrast grains showed no morphological or structural indication of secondary phases by TEM, were consistently identified as non-expanded bcc ferrite in electron diffraction, yet contained ≥ 20 at.% interstitial species.

These remarkable observations raise the question: how is it possible for bcc ferrite to reach such unprecedented levels of interstitial supersaturation given the very limited equilibrium solubilities, yet display no measurable expansion or distortion of the lattice by X-ray or electron diffraction? This discovery is very surprising and was furthermore unpredicted. This section seeks to provide a fundamental answer to this question.

Much of the ensuing discussion has already been described elsewhere [162]. That paper applied specifically to paraequilibrium carburization of 17-7 PH (condition A heat-treated) and 2205. The δ-ferrite in both alloys is of similar composition, though the volume fraction in 17-7 PH (∼ 5 %) is much lower than 2205 (∼ 50%). The same phenomena has been observed in both alloys following nitridation as well. The formation of colossally supersaturated, non-expanded ferrite thus appears to be a general phenomena associated

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1It was mentioned earlier that the distinction whether the 17-7 PH was condition A (primarily austenitic) or condition T (primarily martensitic) heat-treated as it relates to the transformation behavior is important.
with interstitial hardening of $bcc$-based stainless steels, and could be expected in similar grades of stainless steel—those with ferrite or martensite and some volume fraction of austenite. The assertion that some austenite in the starting microstructure is a prerequisite follows from the earlier remarks.

It is useful to begin by noting that the occurrence of supersaturated and decomposed ferrite does have a beneficial effect on surface properties, greatly increasing surface hardness without adversely affecting corrosion resistance or bulk mechanical properties. A synopsis of the general chemical and structural aspects of decomposed ferrite accumulated from a range of characterization techniques in both 2205 and 17-7 PH is as follows:

- **XRD and GI-XRD**
  - evidence of remnant, non-expanded ferrite in the surface layer of most samples
  - significant peak broadening and loss of ferrite signal intensity

- **TKD**
  - very low indexing rate within carburized $\delta$-ferrite grains
  - low quality Kikuchi patterns due to severe internal lattice strain
  - non-indexable regardless of imaging/recording parameters employed

- **Conventional TEM imaging and electron diffraction**
  - appearance of uniform, weak-contrast $\delta$-ferrite grains
  - no morphological or structural evidence of secondary carbides/nitrides
  - diffraction patterns consistently conform to single-phase, non-expanded $bcc$ ferrite
  - high degree of localized strain evident in diffraction patterns (diffuse reciprocal lattice reflections)
  - diffuse ‘tails’ in some diffraction patterns along elastically soft $\langle 001 \rangle_{bcc}$ directions
  - potential indication of local lattice expansion, though unmeasurable tetragonality ($< 5\%$)

- **AES and LEAP microchemical analysis**
  - $\delta$-ferrite grains contain upwards of 20 at.% interstitial carbon or nitrogen (globally)
  - up to 30 at.% local enrichment within Cr-rich clusters
  - random distribution of carbon and nitrogen in Fe-rich and Cr-rich clusters

- **HR-STEM/XEDS**
  - nm-scale phase separation to $\alpha_{Fe}$ and $\alpha_{Cr}'$ within weak-contrast $\delta$-ferrite
  - no decomposition of $\delta$-ferrite below the diffusion layer
  - discernible atoms columns in $\alpha_{Fe}'$; significant distortion in $\alpha_{Cr}'$
7.6. COLOSSAL INTERSTITIAL SUPERSATURATION IN FERRITE

- ≈ 10 at.% Cr in \( \alpha_{\text{Fe}} \) and ≈ 40 at.% Cr-enrichment in \( \alpha'_{\text{Cr}} \)
- edge dislocations observable at ‘interface’ between \( \alpha_{\text{Fe}} \) and \( \alpha'_{\text{Cr}} \)
- strain apparently concentrated within \( \alpha'_{\text{Cr}} \) and interface between \( \alpha_{\text{Fe}} \) and \( \alpha'_{\text{Cr}} \)
- dislocation density estimated at \( \geq 10^{16} \text{ m}^{-2} \) from Burgers circuit analysis of lattice images
- growth of supersaturated, decomposed ‘plates’ along \{001\}_{bcc} \) planes within nominal \( \delta \)-ferrite
- growth of decomposed plates eventually consume the grain

The culmination of these observations suggest that carbon and nitrogen does not reside in conventional interstitial sites. The fact that the \( \delta \)-ferrite below the case has not decomposed confirms that the phase separation is associated with interstitial supersaturation, and not a result of the heat-treat by itself.

The directional phase separation observed in HR-STEM images suggests that the decomposition, which is sensitive to interfacial and strain energy, was enhanced parallel to \{001\}_{bcc} \) planes insofar as \( \langle 001 \rangle_{bcc} \) is the elastically soft direction in ferrite. This is not surprising, considering the non-homogeneous (equibiaxial) stress-state of system.

