KINETICALLY-CONTROLLED NITRIDATION OF TITANIUM ALLOYS

by

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*We also certify that written approval has been obtained for any proprietary material contained therein.
This work is dedicated to all who have taught me the importance of education and hard work, as well as those who have encouraged and supported me during this chapter of my life.
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List of Acronyms and Abbreviations

A₁: Anneal 1, see page 154 for details.
A₂: Anneal 2, see page 154 for details.
B: Beam direction.
BF: Bright-field.
BF/DF: Bright-field, dark-field.
CP Ti: Commercially pure titanium.
CS: Continuous sputtering (during XPS analysis).
CVD: Chemical vapor deposition.
DP: Diffraction pattern.
DF: Dark field.
EBSD: Electron backscatter diffraction.
EELS: Electron energy loss spectroscopy.
EPMA: Electron probe micro-analyzer.
ESI: Electron-spectroscopic imaging.
F₀: Powder-pack furnace.
F₁: Sample furnace.
FIB: Focused ion-beam milling.
HT 1: Heat treatment 1, see page 154 for details.
JEMS: Electron microscopy software.
LOM: Light optical microscopy.
OD: Outside diameter.
OIM: Orientation imaging microscopy.
PS: Sputter performed prior to XPS analysis.
PVD: Physical vapor deposition.
Ra: Average roughness.
SPM: Scanning probe microscopy.
STEM: Scanning transmission electron microscopy.
TEM: Transmission electron microscopy.
XEDS: X-ray energy dispersive spectroscopy.
XPS: X-ray photoelectron spectroscopy.
XRD: X-ray diffractometry.
N: Sample size.
NS: No sputtering (pre nor post XPS analysis).
t: Time.
T: Temperature.
Tₚₚₖ: Temperature of powder pack.
Kinetically-Controlled Nitridation
of Titanium Alloys

Abstract
by
SAMUEL PAUL BARKER

Traditional titanium nitridation techniques increase surface hardness by forming a thin layer of titanium nitrides (Ti$_2$N and TiN) on the substrate surface. Such nitride-forming techniques successfully increase hardness and improve wear resistance, but can result in premature fatigue failure.

A novel method, known as kinetically-controlled titanium nitridation, is capable of diffusing nitrogen into titanium without the formation of undesirable nitrides by providing an extremely low nitrogen pressure. Controlled parameters have yielded nitrogen-stabilized $\alpha$-Ti cases of (10 − 30) $\mu$m in thickness with as much as a three-fold improvement in surface hardness.

Nevertheless, diffusion-affecting features such as structural defects and crystallographic orientation play a significant role in non-uniform nitride nucleation—giving way to unwanted nitrides. Numerous experiments combined with surface analysis techniques such as XRD, XPS, SEM, XEDS, EELS, and TEM were utilized to more fully understand such causes of non-uniform nitridation, as well as methods to control them.
Part 1. Titanium Review

1. History

1.1. Past. Titanium is known to have first been discovered in 1791 by William Gregor, an English mineralogist who found and analyzed a gunpowder-like sand discovered in Cornwall England. Gregor determined that the sand was composed of mostly magnetite and an unknown metallic substance. What Gregor had discovered in the gunpowder-like sand was ilminite (composed of FeTiO$_3$).

Following the discovery, progress in isolating the unknown element from ore was extremely slow and difficult. But, by the end of the 1800’s and beginning of the 1900’s, scientists such as D. K. Kirillov (Russia), Lars Fredrik Nilson and Otto Petterson (Sweden), and Henri Moissan (France) had successfully reached purity levels above 95 percent. A large step forward occurred in 1910 with the successful isolation of Ti in metallic form by Mathew Albert Hunter (USA) who was seeking a better lightbulb filament while working with Rensselaer Polytechnic Institute and General Electric.

Despite the many significant steps previously mentioned by noteworthy scientists, titanium would have remained a laboratory element if it had not been for William J. Kroll of Luxembourg. In 1937, Kroll made vast improvements upon the process used by Hunter, Nilson and Petterson. Using his newly improved batch style process, he produced samples of wire, sheet, turnings, and rods, then made a trip to a few large research organizations in North America to promote his new products. Unfortunately, Kroll’s persuasions were insufficient, developing such a complex and unknown metal was too risky, especially during the great depression. A much larger driving force would be required, the Cold War.

The need for lighter and faster spy planes in the US and faster and deeper diving submarines in the USSR created the titanium industry overnight. Unfathomable amounts of research funding were pumped into the U-2 and SR-71 Blackbird spy planes, resulting in significant advancements in titanium alloys, as well as forming
processes for the new metal. Simultaneously the USSR surged forward with titanium welding technology on the world’s fastest submarines built with titanium hulls. By the end of the Cold War, titanium had stepped out of the darkness and into the spotlight.\[1\]

1.2. Present. Titanium is most commonly known for its low density and high strength, Table 1 demonstrates titanium’s advantage in density and strength compared to a few steel alloys.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Density (g/cm$^3$)</th>
<th>Yield MPa</th>
</tr>
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<tbody>
<tr>
<td>Grade 4, CP Ti</td>
<td>4.5</td>
<td>240 MPa</td>
</tr>
<tr>
<td>Grade 5, Ti-6Al-4V ($\alpha$ &amp; $\beta$)</td>
<td>4.4</td>
<td>855 MPa</td>
</tr>
<tr>
<td>Ti-8Al-1Mo-1V (near $\alpha$)</td>
<td>4.4</td>
<td>910 MPa</td>
</tr>
<tr>
<td>AISI 1020 steel (cold rolled)</td>
<td>7.9</td>
<td>350 MPa</td>
</tr>
<tr>
<td>AISI 4140 steel (normalized and air cooled)</td>
<td>7.9</td>
<td>485 MPa</td>
</tr>
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Pure titanium at room temperature is a single phase HCP crystalline structure known as $\alpha$-Ti. $\beta$-Ti (BCC structure) can be obtained by surpassing the transition temperature of 882°C. In order to improve workability and fabricability, certain elements such as V, Mo, Cr and Cu can be alloyed with Ti to stabilize the $\beta$-phase at lower temperatures. The most common alloy, Ti–6Al–4V, accounts for 45 weight percent of all Ti alloys shipped. Titanium forms a thin TiO$_2$ layer in the presence of oxygen, which acts as a robust diffusion barrier making it a ideal for harsh environments requiring excellent corrosion resistance, such as in maritime applications.\[5\]

Similarly, its inertness with human body fluids gives it prominent application in implantable medical devices such as artificial hips and permanent support braces.\[2\]

These attributes place Ti in its most widely used environment, aerospace. According to the USGS 2008 Mineral Commodity Summary, “an estimated 79 percent of the titanium metal was used in aerospace applications. The remaining 21 percent was used in armor, chemical processing, marine, medical, power generation, sporting goods, and other nonaerospace applications.”\[6\]
Titanium’s excellent corrosion resistance along with its high strength to weight ratio have propelled it to become a highly desired metal for a wide variety of applications, however its high price, largely due to the slow batch-style processing technique, impedes it from rising to prominence as its sister metal Aluminum.

1.3. **Future.** New alloys for specialized applications will most likely be developed in the years to come, but the industry is well aware that the boom of titanium will only happen if a continuous process is successfully developed. Determined inventors and research firms since the 1950’s have sought for such a process with little success. Even William Kroll erroneously predicted in 1959 that a more economical fusion electrolysis process would eventually replace his own within a decade.\[^1\] Despite the failed attempts by giants such as DuPont, Dow, Kennecott Copper and others in the mid 1900’s, developing a new continuous process still remains a common objective today with government and private entities funding the cause. A few of the most promising endeavors are led by Cambridge University, Materials and Electrochemical Research (MER), and International Titanium Powder (ITP).\[^7\]

The FFC/Cambridge process developed by Derek Fray *et al.* at the University of Cambridge during the latter part of the 1990’s has received significant attention for its collaboration with British Titanium, QuinetiQ and TIMET and for having received DARPA funding. Additionally, other organizations such as Metalalysis Ltd. and Norsk Titanium are currently developing spin-offs of the FFC/Cambridge process. The FFC/Cambridge process reduces Ti electrolytically from TiO\(_2\) as opposed to the Kroll process, which utilizes TiCl\(_4\) as the source compound. Successful production of Ti has been accomplished, but only on a laboratory scale.

MER in conjunction with DuPont (world’s largest TiO\(_2\) pigment producer) has developed an electrolytic method utilizing a TiO\(_2\)/carbon graphite anode. A 300 million pound (approximately 490 million U.S. dollars) DARPA grant was awarded to them in 2006 to scale up their process.
ITP was recently purchased by Cristal Global (world’s second largest producer of TiO$_2$) in 2008\textsuperscript{[8]} and has continued in developing and scaling up the Armstrong process. A new plant in Ottowa, Illinois is expected to open in April 2010\textsuperscript{[9]} with a production capability of approximately 1.8 million kg/y (0.8 percent of the 2008 world Ti sponge production).\textsuperscript{[6]} The Armstrong process is unique in that a TiCl$_4$ vapor is injected into the centerline of a molten stream of sodium, wherein reaction occurs. The Na stream carries away the Ti and NaCl, which are filtered later on down the line.\textsuperscript{[7]}

As described, a significant number of techniques are currently being developed in an effort to reduce the processing cost of Ti, which would result in an a widespread increase of overall titanium usage. Ti promoters hope to see it follow in the footsteps of Al, where a new process (Hall/Heroult) enabled a once precious metal to become commonplace all over the world. However, titanium production cost is not its only weakness, a significant disadvantage of Ti relates to its inherent poor tribological properties (high friction coefficient and low hardness values), which subject it to seizing, galling and fretting. Until these weaknesses can be improved, the application of Ti, especially in mechanical applications that require good wear characteristics, will be extremely limited.\textsuperscript{[10,11]}

Part 2. Review of Titanium Nitridation

2. Current Titanium Nitridation Methods

Surface hardening of titanium alloys utilizing nitrogen is typically performed by deposition of a titanium nitride or by inward diffusion of nitrogen into the substrate. The first method is accomplished by depositing a titanium nitride (typically TiN) onto the outermost surface by means of Physical Vapor or Chemical Vapor Deposition (PVD, CVD).\textsuperscript{[12]} The second method encourages the inward diffusion of nitrogen into the substrate, resulting in nitrogen both in solid solution, as well as in new phases
exhibiting higher hardness values. This can be performed by a number of nitridation techniques such as gas, ion implantation, plasma, and laser/gas.\textsuperscript{[13–15]}

Each of these methods has demonstrated the ability to obtain remarkable improvements in increased hardness and wear resistance with the presence of the new nitride layer. However, the new nitride phases (typically TiN and Ti$_2$N are very brittle and have been known to significantly reduce the material’s fatigue resistance.\textsuperscript{[16–18]}

The typical diffusion-affected zone formed in these processes on various Ti alloys contains an outermost layer of TiN and Ti$_2$N, which can be found in the $\mu$m thickness range. Such nitrides can be detected visually by their gold appearance and rough texture.\textsuperscript{[19]} Hardness values of such nitride regions commonly exceed 20 GPa. Below the nitride phase layer lies an $\alpha$-Ti layer rich with nitrogen in solid solution, this layer will typically have a hardness profile reaching values as high as 13 GPa,\textsuperscript{[20,21]} over a two-fold increase compared to that of the substrate. The thickness of such an $\alpha$-Ti layer is highly dependent on the processing parameters, but typically have thicknesses in the of tens of $\mu$m range.

In order to obtain a hardened $\alpha$-Ti case without the formation of nitrides, a new method was developed at Case Western Reserve University. The method utilizes extremely low partial pressures of nitrogen (below $10^{-2}$ Pa), which allows a significant amount of inward nitrogen diffusion while avoiding the formation of titanium nitrides.\textsuperscript{[18,22]}

3. Kinetically Controlled Titanium Nitridation at CWRU

Two methods have been reported successful in nitriding titanium under kinetic control at Case, the powder-pack method and the UHV method. The first notable achievements were performed by Lizhi Liu. A nitrogen-containing powder (CrN) and a titanium alloy (Ti–6Al–4V) were encapsulated in an evacuated fused-quartz ampoule. The ampoule also included a strip of commercially pure titanium (CP Ti) used as a getter to remove or collect residual contaminants from the ampoule prior
to the thermal activation of the Ti–6Al–4V sample. A significant amount of research, experiments, and thermodynamic calculations yielded data for the optimal powder pack composition, as well as a window for treatment time and temperatures for the powder pack and the Ti–6Al–4V sample. Samples treated in this window reportedly yielded more than a two-fold increase in Vickers surface hardness at (50–100) g loads. XRD peak shifts to lower 2θ values indicating lattice parameter expansion caused by nitrogen interstitially dissolved into the Ti was also observed. Nano-hardness tests with a load of 5 mN showed cross-sectional hardness profiles with hardness improvement up to 20 µm deep. These results were extremely encouraging, especially since XRD analysis detected little to no titanium nitrides.[11]

Toward the end of Liu’s Ph.D work, Jason Blush (Masters student) researched the nitridation of CP Ti in a UHV chamber with partial pressures ranging from (6.4 x 10⁻⁴ – 8 x 10⁻⁴) Pa. Such small partial pressures were controlled with a piezoelectric leak valve. Blush reported similar hardness improvement and lattice parameter expansion to that of Liu’s Ti–6Al–4V nitridation research.[23]

Following Liu’s graduation, Soenke Schmidt began research in hopes to optimize certain parameters of the powder-pack method, however, reproducibility became a serious challenge. Under the seemingly same conditions as were recorded by Liu, samples came out of the nitridation heat treatment with ring-like formations composed of nitrides towards the periphery of the circular faces as seen in Figure 7. Lowering the nitrogen partial pressure (accomplished by decreasing the temperature of the powder pack) enabled the suppression of such nitrides, but also drastically minimized any significant hardness improvement. The unforeseen challenge of reproducibility slowed progress, but proved beneficial in gaining experience and developing more efficient analytical methods.
4. Research Objectives

The overall objectives of the research performed for this thesis were first, improve the reproducibility of the powder-pack method for titanium nitridation, and second, gain a deeper understanding of the properties of kinetically-controlled nitrided titanium via experimentation and advanced surface analysis techniques.

Part 3. Experimental Work

5. A Fresh Start

In order to minimize the chances of contamination and random error, it was deemed necessary to thoroughly overhaul and upgrade the equipment used for the encapsulation, standardize the sources of materials inserted in the ampoule (e.g. Ti–6Al–4V, getter and powder pack), and define the encapsulation and heat treatment procedures.

5.1. Equipment overhaul. It was discovered that pressures being reached by the vacuum at commencement of this work were around 20 Pa while those reported by Liu were typically less than 5 Pa. A flushing of the mechanical pump’s oil and cleaning of the lines and joints enabled such pressures to again be reached. The encapsulation procedure was made more robust and repeatable by installing a 3-tip torch (as opposed to the former single-tip torch), and a Kwik-flange to Swagelok \( \frac{1}{4} \text{"} \) connection. This connection provided a tighter and more reliable seal between the fused-quartz tube and the vacuum/argon line, but eliminated the flexibility of the former tube to rubber hose interface. The rubber hose had allowed the operator to heat the tube on all sides with the single-tip torch by manually rotating the fused-quartz tube in the flame. The 3-tip torch resolved this issue as it is capable of heating the fused-quartz tube equally around the tube’s circumference, Figure 1.

The furnaces used in this work were two clam shell style tube furnaces, a Marshall and a Lindberg Heviduty with maximum operating temperatures of 1200°C. For better tube furnace temperature control and monitoring, new programmable furnace
controls were installed, as well as hardware and software to enable temperature data acquisition on a nearby computer.

The furnace used to heat the Ti–6Al–4V and getter (F1) was placed on v-slot pulley tracks to enable easier movement between the gettering and nitridation steps of the process. Accurate and simple positioning of F1 with reference to the sample is critical as only a few centimeters can alter the temperature by a significant amount, Figure 2.

5.2. Materials used. Unknown details regarding materials used in the experimentation, such as the age and conditions to which the preexisting powders had been subjected, were not well known at the commencement of this thesis. During the work of Schmidt and Liu, a few different powders appeared to have been used. Table 2 lists the powder supplier, name and composition of these powders. According to Liu’s dissertation, the CrN from Alfa Aesar was initially used. This powder apparently provided optimal nitridation pressures between (700 − 800) °C. Unfortunately, the
powder was discontinued by Alfa Aesar and most likely the Cr$_2$N powder provided by Princeton Scientific was implemented in the experiment. Liu reports that the optimal temperature window for Cr$_2$N was found between ($600 - 700$)$^\circ$C, indicating a strong difference in generated equilibrium nitrogen pressures as a function of composition. Later during Schmidt’s work, a new powder was again implemented (most likely Cr$_2$N supplied by MatecK) in an effort to identify whether or not the powder had role in the ring-pattern formation of nitrides.

The research performed in this thesis used a preexisting powder in preliminary experiments, but new orders of CrN & Cr$_2$N powder from by Alfa Aesar were used for the remainder of the work.

### Table 2. Powder packs used in experiments.

<table>
<thead>
<tr>
<th>Supplier</th>
<th>Powder Name</th>
<th>Add. Info.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alfa Aesar, MA</td>
<td>CrN</td>
<td>up to 2 wt% Cr$_2$N$^{[11]}$</td>
</tr>
<tr>
<td>Alfa Aesar, MA</td>
<td>Cr$_3$N</td>
<td>99.8% pure</td>
</tr>
<tr>
<td>Alfa Aesar, MA</td>
<td>CrN &amp; Cr$_2$N</td>
<td>50 wt% Cr$_2$N 50 wt% CrN</td>
</tr>
<tr>
<td>Princeton Scientific, NJ</td>
<td>Cr$_2$N</td>
<td>-</td>
</tr>
<tr>
<td>MatecK GmbH, Germany</td>
<td>Cr$_2$N</td>
<td>-</td>
</tr>
</tbody>
</table>

Fused quartz tubes used by Liu and Schmidt of outside diameter ($OD$) 13 mm, wall thickness ($1 - 2$) mm were purchased from Quartzplus Inc. (Brookline, NH)$^{[11]}$. New
tubes of the same dimensions were procured from Technical Glass (Painsville Twp., OH) for this project.

Material for “gettering” had previously been either Ti sponge (Alfa Aesar) or a strip of commercially pure titanium (CP Ti) wrapped in a coil, as seen in Figure 3. All experiments in this thesis used a CP Ti strip.

6. Standardized Experimental Procedures

Nitridation takes place in an evacuated fused-quartz ampoule to prevent atmospheric contamination. The general procedure was described by Liu on page 103 of his dissertation. Figure 3 shows the dimensions of a standard ampoule used in this work with corresponding dimensions and positions of each component. The step-by-step procedures used in Ti–6Al–4V sample preparation, encapsulation, and heat treatment of each run are listed below.

**Figure 3.** Evacuated and sealed ampoule.
6.1. **Ti–6Al–4V sample preparation.**

(1) Ti–6Al–4V samples cut from corresponding bar stock\(^1\) or coupon with SiC blade on Buehler Isomet 4000.

(2) At least one side of sample mechanically polished with Buehler polishing paper in the following order: 1. P400 (35 µm) 2. P800 (22 µm) 3. P1200 (15 µm) 4. P2400 (9 µm).

(3) The other side left as-cut, or polished to P400 (35 µm).

(4) Samples ultrasonically cleaned in ethanol for approximately 10 minutes prior to encapsulation.

6.2. **Electropolishing.** Electropolishing on Ti–6Al–4V was performed for 60 s at room temperature in the following solution:\(^{[24]}\)

\(^1\)Majority of tests performed on 2 mm thick button-shaped samples from stock of 9.5 mm OD.
40 mL H$_2$SO$_4$
13 mL HF
8 mL Glycerin

A current density of (0.7—2) A/cm$^2$ and a voltage of (14—20) DC was implemented. The cathode used was a pure titanium strip with a surface area of roughly 10:1 to that of the anode. The Ti–6Al–4V sample was electropolished for 30 s, then immediately washed with ethanol upon removal from the solution with the current still applied. Such conditions were found to remove approximately 10$\mu$m of material from the surface.

6.3. **Encapsulation.** (Figure 3)

1. Powder end of tube sealed with propane/oxygen flame.
2. Neck #1 created at powder end of tube using flame.
3. Straw (quartz tube of diameter 8 mm) inserted until butted with neck #1.
4. CrN & Cr$_2$N/Cr powder pack poured down straw into chamber #1. As was performed by Liu$^{[11]}$ and Schmidt, the nitrogen containing powders (CrN & Cr$_2$N) were mixed with a Cr powder using a 1:1 ratio (approximately 9:5 by weight, respectively). As specified by MSDS, chromium and chromium nitride powders when not in use were stored in a desiccator within a hood. The quantity of the powder used in each ampoule followed the ratio of 4 g of CrN & Cr$_2$N/Cr for every 200 mm$^2$ of titanium sample surface area.
5. Straw and tube tapped to free loose powder, straw removed from tube.
6. Getter$^2$ inserted into middle chamber (chamber #2), coil diameter slightly exceeding inner diameter of tube to prevent sliding. Dimensions of the CP Ti strip used were based on the volume of the sealed capsule, approximately 1 mm$^2$ of getter for 100 mm$^3$ of ampoule volume. Coil was made by spiraling the CP Ti strip around a glass rod of diameter 6 mm.

