A TWO-STEP CO$_2$ LASER-SUSTAINED PLASMA NITRIDING PROCESS FOR DEEP-CASE HARDENING OF COMMERCIAL TITANIUM

A Dissertation in
Engineering Science and Mechanics
by
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ABSTRACT

Titanium and its alloys possess several attractive properties that include a high strength-to-weight ratio, biocompatibility, and good corrosion resistance. However, due to their poor wear resistance, titanium components need to undergo surface hardening treatments before being used in applications involving high contact stresses. Laser nitriding is a thermochemical method of enhancing the surface hardness and wear resistance of titanium. This technique entails scanning the titanium substrate under a laser beam near its focal plane in the presence of nitrogen gas flow. At processing conditions characterized by low scan speeds, high laser powers, and small off-focal distances, a nitrogen plasma can be struck near the surface of the titanium substrate. When the substrate is removed, this plasma can be sustained indefinitely, away from any potentially interacting surfaces, by the laser beam power and a cascade ionization process. This dissertation explores the unique effects of nitriding titanium in the presence of such a laser-sustained plasma (LSP) in a processing chamber open to the atmosphere, with the ultimate objective of forming wide-area, deep, crack-free, wear-resistant nitrided cases on commercially pure titanium substrates.

First, nitriding experiments were conducted at three processing conditions with and without a prestruck LSP. From optical and scanning electron microscopy, weight measurements, and temperature measurements, it was found that LSP nitriding increased nitrogen intake into the titanium melt pool, reduced surface oxidation, and broadened the energy distribution without causing energy attenuation when compared to conventional laser nitriding; these effects were most pronounced at the highest scan speed and lowest off-focal distance. Next, the effect of processing conditions on surface and cross-sectional microstructures during LSP nitriding was systematically evaluated by studying twenty experimental cases at varying off-focal distances, scan speeds, and gas flow compositions (nitrogen diluted by varying amounts of argon). X-ray diffraction conducted on the top surface of the nitrided trails confirmed the presence of TiN and TiN$_{0.3}$ phases. Although
nitrogen dilution by argon was found to be necessary to prevent crack formation, microstructural characterization and weight measurements revealed that argon addition limited nitrogen intake into the melt pool by reducing Marangoni convection in the melt pool. Elimination of surface cracks thus came at the expense of reduced nitrogen content, shallower melt depths, and a reduced control over the microstructure of the resulting nitrided layer. To overcome these problems, a two-step process was proposed and developed. In the first step, a prestruck nitrogen LSP was used to deposit a single nitrided trail on the substrate; in the second step, a prestruck argon plasma was used to remelt the nitrided trail laid in step one. The nitriding and remelting steps were modeled using an analytical heat conduction solution valid for a moving heat source. Remelting the nitrided trail was found to refine the microstructure and reduce solute segregation, resulting in the formation of deep, hard, homogenous, and crack-free nitrided cases. Optimal processing conditions required to tailor the case microstructure from: (a) a two-phase mixture of TiNₐ dendrites embedded in a titanium matrix, to (b) a uniform solid solution of nitrogen in titanium, α-Ti(N), were identified. Microstructure-property relationships were proposed, and values for the nitrogen flux into the melt pool and the efficiency of nitrogen intake were estimated. The nitriding-remelting treatment resulted in the formation of nitrided cases having depths up to 800 μm, and average Vickers hardness values in the range of 475-730 HV₀.₃. Selected single trail processing conditions were used to deposit multiple overlapping trails to increase surface coverage. For the same processing conditions, an increase in average hardness was observed in the overlapping trail runs compared to the single trail runs. Crack-free nitrided cases of average case hardness values up to 643 HV₀.₃ and case depths up to 600 μm were deposited. Reciprocating ball-on-flat wear tests were conducted to assess their wear resistance. The two-step treatment was found to enhance the wear resistance of the base material by up to 80%.
# TABLE OF CONTENTS

List of Figures .......................................................................................................................... vii

List of Tables ........................................................................................................................... xii

Acknowledgements .................................................................................................................. xiii

Chapter 1 Introduction ............................................................................................................. 1
  1.1 Titanium: benefits and drawbacks ............................................................................. 1
  1.2 Surface engineering of titanium ................................................................................. 3
  1.3 Laser nitriding of titanium ......................................................................................... 6
    1.3.1 Background ..................................................................................................... 6
    1.3.2 Literature review ............................................................................................. 8
  1.4 Dissertation overview ................................................................................................ 21
    1.4.1 Problem statements ......................................................................................... 21
    1.4.2 Organization of dissertation ............................................................................ 21