7.6.1 Segregation of Carbon and Nitrogen to Dislocations in Ferrite

Colossal supersaturation in \( \delta \)-ferrite without traceable lattice distortion can be understood as follows. The \( \delta \)-ferrite grains in both 2205 and 17-7 PH are encompassed by austenite, thereby restricting the \( \delta \)-ferrite to a confined volume. Residual compressive stresses develop during growth of the case. At some point, the \( \delta \)-ferrite grains yield under the strain arising from local volume expansion of the nearby carbon- or nitrogen-supersaturated austenite grains. As dislocations are continuously generated in ferrite, carbon or nitrogen atoms, which diffuse rapidly through ferrite, readily segregate to the dislocation cores to lower the internal lattice strain and thereby reduce the free energy of the system. Due to the very high binding energy between carbon atoms and a dislocation core, carbon atoms are effectively ‘pinned’ and the system is stabilized against further transformation. Eventually, the work-hardened \( \delta \)-ferrite will spinodally decompose (no barrier to nucleation) into Fe-rich and Cr-rich ferrite to further lower the system energy. Carbon or nitrogen atoms then preferentially segregate to Cr-rich regions due to the higher binding energy between these species.

These comments are substantiated by recent atomistic simulations [170] which suggest that dislocation generation may actually be an exothermic process during carburization (and presumably nitridation) of stainless steels. That is, in addition to plastic deformation, dislocations may also form spontaneously as a means to lower system energy. The calculations show that the screw dislocation formation energy is inversely proportional to
the dislocation density, and furthermore that fewer carbon atoms per length are needed to stabilize the dislocations as the density increases.

The dislocation density estimated from HR-STEM lattice images is most likely an underestimate, since it is based on observable edge dislocations in only one viewing direction. Furthermore, a high dislocation density of $10^{16}$ m$^{-2}$—that found in the most severely cold-worked metals—alone is insufficient to explain the observed level of supersaturation. The theoretical limit of carbon supersaturation involving pure edge or screw dislocations in iron has been worked out [171–174], suggesting that a non-conventional array of linear defects may be involved. It is possible that an even higher dislocation density exists, but would still seem insufficient to explain the observed level of supersaturation assuming complete saturation along conventional dislocation cores.

Trapping of carbon in Cottrell atmospheres surrounding dislocation cores in dislocation ‘triangles’ [175] has been observed in a Si-rich ferrous martensite [176]. Severely overlapping Cottrell atmospheres in δ-ferrite may partially explain the level of supersaturation achieved through interstitial-hardening.

A further possibility for this level of carbon/nitrogen accommodation in ferrite is through formation of prismatic dislocation loops of interstitials on \{001\}_bcc planes, analogous to prismatic loops formed by interstitial condensation during neutron irradiation [177]. This hypothesis is consistent with the observation of local lattice expansion on \{001\}_bcc planes, i.e. streaks along \langle 001 \rangle_{bcc} toward smaller reciprocal lattice spacings observed in some diffraction patterns.

### 7.6.2 Dislocation-enhanced Spinodal Decomposition in Fe–Cr System

The most illuminating support of this phenomena follows from a study by Li et al. [178] in which they used phase-field simulations to study the effect of dislocations on the spinodal decomposition process in Fe–Cr alloys. Fig. 7.5 presents the 2D temporal evolution of an Fe–20Cr alloy aged at 262 °C in a microstructure containing two pure-edge dislocations. The conclusion that the stress fields associated with dislocations increase the kinetics and energetics of spinodal decomposition in Fe–Cr fully corroborates the observations presented in this work. Low-temperature carburization leads to an ultra-high dislocation density in δ-ferrite; these dislocations eventually lead to a spinodal decomposition.

The anisotropic evolution of Fe-rich and Cr-rich domains observed in this work was also noted in externally stressed Fe–Cr alloys during low temperature aging [179]. In this study, tensile specimens of a model 15-5 PH alloy (Fe–15Cr–5Ni) were aged at 425 °C with and without application of a uniaxial tensile stress equal to 80% the yield strength. Not only did the tensile stress enhance the kinetics of decomposition, but also significantly affected the morphology of the decomposition products. Elongated Cr-rich domains tended to develop along elastically soft directions, consistent with the HR-STEM images of de-
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Figure 7.5: Phase-field simulation showing the 2D temporal evolution of an Fe–20Cr alloy at 262 °C containing two pure-edge dislocations (shown in the center of each image) [178].

composed δ-ferrite in 2205 (Fig. 6.29). Phase-field simulations of spinodal decomposition in thin (elastically constrained) films [180] with periodic dislocations also demonstrate that dislocation stresses can induce a directional spinodal decomposition.