$^2$Getter and ultrasonically cleaned for 10 minutes prior to insertion in tube.
(7) Neck #2 created at Ti–6Al–4V end of tube.
(8) Ti–6Al–4V inserted into chamber #3.
(9) Open end of Ti–6Al–4V connected to vacuum/argon line, Figure 4.
(10) Tube evacuated until at least 7 Pa.
(11) Tube purged with ultra high purity argon (99.999%) until near atmospheric pressures reached.
(12) Tube evacuated a second time until at least 3 Pa.
(13) Tube purged a second time, following previous instructions.
(14) Tube evacuated a third time.
(15) During third evacuation, entire length of tube heated with torch on low flame setting to de-vaporize inner walls.
(16) Tube sealed once pressure reached 2 Pa.

6.4. **Nitridation heat treatment.** All nitridation heat treatments discussed in this report shall be considered consistent with this list of procedures (notably time of nitridation and temperature of sample being nitrided), unless otherwise specified.

(1) CrN & Cr2N/Cr powder-pack end of ampoule placed in furnace #0 (F0) with the thermocouple (TC) tip hovering above the center of the powder mass.
(2) Furnace #1 (F1) placed over getter with TC tip hovering above center of getter coil.
(3) Gettering run held for 43.2 ks (12 h) with F1 set to 860°C and F0 set to predetermined temperature for desired nitrogen partial pressure.
(4) F1 rolled to position centering TC above Ti–6Al–4V.
(5) Commencement of nitridation.
(6) F0 held for 259.2 ks (72 h), then furnace cooled.
(7) F1 held for 262.8 ks (73 h), then furnace cooled.
(8) Ampoule removed from furnace once Ti–6Al–4V below 200°C, cracked open and Ti–6Al–4V removed for further work.
An exception to the guidelines listed above took place in order to approximate the window of the optimal powder temperature for a 259.2 ks (72 h) treatment period. Such a procedure was needed as temperatures utilized for powders previously used with different compositions were not accurate on the new Cr$_2$N & CrN powder, see Table 2. A number of thin strips of CP Ti were nitrided and observed periodically during the treatment. Every set number of hours, F1 (furnace used for heating the CP Ti) was rolled away and the CP Ti was allowed to cool, a quick inspection was performed and a note was made whether or not nitride spots were visually detectable under a magnifying glass. The furnace was then replaced over the Ti–6Al–4V and the nitridation continued until the next checkup. The simple checkup procedure proved successful in quickly identifying the temperature window, but also allowed a quasi in situ examination of nitride growth.
6.5. **Post nitridation analysis.**

(1) Low magnification light optical microscopy (LOM) imaging performed.

(2) Analyzed by X-ray diffractometry (XRD), step size: 0.03°, dwell time: 3 s, scan range: (2θ) (35−42)°, instrument: Scintag X-1, Cu-Kα crystal, λ = 0.154056 nm.\(^3\)

(3) Vickers hardness measured with loads of (50 − 1,000) g, instrument: Buehler MMT-3.

(4) Sample cut in half to reveal cross-section of α-Ti case, instrument: Buehler Isomet 4000 high-speed cutting saw, SiC blade.


(7) Cross-section of sample etched with Kroll’s etchant (85% distilled water, 10% HNO₃, 5% HF) to reveal nitrogen-stabilized α-Ti case.


(9) Additional surface analysis methods performed (XEDS, SEM, EBSD, XPS, EELS, TEM).

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\(^3\)The size of the nitrided sample required a special fixture, which positioned the sample atop a clay mount, the mount rested within a rigid plastic box, which was placed in the XRD sample holder. To determine the deviation between scans, 8 scans of the same material were performed. After each scan, adjustments to the sample involving resetting the sample position and height atop the clay mount. The standard deviation of the 8 scans was found to be 2θ of 0.03°.
7. Analysis Methods Used

7.1. XRD. The underlying principle behind XRD (X-ray diffractometry) is explained by Bragg’s Law,

\[ n\lambda = 2d_{hkl}\sin\theta. \]

As shown in Figure 5, X-rays are directed toward a crystalline sample surface at angle \( \theta \). The planes that are parallel to the surface of the sample diffract the X-rays at angle \( \theta \) towards the detector (also positioned at angle \( \theta \) to the surface of the sample). The planes that have a spacing such that the Bragg condition is fulfilled are subsequently detected and plotted as intensity or counts per second (CPS) versus the \( 2\theta \) position of the X-ray source (tube or emitter) and the detector. The plot is referred to as a diffractogram. The emitter and detector are incrementally positioned over a range of angles, which allows the detection of numerous plane spacings present in the sample.

**Figure 5.** XRD schematic.
By knowing $\lambda$ (wavelength of X-ray) and the angle ($\theta$) at which the X-ray emitter is aligned to the surface of the sample, $d_{hkl}$ (the distance between atomic planes) can be calculated for Bragg-satisfying $d_{hkl}$-spacings, which show up as peaks in the diffractogram. The peak positions (representative to $d$-spacings) are helpful in identifying which phases are present in the sample.

Peak positions of crystalline materials vary depending on intrinsic properties that affect the plane spacings, e.g. the composition of alloying elements and interstitial impurities. An increase in plane spacing is recognized by a peak shift to lower $2\theta$ angles.

XRD is a valuable technique in determining the effects of nitrogen diffusion into titanium, since it enables a quick scan capable of detecting $\alpha$-Ti, $\beta$-Ti, $\text{Ti}_2\text{N}$, and TiN all within a 7° (35–42)° $2\theta$ scan. Also, lattice parameter expansion caused by the inward nitrogen diffusion is sufficient to cause a detectable peak shift to lower $2\theta$ angles, the amount of the peak shift can be used to roughly calculate the nitrogen concentration.$^{[20]}$

An important aspect of XRD that must be considered in analysis of surface altered materials is the X-ray depth of penetration. According to Cullity,$^{[25]}$ the depth of penetration can be estimated by solving for $x$ with

$$\begin{align*}
(2) & \quad G_x = 1 - \exp\left(-\frac{2\mu x}{\sin \theta}\right) \\
\text{and} & \\
(3) & \quad x = \left(\frac{\ln(0.05\sin \theta)}{-2\mu}\right).
\end{align*}$$

The value of $G_x$ is commonly set at 0.95, which signifies that 95% of all data are collected from the outermost surface layer to a depth of $x$. The term $\mu$ is known as
the linear absorption coefficient, which is listed as $\mu/\rho$ by Cullity. The value of $\mu$ can be obtained for various elements by multiplying by their respective densities ($\rho$). The equation

\[
(4) \quad \left(\frac{\mu}{\rho}\right)_{Ti-6Al-4V} = Wt_{Ti} \left(\frac{\mu}{\rho}\right)_{Ti} + Wt_{Al} \left(\frac{\mu}{\rho}\right)_{Al} + Wt_{V} \left(\frac{\mu}{\rho}\right)_{V}
\]

can be used to solve for the value of $\mu/\rho$ for an alloy, such as Ti–6Al–4V. This result multiplied by the alloy’s density ($\rho$) yields the value of $\mu$ for the alloy.

Solving for Equation 3 indicates that within the scanning angles of $2\theta$ (35–42)$^\circ$, 95% of the data obtained stems from material depths of (5–7)$\mu$m under normal scanning conditions. Glancing at 1$^\circ$(\theta), under the same conditions, collects 95% of the data from within the outermost 0.3$\mu$m.

7.2. Vickers hardness. Vickers hardness testing utilizes a diamond tip (Figure 6) that is pressed into the surface of a sample at a certain load. The depth obtained by the diamond tip is calculated by measuring the corner-to-corner lengths of the square indent ($d_1$, $d_2$) and by knowing the characteristic angle of the diamond tip (136$^\circ$). The size of the impression is inversely proportional to the hardness value (HV) as shown in

\[
(5) \quad HV = \frac{2P\sin(136/2)}{((d_1 + d_2)/2)^2}
\]

where $P$ is the load and $d_1$ and $d_2$ are the diagonal lengths of the indent.\[26\]

The loads used for measuring the surface hardness in these experiments were typically (50 – 100)g as to avoid penetrating more than 3$\mu$m into the case hardened surface. At least five indents were performed for each reported hardness measurement. Conditions such as surface roughness and phases present were considered in selecting the location for each indent. Lena Reichardt, summer student from the
University of Augsburg in Germany, performed much of the micro-hardness testing, LOM imaging, and metallography for this thesis.

Figure 6. Vickers indent.

7.3. **Nanomechanical testing.** Following XRD and microhardness testing, samples were cut in half in order to examine the microstructure and mechanical properties of the nitrogen-diffused cross-section. Nano-hardness was selected to analyze the hardness profile at the surface to enable indents within approximately $(1 - 2) \, \mu m$ from the specimen edge. The instrument used in this work was a TriboScope by Hysitron Incorporated with a Berkovich diamond tip. Each mounted, polished, and etched\textsuperscript{4} cross-section was placed on the instrument’s positioning platform and Scanning Probe Microscopy (SPM) was used to locate the desired regions of the sample for testing.

\textsuperscript{4}Etching enabled distinction between $\alpha$-grains and $\beta$-grains, all hardness results presented in this paper were acquired from $\alpha$-grains. A hardness test comparison between an etched sample and a non-etched sample suggested that etching caused no significant variation in hardness results.
Each hardness indent was held for 5 s, the rate of loading and unloading was 1 mN/s with a maximum load of 5 mN.

In addition to nano-hardness tests, a nano-scratch test was also performed. The procedures of the test are very simple, the diamond nano-tip is pressed into the surface of the desired area at a certain load (in this case 5 mN). The sample is then moved a specified distance allowing the diamond tip to scratch the surface of the sample. Upon completion of the cycle, the tip is removed, the topography is recorded, and the depth and width of the scratch are measured, providing a valuable qualitative comparison.

All work related to the Triboscope (including sample preparation/polishing, nano-hardness tests, nano-scratch tests, and data analysis) was performed by Lena Reichardt.

7.4. XEDS. XEDS (X-ray energy dispersive spectroscopy) is a powerful analytical tool that characterizes the composition of a material by X-rays that are emitted from the material under analysis upon being bombarded by electrons. As the surface of a material in question is bombarded with the electron beam, atoms from within the material subsequently lose electrons that are replaced by those from a higher energy state, causing the emission of X-rays. The X-rays that are not re-absorbed (originating from the outermost few µm of material) escape the sample and can then be picked up by the detector. Differing materials correspond to emitted X-rays of a variety of energy levels, these can be characterized to identify the composition of the material in question. A spectrum is created by plotting the the data as X-ray count versus energy (keV).[27]

XEDS can be used to quickly estimate elemental composition, however, one shortcoming of XEDS in this work relates to the difficulty with peak deconvolution. For example, The Ti-L\(\alpha\) and N-K\(\alpha\) peaks lie within 0.6 keV of each other, 0.45 keV and
0.39 keV respectively. The proximity of the peaks in conjunction with peak broadening makes the deconvolution of nitrogen and Ti very difficult. Despite this setback of differentiating two of the most important elements in question, XEDS methods provided valuable information characterizing the α-Ti case and nitride regions.

Plan-view and cross-sectional samples were analyzed using XEDS on an FEI xT Nova Nanolab 200. A 4010 Bruker Si-drifted detector was used, providing a FWHM (full width at half maximum) resolution (125 eV for Mn-Kα at throughputs of (60 – 90) kcps. Accelerating voltages of 5 keV, 10 keV, and 20 keV were used when performing both XEDS line scans and elemental mapping. Peaks were matched with the standard-less ZAF method.

Precision and accuracy of XEDS measurements were checked with as-received material from suppliers 1 and 2. A 300 µm x 300 µm area was used as the sampling size in 5 different areas of each sample containing α and β grains with an operating voltage of 20 keV. Table 3 displays these results compared with nominal values for Ti–6Al–4V having been processed according to ASM 4928. It can be seen that the quantification for Ti and Al falls within ASM values, while that of V is seen to be a few tenths of a percent higher. This could be representative of high V content, but is more likely due to the impurity elements that were not considered during XEDS quantification, as well as the limited sample area. The standard deviation of the measurements is seen to be less than 0.6 at% for Ti and Al and less than 0.1 at% for V. The last two columns in Table 3 show the increased standard deviation with decreased sampling area and operating voltage. Since quantified regions of XEDS full-spectrum maps were obtained using different sampling area sizes (due to grain size variation), error limits are included with each table of presented data.

7.5. XPS. XPS (X-ray photoelectron spectroscopy) is commonly used for surface analysis due to its capability of accurately characterizing the surface composition

---

5nitrogen, carbon, Fe, and oxygen totaling 1.5 at%.
Table 3. XEDS precision and accuracy (chemical composition in at%).

<table>
<thead>
<tr>
<th>keV µm²</th>
<th>Ti-6Al-4V ASM 4928</th>
<th>α &amp; β Supplier-1 Std.</th>
<th>α &amp; β Supplier-2 Std.</th>
<th>α only Supplier-2 Std.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ti</td>
<td>Al</td>
<td>V</td>
<td></td>
</tr>
<tr>
<td></td>
<td>83.5–86.2</td>
<td>9.3–11.3</td>
<td>3.1–4.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>85.0 ± 0.2</td>
<td>10.7 ± 0.2</td>
<td>4.4 ± 0.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>85.1 ± 0.6</td>
<td>10.8 ± 0.6</td>
<td>4.1 ± 0.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>85.3 ± 0.9</td>
<td>10.1 ± 0.5</td>
<td>4.7 ± 0.9</td>
<td></td>
</tr>
</tbody>
</table>

from within the outermost few nm. The photo-electrons within an element are excited by either a monochromatic X-ray or ultraviolet light. The measured kinetic energy of the excited photo-electrons is used to calculate the binding energy, which is used to identify the atom of origin. An additional advantage of XPS is the ability to distinguish between different bonding types such as TiN and Ti.[28]

This advantage prompted the analysis of a number of samples with a PHI VersaProbe XPS microprobe in an effort to further characterize the surface composition of treated and non-treated Ti-6Al-4V samples.

It was discovered that due to the high affinity of titanium for oxygen, XPS analysis obtained the most consistent results under a continuous argon sputter during analysis. Dynamic sputtering was found to greatly improve the quality and reliability of the data gathered, since the rate at which oxides form at the surface is stabilized during the sputtering.

Some initial work was sputtered under differing parameters, but optimal results were obtained using the following scan/sputter conditions:

1. Initial sputtering for 120 s at 3 keV with a (3 x 3) mm spot size, and an estimated sputter rate of 7 nm/60 s on Ta₂O₅.
2. Continuously sputtered during analysis with argon pressure at 1/5 that of the initial sputtering.
3. Scan performed with pass energy of 93.9 eV.
4. Chamber pressure recorded at 5.3 x 10⁻⁶ Pa.
Table 4 demonstrates the error associated with quantification performed in Phi Multipak software and a sample size of five.

**Table 4.** Quantification error on sample 1012−ep (data in at%).

<table>
<thead>
<tr>
<th></th>
<th>Average</th>
<th>Std.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>78.0</td>
<td>0.7</td>
</tr>
<tr>
<td>Al</td>
<td>6.8</td>
<td>0.5</td>
</tr>
<tr>
<td>V</td>
<td>1.8</td>
<td>0.7</td>
</tr>
<tr>
<td>N</td>
<td>8.5</td>
<td>0.3</td>
</tr>
<tr>
<td>O</td>
<td>5.1</td>
<td>0.7</td>
</tr>
</tbody>
</table>

7.6. **TEM.** Unlike LOM, SEM, or XPS, transmission electron microscopy (TEM) enables sample characterization beyond the surface. This is accomplished by thinning a desired area of a material to such a point that it becomes transparent to an electron beam. The interactions between the crystal structure and the electron beam provide information for both imaging, as well as diffraction work.

TEM samples were prepared by FIB (focused ion beam) milling on two FEI work stations, a Quanta and a Nova. Once the thinned-foil was lifted out of the bulk material, it was mounted on a copper grid and further thinned to (50 – 60) nm. All diffraction work was performed on a FEI Tecnai F30 (300 kV). STEM imaging and EELS were performed on a Zeiss Libra 200FE (200 kV). XEDS was also performed on both instruments. JEMS software was used as a tool for solving and indexing diffraction patterns.
Part 4. Results

8. Initial Observations

Various experiments were performed to address the source of a ring-like nitride\textsuperscript{6} pattern as seen in Figure 7. First, rectangular Ti–6Al–4V samples from sheet-rolled coupons were nitrided as to address whether the ring pattern arose from the material’s intrinsic properties from the as-received condition or from in-house cutting, polishing, and other preparation. Figure 8 shows the typical pattern in which the nitrides formed on the faces of the rectangular samples. The darker vertical stripes on the left hand side of the image are composed of nitride spots. The vertical striped texture shown by the darker nitrides, as well as the general texturing on the remainder of the sample is correlated to the rolling direction of the sample.

\textbf{Figure 7.} Ring pattern formation of nitrides around periphery of sample 821, $T_{ppk}=570\,^\circ\text{C}$.

\textsuperscript{6}TEM diffraction work, as discussed in Section 13, was used to confirm the precipitated phase creating the ring-like pattern to be composed of TiN and Ti$_2$N.
The next experiment was designed to compare whether or not formation of a nitride ring pattern would occur on cylindrical Ti–6Al–4V procured from an alternate supplier, but still having been subjected to the same AMS and ASTM standards. Figure 9 compares two nitrided samples having undergone the same nitridation treatment with the temperature of the powder pack at 550°C. The sample from supplier-1 (left) has a strong ring pattern as expected, but the sample provided through supplier-2 (right) exhibits no obvious ring pattern, nor a significant amount of visibly detectable nitrides.

Sample 94₂ (from supplier-2) was nitrided at 570°C to find out if a ring pattern would develop at a higher N₂ partial pressure on the new material. Figure 10 shows the result having a more even distribution of nitrides compared to sample 82₁, having been treated under the same conditions (Figure 7). Although a thick ring of nitrides did not form on the material from supplier-2 as on material from supplier-1, some clustering of nitrides is found around the periphery of sample 94₂, a closer look is shown in the right image of Figure 10.
Figure 9. Differences in nitride formation between samples from supplier-1 and supplier-2, sample 88R₁ (left), 89R₂ (right), intended surface scratches are explained on page 48.

Figure 10. Higher N₂ pressure on material from supplier-2 yields a mostly uniform distribution of nitride spots over face of sample. However, a zone of clustered nitrides exists near periphery, sample 94₂, $T_{ppk}=570 \, ^\circ C$. 
Figures 11 and 12 show a common feature observed in nitrided samples. Nitride precipitation is more obvious both in the cross-section, as well as the plan-view at the intersection between the face that was cut perpendicularly to the roll direction (0° face) and the circumferential face.\footnote{The precipitated phases observed in cross-sections of samples, such as those shown in Figure 12, were assumed to be nitrides due to their correlation with the nitride spots on the surface. The confirmation of this assumption is discussed in Section 13.}

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{image1}
\caption{Nitride precipitation more prevalent at intersection between 0° face and unseen circumferential face (corner), sample 94\textsubscript{2}, $T_{ppk}$=570°C.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{image2}
\caption{LOM image of etched cross-sections, thicker nitride precipitation at corners of two different samples, 92\textsubscript{2} (left), $T_{ppk}$=575°C, 93\textsubscript{2} (right), $T_{ppk}$=560°C.}
\end{figure}
Both images in Figure 13 also show clusters of nitride spots near the periphery of the exposed faces. Figure 14a shows an SEM image of a substantially large nitride, having grown over the surface of many grains. Figure 14b shows a similar nitride growth illustrating more clearly the transition between the nitride and α-Ti case.

**Figure 13.** LOM, highly concentrated patches of nitride spots near periphery on samples 96\(_2\) (left), 95b\(_2\) (right), \(T_{\text{ppk}}\) for both samples at 570°C.
Figure 14. SEM comparison of nitride spots nucleated on surface of α-Ti.

(a) Sample 1012−ep, $T_{ppk}=570^\circ$C.

(b) Sample 1102−ep−A2, $T_{ppk}=550^\circ$C.
Figure 15 compares a feature common to samples from supplier-1. The coarse-side shows a strong correlation between the abrasive cuts and nitride precipitation in an obvious ring pattern. Figure 15c shows the coarse side at a higher magnification.

![Figure 15](image1.png)

(a) Coarse-polished side.  
(b) Fine-polished side.

![Figure 15](image2.png)

(c) Coarse polished side.

**Figure 15.** LOM images comparing nitride formation on coarse vs. fine-polished faces, sample 831, $T_{ppk}=550^\circ$C.
However, samples from supplier-2 that were similarly treated show the opposite result—a higher concentration of nitrides present on the fine-polished side (Figure 16).