Chapter 2 Experimental details and heat transfer model ......................................................... 23
  2.1 Introduction ................................................................................................................ 23
  2.2 Experimental details ................................................................................................... 23
    2.2.1 Specimen preparation (pre-processing) ........................................................... 23
    2.2.2 Experimental setup .......................................................................................... 24
    2.2.3 Laser-sustained plasma processing ................................................................. 26
    2.2.4 Characterization techniques (post-processing) ................................................ 28
    2.2.5 Wear testing..................................................................................................... 32
  2.2 Heat transfer model .................................................................................................... 33
    2.2.1 Background ..................................................................................................... 33
    2.2.2 Heat conduction due to moving heat source ................................................... 34
    2.2.3 Application to LSP processing ........................................................................ 37
  2.3 Chapter summary ....................................................................................................... 43

Chapter 3 Comparison between LSP nitriding and conventional laser nitriding ..................... 44
  3.1 Introduction ................................................................................................................ 44
  3.2 Methodology .............................................................................................................. 45
  3.3 Results and discussion ............................................................................................... 47
    3.3.1 Effect of LSP on surface morphology ............................................................. 47
    3.3.2 Effect of LSP on energy transfer to substrate .................................................. 50
    3.3.3 Effect of LSP on surface oxidation ................................................................. 56
    3.3.4 Effect of LSP on the nitrogen intake into the melt pool .................................. 58
  3.4 Chapter summary ....................................................................................................... 59

Chapter 4 Effect of processing parameters on microstructure ................................................. 62
  4.1 Introduction ................................................................................................................ 62
  4.2 Methodology .............................................................................................................. 63
4.3 Results and discussion ............................................................................................................. 65
  4.3.1 Nitriding with a pure nitrogen LSP .................................................................................. 65
  4.3.2 Nitriding with a N2-Ar LSP .......................................................................................... 73
  4.4 Chapter summary ................................................................................................................... 82

Chapter 5 A two-step method to perform deep-case hardening of CP-titanium ......................... 85
  5.1 Introduction .......................................................................................................................... 85
  5.2 Methodology ......................................................................................................................... 87
  5.3 Calculations ........................................................................................................................ 89
  5.4 Results and discussion ......................................................................................................... 90
    5.4.1 LSP nitriding .............................................................................................................. 90
    5.4.2 LSP nitriding and remelting ...................................................................................... 95
  5.5 Chapter summary ................................................................................................................... 110

Chapter 6 Effect of two-step treatment on wear resistance ......................................................... 113
  6.1 Introduction ........................................................................................................................ 113
  6.2 Methodology ....................................................................................................................... 114
  6.3 Calculations ......................................................................................................................... 116
  6.4 Results and discussion ........................................................................................................ 118
    6.4.1 Nitrogen intake during multiple overlapping trails ..................................................... 118
    6.4.2 Microstructure .......................................................................................................... 119
    6.4.3 Wear testing .............................................................................................................. 123
  6.5 Chapter summary .................................................................................................................. 131

Chapter 7 Summary and future work .......................................................................................... 133
  7.1 Summary ............................................................................................................................ 133
    7.1.1 Motivation and objectives ......................................................................................... 133
    7.1.2 Key findings ............................................................................................................... 134
    7.1.3 Conclusions .............................................................................................................. 136
  7.2 Recommendations for future work ..................................................................................... 137
    7.2.1 Inverse heat conduction to determine energy flux from LSP .................................... 137
    7.2.2 Atomistic-scale modeling of nitrogen-titanium interface ......................................... 138
    7.2.3 Additional wear testing and rolling contact fatigue testing ....................................... 138
    7.2.4 Addition of TiN thin film after two-step method ....................................................... 138

References .................................................................................................................................... 140

Appendix A  FORTRAN script to calculate melt pool lifetimes ................................................ 152
Appendix B  FORTRAN script to calculate shape of isotherms ................................................ 155
Appendix C  High magnification (2000x) SEM images of wear scar features ............................... 158
LIST OF FIGURES

Figure 1-1. a) Ti-N phase diagram [51], and b) Ti-O phase diagram [52]............................... 4

Figure 1-2. a) Schematic of the laser nitriding process with coaxial nitrogen gas flow, and b) convective transport of nitrogen in the melt pool at the transverse cross-section Y-Y. T and σ indicate temperature and surface tension respectively. CP-Ti denotes commercially-pure titanium. ............................................................................................ 8