7.6.3 Carbon-supersaturated Ferrite in Other Steels

Colossal interstitial supersaturation of ferrite is not a new phenomena. It has been reported in a number of steel systems, albeit never to the extent found in this work, and ultimately achieved through different processing routes. In fact, carbon-supersaturated ferrite is now understood to be the mechanism responsible for the strongest known bulk material: nano-crystalline pearlitic steel wire with an astounding tensile strength of 7 GPa [181]. The subject of immense carbon-supersaturation in ferrite has since become the subject of longstanding scientific interest. Qualitative descriptions often used to explain the nature of this carbon-supersaturated ferrite in the literature include terms such as “heavily entangled dislocation networks”, “dislocation walls”, “dislocation tangles”, “overlapping Cottrell atmospheres”, and “carbon-rich clusters or cells”.

Severe cold-drawing of pearlitic wires is known to lead to decomposition of the ce-
7.7. MARTENSITIC AUSTENITE INDUCED BY ISOTHERMAL NITRIDATION

Cementite, resulting in heavily-dislocated regions of carbon-supersaturated ferrite [181–190], and likewise strain-induced nitride dissolution in high-nitrogen stainless steel [191]. Though most of these studies involved only spatially-resolved chemical characterization, sufficient evidence supports the hypothesis that carbon preferentially segregates to dislocation pile-ups, indicating that carbon is energetically more stable bound to a dislocation core than in cementite [172,192–194]. Indeed, the binding energy of carbon to a dislocation core (0.75 eV) [172] is higher than a carbon atom bound to iron in cementite (0.5 eV) [195]. Chromium further enhances the binding energy between carbon and a dislocation core [196].

Conversely, a high dislocation density in carbon steels can retard precipitation of cementite upon heat-treatment [159,194,197–205]. The trapping of carbon to defects such as dislocations reduces the amount of carbon in solution available to participate in the reaction, thus lowering the driving force for transformation. Recent APT work in the area of nano-crystalline bainitic steels has led to the discovery of carbon-rich clusters with up to 15 at. % carbon in ferrite [159,194,198]. It has also been reported that delayed nitride formation can lead to high nitrogen supersaturation in ferrite [206,207].

In each of these examples, the size and distribution of carbon-enriched clusters was ultimately limited by the initial carbon content of the alloy. Insofar as the paraequilibrium surface hardening treatments used in the present work were conducted in an open system with constant supply of carbon, it is not surprising that a much higher density was observed. Still, all of these discoveries seem applicable the observations presented in this work, and further underscore the immense strength of the carbon–dislocation bond in ferrous alloys. Energetically favorable segregation of carbon and nitrogen atoms to dislocations in δ-ferrite during carburization and nitridation of 2205 effectively delayed precipitation and enabled colossal supersaturation, while maintaining, at least globally, a non-expanded bcc lattice.

7.7 Martensitic Austenite Induced by Isothermal Nitridation

It was proposed in Sec. 6.3 that the isothermal, nitrogen-induced δ → γ reaction in 2205 proceeded by a martensitic transformation, given the partitionless nature, morphology, substructure (closely spaced stacking faults and/or nano-twins), and orientation relationship between parent and product phases in which it formed. These features indicate that the the austenite product formed in such a way so as to minimize strain energy. Moreover, the possibility that the new phase appearing in δ-ferrite was a nitride was considered extensively. Electron diffraction from these features across the spectrum of treatments consistently conformed to an expanded austenite lattice, furthermore supported by all XRD, EBSD, TKD, and MFM analyses.

Although suggested by previous investigators studying interstitial hardening of du-
plex alloys (Sec. 2.3.5), this work represents the first unambiguous evidence for the isothermal nitrogen-induced $\delta \rightarrow \gamma$ transformation. A chemomechanical model was proposed in Sec. 7.4 to explain why carburization did not induce a similar transformation.

This is not the first evidence of 'martensitic austenite' formation in stainless steel, and it is now understood that the same martensitic austenite can form in martensitic stainless steels after similar low temperature nitridation [161, 208]. Before discussing these observations in other stainless steels, it is useful to briefly review the nature of martensitic transformations.

### 7.7.1 The Nature of Martensitic Transformations

The term 'martensite' in a historical context\(^1\) refers to the metastable bct phase found in steels upon the rapid quenching of carbon-supersaturated austenite. Today, it is understood that the same 'martensitic' type of solid-state phase transformation occurring in steels also occurs in a great number of systems, both metallic, ceramic, polymeric, and biological. Though not intending to be exhaustive, a brief overview of the characteristics general to all martensitic transformations is presented here; a number of excellent reviews on the subject can be found in Refs. [209–217].

A martensitic transformation is differentiated from diffusion-controlled nucleation and growth in a number of ways. In contrast with conventional diffusion-controlled nucleation and growth, when a lattice transforms martensitically, the atomic movements are small, occur cooperatively, and a well-defined geometric relation is maintained between the parent and product phases. A distinct change in shape is also observed, often noted by surface relief (tilting), which represents one of the most general and fundamental features of a martensitic reaction. No change in chemistry is involved. For these reasons, martensitic transformations can be described as shear-like, displacive, distortive, and diffusionless.