![LOM images comparing nitride formation on coarse versus fine-polished faces, sample 94₂, Tₚₚk=570°C. Such an observation was also made on samples 93₂, and 97₂. Note the faint ring pattern in the coarse-polished side.](image)

Figure 16. LOM images comparing nitride formation on coarse versus fine-polished faces, sample 94₂, Tₚₚk=570°C. Such an observation was also made on samples 93₂, and 97₂. Note the faint ring pattern in the coarse-polished side.

Figure 17 shows SPM images that were used for the determination of the surface roughness of differently treated samples. The average surface roughness ($Ra$) is defined by

$$Ra = \frac{1}{l} \int_{0}^{l} |f(x)| dx,$$

where $l$ is the length analyzed and $f(x)$ is a plot of the surface topography.\[29\]
(a) Electropolished, $Ra=50$ nm.

(b) Mechanically polished to 9 $\mu$m (p2400), $Ra=90$ nm.

(c) 259.2 ks anneal, $Ra=150$ nm, $A_2$

(d) 259.2 ks nitridation, $Ra=240$ nm, $101_2-ep$.

Figure 17. Comparison of average surface roughness of Ti–6Al–4V samples at different stages, work by Lena Reichardt.
A few experiments were carried out to better understand the effect on nitride formation in the presence of dislocations. Figure 18 shows two samples that were manually scratched with a sharpened titanium tip prior to nitridation, shown in lower magnification in Figure 9. Each sample (from separate suppliers) shows a higher concentration of nitride spots in or near the region of the scratch.

Figure 18. Increased nitride nucleation within scratched region, samples: 88R₁ (left), 89R₂ (right), $T_{ppk}$ for both samples at 550°C.

An additional test was performed in which a Brinell indent was made on the surface of two separate samples, loads of 4.9 kN and 7.4 kN. The 10 mm radius of the Brinell ball was selected to induce the stresses as to limit nitride formation possibly stemming from surface features such as seen on corners and coarse-polished samples. Figure 19 shows three areas of the sample. The left image depicts a region not affected by the indent, the middle image is from the region impressed by the 4.9 kN load and the right image is from the region impressed by the 7.4 kN load. An increased concentration of nitride precipitation exists in the region affected by the 7.4 kN load.
Figure 19. LOM, density of nitride spots increases within Brinell indent of 7.4 kN load, samples 95a$_2$ and 95b$_2$, $T_{ppk}$ for both samples at 570°C.

Nitride spots were observed to initiate on preferred grains of the sample early on in the treatment. They then continued to grow while other grains were free of nitrides for the entire period of the test. This is evident in images previously shown of Ti–6Al–4V samples such as Figures 10 and 13. Figures 20 through 22 show the observed premature precipitation of nitrides on certain grains relative to others on Grade 4 CP Ti samples. Sample 80$_{CP-ep}$ was electropolished prior to nitridation, as described on page 26.

Figure 20. LOM, grain boundary correlation to precipitation of nitrides (dark globular region), sample 76$_{CP}$, $T_{ppk}$=HT 1 (parabolic decrease from 600°C to 500°C).
Figure 21. SEM, formation of nitrides and correlation to grains—darker rough regions are nitrides, sample $80_{\text{CP-ep}}$, $T_{\text{ppk}}=570^\circ\text{C}$, $t$: $86.4\ \text{ks (24 h)}$.

Figure 22. SEM, many nitride spots seen with correlation to grains, sample $80_{\text{CP-ep}}$. 
Premature nitride formation in one region with respect to another was not only observed on certain grains, but also on entire faces. Figure 23 contains a cross-section of sample $101_{2-ep}$ showing the $0^\circ$ face (Figure 24), as well as the circumferential face.

**Figure 23.** LOM, texturing present in sample leads to heavy nitride on vertical edges (circumferential face), while horizontal edge ($0^\circ$ face) is nitride free, sample $101_{2-ep}$, $T_{ppk}=570^\circ$C.

The left and right vertical edges of the sample represent the circumferential face of the rod, the result on this face is a heavy, almost continuous nitride layer with an $\alpha$-Ti layer directly below with a case thickness of approximately 20 $\mu$m. An increased nitride presence was also observed in optical microscopy prior to metallography. The bottom edge represents the $0^\circ$ face of the sample, lying perpendicular to the rolling-direction—no nitrides are visible. This behavior was only found on samples that were electropolished or annealed prior to nitridation. It was also far more obvious on electropolished samples.

In order to determine texturing in Ti–6Al–4V used in this project, XRD was performed on three faces of different orientations. As seen in Figure 24, the cuts were
made at (180, 90, and 45) degrees with respect to the rolling-direction. The faces were then mechanically polished as described on page 26 with the additional final steps of 0.3 μm diamond suspension and 0.05 μm alumina suspension.

**Figure 24.** 90°, 0°, and 45° cuts made for XRD texture analysis.

Figure 25 displays the results of normal XRD scans on each face. As can be seen, the prism planes (\{10\bar{1}0\}) have the strongest presence on the 0° face while the basal planes (\{0002\}) are scarcely represented. The 90° face exhibits inverse results to that of the 0° face. The 45° face supports the 0° and 90° results as the parameter planes (\{10\bar{1}1\}) have the strongest peak.
Figure 25. XRD scans demonstrating texturing of as-received Ti–6Al–4V for 45°, 90°, and 0° faces.

Figure 26. XRD diffractrogram of CP Ti powder.
By comparing these scans with the diffractogram of CP Ti powder in Figure 26, a significant texture appears to be present in the hot rolled Ti–6Al–4V material. The extent of texturing can be quantified by utilizing the Harris method,\cite{30,31} which is

\[
TC_{hkl} = \frac{I_{hkl}/I^\circ_{hkl}}{(1/n) \sum_{i=1}^{n} (I_{hkl}/I^\circ_{hkl})},
\]

where \(I_{hkl}\) is the intensity of peak \(hkl\) from the surface in question. \(I^\circ_{hkl}\) is \(hkl\)'s intensity from a standard powder,\footnote{Standard used for \(I^\circ_{hkl}\) was CP Ti powder supplied by Alfa Aesar of 44 \(\mu\)m size.} \(n\) is the number of distinct \(hkl\)'s used in the \(hkl\) summation. Table 5 shows a breakdown of the TC (texturing coefficient) for the three principal \(\alpha\)-Ti peaks for the 0°, 90°, and 45° faces. Higher values represent an increased texturing relationship for the respective planes.

**Table 5.** Texturing coefficients for principal \(\alpha\)-Ti peaks for the 0°, 90°, and 45° faces.

<table>
<thead>
<tr>
<th></th>
<th>Ti–6Al–4V 0° face</th>
<th>Ti–6Al–4V 90° face</th>
<th>Ti–6Al–4V 45° face</th>
</tr>
</thead>
<tbody>
<tr>
<td>{10\bar{1}0}</td>
<td>2.4</td>
<td>0.1</td>
<td>0.6</td>
</tr>
<tr>
<td>{0002}</td>
<td>0.2</td>
<td>2.8</td>
<td>0.5</td>
</tr>
<tr>
<td>{10\bar{1}1}</td>
<td>0.4</td>
<td>0.1</td>
<td>1.8</td>
</tr>
</tbody>
</table>

The texturing coefficients show that the highest concentration of grains whose basal plane lies perpendicular to the diffusion surface are found on the faces whose normal is parallel to the rolling direction, being the 0° faces, as seen in Figure 27, and as found by Biswas in a similar study on drawn titanium wire.\cite{32}

To further investigate the effect of texturing, a nitrided 90° face (sample 109\textsubscript{2−ep}) was compared to that of a nitrided 0° face (sample 107\textsubscript{2−ep}). Each sample was encapsulated and nitrided with the CrN & Cr\textsubscript{2}N/Cr at 550°C for the usual 259.2 ks (72 hours). Following the nitridation, each sample was analyzed visually and with
Figure 27. Texturing found in Ti-6Al-4V hot rolled bar stock, unit cell’s rotational symmetry about the z-axis is not fixed as shown.

XRD for nitride presence. Figure 28 shows each sample with its corresponding nitrided face. The superimposed border represents equal surface areas used for the visual nitride count of nitrides of diameters greater than approximately 35 µm. The appearance of fewer nitride spots in the 0° face is supported by the absence of a small ε-Ti2N peak for the 0° face (sample Sample 1072–ep) shown in the XRD scan, Figure 29.
Figure 28. Visual nitride-spot comparison of 0° and 90° faces, $T_{ppk}$ of both samples held at 550 °C.
Figure 29. XRD scans showing small $\varepsilon$-Ti$_2$N peak for 90° face (top scan), while $\varepsilon$-Ti$_2$N peak on scan for 0° face is not detectable (bottom scan).

Figure 30. LOM, mechanically polished sample versus mechanically and electropolished sample, 100$_2$ (left), 101$_{2\text{-ep}}$ (right), $T_{\text{ppk}}$ for both samples at 570°C.
Surface uniformity (decrease in average roughness and removal of structural surface defects) brought about by electropolishing was found to greatly suppress the formation of nitrides. Figure 30 shows two samples polished and nitrided under the same conditions in the same ampoule, the only difference being the sample on the right was electropolished prior to nitridation. Figure 17 shows SPM images comparing the 9 µm (p2400) mechanically polished sample versus the electropolished sample (mechanically polished to 9 µm prior to electropolishing). The Ra value (roughness average) calculated for the electropolished sample was almost half that of the mechanically polished sample, (50 and 90) nm respectively.

Figure 31a shows the cross-section of the α-Ti case of the electropolished sample 1012−ep. This even and nitride-free section is representative of the majority of the sample. Figures 31b and 31c show cross-sections of nitrides formed on the same sample.
Figure 31. SEM images of nitrogen-stabilized $\alpha$-Ti case and nitrides in sample 101$_2$ ep.
Initial observations made on samples treated under different conditions and from different suppliers revealed a number of new insights. Nitride precipitation in a ring-like pattern was found to be a function of mill processing on cylindrical rods and not primarily from in-house sample preparation. Even seemingly equal material from different suppliers having been subject to the same ASM standards differed in nitride growth patterns, showing the sensitivity of nitride precipitation. A correlation was found between premature nitride precipitation and one or more of the following: protruding surface features (corners, tips, etc.), the presence of dislocations or defects, and grains favoring orientation with the basal plane parallel to the diffusion surface. Hot-rolled cylindrical Ti–6Al–4V used in this work was found to have a texture favoring grain orientations with the basal plane parallel to the rolling-direction—leading to premature nitride precipitation on such faces. The stress relief and decrease in surface roughness brought about by electropolishing greatly reduced nitride precipitation compared to samples nitried directly after mechanical polishing.
9. LOM, XRD, and Surface Hardness

LOM was used to characterize features of the diffusion-affected zone, such as $\alpha$-Ti case thickness and the presence of nitrides. XRD and Vickers microhardness tests were used to further identify the precipitation of second phases, as well as characteristics of the $\alpha$-Ti diffusion-affected zone. Results will be presented for treated samples from three categories: supplier-1, supplier-2, and supplier–2–electropolished.

9.1. Samples from supplier-1. Figure 32 shows a diffractogram of a series of Ti–6Al–4V samples obtained from supplier-1 having undergone slightly different treatments. Hardness values for samples from supplier-1 are shown in Table 6.

![Figure 32. Comparison of XRD diffractograms on samples from supplier-1.](image)
Table 6. Vickers surface hardness values for samples from supplier-1, measurements from regions without visible nitrides.

<table>
<thead>
<tr>
<th>ID</th>
<th>$T_{ppk}$ (°C)</th>
<th>$H$ (HV50) center</th>
<th>Std. $N$</th>
<th>$H$ (HV50) periphery</th>
<th>Std. $N$</th>
</tr>
</thead>
<tbody>
<tr>
<td>82</td>
<td>570</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>85A</td>
<td>550</td>
<td>445</td>
<td>50</td>
<td>450</td>
<td>55</td>
</tr>
<tr>
<td>84</td>
<td>550</td>
<td>390</td>
<td>45</td>
<td>455</td>
<td>55</td>
</tr>
<tr>
<td>83A</td>
<td>550</td>
<td>390</td>
<td>20</td>
<td>420</td>
<td>25</td>
</tr>
<tr>
<td>A1</td>
<td>NA</td>
<td>330</td>
<td>30</td>
<td>310</td>
<td>20</td>
</tr>
<tr>
<td>AR1</td>
<td>NA</td>
<td>340</td>
<td>15</td>
<td>340</td>
<td>15</td>
</tr>
</tbody>
</table>

Both samples 83A and 84A show almost a 20% increase in surface hardness on regions from the middle of the sample without nitride spots (Table 6). Their cross-sections, a small portion shown in Figure 33, reveal the presence of an uneven $\alpha$-Ti case with periodic nitrides at the surface, and a higher concentration of nitride spots toward the periphery of the 0° face. Samples nitrided at lower temperatures correspondingly have thinner $\alpha$-Ti cases and less nitride formation. Results also indicate that the pre-nitridation anneal (A1 at 790°C for 14.4 ks (4 h) followed with a furnace cool) on sample 84A did not have a noticeable effect on the nitride formation or hardness results.

The diffractogram for sample 85A has an interesting feature, of the four nitrided samples shown in this diffractogram, it is the only one not exhibiting a significant \{0002\} peak (besides the AR sample). The major difference of sample 85A lies in its pre-nitridation anneal (A2), which entailed holding the sample at 925°C for 14.4 ks (4 h) followed with a furnace cool. LOM analysis (plan-view and cross-section) for sample 85A, shown in Figure 33, reveal a surface with a noticeably decreased amount of surface nitrides. The $\alpha$-Ti case for sample 85A, although thinner, is much more uniform across the entire width of the 0° face compared to the other nitrided samples from supplier-1, which exhibited a less-uniform case being thinner toward the center and thicker with a heavier nitride concentration toward the periphery (correlating to ring pattern). Vickers hardness measurements were made
Figure 33. LOM images comparing treated samples from supplier-1, cross-sections show a portion of the diffusion-affected zone.

comparing the center of the nitrided samples to that of the periphery (within 200 µm from the edge). The results for nitrided samples, shown in Table 6, indicate harder values toward the periphery for samples 83₁ and 84₁⁻ₐ₁.

The diffractogram for sample 82₁ shows the effect of raising the powder pack temperature 20°C, the result is the formation of a significant Ti₂N peak at 2θ of 39.3°.
The presence of this peak is supported by the visible nitrides in its image and micrograph shown in Figure 33. Hardness values are not shown for sample 82, due to the difficulty in locating large enough regions without nitride growth.

Heat treating the Ti–6Al–4V samples (with or without nitrogen) at 860 °C is known to cause substantial grain growth. The top two images in Figure 34 show a typical as-received Ti–6Al–4V mill-annealed microstructure, the β-Ti grains are the smaller dark globular particles in the α-Ti matrix. The bottom image shows a typical microstructure after having been annealed for 262.8 ks at 860 °C, the lighter grains are the α-Ti and the darker intergranular grains are β-Ti. An increase in the β-Ti volume fraction can be noticed in these images, as well as in the growth of the β-Ti \{110\} peak in Figure 32.

![Figure 34](image)

**Figure 34.** Typical Ti–6Al–4V microstructures for AR2’s 0° face (top), AR2’s 90° face (middle), and as annealed 0° face, annealed at 860 °C for 262.8 ks (bottom). The β-Ti grains in the AR2 90° face (middle) still show traces of elongated grains from the rolling process.
9.2. **Samples from supplier-2.** Figure 35 compares a series of samples from supplier-2 including as-received ($AR_2$), annealed without nitrogen ($A_2$), and three samples nitrided with the powder pack at temperatures of (550, 560, and 570) $^\circ$C. Figure 36 compares LOM images of each nitrided sample from supplier-2 with a small portion of the corresponding cross-section. A relationship between powder temperature and the formation of nitride spots, as well as thickening of the $\alpha$-Ti case is evident. A comparison of the Vickers hardness measurements from the periphery to the center (Table 7) shows that no such hardness slope exists in nitrided samples from supplier-2 as did in samples from supplier-1. This increased uniformity is also visually evident by the lack of a ring pattern of nitrides.

![Figure 35. Comparison of XRD diffractograms on samples from supplier-2.](image)
Table 7. Vickers surface hardness values for samples from supplier-2, from regions without visible nitrides.

<table>
<thead>
<tr>
<th>ID</th>
<th>( T_{ppk} ) ((^\circ)C)</th>
<th>( H ) (HV50) center</th>
<th>Std.</th>
<th>( N )</th>
<th>( H ) (HV50) periphery</th>
<th>Std.</th>
<th>( N )</th>
</tr>
</thead>
<tbody>
<tr>
<td>94(_2)</td>
<td>570</td>
<td>665</td>
<td>30</td>
<td>5</td>
<td>650</td>
<td>65</td>
<td>5</td>
</tr>
<tr>
<td>93(_2)</td>
<td>560</td>
<td>615</td>
<td>95</td>
<td>5</td>
<td>640</td>
<td>120</td>
<td>5</td>
</tr>
<tr>
<td>97(_2)</td>
<td>550</td>
<td>585</td>
<td>25</td>
<td>5</td>
<td>564</td>
<td>30</td>
<td>5</td>
</tr>
<tr>
<td>A(_2)</td>
<td>NA</td>
<td>350</td>
<td>25</td>
<td>5</td>
<td>355</td>
<td>15</td>
<td>5</td>
</tr>
<tr>
<td>AR(_2)</td>
<td>NA</td>
<td>350</td>
<td>10</td>
<td>5</td>
<td>345</td>
<td>10</td>
<td>5</td>
</tr>
</tbody>
</table>

Figure 36. LOM images comparing treated samples from supplier-2, cross-sections show a portion of the diffusion-affected zone.
9.3. Electropolished samples from supplier-2. Overwhelmingly, optimal nitriding results were obtained with Ti–6Al–4V on samples electropolished before nitriding as described on page 26. The XRD results for electropolished samples from supplier-2 are shown in Figure 37. Substantial peak shifts to lower 2\( \theta \) angles along with the suppression of significant Ti\(_2\)N peaks correlates well with the micrographs shown in Figure 39, as well as hardness results shown in Table 8.

![Figure 37. Comparison of XRD diffractograms on electropolished samples from supplier-2.](image)

<table>
<thead>
<tr>
<th>ID</th>
<th>( T_{ppk} ) (°C)</th>
<th>( H ) (HV50) center</th>
<th>Std.</th>
<th>( N )</th>
<th>( H ) (HV50) periphery</th>
<th>Std.</th>
<th>( N )</th>
</tr>
</thead>
<tbody>
<tr>
<td>103(_2)-ep(-A_2)</td>
<td>570</td>
<td>890</td>
<td>85</td>
<td>5</td>
<td>875</td>
<td>100</td>
<td>5</td>
</tr>
<tr>
<td>101(_2)-ep</td>
<td>570</td>
<td>680</td>
<td>90</td>
<td>10</td>
<td>640</td>
<td>30</td>
<td>10</td>
</tr>
<tr>
<td>110(_2)-ep(-A_2)</td>
<td>550</td>
<td>550</td>
<td>50</td>
<td>12</td>
<td>520</td>
<td>30</td>
<td>6</td>
</tr>
<tr>
<td>107(_2)-ep</td>
<td>550</td>
<td>605</td>
<td>65</td>
<td>12</td>
<td>630</td>
<td>60</td>
<td>12</td>
</tr>
<tr>
<td>A(_2)-ep</td>
<td>NA</td>
<td>330</td>
<td>20</td>
<td>5</td>
<td>315</td>
<td>15</td>
<td>5</td>
</tr>
<tr>
<td>AR(_2)-ep</td>
<td>NA</td>
<td>340</td>
<td>10</td>
<td>5</td>
<td>350</td>
<td>15</td>
<td>5</td>
</tr>
<tr>
<td>AR(_2)</td>
<td>NA</td>
<td>350</td>
<td>10</td>
<td>5</td>
<td>345</td>
<td>10</td>
<td>5</td>
</tr>
</tbody>
</table>
The micrographs in Figure 39 show a stark drop in the concentration of formed surface nitrides compared to non-electropolished samples nitrided under the same conditions, compare to Figure 36. Samples 107$_{2-ep}$ and 110$_{2-ep-A2}$ (both nitrided with the powder pack at 550°C) show no XRD peak indicating the presence of nitrides, yet still show a (60-90)% increase in hardness with a 0.49 N load. However, LOM reveals that limited nitride spots have indeed precipitated. Samples 101$_{2-ep}$ and 103$_{2-ep-A2}$, nitrided with powder pack at 570°C, both show a noticeable increase in nitride presence both visually and in the diffractogram. This increase is accompanied by a surface hardness improvement from (50-170)%.

Possible causes for this are believed to be the increased surface roughness, as well as variations associated with differently oriented grains.

In an effort to compare the lattice parameter expansion in the $c$-direction versus the $a$-direction, a 90° face was prepared on two samples, one to be nitrided and the other annealed. This enabled XRD scans of a face with a dominant concentration of basal planes parallel to the surface, yielding the $\{0002\}$ peak. The diffractogram in Figure 38 shows a clear peak shift to the left and a small Ti$_2$N peak. The $\{0002\}$ peak also shows a larger shift than the $\{10\bar{1}1\}$ peak. The LOM image for this sample can be seen in Figure 28b.