Figure 1-3. (a) Schematic of Nassar et al.’s [107] LSP nitriding process with the substrate perpendicular to the laser beam, (b) CCD image of freestanding nitrogen LSP, and (c) schematic of Black et al.’s [108] LSP nitriding process with the substrate parallel to the laser beam. Images (a) and (b) reproduced from Ref. [107], and image (c) reproduced from Ref. [108].............................................................................................. 19

Figure 2-1. Theoretical intensity profile of the Q-mode CO₂ laser beam shown as a superposition of four fundamental TEM modes. .................................................................................................................. 24

Figure 2-2. a) Experimental setup, b) Schematic of LSP nitriding process, c) CCD image of a freestanding nitrogen LSP (green arrow points in the direction of the laser beam). .......................................................................................................................................... 26

Figure 2-3. Schematic of a linear reciprocating ball-on-flat wear test. Image reproduced from the ASTM G133-05 standard [117]. .......................................................................................................................... 32

Figure 2-4. Schematic of a Gaussian heat source moving over a semi-infinite substrate, z > 0........................................................................................................................................................................... 34

Figure 2-5. Determination of the energy absorption efficiency (η) for a) argon LSP melting (7 mm off-focal distance) and b) LSP nitriding (8 mm off-focal distance) experiments. The error bars indicate a range of ±5% around the measured widths. ............................. 42

Figure 2-6. a) Melt isotherm (shown in red) plotted using Equation 2-11, superimposed upon transverse cross-section of melt pool obtained by LSP nitriding at a speed of 30 mm/s and off-focal distance of 8 mm, b) corresponding width and depth of the melt pool as a function of time. .................................................................................................................. 42

Figure 3-1. Experimental conditions studied (denoted by triangles) to quantify the effect of LSP in nitriding. The conditions are overlaid on a LSP nitriding processing window plot, reproduced from Nassar et al. [21] with minor modifications. .................................................. 45

Figure 3-2. Schematic of temperature measurement in parallel configuration with location of the thermocouples. ............................................................................................................................................... 47

Figure 3-3. SEM images of nitrided surfaces for all the six conditions listed in Table 3-1. List of nitriding experiments. The scale marker (500 μm) is the same for a given OFD/speed combination with and without LSP, but is different for different conditions. The white arrow in (c) points in the direction of the laser beam velocity
relative to the substrate, and applies to all micrographs. The nitrided zone (N), the transition zone (T), and the substrate (S) have been labeled in (a).

Figure 3-4. Optical profilometry of nitrided surface at processing conditions of 8 mm OFD and 90 mm/s speed from Table 3-1 for (a) no LSP (run 3) and (b) LSP (run 4).

Figure 3-5. Temperature rise, $\Delta T$ (°C), recorded by two thermocouples TC1 and TC2 at the end of 5 seconds. The location of the thermocouples can be found in Figure 3-2.

Figure 3-6. a) Schematic of the sphere-plate geometry for view factor calculation, b) $Q_{inc}/F$ plotted for distances $d \geq 9$ mm. The vertical error bars denote a range of ±10% around the respective data points.

Figure 3-7. Theoretical irradiance profiles for an ideal case of a point source radiating energy on to a large plate for various distances $d$. The point source was assumed to radiate energy at the rate of 998 W.

Figure 3-8. Nitrided samples for the experiments listed in Table 3-1. The numerical labels indicate the run # for the respective coupon from Table 3-1.

Figure 3-9. Optical micrographs of transverse cross-sections of all six nitrided samples listed in Table 3-1. The scale marker for each pair of micrographs is indicated in the bottom figure.

Figure 4-1. Processing conditions from the literature [62, 65, 69, 72, 78, 79, 135] and this work. 'C' denotes controlled environment and 'O' denotes open atmosphere.

Figure 4-2. Effect of off-focal distance on surface morphology: a) 8 mm OFD b) 10 mm OFD c) 12 mm OFD d) 14 mm OFD at processing conditions of 3.5 kW power, 90 mm/s speed, 16 slpm N2. Laser scan direction is from top to bottom. Some black patches in (a) are arrowed and labeled. Scale marker of 1 mm shown on the bottom right is common for all micrographs.

Figure 4-3. Effect of scan speed on surface morphology: a) 135 mm/s b) 180 mm/s c) 225 mm/s d) 270 mm/s e) 300 mm/s at processing conditions of 3.5 kW power, 8 mm OFD, 16 slpm N2 flow. Some cracks, black patches, and longitudinal ridges have been arrowed and labeled. Scale marker of 1 mm shown on the bottom right is common for all micrographs.