The surface distortion observed in martensitic transformations implies that the product martensite, though having a different crystal structure, remains highly coherent with the parent phase. A further fundamental aspect of martensitic transformations concerns the plane which separates the parent and product phase. The interface, or habit plane, is an undistorted and unrotated (invariant) plane in the parent structure.

Central to the kinetic and thermodynamic characteristics of martensitic transformations is that, owing to the coherent nature of martensite reactions, strain energy contributions to the total driving force are important. The reaction may proceed only when the chemical driving force for the atoms to obtain a more stable configuration can overcome the retarding strain energy. Martensites thus form in such a way so as to minimize the

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\(^1\)Named in honor of Adolf Martens, a pioneering metallurgist in the late 19th century, who, although made many significant contributions to the field, never worked directly in the area of martensitic transformations.
Martensites can form in a number of different ways. Most often the reaction is found to be athermal, such that the amount of martensite formed is a function of temperature only. Depending on the degree of undercooling, a certain percentage of the material will transform, which increases with further undercooling. Once initiated, the growth of individual martensite variants proceeds at an appreciable rate, approaching the speed of sound in the material. This ‘burst’ phenomena is contrasted with isothermal martensites [218], whereby the amount of martensite formed increases at a constant temperature as a function of time. The isothermal mode of martensite transformation mainly occurs by nucleation and growth of new plates rather than by growth of existing ones, but individual plates may themselves grow with increasing time at constant temperature.

Analogous to the effect of temperature on the chemical driving force, an applied stress can also induce a martensitic reaction from the influence of the strain energy component to the total driving force. The influence of applied stress however is more complex than temperature, where a lowering of temperature always increases the chemical driving force. An applied stress may have a positive or negative contribution to the strain energy component, depending upon its orientation with respect to individual variants.

Theories concerning nucleation and growth of martensites often involve a framework of dislocation arrays. Numerous ‘small particle’ experiments have demonstrated that martensitic transformations can be suppressed when the particle size is small enough, most often interpreted as a lack of heterogeneous nucleation sites [219–221]. Alternatively, it has been observed that martensitic transformation in such small austenite particles can proceed only after plastic deformation when dislocations have been produced [222].

These characteristics of martensite transformations are consistent with the present observations. The diffusionless and shear-induced growth were comprehensively demonstrated by TEM, while the surface relief associated with the nitrogen-induced $\delta \rightarrow \gamma$ transformation is evident in Fig. 5.5.

### 7.7.2 Martensitic Austenite in Other Stainless Steels

#### 7.7.2.1 Analogy in Closed Systems

Southwick and Honeycombe [223] were the first to report martensitic austenite formation from supersaturated ferrite. In their study, samples of a duplex stainless steel (26Cr–5Ni–1.3Mo–0.03C) were solution treated within the ferritic regime (1300 °C) and rapidly quenched to room temperature, thereby producing a metastable, fully ferritic microstructure supersaturated with carbon. The samples were then isothermally aged between 300–1200 °C to study the decomposition of $\delta$-ferrite to austenite. Between 300-650 °C they observed austenite formation via an athermal martensitic mechanism, very similar to that observed in this work. Fig. 7.6 shows a BF and high-resolution TEM micrograph
of the martensitic austenite, along with an SAED pattern. They found that the martensitic austenite maintained a N–W OR with the parent $\delta$-ferrite, and grew with a \{133\}_$\delta$ habit plane.

**Figure 7.6:** (a) BF TEM micrograph of martensitic austenitic, (b) SAED from martensitic austenite with pronounced streaking, (c) HR-TEM lattice image showing \{110\}_$\alpha$/\{111\}_$\gamma$ fringes and stacking faults (arrowed) [223].
In a later study, Tomida et al. [224] investigated the $\delta \rightarrow \gamma$ transformation in melt-quenched duplex stainless steel ribbons. They also found a plate-like austenite product within the $\delta$-ferrite matrix, which presumably formed martensitically by the rapid quenching. Interestingly, some of the austenite transformation product showed 18R stacking in diffraction patterns, which could also explain some of the atypical diffraction patterns obtained in this work.

With the exception of these two publications, there has not been much work in the area of a ferrite-to-austenite transformation via a martensitic reaction. It has been reported that a ‘reverse martensite-to-austenite’ transformation can occur by a martensitic shear reversion upon the very rapid heating of steels [225–229].

### 7.7.2.2 Analogy in Open Systems

The final point to be made is that $\gamma'_M$ has been observed in martensitic stainless steels following gas-phase nitridation. Two examples of a $\gamma'_M$ microstructure in 17-7 PH and 15-5 PH are shown in Figs. 7.7 and 7.8, respectively. The plate-like morphology, internal structure, partitionless chemistry, etc. are consistent with the many observations made here.
7.7. MARTENSITIC AUSTENITE INDUCED BY ISOTHERMAL NITRIDATION

Figure 7.8: (a) BF TEM micrograph of martensitic austenitic in 15-5 PH following nitridation at 400 °C and \( n_{N_2} = 7,400 \), (b) double exposure DF image showing region from which (c) SAED pattern was obtained [208].
Significant improvement in the desirable surface properties of the 2205 duplex alloy has been demonstrated by means of novel low-temperature gas-phase nitridation or carburization. The surface hardness and case depth can be tailored with the thermodynamically-controllable gas-phase process. Nitridation or carburization of the alloy at or below 400 °C is deemed relatively safe for reasonable processing durations.