![Figure 38](image.png)

**Figure 38.** Comparison of XRD diffractograms from 90° face on electropolished samples from supplier-2.
Figure 39. LOM images comparing electropolished-nitrided samples from supplier-2, cross-sections show a portion of the diffusion-affected zone.

A peak shift to larger $2\theta$ angles for all present peaks following electropolishing or annealing is observed on virtually all diffractograms for samples having undergone either treatment$^9$ (See Figures 32, 35, and 37). This apparent lattice parameter contraction upon electropolishing or annealing spurred further investigation.

$^9$The same peak shift to higher $2\theta$ angles was also observed upon electropolishing CP-Ti.
In order to better understand the cause, a few simple experiments were performed in reverse order to that of the initial observation. An annealed sample (259.2 ks at 850°C) and an electropolished sample were both scanned five times with XRD under normal and glancing conditions. Each sample was then mechanically polished as described on page 26. Five more XRD scans (normal and glancing conditions) were then performed on the new mechanically polished surface. Table 9 shows the average peak positions for each condition, as well as the observed shift. Results for both samples indicate a lattice parameter expansion in planes parallel to the scanning surface as a result of compressive residual stresses induced by mechanical polishing.

Table 9. \(\{10\bar{1}1\}\) peak positions and shift due to mechanical polishing.

<table>
<thead>
<tr>
<th></th>
<th>Annealed</th>
<th>MP</th>
<th>2θ shift</th>
<th>Std.</th>
</tr>
</thead>
<tbody>
<tr>
<td>normal</td>
<td>35.37</td>
<td>35.35</td>
<td>-0.02</td>
<td>± 0.01</td>
</tr>
<tr>
<td>glancing</td>
<td>35.39</td>
<td>35.31</td>
<td>-0.08</td>
<td>± 0.01</td>
</tr>
<tr>
<td>EP</td>
<td>35.48</td>
<td>35.44</td>
<td>-0.04</td>
<td>± 0.01</td>
</tr>
<tr>
<td>MP</td>
<td>35.41</td>
<td>35.34</td>
<td>-0.07</td>
<td>± 0.01</td>
</tr>
</tbody>
</table>

In summary, LOM, XRD, and surface hardness results from each batch of samples contain key findings that have aided in better understanding the nitridation process. Namely, the \(\alpha\)-Ti case, formed below nitrides, was always found to be thicker than regions without nitrides, indicating a greater content of \(\alpha\)-stabilizing nitrogen. \(\alpha\)-Ti cases formed on samples from supplier-1 were observed to grow thicker toward the periphery of the sample, in conjunction with the ring-like surface nitrides. This increase in nitrides and \(\alpha\)-Ti-case thickness toward the periphery of the sample was supported by increased hardness values from \((8 - 17)\%\) compared to the center. The one exception to this observation was sample 851−A2, which was annealed at 925°C prior to nitridation. Such an anneal also suppressed the formation of the XRD peak representing \(\{0002\}\) planes. It was discovered that nitrided samples, such as 831, 841−A1, 851−A2, and 1072−ep, with visible nitride spots did not contain a large enough volume fraction to be detected by XRD under the used scanning conditions. Nitrided
samples from supplier-2 were found to precipitate a distribution of nitrides in a much more even manner over the face of the sample, exhibiting no ring-pattern of nitrides. The only samples exhibiting a significant peak shift to lower 2θ values without heavy nitride precipitation were electropolished prior to nitridation. These samples also were measured to have an increase in surface hardness from (1.5–2.5) times that of a sample treated equally, but without the presence of nitrogen (AR_{2–ep}). XRD showed a greater expansion of the lattice parameter in the c-direction to that of the a-direction. And a peak shift to higher 2θ angles was observed on all samples after annealing or electropolishing, indicative of residual stress relief.
10. Nanomechanical Tests

As a reference, Figure 40 shows the nano-hardness results from nitrided Ti–6Al–4V performed by Liu. The profile was acquired from a sample nitrided under kinetically-controlled conditions exhibiting no XRD-detectable nitride peaks. The nitrogen-diffused layer within the outermost 5 µm demonstrates a (2–3) fold increase in hardness.

![Graph showing nano-hardness results on Ti–6Al–4V from Liu.](image)

Figure 40. Nano-hardness results on Ti–6Al–4V from Liu.\[11\]

As mentioned on page 34, all work relating to nano-hardness/scratch tests in this theses was performed by Lena Reichardt.

Nano-hardness tests were performed for each set of samples (supplier-1, supplier-2, and supplier-2-electropolished) from α-grains located beyond the diffusion-affected zone to obtain the “core hardness.” Numerous grains were selected at the core from which measurements were taken to obtain an average core hardness.
10.1. **Nano-hardness on samples from supplier-1.** Due to the inhomogeneous ring pattern formation of nitrides, profiles were performed on two different regions on samples from supplier-1, in the center of the sample, or hole of the ring pattern and from within the ring pattern. Figure 41 shows an example of these two regions, the center of the ring pattern shows an absence of nitrides, as seen in the plan-view, as well as the cross-section. The region from within the ring pattern shows prominent nitrides penetrating sometimes up to depths of 15 µm.

![Figure 41](image)

**Figure 41.** Locations selected for nano-hardness profiling.

Figure 42 shows how significant hardness improvement is observed in α-Ti regions under nitrides,\(^\text{10}\) while thinner α-Ti regions without nitrides only exhibit a small improvement, if any. Figure 43 shows an SPM image of one of the profiles from sample 83\(_1\). The measurements were preferentially performed on α-grains.

\(^{10}\)Nano-hardness values above 15 GPa are most likely from the nitride or on the nitride α-Ti interface.\(^{21}\)
Figure 42. Various nano-hardness profiles for samples from supplier-1.

Figure 43. SPM image of actual nano-hardness profile path from sample 831 underneath nitride. Indents only from nitride region and α-Ti grains. Scale is consistent with Figure 42.

Figure 44 shows a few profiles for samples from supplier-1, having undergone pre-nitridation anneals. The profiles from regions without nitrides show a small hardness improvement compared to the core hardness. The core hardness was measured to be slightly less than that of samples not having undergone a pre-nitridation anneal (from 6 GPa to 5 GPa). The profile taken near a nitride shows the commencement of
a steeper profile with higher values, but measurements on the nitride itself were not performed, explaining the lack of data points below 12 µm.

Figure 44. Nano-hardness profiles for samples from supplier-1 having undergone pre-nitridation anneal.

10.2. **Nano-hardness on samples from supplier-2.** A comparison of profiles from nitride-bearing regions and non-nitride-bearing regions is shown in Figure 45 for samples from supplier-2. The results support observations made on samples from supplier-1 in that profiles from underneath nitrides exhibit a steeper hardness profile. However, the profile for sample 94 shows a significant improvement in the α-Ti case without a nearby nitride, it was correspondingly nitried with the powder pack at the highest temperature (570°C) of the set.

10.3. **Nano-hardness on electropolished samples from Suppliers 1 & 2.** The first electropolished sample (811−ep) from supplier-1 was only nitried for 86.4 ks (24 h) but still shows a significant hardness slope (Figure 46) and exhibited no ring pattern formation of nitrides. Figure 46 also shows profiles from electropolished samples from supplier-2, which show similar hardness profiles in locations absent of nitrides. The profiles show almost a 3-fold improvement in hardness in the outermost few µm.
Figure 45. Various nano-hardness profiles for samples from supplier-2.

Figure 46. Various nano-hardness profiles for electropolished samples from Suppliers 1 and 2.
Figure 47. Location of hardness profile on sample 1012–ep without nitride present.
10.4. **Nano-scratch tests.** Nano-scratch tests were performed in two regions of sample 1012−ep, the left side of Figure 48 shows two scratches performed on an α-Ti grain at the core of the nitrided sample while the right side shows a scratch from the α-Ti hardened case. The depths of the scratches were measured and are presented in Table 10. The nitriding effectually reduced the depth of the scratch by \(\approx 60\%\).

![Image of nano-scratch tests](image)

**Figure 48.** Nano-scratch tests comparing α-Ti-grain from core (left) to α-Ti-grain from the diffusion-affected zone (right), sample 1012−ep.

<table>
<thead>
<tr>
<th>Location</th>
<th>Depth (nm)</th>
<th>Std.</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Core, α-Ti grain</td>
<td>240</td>
<td>30</td>
<td>6</td>
</tr>
<tr>
<td>α-Ti case</td>
<td>90</td>
<td>30</td>
<td>6</td>
</tr>
</tbody>
</table>

**Table 10.** Comparison of nano-scratch depths.

Results from nanomechanical testing showed that unless the sample was electropolished prior to nitridation, (2–3) fold hardness improvement in the α-Ti case was only found in regions below nitrides—indicating a higher nitrogen content in such regions. The one exception to this was one of the four profiles from sample 942 in regions without visible nitrides. Also, a small improvement (20% in the outermost 5 µm) was observed on samples from supplier-1 that were annealed prior to nitridation (841−A1 and 851−A2).
11. XEDS

Figure 49 shows full-spectrum maps, or hypermaps, to illustrate some major compositional differences between the surface nitride spots and the $\alpha$-Ti regions. This qualitative comparison indicates that the nitrides are depleted of Al content and contain less V compared to the $\alpha$-Ti regions.

Figure 50 shows two XEDS spectra from boxed regions 1 and 2 in Figure 49b. The absence of the Al in region 1 (nitride) is indicated by the missing Al-K$\alpha$ peak at 1.49 keV. But, region 2 ($\alpha$-Ti) appears to contain a significant Al-K$\alpha$ presence. The two Ti-K$\alpha$ peaks at 4.51 keV (from regions 1 and 2) are normalized with each other, revealing a peak-height mismatch between the two region’s Ti-L$\alpha$ peaks at 0.45 keV, with the peak representing region 1 (nitride) being significantly larger. Quantitative analysis, shown in Table 11, was performed in each box from the Ti, Al, and V peaks while ignoring the presence of nitrogen. The most noteworthy difference between the two regions is found in the fraction of aluminum.

Table 11. XEDS quantitative comparison of regions 1 and 2 from sample 94. Error of $\pm$ 0.5%.

<table>
<thead>
<tr>
<th>Element</th>
<th>Region 1, Nitride (at%)</th>
<th>Region 2, $\alpha$-Ti (at%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>96.5</td>
<td>88.0</td>
</tr>
<tr>
<td>Al</td>
<td>0.5</td>
<td>9.0</td>
</tr>
<tr>
<td>V</td>
<td>3.5</td>
<td>3.5</td>
</tr>
</tbody>
</table>
Figure 49. XEDS full-spectrum maps from 0° face of sample 942.

Figure 50. XEDS spectra for select regions from sample 942, regions shown in Figure 49b (spectra normalized with Ti-Kα).
Figure 51 displays XEDS full spectrum maps from the cross-section of sample 101$_{2-ep}$. Although the sample preparation and treatment conditions differed slightly (see page 154), these results correlate well with the plan-view full-spectrum map from sample 94$_2$, Figure 49. Specifically, Ti is present in all phases and Al is absent in the outermost layer of the nitride. Interestingly, an Al-rich band exists at the interface of the nitride and the $\alpha$-Ti case. This Al-rich band is present below all other observed nitrides and not seen in $\alpha$-Ti regions without nitride formation. The $\beta$-Ti grains appear to be rich in vanadium (as expected), and a vanadium presence is found in the nitride region unlike Al.

The XEDS spectrum in Figure 52 for region 2 clearly shows an increased Al concentration compared to regions 1 and 3. The spectrum representing region 1 (nitride) also appears to have an increased nitrogen concentration as its Ti-L$_\alpha$ peak at 0.45 keV is slightly larger than the Ti-L$_\alpha$ peak for region 3 ($\alpha$-Ti grain). Table 12 contains the quantitative analysis (ignoring nitrogen) for the 6 regions shown in Figure 51d. The results for region 1, from the surface-most portion of the nitride, match nicely with those from the nitride region 1 from sample 94$_2$ shown in Table 11. Region 2, the Al-rich band, is estimated to contain 19 at% Al compared to 10 at% of region 3 ($\alpha$-grain) and 1 at% in region 1(nitride). Table 12 also contains quantitative results for regions a, b, and c, shown in Figure 51d. No apparent compositional difference is detectable with XEDS as a function of depth into the $\alpha$-Ti case.
Figure 51. XEDS full-spectrum mapping on cross-section of sample 101$_{2-ep}$.

Table 12. XEDS quantitative comparison of regions 1, 2, 3, a, b, and c on sample 101$_{2-ep}$ in the presence of a nitride, see 51d. Error ± 1%.

<table>
<thead>
<tr>
<th>Element</th>
<th>Region 1 Nitride at%</th>
<th>Region 2 Al-rich at%</th>
<th>Region 3 α-grain at%</th>
<th>Region a α-Ti case at%</th>
<th>Region b α-Ti case at%</th>
<th>Region c α-Ti case at%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>96</td>
<td>77</td>
<td>86</td>
<td>86</td>
<td>87</td>
<td>87</td>
</tr>
<tr>
<td>Al</td>
<td>1</td>
<td>19</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>V</td>
<td>2</td>
<td>5</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
</tbody>
</table>
Figure 52. XEDS from three distinct regions (see Figure 51d) on cross-section of sample 101$_{2-\text{ep}}$ in the presence of a nitride (spectra normalized with Ti-K$_\alpha$).

Figure 53 shows XEDS full-spectrum maps from a cross-section of sample 101$_{2-\text{ep}}$ in an area absent of nitrides. The full-spectrum maps along with the spectra as seen in Figure 54 indicate a clean $\alpha$-Ti case without secondary phases, such as nitrides or peculiar Al-rich bands. This is representative of the $\alpha$-Ti case throughout the sample. Table 13 displays quantitative analysis from selected regions shown in Figure 53d. A comparison of regions 2, a, b, and c indicates that no significant compositional difference (considering Ti, Al, and vanadium) exists between $\alpha$-grains at different depths into the sample. The same appears to be true for $\beta$-grains by comparing regions 3 and 4.
(a) Ti-rich regions.

(b) Al-rich regions.

(c) V-rich regions.

(d) SEM image of regions selected for XEDS.

**Figure 53.** XEDS on cross-section of sample 101$_{2-ep}$, without nitride.

**Table 13.** XEDS quantitative comparison of regions 2, 3, 4, a, b, and c on sample 101$_{2-ep}$ without the presence of a nitride, see 53d. Error for $\alpha$-Ti grains of ±0.5%, $\beta$-Ti grains of ±1%.

<table>
<thead>
<tr>
<th>Element</th>
<th>Region 2 $\alpha$-grain at%</th>
<th>Region 3 $\beta$-grain at%</th>
<th>Region 4 $\beta$-grain at%</th>
<th>Region a $\alpha$-Ti case at%</th>
<th>Region b $\alpha$-Ti case at%</th>
<th>Region c $\alpha$-Ti case at%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>86.5</td>
<td>80</td>
<td>81</td>
<td>88.0</td>
<td>86.0</td>
<td>86.5</td>
</tr>
<tr>
<td>Al</td>
<td>9.5</td>
<td>7</td>
<td>7</td>
<td>9.0</td>
<td>10.0</td>
<td>9.5</td>
</tr>
<tr>
<td>V</td>
<td>4.0</td>
<td>13</td>
<td>12</td>
<td>3.0</td>
<td>4.0</td>
<td>4.0</td>
</tr>
</tbody>
</table>
Figure 54. XEDS from three distinct regions (see Figure 53d) on cross-section of sample 101$_{2-ep}$ (spectra normalized with Ti-K$\alpha$).

Figures 55 and 57 show XEDS line scans (y-axis plotted as intensity) along with an SEM image placed below the scan corresponding to the area selected for the scan. Figures 56 and 58 show line scans with at% plotted on the y-axis. Characteristics previously observed in the full-spectrum maps, selected-area spectra, and quantitative analysis are also observed in the line scans. The characteristic features include the Al-deficient nitride, an Al-rich band at the nitride/$\alpha$-Ti case interface, and compositional changes between $\alpha$-Ti and $\beta$-Ti grains. The high Al concentrations found at the surface of the sample are from the mounting compound.
Figure 55. XEDS line scan plotting intensity versus distance, sample 1012-ep, note: sample rotated 45°.

Figure 56. XEDS line scan plotting at% versus distance, sample 1012-ep, note: sample rotated 45°.
Figure 57. XEDS line scan plotting intensity versus distance in region without nitride, sample 101$_{2-ep}$.

Figure 58. XEDS line scan plotting at% versus distance in region without nitride, sample 101$_{2-ep}$.
XEDS full-spectrum mapping and chemical quantitative analysis consistently showed a significant increase of carbon presence within the nitride regions, Figure 59. This led to the investigation of whether the presence of carbon stems from the formation of a new phase such as TiC or Ti(CN) during the nitridation or simply a result of contamination introduced before, during, or after the nitridation.

Quantification of various positions on the cross-section of the nitride showed carbon concentrations between (12 and 14) at% compared to (8 to 10) at% in non-nitride regions such as the $\alpha$-Ti case, Al-rich band, and $\beta$-Ti grains. Quantitative comparisons made between an $\alpha$-Ti region (without nearby nitride) and a nitride, both at the same distance from the mount/sample interface, show that the increased carbon presence is only seen in the nitride, suggesting the results not to be merely a factor of proximity to the mount. Additional evidence is the increased carbon detected in nitride from the plan-view of the sample surface where no mount is present, Figure 59. Page 137 discusses why this detected carbon is considered only a contaminant.

XEDS proved extremely valuable in showing compositions in different regions of nitrided samples. The most important being the discovery of the Al-rich band (18 at% Al) and of normal ratios of Ti, Al, and vanadium in the $\alpha$-Ti case, as well as $\alpha$-Ti and $\beta$-Ti grains below the $\alpha$-Ti case.
12. XPS

Figure 60 shows XPS spectra representing four unique samples: AR\(_1\) (as-received), 43\(_1\) (nitrided with a high nitrogen partial pressure), A\(_{2-ep}\) (annealed for 262.8 ks), and 101\(_{2-ep}\) (nitrided for 259.2 ks).\(^{11}\) The contrasting surface appearance of three of the four samples investigated is shown in Figure 61.

These spectra, as well as their quantitative results shown in Table 14, reveal important compositional differences between the samples, which correspond not only to their treatment, but also to their scanning/sputtering parameters. Table 14 shows that with no sputtering (NS), sample AR\(_1\) contains 16 at% carbon and a ratio of oxygen to titanium at levels fairly close to stoichiometric TiO\(_2\). But, after performing a pre-analysis argon sputter (PS) on the surface to be analyzed for 30 s, a (3 – 5) nm layer is estimated to have been removed. The carbon contamination was then reduced and the oxygen to titanium ratio was found to be much closer to the stoichiometric value of 2:1.

Table 14. XPS quantitative analysis results, values in at%. The dash (-) means that the corresponding element was not detected. Error of less than ±1 at% for each element.

<table>
<thead>
<tr>
<th>Element</th>
<th>AR(_1) (NS)</th>
<th>AR(_1) (IS)</th>
<th>43(_1) (IS)</th>
<th>A(_{2-ep}) (CS)</th>
<th>101(_{2-ep}) (CS)</th>
<th>110(_{2-ep}) (CS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti(_{2p})</td>
<td>22</td>
<td>29</td>
<td>32</td>
<td>76</td>
<td>78</td>
<td>75</td>
</tr>
<tr>
<td>Al(_{2p})</td>
<td>5</td>
<td>6</td>
<td>2</td>
<td>6</td>
<td>7</td>
<td>9</td>
</tr>
<tr>
<td>V(_{2p3})</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>12</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>O(_{1s})</td>
<td>53</td>
<td>60</td>
<td>9</td>
<td>6</td>
<td>5</td>
<td>9</td>
</tr>
<tr>
<td>N(_{1s})</td>
<td>1</td>
<td>&lt;0.5</td>
<td>41</td>
<td>–</td>
<td>9</td>
<td>4</td>
</tr>
<tr>
<td>C(_{1s})</td>
<td>16</td>
<td>4</td>
<td>5</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Cr(_{2p})</td>
<td>–</td>
<td>–</td>
<td>9</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Cu(_{2p3})</td>
<td>2</td>
<td>&lt;0.5</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

\(^{11}\)Samples AR\(_1\) and 43\(_1\) were analyzed with an operating voltage of 93.9 eV while the operating voltage for A\(_{2-ep}\) and 101\(_{2-ep}\), was 117.4 eV
Figure 60. XPS spectra comparing samples having undergone different treatments, PS: pre-analysis sputter, CS: continuously sputtered during analysis after pre-analysis sputter.
Figure 61. Surface appearance of select samples analyzed with XPS. Red box in Figure 61c indicates the 300 µm spot size of the XPS scan area.
Figure 62 shows a closer look at the Ti$_{2p}$ peak for each sample. Variations in peak shape and position are seen. An additional spectrum representing AR$_1$ (NS) is also shown for comparison.