Figure 4-4. a) SEM image (20x) of the top surface of run 1 at 135 mm/s scan speed. Inset image shows a magnified image (200x) of one of the rough 'black spot' regions in the optical micrographs of Figure 4-3. Black arrow indicates the direction of the laser beam scan. b) Optical profilometry images show surface topography in 2 and 3 dimensions. The vertical scale ranges from -19.6 to 45.2 µm.

Figure 4-5. a) Surface (scanning electron micrograph) and transverse cross section (optical micrograph) of run 12 in Table 4-1 (90 mm/s speed, 16:0 N2:Ar gas flow ratio, 3.5 kW power and 8 mm OFD). A, B and C represent different surface morphologies. Surface topography contours obtained from optical profilometry are shown at the top,
with the height scale ranging from -35.5 to 43.6 µm shown on the bottom left of the profilometry image. A melt isotherm (drawn in red) of the trailing side of the melt pool has been superposed on the SEM image. The topography contour plot, the melt isotherm, and both the scanning electron and optical micrographs are drawn to the same scale (500 µm scale shown at the bottom). The arrow shows the beam scan direction. b) Higher magnification scanning electron micrograph of the cellular features of region A and the transition from A to B. The scale marker is 50 µm and is shown at the top. The arrow shows the beam scan direction.

Figure 4-6. Scanning electron micrographs of the surface of run 12 (90 mm/s, 16:0 N₂:Ar ratio, 3.5 kW power, 8 mm OFD): a) before and b) after grinding with 200 grit sandpaper for 15 seconds.

Figure 4-7. SEM images of nitrided surfaces at N₂:Ar ratios of 16:0 to 16:3 and speeds of 90, 70, and 50 mm/s, corresponding to runs 10 through 21 in Table 4-1 (3.5 kW power, 8 mm OFD). Laser scan direction is from right to left as indicated by the white arrow in (e). All micrographs were obtained at the same magnification, and the scale marker on each micrograph is 1 mm.

Figure 4-8. Optical micrographs of transverse cross sections at N₂:Ar ratios of 16:0 to 16:3 and speeds of 90, 70, and 50 mm/s, corresponding to runs 10 through 21 in Table 4-1 (3.5 kW power, 8 mm OFD). Scale marker of 500μm shown below the images is common for all micrographs.

Figure 4-9. Weight change per unit nitrided length of substrate as a function of argon flow in 16 slpm nitrogen flow (runs 12, 15, and 18 from Table 4-1) at processing conditions of 3.5 kW power, 8 mm OFD, and 90 mm/s scan speed. The corresponding transverse cross-sectional micrographs are shown as inset images.

Figure 4-10. Three-dimensional surface topography images obtained using optical profilometry for four different N₂:Ar ratios: a) 16:0 b) 16:1 c) 16:2 and d) 16:3 slpm:slpm. The smoothing effect of argon gas flow on the nitrided surface can be clearly seen. Sa is the (arithmetic) mean surface roughness, Sq is the root mean square (RMS) roughness and Sz is the height difference between the highest and the lowest points on the measured surface. The roughness profile (in microns) for representative transverse cross-sectional planes is shown below each three-dimensional surface profile.

Figure 4-11. (a) Optical and (b) scanning electron micrographs of transverse cross section for run 13 in Table 4-1 (50 mm/s speed, 16:1 N₂:Ar ratio, 3.5 kW power and 8 mm OFD). The microstructural features and their corresponding phases are labeled. A thin continuous TiN layer can be seen at the top.

Figure 4-12. X-ray diffraction analysis conducted at the top surface of run 13 in Table 4-1 (N₂:Ar 16:1, speed 90 mm/s, 3.5 kW power and 8 mm OFD).

Figure 5-1. Schematic for LSP nitriding and remelting experiments.
Figure 5-2. Isotherm lifetimes calculated for three temperatures, plotted against the inverse of: a) four LSP nitriding speeds, and b) four remelting speeds.................................90

Figure 5-3. Optical micrographs of transverse cross-sections of all the experimental cases (with corresponding run #) listed in Table 5-1. Scale marker of 1 mm shown at the bottom is common for all micrographs.................................................................91

Figure 5-4. Higher magnification optical micrographs of LSP nitrided coupons at speeds of 60 mm/s (run 11) and 75 mm/s (run 16). The scale marker of 200 μm shown at the bottom is common for both micrographs. The regions that did not exhibit TiN dendrites are indicated by black arrows.................................................................92

Figure 5-5. Weight gain of nitrided samples measured at five LSP nitriding speeds (8 mm OFD, 3.5 kW power), plotted against the inverse of nitriding speed.................................93