Detailed chemical and structural aspects of the transformation behavior occurring within the diffusion layer giving rise to these improvements were obtained through a suite of characterization techniques.

The austenite in 2205 responds analogously to paraequilibrium nitridation and carburization of single-phase austenitic grades: a precipitate-free, ‘colossal’ supersaturation of interstitial solutes is realized. A similar decomposition sequence of the austenite to partitionless carbides is also observed during prolonged carburization: $\gamma \rightarrow \gamma_C \rightarrow M_5C_2 \rightarrow M_7C_3$.

There are two microstructural responses of the $\delta$-ferrite for treatments $325 \leq T \leq 400 \, ^\circ C$: nitridation (primarily) induces martensitic formation of austenite ($\gamma'_M$), while carburization (and to a lesser extent, nitridation) leads to a spinodal decomposition of ferrite to nm-scale Fe-rich ($\alpha_{Fe}$) and Cr-rich ($\alpha'_{Cr}$) domains. Both the martensitic austenite and decomposition products contain colossal supersaturation of interstitial solutes orders of magnitude higher than predicted equilibrium values.

During nitridation, the exceptionally large chemical driving force due to the potent austenite-stabilizing nature of nitrogen, combined with favorable strain energy contributions imposed by neighboring nitrogen-supersaturated austenite grains enables the isothermal $\delta \rightarrow \gamma$ reaction. Nucleation of austenite is suggested to occur at dislocations within the supersaturated, work-hardened $\delta$-ferrite and proceeds by a shear-like martensitic reaction. The high-aspect-ratio plates of $\gamma'_M$ are heavily twinned, contain significant substructure, and maintain an orientation relationship with the parent ferrite between the common N–W and K–S type. The supersaturation of nitrogen in the $\gamma'_M$ varies with depth in similar fashion to the parent austenite, though being measurably higher at the surface.
The $\gamma'_M$ case also extends deeper than in parent austenite grains, due to accelerated nitrogen diffusion through $\delta$-ferrite prior to the transformation.

For carburization, the $\delta \rightarrow \gamma$ reaction is largely inhibited by the lower chemical driving force and/or lower stress imposed by neighboring carbon-supersaturated austenite grains. It is also suggested that fewer dislocations, necessary for early-stage heterogeneous austenite nucleation, exist in carbon-supersaturated ferrite, due to the slower buildup of carbon in adjacent austenite grains.

Instead, inhibited austenite nucleation during carburization enables colossal supersaturation of the ferrite through energetically favorable segregation and ‘trapping’ of carbon atoms along dislocation cores, while maintaining, at least globally, an undistorted bcc lattice. The high-density dislocation network eventually enhances spinodal decomposition of the $\delta$-ferrite with no such barrier to nucleation. The resulting morphology of $\alpha_{Fe}$ and $\alpha'_{Cr}$ is highly directional due to the anisotropic stress state of the system. Such grains of decomposed ferrite display a uniform, weak-contrast in the TEM due to overlapping strain fields associated with the $\alpha_{Fe}$ and $\alpha'_{Cr}$ decomposition products and the ultra-high density dislocation network. Once decomposed, the supersaturated ferrite sustains no further transformation due to the strong carbon–dislocation interaction.

8.1 Suggestions for Future Research

More detailed crystallographic characteristics concerning the nature of martensitic austenite are considered most germane for future study. To reduce anomalies in diffraction patterns, it is suggested to precede site-specific foil extraction with the protocol mentioned earlier: compress samples by a few pct. strain so as to mitigate the residual stress and thereby allow preparation of thinner TEM foils.