![XPS spectra contrasting variations between Ti$_{2p}$ doublet peak from a number of samples, NS: no sputter, PS: pre-analysis sputter, CS: continuously sputtered during analysis after pre-analysis sputter.](image)

Figure 62. XPS spectra contrasting variations between the Ti$_{2p}$ doublet peak from a number of samples, NS: no sputter, PS: pre-analysis sputter, CS: continuously sputtered during analysis after pre-analysis sputter.

The close-up look on the N$_{1s}$ peak (Figure 63) shows that significant amounts of nitrogen were only detected in samples 43$_1$ and 101$_2$-ep, as anticipated. The quantified values of nitrogen for each of these samples are shown in Table 14.

The initial sputtering of samples 101$_2$-ep, A$_2$-ep, and 110$_2$-ep was held for 120 s in contrast to the 30 s used for samples AR$_1$ and 43$_1$. The longer time was implemented in an attempt remove nearly 15 nm of the original TiO$_2$-containing surface. The longer sputter time seems to have effectively reduced the unwanted oxygen signal, and removed the carbon contamination.
As mentioned on page 36, the peak positions can be used to identify the bonding type for the element in question. The transition from the sharp doublet Ti\textsubscript{2p} peaks in AR\textsubscript{1} (NS) to the broader doublet in AR\textsubscript{1} (PS) along with a shift to lower binding energy can be explained by the initial sputtering-away of the TiO\textsubscript{2} film (62). Following the sputtering, information appears to have been gathered from both Ti in TiO\textsubscript{2}, as well as metallic Ti. This resulted in a merging of a Ti\textsubscript{2p} primary peak at 459\,keV (TiO\textsubscript{2}) and at 454\,keV (Ti metallic). A significant difference in the Ti-peak shape and location also exists between sample 43\textsubscript{1} and those of samples A\textsubscript{2–ep} and 101\textsubscript{2–ep}. Sample 43\textsubscript{1}, as seen in Figure 61a, was nitrided with a high enough nitrogen partial pressure to create a continuous gold-colored titanium nitride coating. Samples A\textsubscript{2–ep} and 101\textsubscript{2–ep} retained their original Ti-color. The Ti\textsubscript{2p} peak from 43\textsubscript{1} appears to be located at a slightly higher binding energy than those of A\textsubscript{2–ep} and 101\textsubscript{2–ep}. This

\footnote{In the case of nitrogen, it is not possible to distinguish between nitrogen from nitrides and nitrogen in solid solution with a metal, as the peak positions are too close to one another.}
corresponds to the known Ti$_{2p}$ peak position at 456 keV from nitrides compared to the position at 454 keV for metallic titanium.$^{[34]}$

One disclaimer related to XPS work is that it can be difficult to ensure that the selected area for analysis is performed in a region void of nitrides in samples exhibiting scattered nitride spots, such as 101$_2$-ep. The red square seen in Figure 61c is scaled to represent the 300 µm spot size of a typical scan area. It can be seen that a possibility exists of inadvertently selecting a region containing a nitride, as well as α-Ti. In order to reduce the likelihood of such a circumstance, care was taken to scan regions free of nitride spots on samples 101$_2$-ep and 110$_2$-ep–A2. Also, the fact that normal Al content is seen in each sample shows that a nitride was not likely in the scan area, as Al was discovered to be absent in the nitride regions. Additional scans were also performed on each sample, which resulted in consistent nitrogen concentrations.

XPS successfully provided compositional quantification of the surfaces of samples nitrided under various conditions. Optimal results were obtained when implementing a continuous sputter during analysis. The gold coating found on sample 43$_1$ was found to have a Ti to nitrogen ratio consistent with that of TiN. The presence of (9 and 4) at% nitrogen was found in samples 101$_2$-ep and 110$_2$-ep, respectively. Since the analysis for the latter two samples was taken from regions void of visible nitrides, the nitrogen presence is assumed to be from solid solution.
13. TEM Analysis

Three TEM specimens were prepared by focused ion-beam milling (FIB) using the lift-out technique. The lift-outs were prepared from the following samples in order to investigate a precipitated nitride, the surface of an annealed sample (259.2 ks), and a nitride-free stabilized-α-Ti case from a sample having been nitrided for 259.2 ks:

1. $84_{\text{A1}}$, $T_{\text{ppk}}=550^\circ\text{C}$, $t=259.2\text{ ks}$.
2. $A_{2\text{-ep}}$, $T_{\text{ppk}}=\text{NA}$, $t=259.2\text{ ks}$.
3. $101_{2\text{-ep}}$, $T_{\text{ppk}}=570^\circ\text{C}$, $t=259.2\text{ ks}$.

13.1. Sample $84_{\text{A1}}$. Figure 64 depicts sample $84_{\text{A1}}$ in the location selected for thin-foil lift out. The Pt was deposited on the surface of a visible nitride spot. Figure 65 shows three dark-field STEM images of the lift-out. The precipitated nitrides can be seen at the Pt/Ti interface. The small black holes seen in Figure 65b are suspected to be porosity in the nitride.\textsuperscript{[11,19]} The larger holes, as well as the vertical parallel lines (curtain effect) in Figure 65a are a product of milling. Figure 65c, shows a close-up of the nitride layer with its curious ribbon-like patterns whose orientations differ from grain to grain.

![Figure 64. Pt deposited on the surface of a visible nitride spot for a TEM lift-out procedure, sample $84_{\text{A1}}$.](image)
Figure 65. DF-STEM images of TEM foil prepared by FIB from sample $84_{1-A1}$. 
Figure 67 shows six diffraction patterns acquired from the labeled regions shown in Figure 66. Three different types of patterns were observed at different depths along the length of the sample. The most striking features are the grains at the outermost surface exhibiting striped or ribbon-like patterns in STEM imaging, as well as a more-complex diffraction pattern—see regions 1a, 1b, and 1c in Figure 67. Grains at depths of below \((3-5) \mu m\) were typically without obvious features in STEM imaging, and had fairly simple diffraction patterns (region 3). Grains found between regions 1 and 3 were observed with STEM to have more contrast than that of region 3 and diffraction patterns with ordering-like spots between the primary reflections (regions 2a and 2b).

**Figure 66.** DF-STEM image showing regions used for diffraction patterns, sample 841-811.
Figure 67. Diffraction patterns from different regions in sample $84_{1-A1}$. 

(a) Region 1a. 
(b) Region 1b. 
(c) Region 1c (not shown in Figure 66). 
(d) Region 2a. 
(e) Region 2b. 
(f) Region 3.
Despite the different camera lengths and exposure time, it can be seen that matching patterns are found for regions 1a and 1b, as well as regions 2a and 2b. The intense reflections found in regions 2a and 2b match nicely with the reflections from region 3.

Region 3 was identified as $\alpha$-Ti viewed along the $[2\bar{1}\bar{1}0]$ zone axis. Figure 68 shows the indexed pattern, as well as measurements used to match it with known spacial frequency ratios given for HCP crystals, shown in Table 15.\[^{[35]}\]

![Figure 68. Region 3's diffraction pattern, identified as $\alpha$-Ti, $\vec{B}$ (beam direction) = [2\bar{1}\bar{1}0], sample 84$_1$-A$_1$.](image)
Table 15. Measured values from regions 2a and 3 compared with standard spacial frequency ratios for HCP crystals.\cite{35}

<table>
<thead>
<tr>
<th></th>
<th>c/a (mm)</th>
<th>b/a (mm)</th>
<th>&lt;ab</th>
<th>&lt;bc</th>
</tr>
</thead>
<tbody>
<tr>
<td>Williams &amp; Carter</td>
<td>1.1</td>
<td>1.1</td>
<td>28.6°</td>
<td>61.4°</td>
</tr>
<tr>
<td>Region 3</td>
<td>1.1</td>
<td>1.1</td>
<td>28.3°</td>
<td>61.7°</td>
</tr>
<tr>
<td>Region 2a</td>
<td>1.1</td>
<td>1.1</td>
<td>28.6°</td>
<td>61.4°</td>
</tr>
</tbody>
</table>

Table 15 also contains the measurements from region 2a, which are shown in a partially indexed diffraction pattern in Figure 69. The more-intense spots are shown to match \(\alpha\)-Ti in the \([2\bar{1}\bar{1}0]\) zone axis. The less-intense spots appear to be from the \(\text{Ti}_3\text{Al}\) particles, which apparently precipitated during the nitridation. The simulated diffraction patterns for \(\alpha\)-Ti and \(\text{Ti}_3\text{Al}\) are shown in Figures 70 and 71.

\textbf{Figure 69.} Region 2a’s diffraction pattern, intense reflections match well with \(\vec{B} = [2\bar{1}\bar{1}0]\) for \(\alpha\)-Ti, however less-intense intermittent reflections also exist.
Figure 70. Diffraction pattern simulations from $\alpha$-Ti and Ti$_3$Al.

(a) Indexed DP of $\alpha$-Ti, $\vec{B} = [2\overline{1}10]$.  

(b) Indexed DP of Ti$_3$Al, $\vec{B} = [11\overline{2}0]$. [36]

Figure 71. Indexed diffraction pattern simulations.
The diffraction pattern for region 1a is shown in Figure 72. The simulated matches are superimposed in different colors. These simulations suggest the presence of both TiN and Ti$_2$N.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{diffraction_pattern.png}
\caption{Solved diffraction pattern from region 1a, sample 84$_{1\text{--}A1}$.}
\end{figure}
Figure 73 displays another diffraction pattern from a grain with ribbon-like features near the surface of the sample, similar to that of regions 2a and 2b. However, the region is not marked on the STEM image in Figure 66. The diffraction pattern reveals again the presence of twinned TiN with the 71° relationship. The diffraction pattern does not contain reflections indicating the presence of Ti$_2$N.

Figure 73. Solved diffraction pattern from ribbon-like grain, sample 84$_{1-A1}$. 
Bright-field and dark-field images are shown in Figure 74, which were taken from the region used for the diffraction pattern shown in Figure 73. The dark-field image shows better contrast, but does not seem to do much more than form an inverse image of the bright-field. This can be explained by referring back to the diffraction pattern in Figure 73. It can be seen that both g1 and g2 are positioned in such a way that a reflection is selected from both the primary and twinned TiN crystals. Ideally only one reflection would have been selected at g2 by shifting the objective aperture’s position, thus creating contrast between the TiN crystal and its twin. However, it was not known at the time of analysis that twinned TiN was the material under question. DF work was performed with the diffracted beam on-axis.

Figure 74. BF/DF imaging from ribbon-like grain in sample 841−A1.
A elemental map was created by ESI (electron-spectroscopic imaging) from the ribbon-like grain shown in the BF image in Figure 75a. The map, Figure 75b, shows a stronger nitrogen presence in the ribbon-like grain compared to the α-Ti grain.

Figure 75. Elemental map for nitrogen obtained by ESI, 84₁₋₁₆₁.

EELS spectra were created for regions 1b, 2a, and 3 from sample 84₁₋₁₆₁ (Figure 66), results are shown in Figure 76. An obvious nitrogen edge is present for the ribbon-like grain of region 1b, and slight edges are present for regions 2a and 3.

Figure 77 shows an EELS spectrum for region 1b, performed in the area predicted to have an increased carbon content by XEDS. However, an insignificant fraction of carbon is observed.
(a) Region 1b.

(b) Region 2a.

(c) Region 3.

**Figure 76.** EELS spectra showing the nitrogen edge at 397 eV, $\tilde{\text{A}}_{1}$. 
Figure 77. EELS results showing little carbon presence at 284 eV from region 1b of 84₁₋ₐ₁.

13.2. **Samples A₂₋ₑₑ and 10₁₂₋ₑₑ.** Samples A₂₋ₑₑ and 10₁₂₋ₑₑ were also analyzed with conventional TEM methods. Since sample A₂₋ₑₑ was only annealed, and no second phases were present on the surface, the lift-out was selected from a surface with normal characteristics. Figure 78 shows a bright-field image of A₂₋ₑₑ with regions used for diffraction work. The bright-field image reveals a few different distinguishable grains along with image artifacts, such as thickness and bend contours. As expected, the TEM results reveal nothing out of the ordinary—each diffraction pattern is identified as α-Ti. An LOM micrograph (Figure 39) of an etched portion of sample A₂₋ₑₑ shows that the β-Ti phase does indeed exist at the surface, but no β grains were found in the thin-foil constituting the TEM.
Figure 78. Diffraction patterns from different regions in sample A$_2$-ep.
The first lift-out sample from $101_2^{-ep}$ was used for diffraction work, but was then unfortunately damaged and lost. A second was then prepared, upon which diffraction work was repeated, as well as EELS work. Both lift-out samples were intentionally prepared from a nitrided surface without nitrides, and included at least 1 grain boundary on the surface as shown in Figure 79.

![Figure 79](image)

**Figure 79.** Representation of location used for lift-out samples from $101_2^{-ep}$. The shaded box, labeled Pt, indicates a region similar to those actually used for lift outs from $101_2^{-ep}$. In the lift-out technique, Pt (platinum) is deposited over the desired feature or region to protect it during ion milling. In the case of $101_2^{-ep}$, the desired area was a region free of visible nitrides at a grain boundary.

TEM work for the first lift-out from sample $101_2^{-ep}$ (Figure 80) revealed no curious ribbon-like grains at the surface. The few triangle-like shapes in grain 1 at the Pt/Ti interface are possibly a result of some stacking fault or twinning. The patterns are identified as $\alpha$-Ti and no evidence of any second phases is found.
TEM results from the second lift-out from sample 101$_{2-ep}$ are shown in Figure 81. Three grains are visible, grain 1 shows a number of curious shaped bend and thickness contours. The diffraction pattern from grain 1 was identified as $\alpha$-Ti, no evidence of any second phases was found in the diffraction patterns nor BF/DF imaging.

EELS was performed on the second lift out from sample 101$_{2-ep}$ in grain 1 shown in Figure 81a. The spectrum in Figure 82 shows an obvious Ti edge, but nothing at 397 eV to represent the presence of nitrogen.
Figure 81. TEM image and solved diffraction pattern of second lift out from sample 101$_{2-ep}$.

Figure 82. No nitrogen edge present at 397 eV, sample 101$_{2-ep}$.

Starting at the outermost surface on sample 84$_{1-A1}$, TEM methods confirmed the suspected nitrides to indeed be TiN and Ti$_2$N as anticipated. The 71° relationship of the TiN diffraction patterns indicates twinned grains. The Al-rich band below the nitrides was found to contain Ti$_3$Al and α-Ti. α-Ti was the only phase identified below the Al-rich band. EELS work confirmed a strong presence of nitrogen in the
nitride regions and small presence in a Ti$_3$Al-containing grain, as well as an $\alpha$-Ti grain, both below the nitride. Only the phase of $\alpha$-Ti was observed in the nitrided sample 101$_{2-ep}$ and the annealed sample A$_{2-ep}$. But, no edge for nitrogen was detected anywhere the $\alpha$-Ti case of the lift-out for 101$_{2-ep}$. 
Part 5. Discussion

Much understanding had been obtained by Lizhi Liu, Jason Blush, and Soenke Schmidt regarding the feasibility of kinetically-controlled titanium nitridation. Both Liu and Blush broke the ice on this project by showing theoretically and empirically the feasibility of this technique by two separate methods. Both reported obtaining nitrided samples without the formation of nitrides and exhibiting a (2–3) fold improvement in surface hardness. XRD was also implemented by both to estimate the lattice-parameter expansion. Schmidt made significant advances in XPS methods and began TEM work, but experienced difficulty in obtaining hardness improvement without the formation of substantial nitrides, especially in a ring-like pattern.\textsuperscript{[11,23]}

The most significant contributions made during this thesis have been a better understanding of reasons for premature nitride formation, ways to avoid it, and characterization of the diffusion affected zone by TEM and XEDS.

14. Mechanisms Affecting Premature Nitride Formation


In order for a secondary phase to form within a primary phase, the formation must be energetically favorable (a decrease in free energy). The total free energy change that takes place during the homogeneous formation of a second phase is described as

(8) \[ \Delta G = \frac{4}{3} \pi r^3 \Delta G_v + 4 \pi r^2 \gamma. \]

The term containing \( \Delta G_v \) represents the decrease in energy associated with the volume of the newly formed second phase. And the term containing \( \gamma \) represents the
increase in energy associated with the newly formed surface area. Figure 83 shows the contribution of each term to the total free energy change.

![Figure 83. Total free energy change associated with nucleation.][37]

It can be seen that a critical amount of energy (ΔG* or activation energy) is needed to form a nucleus of size r* to prevent the nucleated embryo from dissolving back into the primary phase. The nucleation rate is then dependent on the number of nuclei of critical size r*, and the capability of the required atoms to diffuse to the nucleus of size r*. The conditions described thus far have been for homogeneous nucleation, which is defined by the formation of a spherical nucleus within the primary phase. However, the formation of titanium nitrides on the surface of a sample is more accurately described by heterogeneous nucleation. The activation energy required for heterogeneous nucleation is less than that required for homogeneous nucleation. This is due to the decrease in the surface free energy term (γ) associated with nucleation on a surface. Other than this difference, the fundamental principles are the same between the two types of nucleation, in that the nucleation rate is dependent on the
ability to overcome the activation energy and that the diffusivity is high enough to supply the required atoms (both interstitial and substitutional) to the nucleus.

As heterogeneous nucleation occurs on a pre-existing surface, certain surface features can provide favorable conditions for nucleation compared to others. For example, the excess free volume associated with terraces, voids, high angle grain boundaries, and dislocations can reduce the surface free energy term $\gamma$—decreasing the activation energy ($\Delta G^*$) required, and thus increasing the probability of nucleation with radius of size $r^*$.\textsuperscript{[37–39]} Moreover, extended structural defects, such as dislocations and high angle grain boundaries, can act as channels through which rapid diffusion can occur, enabling quick supply of the needed atoms for nucleation.\textsuperscript{[40]}

Of the many conditions known to affect nucleation, three were investigated more so during this thesis, these being: structural defects and residual stresses, increased surface area per unit area of substrate, and diffusion-affecting crystallographic orientations.

14.2. **Structural defects and residual stresses.** The Ti–6Al–4V used in these experiments is known to be hot-rolled, mill-annealed, centerless-ground, cut, and mechanically polished. Each of these processes will in some way affect the density of dislocations and defects, and in turn, residual stresses. Extended structural defects, such as dislocations, have been known to significantly affect the rate of diffusing species into crystallographic structures. Akbulut, in a study regarding plasma nitriding of explosively welded Ti–6Al–4V, reported enhanced nitrogen diffusivity thought to be due to the increased dislocation density induced by the explosive welding process.\textsuperscript{[41]} Additionally, premature formation of nitrides and carbides in steels has been credited to the presence of dislocations introduced by cold working by a mechanism referred to as “trapping.” Trapping occurs when interstitial atoms jump into a defect which requires an increased amount of activation energy to jump to a defect-free site.\textsuperscript{[42]} Hirsch and Dornelles reported a decrease in the diffusion rate and diffusion
layer while nitriding steels in the presence of induced compressive residual stresses by mechanical polishing, as well as sand blasting. The compressive residual stress for the mechanically-polished state was estimated to be $-800 \text{ MPa}$, and that of the sand blasted samples between $(-1,000 \text{ and } -1,600) \text{ MPa}$. Also, diffusion tests on mechanically stressed samples (tension of $754 \text{ MPa}$ and compression of $-1,050 \text{ MPa}$) supported their initial claims by showing a $20\%$ increase in the diffusion layer for the sample stressed in tension.$^{[43,44]}$

Significant time was devoted to better understand the reasons for the formation of the ring-pattern of nitrides on the $0^\circ$ face of samples from supplier-1, while samples from supplier-2 formed a mostly random dispersion of nitrides on the same face. It was discovered through the literature and through contact with the Ti–6Al–4V suppliers that the mill-anneal of hot rolled Ti–6Al–4V can vary significantly from mill to mill. As stated by Lutjering & Williams,$^{[45]}$ the mill-anneal on Ti–6Al–4V is about $700^\circ \text{C}$ and can be held for “as short as 1 hour or as long as 8 hours.” The technical data from the mill source for supplier-1,$^{[46]}$ show that their mill-anneal varies between $\frac{1}{2} \text{ h}$ and 2 h with either an air or furnace cool. Supplier-2 was hesitant to reveal the mill from where their Ti–6Al–4V originated, but did say that the Ti–6Al–4V was mill-annealed for 2 h at 1300 F ($\approx 700^\circ \text{C}$) followed by an air cool, and then centerlessly ground to fall within tolerances. It is very possible that differences in the mill-anneal/quenching conditions and the parameters of the centerless grinding process affect the defect density and residual stresses. These in turn alter the nitridation behavior and specifically the ring-pattern nitride formation. For example, centerless grinding would introduce new defects and dislocations into the outermost tens of $\mu \text{m}$ of the circumferential face.$^{[43]}$ Differing quenching rates could create a residual stress gradient as the exterior of the sample would cool faster than the core.