Time-variant paraequilibrium nitridation treatment of metastable ‘ferritized’ duplex alloys will also be useful for studying the underlying mechanisms governing the isothermal nitrogen-induced $\delta \rightarrow \gamma$ transformation. That is, to determine if the nitrogen-induced $\delta \rightarrow \gamma$ transformation is dictated primarily by chemical or strain energy effects. To that end, it is also of interest to determine if growth of the martensitic austenite lamellae is athermal, occurring as a burst at some point during treatment, or if growth proceeds thermoplastically, whereby individual variants grow with increasing time. In-situ heating and cooling experiments in the TEM may prove useful in that regard.
Appendix A
(a) Cross-sectional BF micrograph of specimen from a single δ-ferrite grain in cast material after nitridation at $T_N = 400 \, ^\circ\text{C}$ and $a_{N_2} = 4.0 \times 10^9$, along with a near-surface, horizontal XEDS line-scan of nitrogen. (b) BF micrograph of TEM specimen under different diffracting conditions with inset SAED pattern along a [011]$_{fcc}$ directions with twinning; XEDS line-scan and elemental nitrogen map obtained near middle of the specimen showing the decrease in nitrogen concentration with increasing depth, consistent with the AES analysis of this sample.
SAED pattern and corresponding BF and DF images formed using encircled $\vec{g}$ vectors from TEM specimen of single $\delta$-ferrite in cast material after nitridation at $T_N = 400 \, ^\circ\text{C}$ and $a_{N_2} = 4.0 \times 10^9$. 
(a)–(d) STEM images at increasing magnification of former δ-ferrite in wrought sample nitrided at $T_N = 350 \, ^\circ\text{C}$ and $a_{N_2} = 1.8 \times 10^2$. (e) SAED pattern consisted with $[112]_{f\text{cc}}$ showing forbidden $\frac{1}{2}[113]$ reflections.
BF micrographs of near-surface δ-ferrite grains in wrought sample nitrided at $T_N = 350 \, ^\circ\text{C}$ and $a_{N_2} = 1.8 \times 10^2$. Inset nano-diffraction pattern from lower region of δ-ferrite grain showing the usual contrast confirmed as $[001]_{bcc}$ zone-axis pattern.
BF micrographs from sub-surface $\delta$-ferrite grains in wrought sample nitrided at $T_N = 350$ °C and $a_{N_2} = 1.8 \times 10^2$ showing partial transformation to austenite. Diffuse SAED pattern acquired from transformed region showing heavy streaking, indexable as a $[011]_{fcc}$ viewing direction.
Series of SAED and nano-diffraction patterns obtained from wrought sample nitrided at $T_N = 350$ °C and $a_{N_2} = 1.8 \times 10^2$. Indexing indicated in each pattern.
(a) STEM and (b) BF images from wrought sample nitrided at $T_N = 350$ °C and $a_{N_2} = 5.8 \times 10^4$. (c) BF and (e) DF image from the SAED pattern in (d) along $[011]_{fcc}$ zone-axis with twins.
(a) STEM image of wrought sample nitrided at $T_N = 350$ °C and $a_{N_2} = 5.8 \times 10^4$. (b) SAED pattern from transformed $\delta$-ferrite grain (c) containing a $[013]_{\text{fcc}}$ and $[011]_{\text{fcc}}$ zone-axis. (d) and (e) DF from encircled $\bar{g}$ showing that both reflections originate from the same region of the grain.
(a) STEM and (b) BF image from wrought sample nitrided at $T_N = 325$ °C and $a_{N_2} = 3.0 \times 10^3$. (b) and (c) Two SAED patterns acquired from fully transformed δ-ferrite grain (a) with zone-axis indicated. (d) and (e) DF images from encircled $\bar{g}$ in (c).
(a) STEM and inset BF image of wrought 2205 sample nitrided at $T_N = 380 \, ^\circ\text{C}$ and $a_{N_2} = 1.4 \times 10^5$. 
BF and DF images of austenite transformation product in $\delta$-ferrite after nitridation at 380 °C and $a_{\text{Na}} = 1.4 \times 10^5$. Inset SAED pattern along a $[011]_{\text{fcc}}$ direction with twins. DF images formed using encircled $\vec{g}$ vectors.
Wrought 2205 sample nitrided at $T_N = 380 \, ^\circ\text{C}$ and $a_{N_2} = 1.4 \times 10^5$. (a) SAED pattern along a $[114]_{\text{fcc}}$ zone-axis with interior $[011]_{\text{fcc}}$ twins, (b) BF image, (c)–(d) DF images formed using the encircled $\bar{g}$ vectors in (a).
Wrought 2205 sample nitried at $T_N = 380 \, ^\circ C$ and $a_{N_2} = 1.4 \times 10^5$. (a) SAED pattern consistent with [112]$_{fcc}$ zone-axis with additional $1/2\vec{g}_{113}$ vectors. (b) Same SAED pattern in (a) with adjusted intensity levels. (b) Corresponding BF image, (d)–(f) DF images formed using the encircled $\vec{g}$ vectors in (a).
Appendix B

Elastic Anisotropy in Nitrided 316L Stainless Steel

In parallel with the investigation on 2205, a series of synchrotron-based experiments were conducted at the Advanced Photon Source (APS) facility at Argonne National Laboratory on a low-temperature gas-phase nitrided 316L austenitic stainless steel. The aim of the synchrotron experiments was to investigate the elastic anisotropy of expanded austenite giving rise to peculiar XRD data.

The X-ray micro-diffraction technique permits lattice parameter measurements in individual grains, in three dimensions, as a function of depth below the surface. This is a most useful, non-destructive method for studying orientation-dependent deformation mechanisms in layers of expanded austenite. Conventional XRD has its own limitations. First, it is only suitable for measuring lattice strain normal to the surface, in different populations of grains. Second, the sample tilting $\sin^2 \psi$ technique for measuring residual stress assumes that all grains have the same lattice parameter, which is clearly not the case in most layers of expanded austenite. The residual strain measured using different diffracting planes can vary by a factor of 10, which is significantly greater than ever seen in an fcc metal (Zener anisotropy ratio of 316L is 3.62). In order to better understand if the effect is due to elastic anisotropy, Laue micro-diffraction mapping with strain tensor measurement is desired in order to understand if the anisotropy is observed in individual grains as well.