The effect of in-house mechanical polishing (as described on page 26) on induced residual stresses and defects was also investigated. The diffractograms for samples from supplier-1 (Figure 32) show peak thinning as a result of annealing the sample
AR₁ (as-received mechanically polished face) for 259.2 ks at 850°C. This is most likely representative of the annealing out of dislocations. The strain fields of dislocations cause local compression and tension on the lattice parameter—hence the broadened peaks. Not only is peak thinning brought about by annealing, but also a slight peak shift to higher 2θ. Table 9 shows the peak shift brought about by mechanically polishing the surfaces of electropolished and annealed samples. The reason for this peak shift is due to residual compressive stresses induced during mechanical polishing. Feng reported compressive residual stresses as deep as 60 µm due to mechanical polishing in a study on compressive residual stresses on the Ti alloy TC4-DT (similar composition to Ti–6Al–4V).\cite{47} The compressive in-plane residual stresses (x and y directions) lead to an in-plane compressed lattice parameter, known as the Poisson effect. But, the out-of-plane strain (z-direction) at the free surface will naturally be expanded and detected by XRD as such. Holding the sample at elevated temperatures can anneal out the dislocations and relieve the compressive residual stresses, allowing the expanded out-of-plane strain to return to its stress-free plane spacing.

The conditions of electropolishing were measured to remove nearly 10 µm from the surface, thus allowing the removal of a substantial portion of the most damaged and strained region. If the peak position of the annealed or electropolished samples is considered a stress free state, the average strain in the z-direction can be estimated for the mechanically polished surface by the severity of the peak shift. By knowing the strain in the z-direction, the average residual stress present in the x or y directions can also be estimated from within damaged surface.

Hooke’s generalized law for strain in the z-direction (εz) is

\begin{equation}
ε_z = \frac{1}{E} [σ_z - ν(σ_x + σ_y)],
\end{equation}
where $E$ is the modulus of elasticity (114 GPa for Ti–6Al–4V), $\sigma$ is stress, and $\nu$ is Poisson’s ratio (0.34 for Ti-6Al-4V). Since $\sigma_z$ is 0, and $\sigma_x$ and $\sigma_y$ are equal to each other, equation 9 can be transformed to

$$\sigma_x = -\frac{E\epsilon_z}{2\nu}$$

to enable solving for the average in-plane residual compressive stress in the $x$ or $y$ directions. Figure 84 plots residual in-plane compressive stresses on the y-axis versus out-of-plane strain or peak shift to lower 2$\theta$ angles on the x-axis.

![Figure 84](image)

**Figure 84.** Residual in-plane compressive stresses as a function of out-of-plane strain.

Comparing the observed peak shifts from mechanical polishing in Table 9 with the plot in Figure 84 demonstrates the gradient of residual stress that exists from the outermost surface towards the core. For example, the average compressive residual stress within the outmost 6 $\mu$m (normal scanning conditions) is estimated to be less than 200 MPa, while from within the outermost 0.3 $\mu$m (glancing) the stress level reaches nearly 400 MPa, a little less than half of the yield stress of Ti–6Al–4V (855 MPa).
The anneals of A1 and A2 were implemented in an effort to eliminate the ring-pattern nitride formation. A2 is recommended by Welsch to obtain a more reproducible equiaxed structure compared to resultant microstructure following the mill-anneal—which can be “very dependent upon previous working.” Under similar conditions, the annealing of samples prior to nitridation (both electropolished, as well as only mechanically polished) seemed to have an effect of suppressing the formation of nitrides. This is slightly evident in a visual comparison, but more so in a comparison of hardness values from the center and the periphery of samples 83\textsubscript{1}, 84\textsubscript{1}−A1, and 85\textsubscript{1}−A2, shown in Table 6. Although the high error limits make definite conclusions difficult, it can be seen that the higher temperature anneal A2 (925 °C), performed on sample 85\textsubscript{1}−A2, had the effect of equalizing the hardness variation between the center and the periphery of the sample. Such an equalization of hardness values due to the anneal is also supported by the fact that the cross-sections of the α-Ti case in sample 85\textsubscript{A2} show a more-uniform thickness across the entire diameter of the sample than that of sample 84\textsubscript{1}−A1, and especially 83\textsubscript{1}. This more-uniform diffusion and suppression of nitride nucleation was initially believed to result from the annealing out of structural defects and residual stresses present in the sample from processing and mechanical polishing. But, a more in-depth look at the results and the annealing temperatures hints that residual stresses do not play such a large factor in premature nitride nucleation as originally suspected. Both samples 84\textsubscript{1}−A1 and 85\textsubscript{1}−A2 were mechanically polished prior to their respective anneals, leaving an in-plane compressive residual stress estimated to be near 400 MPa (Figure 84). According to Donachie,\textsuperscript{[33]} compressive residual stresses in Ti–6Al–4V are decreased to values lower than 50 MPa in as little as 3.6 ks (1 h) at 620 °C. This shows that A1 (14.4 ks at 725 °C) was more than adequate to limit any major effect of compressive residual stresses on nitride nucleation. Yet, sample 84\textsubscript{1}−A1 still exhibited a ring-like
pattern of nitrides and hardness variation between the center and the periphery similar to that of the un-annealed sample. This may be due to the fact that such stress-relief anneals still leave “traces of cold or warm working in the microstructures.”

The temperature of the higher anneal (A2) at 925 °C is above the recrystallization temperature of Ti–6Al–4V, temperatures for recrystallization anneals of Ti–6Al–4V are typically between (800 – 900) °C. The higher temperature, in the recrystallization zone, is believed to have substantially reduced the structural defects, allowing for a more-uniform nitridation.

Additional support indicating increased nitride nucleation in the presence of structural defects stems from increased nitride nucleation in the presence of the mechanically scratched regions, page 48. A problem associated with drawing conclusions from the scratch test lies in the fact that scratching the sample creates new surface features (edges), which possibly affect nitride nucleation as described in Section 14.3. The increased nitride presence within the Brinell indent of 7.4 kN compared to an area unaffected by the indent, as seen on page 49, also attests to the increased nitride precipitation in the presence of structural defects. The relatively large-radiused ball prevented odd surface features from developing as did during the scratching process. Although, another factor that could alter the premature nitride formation, besides the induced defects, is the texturing that is known to occur upon the application of stress in Ti–6Al–4V, as discussed on page 51.

The reason for the premature nucleation of nitrides in one region with respect to the other is believed to be strongly related the surface defects and dislocations introduced during the material processing and in-house mechanical preparation (high-speed cutting and mechanical polishing). The residual compressive stresses are not suspected to play a direct role in premature nitride nucleation. The structural defects provide surface sites not only with an excess of free volume (reducing the surface free energy

\[ \text{The term “excess free volume” is used to describe the cavity or emptiness associated with voids, edge dislocation cores, high angle grain boundaries, etc.} \]
term \( \gamma \) in Equation 8), but also with diffusion channels allowing for increased diffusivity. The increased diffusivity provided by the channels may explain the increased thickness of the \( \alpha \)-Ti case in regions of the sample exhibiting a higher volume ratio of nitrides. The channels would act not only as a diffusion path into the sample for the \( \alpha \)-Ti-stabilizing nitrogen, but also for the exiting vanadium atoms as the vanadium-rich \( \beta \)-Ti grains are overtaken by the \( \alpha \)-Ti grains. These defects were successfully removed by both annealing and more so by electropolishing—resulting in the suppression of premature nitride formation and the formation of an \( \alpha \)-Ti case with greater thickness uniformity.

14.3. **Increased surface area per unit area of substrate.** Proper conditions of time, temperature, and pressure allow the concentration of a diffusing species, such as nitrogen, to increase in solid solution, as the nitrogen atoms jump between octahedral sites\(^{[11,51]}\) until the maximum solubility limit is reached. At the elevated temperature of 860 °C, the maximum solubility level of nitrogen in \( \alpha \)-Ti is in the \((13 - 15)\) at% range. At such a point, thermodynamics predicts the precipitation of Ti\(_2\)N, as seen in the Ti/N phase diagram in Figure 85.

Diffusion modeling enables predictions of appropriate values for time, temperature, and pressure as to achieve the maximum concentration of nitrogen in solid solution while avoiding the precipitation of nitrides. Liu and Blush made significant advancements in predicting the nitrogen diffusion profiles in titanium alloys under kinetically-controlled conditions.\(^{[11,23]}\) However, the concentration estimates of the diffusing species are based on a model with an ideally flat surface. A common feature was observed in nitrided samples in this work, as well as that of others,\(^{[19]}\) where nitrides formed on 90°-facial intersections more so than on flat surfaces. The cross-sections of two separate nitrided samples are shown in Figure 12. Notice how the nitride phases in each sample grow thicker as the corner is approached. This feature is also evident in the plan-view of samples such as those shown in Figure 11.
The left side of Figure 86 shows how surface roughness or corners expose a greater surface area per unit area of substrate to the diffusing species. The corners, or tips of the peaks, then become likely regions for nitride nucleation as a higher flux of nitrogen at the surface will lead to premature saturation of nitrogen in solid solution.

Figure 15 and 16 illustrate a strong correlation of nitride growth along the abrasive cuts of the course-polished (35 µm grit size) side compared to the fine-polished side (9 µm grit size). A number of possible explanations exist for this observation. The
first relates to the increase in structural defects at the surface, as discussed in the previous section. The second has to due with stress-induced recrystallization to grain orientations favorable to nitride precipitation (see page 125). And the third could relate to the increased surface area per unit area of substrate caused by the coarse abrasive cut—leading to the increased nucleation of nitrides at protruding edges along the cut path. If rough surfaces indeed play a role in premature nitridation formation, it is no wonder that electropolishing prior to nitridation greatly reduces nitride formation. Recall that the $Ra$ value for an electropolished sample is almost half that of the mechanically-polished sample of 9 µm grit size. The difficulty in such a claim lies in the removal of the structural-defect-containing surface layer by electropolishing, in addition to the surface smoothing. Determining the extent to which the precipitation of nitrides is effected by protruding surface features, or structural defects can be challenging, as individual components can be intertwined with the others.

14.4. **Diffusion-affecting crystallographic orientations.** Minkwitz and Herzig researched carbon diffusion in $\alpha$-Ti comparing diffusion parallel and perpendicular to the $c$-axis, Figure 87. At 827°C, diffusion parallel and perpendicular to the $c$-axis yielded ($3.8 \times 10^{-14}$ and $8.8 \times 10^{-14}$) m$^2$s$^{-1}$, respectively. “The diffusivity parallel to the basal plane is remarkably faster than parallel to the $c$-axis.” [53] Foquet et al. also observed a measurable difference in the diffusion coefficient of nitrogen into $\alpha$-Ti, with results indicating faster diffusion in grains with the basal plane perpendicular to the surface being nitrided.[54]

OIM or EBSD was attempted on nitrided samples of CP-Ti and Ti–6Al–4V to understand more regarding nitride formation with respect to grain orientation. However, surface conditions brought about during nitridation, such as the roughness on the $\alpha$-Ti grains and especially on the nitrides, created undesirable conditions. The
increased roughness and stresses associated with nitrogen diffusion reduced the capability of generating Kikuchi patterns of high enough quality for accurate measurements or software recognition and phase matching. However, the texturing found in hot-rolled Ti–6Al–4V, as discussed in pages 51 through 56, was found to provide optimal conditions for obtaining information regarding this topic.

Considering that the fastest diffusion occurs on grains whose basal plane lies perpendicular to the diffusion surface, it should be expected to see a smaller concentration of nitrides on the 0° face compared to the 90° face and circumferential face. As the latter two favor a texture with the basal plane parallel to the diffusion surface. This stipulation assumes that all other major diffusion rate controlling variables are removed or suppressed by electropolishing. This premature nitride formation on the 90° and circumferential faces would principally be due to the build up of nitrogen at the surface caused by a lower inward flux of such orientations. The results, shown in
Figures 23 and 28, concord with this stipulation, as the circumferential and 90° faces more readily nucleated the nitrides than the 0° face.

Again, a major key to avoiding the formation of nitrides in kinetically-controlled titanium nitridation is to ensure that the inward diffusion of nitrogen is fast enough to prevent the build up of high nitrogen concentrations at the surface. This is accomplished by providing extremely small partial pressures at the substrate’s surface. Thus, a grain or a face of grains exhibiting a significantly slower rate of inward diffusion could very well permit such a build up of nitrogen concentration enabling the formation of the unwanted nitrides.\[11\]

It should be emphasized that this occurrence of unequal nitride formation on such faces was only obvious on samples that had been annealed for 14.4 ks at 925 °C (A2) or electropolished prior to nitridation. As mentioned above, these procedures are believed to reduce the effect of other diffusion-affecting variables.

Recall that the coarse-polished side of sample 83\(_1\) led to thicker nitride growth than the fine-polished side, Figure 15. A close look at the diffractograms of each side (Figure 88) reveals an impressively large \{0002\} peak on the scan representing the coarse-polished side. This was originally believed only to be due to the energetically favorable orientation allowing the c-axis to expand into free space, as the c-axis is known to expand more so than the a-axis.\[20\] After more closely analyzing the diffractograms representing a coarse and fine-polished face from an untreated sample, further insight was gained. Figure 89 shows that a much larger surface area fraction of basal planes parallel to the surface exists on the as-cut face, represented by the larger \{0002\} peak. Since such a large difference in texturing would not be expected in the same sample on parallel faces separated by only 2 mm, the increased presence of the \{0002\} peak is suspected to be caused by stress-induced recrystallization due to the stresses incurred during high-speed cutting and/or coarse-mechanical polishing compared to fine-mechanical polishing. Such stress-induced recrystallization appears to decrease the texturing caused by the hot rolling and create a condition more similar to
that found in an isotropic sample, Figure 26. So, the large \{0002\} peak seen in Figure 88 appears not only to be a factor of stress-induced recrystallization from the nitrogen diffusion, but also has a significant jump start from already present \{0002\} planes parallel to the diffusion face. The increased presence of these planes having been obtained by the stresses induced by mechanical deformation prior to treatment. The temperature of the nitridation (850 °C) does fall within recrystallization annealing temperatures used on Ti–6Al–4V, which are typically between (800 – 900) °C.\[45,50\]

![Diagram](image)

**Figure 88.** Growth of \{0002\} peak during nitridation on corse-polished versus fine-polished side, sample 831.

Note the presence of the \{0002\} peak on the fine-polished sides of all nitrided samples from supplier-1 (Figure 32). The exception to this observation is sample 851–A2, which shows no \{0002\} peak presence on the fine-polished side (Figure 32). It seems that the grains of alternate orientations overtook the grains whose basal plane lied parallel to the 0° face during the recrystallization anneal. However, the diffractogram for the nitrided coarse-polished side of 851–A2 does contain a significant \{0002\} peak similar in size ratio to that seen in the diffractogram for the as-cut sample (not nitrded) 88R1 in Figure 89. Indicating that no significant peak growth occurred on the coarse polished side during nitridation.
So, the high-speed cutting, or coarse-mechanical polishing introduces enough stress to cause significant recrystallization for the \{0002\} peak to more-strongly appear prior to nitridation (Figure 89). The continuation of mechanical polishing to smaller grit sizes can subsequently remove the highly damaged layer. Thus explaining the difference between the \{0002\} peak size for coarse and fine-polished sides (pre-nitridation). Take for example a sample that is nitrided with one coarse and one fine-polished side. After nitridation, the result will be a much larger \{0002\} peak growth on the coarse polished side. This being credited to the already present grains of such orientation and to the extra compressive residual stresses present in the coarse-polished side. These are believed to provide an additional driving force for recrystallization during nitridation—allowing the expansion of lattice parameter $c$ into free space. But, if samples are annealed prior to nitridation, such as $85_{1-A2}$, little, if any, \{0002\} growth will occur on the coarse-polished side and almost no presence will be found on the fine-polished side. This being due to the recrystallization suppressing the presence of such oriented grains, and the annealing away of the residual stresses. If samples are
electropolished prior to nitridation, the electropolishing will have removed the outermost 10 µm containing the highest residual stresses and defects. It will also have removed the mechanically polished stress-induced recrystallized grains with the basal plane parallel to the 0° face. The result, after nitridation, will be very little, if any, \( \{0002\} \) peak presence. This can be seen in Figure 37.

On samples from supplier-1, the increased presence of \( \{0002\} \) planes parallel to the surface on the 0° face on nitrided-coarse-polished samples is associated with a more-dense surface coverage of nitrides. This is evident in the diffractogram shown in Figure 88 and in the LOM images shown in Figure 15. This seems to support the observations of nitrides forming more quickly on faces with a higher texturing of basal planes parallel to the diffusion surface, as discussed earlier in this section. However, the opposite was observed in samples from supplier-2. Figure 16 shows a higher density of nitrides on the fine-polished surface, than that of the as-cut surface. XRD diffractograms of the fine-polished versus the as-cut surface show matching results to that of samples from supplier-1. That is, the increased presence of the \( \{0002\} \) peak after high-speed cutting or coarse polishing. XRD diffractograms (Figure 90) for the nitrided-sample 932, from supplier-2, also support the observation made on samples from supplier-1 (Figure 89), showing huge \( \{0002\} \) peak growth during nitridation on the as-cut side. But, as the LOM images reveal for samples from supplier-2, the diffractogram also shows a much larger volume fraction of nitrides on the fine-polished side compared to the as-cut side.

The observation of a higher volume fraction of basal planes parallel to the nitriding surface on samples from supplier-2 and the presence of fewer nitrides appears contradictory. It seems not only to contradict the observations made on samples from supplier-1, but also the hypothesis that grains exhibiting a slower diffusivity will have a higher chance of nucleating nitrides. If the increased precipitation of nitrides, such as observed in Figures 23 and 28, is not due to the texture itself, what are some other possibilities? One route worth investigating would be to electropolish the sample for
longer times, removing more material. Perhaps the centerless grinding operation performed after the mill-anneal is severe enough to introduce substantial defects below the 10 $\mu$m removed by current electropolishing conditions. The presence of these defects then increases the likelihood of nucleation on the circumferential face. But, this would not explain the observation shown in Figure 28, where a greater volume fraction of nitrides nucleated on the 90$^\circ$ face compared to the 0$^\circ$ face. Then again, the observation could be only a function of the samples having been nitrided in different ampoules at separate times. Conditions such as the ratio of the powder pack to sample surface area might not have been quite equal, or position of the powder pack in the center of the furnace was askew, despite best efforts.

Untangling the relationship between nitride nucleation and factors such as structural defects, surface area per unit area of substrate, and diffusion-affecting crystallographic orientations has proven to be challenging. The reasons for all observed behaviors and contradictions are not known at this time, but these observations surely show how sensitive nitride nucleation is to the defects and texturing introduced by
mechanical polishing—strongly supporting the reasons why electropolishing drastically improves uniformity.

If titanium nitridation is so sensitive to defects and texturing introduced by mechanical polishing, how is it that both Liu and Blush reported nitride-free samples with increased hardness and lattice parameter expansion? It is believed that each did obtain samples free of nitrides, that is according to the resolution of XRD. Every sample nitrided in this thesis\(^{14}\) that exhibited more than a 50% improvement in hardness was found to contain at least a hand-full of nitride spots. But, the volume fraction of these nitrides was not large enough to be detected by XRD methods used. See samples 83\(_1\), 84\(_{1-A1}\), 85\(_{1-A2}\), 107\(_{2-ep}\), and 110\(_{2-ep-A2}\) in section 9. It has been shown that high-speed cutting and coarse-mechanical polishing can greatly increase nitride nucleation compared to the fine-polishing. It is possible that the optimal samples obtained by Liu and Blush were prepared in a more delicate manner. Perhaps low-speed saws were used and less force was applied when polishing—limiting the defect density and recrystallization. Through conversation with Liu by telephone, it was learned that only a few button-shaped samples of Ti–6Al–4V were obtained with increased hardness and a nitride-free surface in his work. Liu also explained the difficulty encountered while nitriding longer tensile specimens, nitrides seemed to form more readily at the sample end closer to the powder, see Section 19. Contact with Blush was not made, nor were samples investigated from his work.

14.5. **Additional factors.** As has been discussed in this section, the formation of nitrides under kinetically-controlled conditions can be affected by a number of variables. Understanding these variables can be difficult as each one seems to be intertwined in someway with the others. Additional factors not discussed in this thesis may also play a role in nitridation behavior, such as grain growth (Figure 34), grain boundaries, changes in composition, and the transformation of $\beta$-Ti grains to $\alpha$-Ti grains as they

\(^{14}\)Electropolished samples included.
grow and saturate with nitrogen simultaneously. Interestingly, the diffusion rate in $\beta$-Ti is known to be higher than in $\alpha$-Ti.\textsuperscript{[20,54]} It is also known that as $\beta$-Ti grains grow, the vanadium content per grain volume decreases, which in turn increases the lattice parameter due to the larger atomic radius of Ti atoms.\textsuperscript{[55]} Such a peak shift is actually visible in Figure 37. From the as-received condition to the electropolished state, the $\beta$-Ti peak shifts to higher angles, indicative of the compressive residual stress relief. Then upon annealing, the peak shifts to lower values and grows in intensity as the lattice parameter and overall volume of $\beta$-Ti grains increase.