This preliminary work enabled strain vs. depth measurement normal to the surface in four grains with the following orientations: $\langle 001 \rangle$, $\langle 111 \rangle$, $\langle 011 \rangle$, and $\langle 113 \rangle$. Full 3D strain measurement was made in two orientations: $\langle 113 \rangle$ and $\langle 135 \rangle$. In order to make conclusive statements about the elastic anisotropy of expanded austenite, future experiments should be aimed at 3D strain measurement in the two extreme cases: $\langle 111 \rangle$ and $\langle 001 \rangle$-oriented grains.

The particular sample of 316L under investigation was gas nitrided at 440 °C with a nitrogen activity of 7,400 for a total of 20 h. This sample displayed enormous lattice parameter anisotropy by XRD. The austenite lattice parameter measured according to
different peaks in conventional $\theta$-$\theta$ XRD in this, and other samples nitrided at different nitrogen activities are shown in Fig 1(a). The case depth also varies between differently oriented grains (i.e. those whose surface normal corresponds to different crystallographic directions). The largest case depths are always observed in grains whose surface normal is parallel to a $\langle 001 \rangle$ direction, and shallowest for grains with surface normal parallel to a $\langle 111 \rangle$ direction. This is demonstrated in Fig. 1(b) by the AES composition-depth lines scans conducted through a $\langle 111 \rangle$ and $\langle 001 \rangle$-oriented grain in the sample nitrided with $a_{N_2} = 7,400$ [94].

This orientation dependent lattice expansion was ultimately attributed to the elastic anisotropy of 316L, and exacerbated by a para-to-ferromagnetic transition [94]. Grains with surface normal orientation parallel to $\langle 111 \rangle$ yield first and undergo more strain hardening than $\langle 001 \rangle$ oriented grains. Due to the higher compressive stress, the solubility, and thus level of expansion, is lower in $\langle 111 \rangle$-oriented grains relative to $\langle 001 \rangle$-oriented grains, and intermediate for other orientations. The lower compressive stress in $\langle 001 \rangle$ and thus higher surface concentration of nitrogen also has the effect of increasing the case depth. The much larger lattice parameter in $\langle 001 \rangle$-oriented grains (0.390 nm) relative to $\langle 111 \rangle$ grains (0.375 nm) is not the direct result of increased lattice dilation from a 3% increase in surface concentration of nitrogen. Rather, the additional increase in these grains is attributed to a ferromagnetic transition that begins at $\approx 14\%$ and reaches completion at 18...
at% nitrogen \cite{94,103}.

The micro-diffraction setup at APS beamline 34-ID-E is well suited for studying deformation mechanisms in individual grains. The non-destructive technique allows for full strain tensor measurement in individual grains using a high-intensity focused X-ray beam. The polychromatic or monochromatic X-ray beam is focused using a non-dispersive elliptical Kirkpatrick-Baez (K-B) mirror pair to a focal spot \(\approx 300\) nm in diameter. Three 2D X-ray detectors are used to determine individual grain orientations and lattice plane spacings normal and parallel to the surface. A differential aperture enables depth-dependent diffraction data. A schematic illustration of this apparatus is shown in Fig. 2. More information on the technique can be found in Refs. \cite{230–233}.

The experimental procedure for 3D strain measurement in individual grains is as follows. The beam is first focused on a grain of interest. The orientation of the grain is then determined according to a white Laue micro-diffraction pattern recorded on the topmost CCD detector (indexed by software). An optical image of the nitrided 316L sample surface along with a previous EBSD orientation map used as a reference is shown in Fig. 3. A Laue pattern from non-treated 316L, Fig. 4(a), is contrasted with a Laue pattern obtained from the nitrided sample in Fig. 4(b). The sharp reflections in non-treated material are indicative of minimal lattice strain, whereas the reflections in nitrided material show elongated diffuse 'tails', indicating a large degree of lattice strain and lattice rotation relative to the non-treated core.
The topmost CCD X-ray detector captures the surface normal orientation of the grain. The two side CCD detectors record the Laue pattern from lattice planes that are inclined by some angle relative to the surface. Once a grain with the desirable orientation has been identified (e.g. \(\langle 001\rangle\), \(\langle 111\rangle\), or \(\langle 113\rangle\)), the sample is rotated until the desirable in-plane reflections are captured by the two side detectors. A stereographic projection useful for this purpose is shown in Fig. 5 for example. This grain was oriented very near a \(\langle 113\rangle\) direction, and was rotated such that the \{002\} and \{022\} in-plane lattice reflections were captured by the side detectors. To obtain 3D strain measurement, a differential aperture (Pt wire) is scanned across three reflections, one from each detector, through a range of incident beam energies, thus enabling depth-dependent measurement of lattice plane spacings.