Another factor known to alter the surface conditions, and possibly the nitridation behavior, is the roughness known to develop during annealing, as well as nitridation. After 259.2 ks at 850 $^\circ$C, the average surface roughness increases three-fold to that of an electropolished surface. With nitrogen present, the average roughness increases almost five-fold by the end of the 259.2 ks treatment. Figures 20 and 21 illustrate nicely the faceted planes that seem to develop on certain grains at elevated temperatures while others remain relatively flat. The impact on diffusion behavior due to this increase in roughness developed during annealing is not known at this time. But, others such as Wallace have seen such correlations between nucleation on faceted planes.\textsuperscript{[39]}

Such factors as these may indeed play a role in affecting nitridation behavior as the movement of other atoms occurs simultaneously. However, these issues were not considered in depth in this thesis as results did not suggest their contribution to take precedence over issues such as structural defects, ratio of surface area per unit area of substrate, and grain orientation with respect to the diffusion direction.

15. Nitrogen in Solid Solution

Perhaps one of the most fundamental questions regarding this research is whether or not nitrogen is indeed the cause of the increased surface hardness, and formation
of the $\alpha$-Ti case. Numerous results indicate the affirmative. A number of these evidences are discussed in this section.

The results for sample A$_1$ (annealed without the activation of the nitrogen-containing powder pack) show a slight decrease in hardness (Table 6). This is attributed to the annealing out of dislocations from mill processing and mechanical preparations. The cross-section for sample A$_1$, shown in Figure 33, confirms that when no nitrogen is supplied from the powder pack, the $\alpha$-Ti case does not form. It is also evident that a relationship exists between surface hardness values and the temperature at which the nitrogen-containing powder pack CrN & Cr$_2$N/Cr is held during the nitriding process. Increased powder-pack temperature leads to a higher partial pressure of nitrogen, which leads to nitride formation (confirmed visually, as well as with XRD), a thicker $\alpha$-Ti case, increased surface hardness, and $\alpha$-Ti peak shifts to lower 2$\theta$ angles. A closer look at the peak shifts, changes in peak intensity, and peak appearance/disappearance aids in understanding the interaction of nitrogen with the Ti–6Al–4V sample.

XRD diffractograms for each set of samples show that following substantial nitridation, the $\beta$-peak disappears from the diffractogram as the $\alpha$-Ti case is formed in the outermost (10 − 20)$\mu$m. Since the majority of the data collected in the normal XRD scan stem from only the outermost (5 − 7)$\mu$m, only $\alpha$-Ti phases stabilized by the diffused nitrogen are present in XRD scans. This suggests that the inward diffusion of nitrogen ($\alpha$-stabilizer) transforms the $\beta$-Ti phase into $\alpha$-Ti. The disappearance of the $\beta$-Ti phase in the outermost surface is only observed when a substantial partial pressure of nitrogen is provided.

Significant peak shifts on a few samples in Figures 32 and 35 to lower 2$\theta$ positions are not observed for the $\{10\bar{1}0\}$ nor the $\{10\bar{1}1\}$ peaks, but appear to be evident for the $\{0002\}$ peak. This can be explained by an uneven lattice parameter expansion in the c-direction versus the a-direction.[56] Utilizing nuclear reaction techniques, Bars
reported that the addition of 9 at% nitrogen in α-Ti caused a c-direction expansion of almost 5 times that of the a-direction.\textsuperscript{[20]}

It can be seen in samples bearing the \{0002\} peak, such as 109\textsubscript{2−ep}, 83\textsubscript{1}, 84\textsubscript{1−A1}, 93\textsubscript{2}, and 109\textsubscript{2−ep}, that a larger shift does occur in peaks bearing the c-axis. The quantification of this shift has a large deviation due to the less-than-desirable method of performing XRD scans with the sample elevated on a clay mount, but does seem to fall close to work by Bars. For example, by measuring the shift of the \{0002\} peak for sample 109\textsubscript{2−ep}, the expansion in the c-direction is calculated to be \((8 − 16) \times 10^{-4}\) nm. The calculated a-direction lattice parameter expansion from the \{10\textsubscript{10}\} peak shift from the similarly treated sample 101\textsubscript{2−ep} lies between \((1 − 5) \times 10^{-4}\) nm. Comparing the mean values yields a c-direction expansion of four-times that of the a-direction, slightly less than that observed by Bars. The discrepancy could very well be from the large deviation, as well as the fact that the two samples were treated in separate ampoules where the slight differences in positioning of the powder in the hot zone of the furnace can cause deviation in the generated partial pressure. Another reason could relate to the lower diffusivity perpendicular to the basal plane, as the c-direction lattice expansion measurement is made on grains whose basal plane lies parallel to the surface.

Table 16 compares the \{10\textsubscript{10}\} peak shift with the expansion of lattice parameter a, nitrogen fraction, and Vickers hardness for unalloyed α-titanium, table information from Bars \textit{et al.}\textsuperscript{[20]} A quick comparison can be made of the lattice parameter expansion of α-Ti in Ti–6Al–4V in this work to that of CP Ti in work of Bars. Sample 93\textsubscript{2} exhibits a \{10\textsubscript{10}\} peak shift of \(-0.10° \pm 0.03°\), which means, according to Table 16, an expansion of lattice parameter a of just over 0.2% and hardness of almost 600HV100. Table 7 shows the measured average surface hardness to be 615HV50. Measurements with the higher load of 0.980 N (100 gf) were also performed, yielding an average of 575HV with a standard deviation of 50 and a sample size of 5. Results for 93\textsubscript{2} appear to fall in line with the work performed by Bars \textit{et al.} but other samples do not follow
as closely. For example, the peak shift of \{10\overline{1}0\} for sample 101_{2-ep} is measured to be \(-0.04^\circ \pm 0.01^\circ\), which according to Bars should contain near 3.6 at% nitrogen and have an average Vickers hardness of 480HV100. Five hardness measurements with a 0.980 N (100 gf) load yielded an average of 660HV and a standard deviation of 72.

The calculated at% of nitrogen by XPS on 101_{2-ep} is seen in Table 14 to be 9 at%. Again, the deviation in XRD peak position may be a factor, but the differing nitriding methods and alloys between this work and that of Bars should also be remembered (Ti–6Al–4V and gas nitridation versus and plasma and commercially pure titanium, respectively).

Table 16. Comparison between peak shift, lattice parameter expansion, at% nitrogen, and hardness (HV100) according to Bars et al.\textsuperscript{[20]}

<table>
<thead>
<tr>
<th>{10\overline{1}0} Peak Shift (2\theta)</th>
<th>% Increase latt. par. (a)</th>
<th>at% (nitrogen)</th>
<th>HV100</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.01</td>
<td>0.05</td>
<td>0.1</td>
<td>230</td>
</tr>
<tr>
<td>-0.04</td>
<td>0.10</td>
<td>3.6</td>
<td>480</td>
</tr>
<tr>
<td>-0.09</td>
<td>0.20</td>
<td>4.8</td>
<td>590</td>
</tr>
<tr>
<td>-0.14</td>
<td>0.35</td>
<td>6.0</td>
<td>700</td>
</tr>
<tr>
<td>-0.20</td>
<td>0.50</td>
<td>8.0</td>
<td>890</td>
</tr>
<tr>
<td>-0.23</td>
<td>0.55</td>
<td>9.1</td>
<td>–</td>
</tr>
<tr>
<td>-0.26</td>
<td>0.60</td>
<td>12.5</td>
<td>–</td>
</tr>
</tbody>
</table>

Nano-hardness results shown in Figures 42, 44, 45, and 46 provide an important insight regarding the inward diffusion of nitrogen into the sample. Each plot, for non-electropolished samples, shows that only a slight nano-hardness slope is found in profiles from regions absent of nitrides. Although LOM cross-sections reveal the presence of some \(\alpha\)-Ti case, the nitrogen content is not sufficiently high to make a significant impact. The plots also show that profiles from below (or near) a nitride have slopes that support a two-fold increase in hardness in the \(\alpha\)-Ti case prior to reaching the nitride region. This seems to suggest that nitride formation occurs on surfaces above regions where the nitrogen concentration in solid solution has surpassed its solubility limit. Extended structural defects, such as dislocations, are thought allow the rapid inward diffusion of nitrogen in such regions. The excess free volume associated
with the structural defects at the surface could also facilitate the nucleation of nitrides. The nano-hardness plot for the electropolished samples (Figure 46) shows that almost a three-fold improvement can be obtained in the $\alpha$-Ti case with very little nitride formation. The removal of structural defects and the surface uniformity brought about by electropolishing appear to allow a more uniform increase in nitrogen concentration across the surface of the sample. For example, assume an electropolished sample and a non-electropolished sample with grain orientation of similar diffusivity are nitrided under the same conditions until complete nitride coverage occurs. The time window in which 100% of the surface would be covered with nitrides would be much shorter for the electropolished sample as each grain or region would reach its maximum solubility of nitrogen relatively at the same instance. In contrast, the non-electropolished and less-uniform sample would begin nitride formation earlier, and the time window of 100% coverage would be longer.

It was pointed out in Section 11 that the Ti-L$_\alpha$ peak, just under 0.5 keV, is substantially larger in regions known to bear nitrogen (when the Ti-K$_\alpha$ peaks from each region are normalized with each other). This being due to the presence of the N-K$_\alpha$ peak at 0.39 keV. However, even with the Ti-K$_\alpha$ peaks being normalized with each other, the Ti-L$_\alpha$ peak for the $\alpha$-Ti case (no nitride present) shown in Figure 54 does not appear to be measurably larger than that of the $\alpha$-Ti grains from the core. Nevertheless, the fact that the a significant height difference is observed comparing nitride regions to non-nitride regions is qualitative evidence that nitrogen is present in the sample. As mentioned earlier, the XEDS is not capable of accurately separating the N-K$_\alpha$ and the Ti-L$_\alpha$ due to the broad overlap of relevant peaks.

One of the strongest sources witnessing to nitrogen in solid solution are the XPS results (page 89). Results indicate that nitrogen is introduced into the Ti sample during the nitridation process. Higher pressures, such as those used on sample 43$_1$, showing the formation of a visible gold or brown-colored surface, yielded nitrogen concentrations expected by a combination of TiN and Ti$_2$N phases. Samples nitrided
with lower pressures (101$_{2−ep}$ and 110$_{2−ep}$) that were analyzed from nitride-free regions resulted in nitrogen atomic percentages of (9 and 4) at%, respectively.

Considering the observation of hardness improvement, $\alpha$-Ti peak shifts to lower 2\(\theta\), disappearance of $\beta$-Ti peaks, formation of nitrides, qualitative and quantitative detection of nitrogen with XEDS and XPS all due to nitridation, nitrogen is determined to have been introduced into the sample in sufficient quantity, and in solid solution. However, EELS did not confirm these results.

The EELS results presented in Section 13, starting on page 105, show that nitrogen edges are recognizable for regions 2a (Ti$_3$Al) and 3 ($\alpha$-Ti), from sample 84$_{1−A1}$, see Figure 66. But, EELS results seen in Figure 82 from region 1 ($\alpha$-Ti) of sample 101$_{2−ep}$ show no nitrogen edge. The small nitrogen edges in regions from sample 84$_{1−A1}$ and the lack of an edge for sample 101$_{2−ep}$ are surprising, as nano-hardness tests performed on each of these samples yielded more than a two-fold hardness improvement in similar areas, see Figures 42 and 46.

Consideration must be given to the conditions of the ion milling, as well as the TEM analysis. Could it be possible that unwanted nitrogen diffusion occurs from the specimen into the instrument’s vacuum as the sample is consequently heated and altered during ion milling and TEM analysis. The conditions may be such that the nitrogen in solid solution departs a significant amount by the time EELS spectra is performed. The possibility of this nitrogen exodus being credited to merely diffusion can be quickly estimated from

\[ d = \sqrt{Dt}. \]  

In order for a diffusion distance \(d\) of 10 nm, a time \(t\) of 10 ks (2.7 h) at 500°C would be required \((D = 10^{-16} \text{cm}^2/\text{s})\). But, temperatures incurred during ion milling on stainless steel samples are known to not exceed 200°C during typical milling
conditions.\[58\] TEM irradiation is believed to raise the sample temperature no more than \((10 - 20) ^\circ C\) while operating under 300 keV. However, Stratton et al. and Kaoumi et al., credit grain growth observed during TEM analysis on amorphous Al alloys and Zn-Fe alloys not to temperature rise, but rather to what is termed as “knock-on collisions” or “collisional processes.” The energy transfer from the imaging electrons and the sample is thought to be great enough to cause atomic displacement. The possibility of “collisional processes” reducing the concentration of nitrogen within the TEM should be investigated further as to conclude whether the absence of nitrogen observed by EELS in the nitrided thin-foil is due to analysis conditions.\[59,60\]

This explanation of nitrogen being lost out of solid solution during TEM analysis is not supported by Moskalewicz\[61\], who reported (14-16) at\% of nitrogen in \(\alpha\)-Ti in solid solution by EELS. Also, the Tecnai F30 TEM was used to perform EELS on a lift-out sample (supposedly from the \(\alpha\)-Ti case) from previous work on this project (by Schmidt), results are shown in Figure 91. An obvious nitrogen edge exists, but no diffraction work was found with these results confirming the location of the EELS to be \(\alpha\)-Ti. EELS was not attempted on the Tecnai during this thesis due to technical problems associated with the instrument at the time the research was being carried out.

16. Contamination and other Phases Formed

16.1. Carbon contamination. It was pointed out on page 88 that increased carbon content was detected in plan-view and cross-sections of nitrides compared to other phases.

The \(\delta\)-phase of TiC has the same crystal structure and space group as \(\delta\)-TiN, and a lattice parameter within a 2% match. Restrepo\[62\] reported the precipitiation of mentioned TiC and TiN in the same crystallographic orientation during plasma carbo-nitridation. Restrepo was able to deconvolute the overlapping TiC and TiN XRD peaks (TiC at lower 2\(\theta\) angles). But, such a procedure is not possible on
Figure 5: EELS spectrum from N Ti–6Al–4V processed at \( T_s = -33 \) Kx. The sample was prepared by FIBv and the spectrum was recorded from an area close to the specimen edge. The absorption edges of nitrogen and titanium are clearly visible.

The processing scheme was improved significantly by applying a higher temperature to the specimen without changing the temperature of the powder packs. Our results indicate that the diffusivity of nitrogen increases faster with increasing temperature than the impingement rate of nitrogen on the specimen surface. Accordingly, increasing the specimen temperature needs to result in larger case depths and shorter times without increasing the likelihood of nitride precipitation.

The threefold increase of the case depth we have accomplished makes the nitridation under kinetic control even more attractive for technical applications. First experiments were successfully carried out to study the effect of nitridation on the surface topography the hardness–depth profile. Apparently, nitridation induces a substantial increase in surface...

Figure 91. EELS work on sample prepared by Schmidt, supposedly from the \( \alpha \)-Ti case. EELS performed on Tecnai F30.

samples produced in this work due to the relatively small presence of TiN, let alone TiC (if present). Even on samples with significant TiN peaks, such as 90x (Figure 92), evidence of a the \{111\} TiC peak is not found within the \{111\} TiN peak (2\( \theta \) 36.7\( ^\circ \)) as in Restrepo’s work.

If the increased carbon presence is indeed a factor of the existence of TiC, or a form of a titanium carbonitride, it is not supported by XRD, nor EELS from the nitride region. The lack of a carbon edge at 284 eV in Figure 77 suggests the extra carbon detected by XEDS to be from contamination rather than as a phase such as TiC.

Following nitridation, each sample was exposed to contaminants during high-speed cutting (to make cross-sections), either by the high-speed cutting fluid, or by protectant tape. Tape was used in an effort to protect the nitrided surface during the
cutting process. The cutting fluid and the residue of the tape may not have been removed sufficiently during the acetone and ethanol ultra-sonic cleaning. Samples were also stored in plastic bags where the sample surfaces would have rubbed with the bag interior. But, neither the tape nor the bag would have the capability of introducing carbon so uniformly around the periphery of the nitride as seen in Figure 59. Neither would it be logical to assume the increased carbon presence detected below the surface (from the cross-section) in the nitride to be caused by either of these sources. The source of the carbon detection may lie in the porosity of the nitride. Figures 21, 14a, 14b, and 65b show the increased roughness and porosity of the nitride compared to $\alpha$-Ti. The porosity could very well be a trap for the cutting fluid, as well as carbon available in atmospheric conditions.

16.2. **Titanium nitrides.** The precipitated spots on the surface of the Ti–6Al–4V substrate that are known to eventually cover the entire surface under proper conditions of time and temperature were always assumed to be titanium nitrides due to their color, hardness, and representative peaks identified by XRD. XEDS results also show an increased amount of nitrogen in the suspected nitride regions. Even the XPS
results showing 40 at\% of nitrogen in sample 43 seem to be in line with the expected nitrogen at\% of a surface coating composed of TiN and Ti$_2$N. But, TEM provides the most in accurate identification of the precipitated titanium nitrides.

The ribbon-like grains of titanium nitrides are very interesting, much time was spent in searching for a similar observation in the literature, but nothing quite like it was discovered. However, the finding of Ti$_2$N and TiN together is an occurrence typically observed in many different types of titanium nitridation. Diffraction work on 97 shows that region 1c contains only TiN, while regions 1a and 1b contain TiN and Ti$_2$N. This is a possibility as Ti$_2$N will eventually give way to TiN if enough nitrogen is available. Or it may simply be due to the area of the grain selected. Perhaps if a larger SAD aperture were used, the greater volume analyzed would show reflections from Ti$_2$N. The smallest aperture (OD of 200 µm) was implemented in this case as to select only the grain with ribbon-like features.

The twinning in FCC crystal structures, starting on page 102, is a common occurrence, neighboring grains interface with each other on the \{111\} densely-packed plane and a 71° rotational relationship. Han and Weatherly observed this type of twinning in titanium carbonitride (Ti(C,N)).\cite{63}

16.3. **Aluminum-rich band.** XEDS full-spectrum maps and line scans in Section 11 reveal the Al-rich zone below the nitride. The precipitation of Ti$_2$N and TiN appears to expel aluminum to the nearest grain boundary, when a high enough at\% is reached, the precipitation of Ti$_3$Al then occurs. According to the Ti-Al phase diagram shown in Figure 93, at 850°C both Ti$_3$Al and α-Ti are present between (16 and 22) at\% Al. XEDS quantified values from the Al-rich band were found to be 19 at\% Al, 77 at\% Ti, and 5 at\% vanadium, with a standard deviation of less than 1 % for each element, and a sample size of 5.

It is assumed that region 2a and possibly region 3 in Figure 66 fall within the Al-rich band. Such Al-rich bands have been observed by Rolinski and Ponticaud underneath
nitrides during titanium nitridation.\cite{13,64} According to Donachie, precipitation of Ti$_3$Al has been known to occur in a special orientation relationship (ordering) with the α-Ti phase.\cite{33} Page 100 shows the diffraction pattern from region 2a, which matches nicely with the [1120] zone axis of Ti$_3$Al and the brighter spots match nicely with the [2110] zone axis of α-Ti. Ti$_3$Al has a DO$_{19}$-type crystal structure, which is a structure with the P6$_3$/mmc space group. The difference between the DO$_{19}$ structure and HCP (α-Ti) is very small. As shown in Table 17, the lattice parameter $c$, for each phase, falls within 0.5% of each other. If the lattice parameter $a$ of α-Ti is doubled, it falls within 0.1% of lattice parameter $a$ for Ti$_3$Al. These conditions allow for the precipitation of Ti$_3$Al within the α-Ti matrix, producing diffraction patterns such as those found in Figures 69 and 70. The faint intermittent reflections are a result of the lattice parameter $a$ in Ti$_3$Al being double that of α-Ti. Indexed patterns of the zone axes of [2110] and [1120] for α-Ti and Ti$_3$Al (respectively) are found in Figure 71.

<table>
<thead>
<tr>
<th>Phase</th>
<th>$a$ (nm)</th>
<th>$c$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-Ti</td>
<td>0.2925</td>
<td>0.4670</td>
</tr>
<tr>
<td>Ti$_3$Al</td>
<td>0.5792</td>
<td>0.4648</td>
</tr>
</tbody>
</table>

The size of the Al-rich band, shown in Figure 51b, suggests that region 3 from Figure 66 to be Al-rich as well. Diffraction work, shown in Figure 68, indicates the region to be α-Ti in the [2110] zone axis. BF/DF work was attempted on the Ti$_3$Al-containing grain, labeled 2a, in hopes of identifying the grain as purely Ti$_3$Al or a mixture of Ti$_3$Al and α-Ti. However, the BF/DF did not detect any obvious second phase. This could be an indication of the grain being a single crystal of Ti$_3$Al, or be due to the high coherency that exists between α-Ti and Ti$_3$Al. The fact that region 3 most likely falls within the Al-rich band and was identified as α-Ti with an orientation perfectly coherent to that of the orientation of Ti$_3$Al in region 2a, it is suspected that 2a is a single crystal of Ti$_3$Al precipitated in the Al-rich α-Ti. But,
this would have to be verified with additional TEM diffraction and BF/DF work, taking better note of sample tilt and the orientation relationship between the two regions. Also note that the position of the two grains identified as Ti$_3$Al (2a and 2b) are butted up with the nitride layer where the Al concentration would be the highest, promoting the transformation from Al-enriched $\alpha$-Ti to Ti$_3$Al.