The lattice strain as function of depth below the surface was measured in four grains,
Figure 4: White beam Laue pattern from single grain in polycrystalline (a) non-treated 316L and (b) nitrided 316L near $\langle 111 \rangle$ surface normal orientation.
FIGURE 5: Stereographic projection for nitrided 316L grain near ⟨113⟩ surface normal orientation. 110 and 001 planes recorded by two side CCD detectors.

with surface normals near: ⟨111⟩, ⟨001⟩, ⟨011⟩, and ⟨113⟩ directions. The (444) X-ray diffraction peak from the grain near ⟨111⟩ orientation is shown in Fig. 6(a) plotted as intensity vs. lattice parameter as a function of depth. The non-treated core displays a lattice parameter of 0.360 nm (depths greater than 7 µm), in agreement with the nominal lattice parameter of 316L and case depth measured by AES depth profiling. At shallower depths,
Figure 6: Lattice parameter as a function of depth below the surface for two grains in nitrided 316L: (a) near ⟨111⟩-oriented grain, and (b) near ⟨100⟩-oriented grain.
the lattice parameter gradually increases, due to the increasing interstitial nitrogen concentration. At the surface, the lattice parameter is 0.375 nm, which agrees with the results for the 111 and 222 XRD peak positions for this sample shown in Fig. 1(a).

The lattice strain normal to the surface was also determined in a grain with a surface normal near ⟨001⟩. The (008) XRD signal from this grain as a function of depth into the sample is shown in Fig. 6(b). The non-treated core can be seen at depths greater than 10 µm. At depths less than 10 µm, the lattice parameter gradually increases, due to the increasing interstitial nitrogen concentration. At a depth of 4–5 µm, there is an abrupt change in the lattice parameter from 0.38 nm to 0.39 nm nearer the surface. The surface lattice parameter of 0.39 nm agrees with the results for the 002 and 004 XRD reflections for this sample shown in Fig. 1. Without the abrupt increase to 0.39 nm, the lattice parameter would have remained 0.38 nm, and the anisotropy shown in Fig. 1 would have been similar to the samples with lower anisotropies (i.e. \( a_{N_2} = 1, 200, \) or \( 4 \times 10^9 \)). The near-surface region with very large lattice parameter corresponds to the ferromagnetic region. Below this region is nitrogen-expanded austenite which has not become ferromagnetic.

The lattice strain (measured according to the peak in the intensity profile) vs. depth in these two grains and those near ⟨011⟩ and ⟨113⟩ orientations are summarized in Fig. 7. The lattice parameters at the surface of each grain are consistent with those measured by XRD in Fig. 1(a), and the case depths consistent with AES depth-profiling in Fig. 1(b). The additional strain in the ⟨001⟩ grain is attributed to the ferromagnetic transition. Likewise, the ⟨113⟩-oriented grain with ≈ 14-17 at.% nitrogen has begun its ferromagnetic transition, accompanied by an additional volume expansion. Without understanding the difference in residual compressive stress in each of these grains, the known elastic constants for 316L cannot be used for predicting lattice strain. 3D strain measurement in individual grains is necessary for that purpose.

Full 3D strain mapping was conducted in three grains—two oriented near ⟨113⟩ and one oriented near ⟨135⟩ (half way between ⟨113⟩ and ⟨011⟩). The surface normal and in-plane strains for these three grains are shown in Fig. 8. 3D strain measurement was attempted in the ⟨111⟩ and ⟨001⟩-oriented grains (G5 and G6), but the in-plane reflections were insufficiently intense on the two side detectors to be measured.

The most difficult aspect of such experiments is undoubtedly in locating suitable grains. Not only must the surface normal orientation be very close to the desirable ⟨111⟩, ⟨001⟩, and ⟨113⟩ orientations, but the in-plane lattice reflections must also be indexable within the angular distribution provided by the two side detectors. Moreover, the intensity of the in-plane reflections should be sufficiently high so as to reduce the signal-to-noise ratio and therefore improve the accuracy of peak identification in the diffraction patterns. The error in peak-identification on the two side detectors was high in each case high, due to the low intensity of the signal (relative to the topmost detector). Since these experiments were conducted, the two side detectors have recently been upgraded at 34-ID-E and will...
allow for more accurate measurements. Future experiments to conclude whether or not expanded austenite exhibits extreme elastic anisotropy will require 3D strain vs. depth in two additional grains: one with \( \langle 001 \rangle \) and \( \langle 111 \rangle \) surface normal orientation.

**Figure 7:** Lattice strain as a function of depth below the surface through four grains as a function of surface normal orientation.
FIGURE 8: Surface normal and in-plane lattice strain as a function of depth below the surface for three grains in nitrided 316L: (a) and (b) near ⟨113⟩-oriented grains, and (c) near ⟨135⟩-oriented grain.
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