An alternate explanation may be found as to why the nitrogen edge is not as strong as expected for regions 2a, shown in Figure 66. Ponticaud et al. estimated an Al-enriched zone below the nitride region to contain 25 at% Al. Their work did not identify the phase, but did quantify the Ti, Al, vanadium, and nitrogen with EPMA for each phase. Their results show near 40 at% nitrogen in the nitride zone, then abruptly dropping to below 5 at% nitrogen in the Al-rich zone. Upon resuming to the region below the Al-rich zone, the nitrogen jumps upward to 25 at% nitrogen. A definite answer is not given on how such a nitrogen gradient could be possible, speculation is made, however, that it could deal with porosity in the Al-rich phase, or that the phase is not continuous throughout. The Al-rich band found by Ponticaud contains an estimated 25 at% Al, which, according to the Ti-Al phase diagram, would contain only Ti$_3$Al. The Al-rich band in this work is estimated to contain slightly under 19 at% Al by XEDS, which falls within the two-phase region of both $\alpha$-Ti and Ti$_3$Al. The differences in composition are reasonable as the partial pressure of nitrogen used in the work by Ponticaud was recorded to be between (10$^4$ and 10$^5$) Pa compared to the 10$^{-4}$ Pa used by Blush and estimated by Liu for the nitridation method used in this work.$^{[11,13,23]}$ Such high pressures would have the tendency to form much thicker nitrides, expelling more Al, and thus creating a continuous Ti$_3$Al phase. Hence, the lack of a nitrogen edge in region 2a could very well be supported by Ponticaud’s work. But, this would still not explain the lack of a nitrogen edge on sample 101$_2$-ep (page 110), which was performed in the $\alpha$-Ti case from a region absent of nitrides. Nor does it answer all the questions regarding the lack of a significant nitrogen edge from region 3, which does not contain Ti$_3$Al.
Figure 93. Ti-Al phase diagram. [65]
Part 6. Conclusions and Future Work

17. Conclusions

The work in this thesis has made critical advancements toward making kinetically-controlled nitridation an applicable engineering process. The experiments and analytical work carried out during this project proved very successful in better understanding reasons for non-uniform nitride formation. Procedures such as pre-annealing and electropolishing aid in suppressing the formation of unwanted nitrides. Methods such as hardness testing (micro and nano), XRD, XEDS, XPS, EELS and TEM have provided a greater understanding of phase transformations during the nitridation process and changes in microstructure due to the heat treatment and induced nitrogen.

A strong relationship between premature precipitation of nitrides in one region with respect to another was found to correlate to one or more of the following: structural defects, surface area per unit area of substrate, and diffusion-affecting crystallographic orientations. Differentiating between them proved to be the most challenging aspect of the project. Nevertheless, results support increased nitride nucleation in the presence of structural defects. Texturing developed during mill processing was found to favor the orientation of the α-Ti unit cell with the basal plane parallel to the rolling-direction. Faces parallel to the rolling-direction were found to saturate with surface nitrides more quickly than those perpendicular to the roll direction. Regions with the increased ratio of surface area per unit area of substrate, such as intersecting faces were also found to encourage premature and increased nitride precipitation.

The most effective nitridation conditions were obtained by electropolishing the Ti–6Al–4V sample prior to nitridation. Electropolishing enabled removal of the structural defects introduced by processing, cutting, and mechanical polishing, in addition to creating a more-uniform surface. These factors suppressed the premature nucleation of nitrides and eliminated the previously observed ring-pattern formation of nitrides. The thickness of the nitrogen-stabilized α-Ti cases ranged between $(10 − 30) \mu m$, 
depending on the partial pressure of nitrogen. The improvement of surface hardness was found to be (1.5−2.5) times the initial value of 350HV50. Nano hardness profiling showed a (2−3) times increase in hardness within the outermost 5µm. The volume of precipitated nitrides on few of such samples (1072−ep and 1102−ep−A2) was below the threshold to enable detection by XRD methods. According to the XRD peak shift to lower 2θ angles on nitrided samples, lattice parameter expansion of α-Ti in the a-direction was estimated to be near 0.3%. The composition of the α-Ti case was found to be within a few at% of nominal values by XEDS methods.

The precipitated nitride spots were found to be composed of twinned TiN in conjunction with Ti2N by TEM diffraction work. An Al-rich band composed of α-Ti (rich in Al) and precipitated Ti3Al was discovered under each nitride as a result of expelled Al from the region of nitride growth. The Al fraction was estimated to be just under 20 at%.

Even though XRD methods used in this work were not able to detect precipitated nitrides on optimal samples, due to their small volume fraction, surface nitrides were detected with LOM on every nitrided sample that exhibited significant α-Ti hardness improvement. It is understood that samples nitrided by Liu and Blush also contained similar characteristics. Thus, despite the critical advancements made in this work with regard to avoiding non-uniform nitridation, the kinetically-controlled nitridation process is not yet ready for engineering applications. However, promising results obtained by electropolishing and annealing prior to nitridation, samples such as 1072−ep and 1102−ep−A2, suggest that continued research will enable the process to arrive to such a point. The kinetically-controlled nitridation method has progressed substantially and remains full of potential for future research.

18. Future Work

Listed below are a number of the most promising aspects of kinetically-controlled titanium nitridation ready for research:
(1) OIM. A greater understanding of nitride formation on grains of various orientations could be studied in a fairly simple manner by pre-annealing a CP-Ti sample. The CP-Ti would simplify the experiment by reducing the pre-existing phases to only $\alpha$-Ti. The pre-anneal would allow for grain growth to stabilize, and thus easier identification of grains and grain orientation via OIM before and after nitridation. After the annealing, mechanical polishing and electropolishing would be performed to prepare the surface for OIM work. Nitridation would then take place, just long enough to commence precipitation of nitrides on a limited number of grains. The shorter nitridation time would also prevent excessive surface roughness, which is known to limit the ability to recognize Kikuchi patterns in EBSD mode. The nitrided sample would then have OIM work performed on it in the same region used prior to nitridation. A better understanding of diffusivity and nitride formation on grains of different orientations is necessary for the end goal of this project—nitrogen in solid solution, without the formation of nitrides.

(2) Much understanding could be obtained by performing XRD scans on electropolished samples having been nitride for increasing time intervals. Times in this work on electropolished samples were maximized at 259.2 ks, but continuation would enable a more-detailed observation of the preferential disappearance of certain $\alpha$-Ti peaks to form Ti$_2$N and TiN peaks. This would add evidence in identifying which grains orientations promote the premature formation of nitrides.

(3) A greater understanding of the the twinned TiN, Ti$_2$N, and Ti$_3$Al (Al-rich band) should be obtained by additional investigation with TEM techniques. The knowledge extracted from the initial TEM work presented in this thesis will greatly facilitate further investigation. Particularly in knowing which reflections to use for best phase contrast in BF/DF on the twinned TiN grains, as well as Ti$_3$Al.
(4) Experiments could be carried out to show whether or not suspected interstitially dissolved nitrogen diffuses out of the TEM specimen during TEM irradiation. A region such as that of region 3 in Figure 66 that is known to have a small nitrogen edge could be irradiated with the electron beam for a set time, then quantified again. This step could be repeated as desired.

(5) Experimentation with different annealing and quenching parameters at temperatures above the β-transus temperature would be ideal as to eliminate texturing and residual stresses from mill processing and mechanical polishing prior to nitridation.

(6) Electropolishing parameters could be optimized as to most efficiently remove the damaged surface layer.

(7) Much room for optimization of nitriding parameters exists, for example, shorter times and higher nitrogen partial pressures showed promising results on sample 811–ep. Another region worth investigating would be nitriding with a decreasing powder-pack temperature as a function of time. Successful samples were reported by Liu by using such a method.[11]

(8) Further understanding could be gained regarding the effect of the ratio of surface area per unit area of substrate by masking one of the intersecting faces prior to nitridation with a platinum deposit.

Once (and if) the process arrives to the desired successful state, additional testing of corrosion, fatigue, friction, impact, tensile, compression, and others should be undertaken.
Appendix 1
Additional Experiments and Observations

19. Partial Coverage

Prior to performing the actual nitridation experiments, as discussed in the main body of this paper, a number of practice runs were performed to get accustomed to the encapsulating and heat-treating equipment. These practice runs were performed in ampoules of around 25 cm in length. Figure 94 shows an illustration representing the sealed ampoule with the powder pack in one end and the Ti–6Al–4V in the other, no Ti-getters were used.

![Figure 94. Components of a practice amoule.](image)

Practice ampoules were nitrided by placing the entire ampoule in a single furnace with the Ti–6Al–4V at the center. Nitridation times typically varied from $(0.6-36)$ ks, but the sample was always held at $850^\circ$C. This temperature was selected to intentionally provide a high enough partial pressure to form visually detectable nitrides. Tests were performed with various powder quantities ranging from $(0.1-8)$ g using a 1:1 ratio of Cr$_2$N to Cr, the Cr$_2$N was provided through Princeton Scientific. As with latter experiments, ampoules were backfilled with ultra high purity argon twice and subsequently evacuated, however some practice samples were backfilled with argon a third time to a pressure estimated to be just below atmosphere, then sealed. These practice runs proved beneficial in mastering the encapsulation process,
testing the heat treating equipment, selecting an adequate powder quantity, and identifying the condition under which curious nitride-formation behavior occurred.

The very first samples encapsulated were only nitrided for 0.6 ks (10 min) or less, removed from the furnace and then quenched in air or water (without breaking the ampoule). Upon cooling, a gold-colored surface was observed on the portion of the sample closest to the powder pack as illustrated in Figures 94 and 95.

![Figure 95. Partial coverage of gold coating, nitrided 0.6 ks (10 min), sample 28₁.](image)

A simple experiment was performed in order to determine whether the gold-colored precipitates occurred due to orientation with respect to the powder, or some feature in the sample itself. An ampoule was prepared and nitrided for a few minutes, after the golden color was observed upon cooling, the ampoule was agitated such that the sample rotated about 90° from its original position. The ampoule was replaced in the furnace and removed after a few more minutes. The original gold region had since begun to fade and a new region (closest to the powder) had formed.

Hardness values were performed on both the gold-colored and titanium-colored sides of sample 28₁, at least a 25% increase was observed for both sides. The results, shown in Table 18, do not support a significant hardness difference between sides under the testing conditions of a 0.980 N (100 gf) load. This is assumed to be due
to the small nitridation time of 0.6 ks not allowing the growth of a sufficiently thick phase to affect the hardness with such a load. At the measured hardness values, the depth of the diamond indent would be about 4 μm.

Table 18. Vickers hardness (HV100) for distinct regions of sample 28₁.

<table>
<thead>
<tr>
<th></th>
<th>Gold colored</th>
<th>Titanium colored</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average</td>
<td>441</td>
<td>435</td>
</tr>
<tr>
<td>Standard Dev.</td>
<td>15</td>
<td>20</td>
</tr>
<tr>
<td>Sample Size</td>
<td>5</td>
<td>5</td>
</tr>
</tbody>
</table>

XRD and XPS work was performed on both the gold and titanium-colored sides of sample 46₁, which was nitrided for 27 ks (7.5 h). Sample 46₁ was cut in such a way that the cut faces lied perpendicular to the length of the ampoule. This orientation led to the formation of the golden color on the cut and circumferential faces closest to the powder pack as seen in Figure 96. Notice the defined transition from the golden color to the titanium color on the circumferential face.

Figure 96. Partial coverage of gold coating, nitrided 18 ks (5 h), sample 46₁.

In addition to α-Ti phases, the XRD diffractogram for the gold side of sample 46₁, seen in Figure 97, shows a strong presence of {111} planes for ε-Ti₂N at 2θ of 39.3° as well as a noticeable presence of {200} ε-Ti₂N and {111} TiN at 2θ (36.3 and
36.7)° respectively. The diffractogram for the titanium-colored side does not reveal any obvious TiN peaks, but perhaps has a small presence of ε-Ti$_2$N indicated by the small peak just under 2θ 39.5°. Keep in mind that under glancing conditions only the outermost 0.3 µm provides 95% of the collected data. This suggests that despite the new phases present on the surface of the golden side, a sufficient amount of α-Ti exists within the outermost 0.3 µm to form recognizable α-Ti peaks.

![Diffractogram showing phases present from each side of sample 13.](image)

**Figure 97.** Glancing XRD diffractograms showing phases present from each side of sample 13$_1$.

XPS was performed on sample 46$_1$ after sputtering the surface for 30 s, removing an estimated (3 to 4) nm. The elemental quantification (Table 19) of each side appears to correlate with the phases identified by XRD. The golden side contains almost a 1:1 ratio of Ti to nitrogen while the titanium-colored side is closer to 2:1 in favor of Ti.

LOM work on an etched cross-section of sample 46$_1$ revealed a (5 – 10) µm-thick α-Ti case for both the gold and titanium-colored sides. The gold-colored side also contained a layer as thick as 2 µm on top of the α-Ti case, suspected to be TiN. No additional surface layer, such as seen with the gold-colored side, was detectable by LOM on the titanium-colored side. LOM images from the described areas are
Table 19. XPS quantified comparison of gold and titanium-colored sides of sample 46_1.

<table>
<thead>
<tr>
<th></th>
<th>Gold colored (at%)</th>
<th>Titanium colored (at%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>42</td>
<td>42</td>
</tr>
<tr>
<td>N</td>
<td>43</td>
<td>25</td>
</tr>
<tr>
<td>O</td>
<td>14</td>
<td>33</td>
</tr>
<tr>
<td>V</td>
<td>1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Al</td>
<td>&lt;1</td>
<td>1</td>
</tr>
</tbody>
</table>

shown in Figure 98. Since the gathered XPS data come from only the outermost few nanometers, the precipitating phases of TiN and Ti_2N predominantly provided the data for the quantified results.

Figure 98. LOM images of cross-section of sample 46_1, notice the bright precipitates on the surface from the gold-colored side.

Despite the initial appearance that only the gold-colored portion of the sample was subject to significant nitrogen diffusion and nitride precipitation, XRD, XPS, and Vickers hardness results show that the titanium-colored side did receive significant inward diffusion of nitrogen, but less nitride precipitation.

According to lab notes, the only samples that exhibited the partial nitridation phenomenon were those sealed under high argon pressures. The behavior of gas in a sealed ampoule is known to be random, but perhaps the sample position with respect to the powder and the mean free path play a role in creating the condition in which the partial nitridation occurs. The mean free path of an argon atom in an ampoule sealed under high (101,000 Pa) and low (26 Pa) argon pressures was calculated to
be 44 µm and 170 mm respectively. Perhaps in high argon pressures, the shortened mean free path increases the likelihood that each N₂ molecule strikes the front of the sample more so than the rear. The increased availability of nitrogen at the surface towards the front of the sample would then increase the probability of forming TiN, thus causing the golden color.

Once it was discovered that the high argon pressures provided the conditions for partial nitridation, all ampoules were sealed under the lowest possible pressure. Following this step, no more samples were observed to exhibit partial nitridation, and thus ceased the investigation of explaining the phenomenon. However, Lizhi Liu reported in a phone conversation that while nitriding longer tensile specimens sealed under low argon pressures, such a phenomenon was observed.

20. Aluminum Deposition on Ampoule Wall

Figure 99 shows an ampoule containing a reflective deposition on the interior of the ampoule wall surrounding the location of the Ti–6Al–4V sample during heat treatment (sample was moved to position shown in image after the heat treatment). This deposition was a rare occurrence among annealed samples. XPS was used to identify the deposition as containing Al and Ti. It is assumed that such depositions are a result of off-gassing coming from the sample during heat treatment. This deposition was only observed in some annealed samples and not in nitrided samples.

Figure 99. Deposition composed of aluminum and titanium on inner wall of annealed Ti–6Al–4V sample.
Appendix 2

Relevant Information

21. List of Sample Heat Treatments

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>$T_{ppk}$</th>
<th>Time (ks)</th>
<th>Power pack qty. (g)</th>
</tr>
</thead>
<tbody>
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<td>AR₁</td>
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<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>AR₂</td>
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<td>NA</td>
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</tr>
<tr>
<td>A₁</td>
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<td>262.8</td>
<td>NA</td>
</tr>
<tr>
<td>A₂</td>
<td>NA</td>
<td>262.8</td>
<td>NA</td>
</tr>
<tr>
<td>A₂‐ep</td>
<td>NA</td>
<td>262.8</td>
<td>NA</td>
</tr>
<tr>
<td>73₃</td>
<td>HT 1</td>
<td>259.2</td>
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</tr>
<tr>
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<td>HT 1</td>
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<td>4</td>
</tr>
<tr>
<td>81₃‐ep</td>
<td>570</td>
<td>86.4</td>
<td>4</td>
</tr>
<tr>
<td>82₁</td>
<td>570</td>
<td>259.2</td>
<td>4</td>
</tr>
<tr>
<td>83₁</td>
<td>550</td>
<td>259.2</td>
<td>4</td>
</tr>
<tr>
<td>8₄₁−A₁</td>
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<td>259.2</td>
<td>4</td>
</tr>
<tr>
<td>8₅₁−A₂</td>
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<td>259.2</td>
<td>4</td>
</tr>
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<td>575</td>
<td>259.2</td>
<td>4</td>
</tr>
<tr>
<td>9₃₂</td>
<td>560</td>
<td>259.2</td>
<td>4</td>
</tr>
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<td>570</td>
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</tr>
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<td>8</td>
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<td>8</td>
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<tr>
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<td>4</td>
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<tr>
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<td>4</td>
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<tr>
<td>1₀₉₂‐ep</td>
<td>550</td>
<td>259.2</td>
<td>2.4</td>
</tr>
<tr>
<td>1₁₀₂‐ep−A₂</td>
<td>550</td>
<td>259.2</td>
<td>4</td>
</tr>
</tbody>
</table>

- Subscripts ₁, ₂, and ₃ represent the different suppliers of the Ti–6Al–4V used.
- Subscript CP indicates sample is commercially pure Grade 4 titanium.
• Subscript \( A_1 \) signifies sample was annealed at 790°C for 14.4 ks, followed with a furnace cool.

• Subscript \( A_2 \) signifies sample was annealed at 925°C (still below \( \beta \)-transus temperature) for 14.4 ks, followed with a furnace cool.

• Subscript \( \text{ep} \) indicates sample was electropolished, see page 27.

• HT 1 means that the temperature of the powder pack was decreased from 600°C to 495°C at set time increments throughout the 259.2 ks (72 h) nitridation.

All samples were held at 860°C. Samples paired in table were treated in the same ampoule. After the designated heat treatment time was reached, all samples from 80\( \text{CP}_{-\text{ep}} \) to 110\( _2^{-\text{ep}-A_2} \) commenced furnace cooling 3.6 ks (1 h) after furnace cooling had begun on powder pack. For this reason, nitrided samples are identified as being treated for 259.2 ks while annealed samples (\( ^\dagger \)) are labeled as having been annealed for 262.8 ks. The samples with an asterisk (*) by the treatment time were visually observed periodically during heat treatment by removing F1, observing, then replacing the furnace over the sample.
22. Crystallographic Information

<table>
<thead>
<tr>
<th>Phase</th>
<th>Crystal System</th>
<th>$a$ (nm)</th>
<th>$c$ (nm)</th>
<th>Space Group</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-Ti (Ti–6Al–4V)</td>
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<td>0.467</td>
<td>P6$_3$/mmc</td>
</tr>
<tr>
<td>citewelsch ε-Ti$_2$N</td>
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<td>0.3036</td>
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<tr>
<td>δ-TiN</td>
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<td>0.4239</td>
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<td>Fm$3m^{[66]}$</td>
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<td>Cubic</td>
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<td>Ti$_3$Al</td>
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<td>0.577</td>
<td>0.462</td>
<td>P6$_3$/mmc$^{[66]}$</td>
</tr>
</tbody>
</table>

23. Composition of As Received Material

Ti–6Al–4V (values for N, C, H, Fe, and O shown as limits)$^{[4]}$

<table>
<thead>
<tr>
<th>Element</th>
<th>Ti</th>
<th>Al</th>
<th>V</th>
<th>N</th>
<th>C</th>
<th>H</th>
<th>Fe</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>at%</td>
<td>83.5–86.2</td>
<td>9.3–11.3</td>
<td>3.1–4.0</td>
<td>0.2</td>
<td>0.4</td>
<td>0.3</td>
<td>.2</td>
<td>.06</td>
</tr>
</tbody>
</table>
References


[31] Damrongsak Jadsadapattarakul, Chanipat Euvananont, Chanchana Tay-
achayanont, and Tawan Sooknoi. (200) Preferred Orientation SnO$_2$ Film pre-