Figure 5-6. SEM image (backscatter mode) of transverse cross section of (a) run 4 (30 mm/s nitriding speed, 15 mm/s remelting speed), and (b) run 1 (30 mm/s, no remelting) near the surface. The scale marker for (a) is 200 μm and for (b) is 20 μm. Five distinct microstructural features have been labeled in the micrographs.................96

Figure 5-8. Higher magnification optical micrographs showing the effect of remelting on samples nitrided at 30 mm/s: a) remelting at 10 mm/s speed (run 5), b) no remelting (run 1), and c) remelting at 25 mm/s (run 2). Isotherms corresponding to remelting speeds of 10 mm/s and 25 mm/s for 1670 °C (red), 2350 °C (green), and 3290 °C (blue) are superposed upon micrographs in (a) and (c) respectively. The scale marker of 400 μm shown in (c) is common for all micrographs.................................100

Figure 5-9. a) Hardness profile for sample nitrided at 30 mm/s and remelted at two different speeds of 25 mm/s (run 2) and 10 mm/s (run 5), and b) EDS line scan results showing qualitative depth profiles of nitrogen content (atomic %) in the melt pool. .....................102

Figure 5-10. Linear correlation between Vickers hardness number (VHN) and dendrite volume fraction (DVF)................................................................................................102

Figure 5-11. XRD data showing the effect of remelting on phase transformation in a sample nitrided at a speed of 75 mm/s. .........................................................................................103

Figure 5-12. Optical micrographs showing the effect of remelting multiple times at a nitriding speed of 45 mm/s and a remelting speed of 15 mm/s. a) Original nitried layer (no remelting), b) remelted once, and c) remelted eight times. The scale marker of 400 μm shown in (a) is common for all three micrographs.................................106

Figure 5-13. SEM images (50x magnification) of the top surface of LSP nitrided-remelted samples for two nitriding conditions that were remelted using the following conditions: no remelting, remelting at speeds of 20 mm/s and 10 mm/s. Cracks are denoted by white arrows. Scale markers on all the micrographs indicate a length of 500 μm. The direction of laser beam scan was from left to right. .................................108
Figure 5-14. 3D contours and corresponding surface profiles along a line across the width of nitrided surface for: a) no remelting (run 16), b) remelting at 20 mm/s (run 18), and c) remelting at 10 mm/s (run 20) speed. The nitriding speed was 75 mm/s. ..................109

Figure 6-1. Schematic of transverse cross section of a) multiple overlapping trails (this Chapter), and b) a single trail (Chapter 5), during LSP nitriding. Region 1+2 represents the current trail in the process of being deposited, region 2+3 represents the last trail that was deposited, and region 2 represents the overlapping region between the successive trails. The direction of the laser beam scan is normal to the plane. ..................116

Figure 6-2. Variation of nitrogen intake per nitrided trail with inverse of nitriding speed, shown for single trail measurements (Chapter 5), multiple overlapping trail measurements (present Chapter), and multiple overlapping trail calculations................118

Figure 6-3. Optical micrographs of the transverse cross-sections of runs 1-5 in Table 6-1. The scale marker shown in (d) is 2 mm and is common to all micrographs. Hot tearing cracks in (a) and (e) are indicated by white arrows.........................................................120

Figure 6-4. (a) Average case hardness (with standard deviation) and nitrogen content (at. %) in the melt pool as a function of nitriding speeds; optical micrographs taken near the center of the melt pool for (b) run 1, (c) run 2, (d) run 3, and (e) run 4 from Table 6-1. The scale marker of 280 μm shown at the top is common to all the micrographs....121

Figure 6-5. XRD spectra for runs 1-4 from Table 6-1............................................................122

Figure 6-6. Low magnification SEM images of wear scar for: (a) untreated CP-titanium, (b) run 4 (75 mm/s nitriding speed), (c) run 3 (60 mm/s nitriding speed), and (d) run 2 (45 mm/s nitriding speed), where (b)-(d) were all remelted at a speed of 20 mm/s. ....124

Figure 6-7. High magnification SEM images taken at the middle of the wear scar for: (a) untreated CP-titanium, (b) run 4 (75 mm/s nitriding speed), (c) run 3 (60 mm/s nitriding speed), and (d) run 2 (45 mm/s nitriding speed), where (b)-(d) were all remelted at a speed of 20 mm/s.................................................................125

Figure 6-8. (a) Measured wear scar volumes; (b) Variation of coefficient of friction over the test duration; wear scar profiles in the (c) longitudinal and (d) transverse directions. The symbol NX in the figures denotes ‘nitrided at X mm/s speed’. ............128

Figure C-1. High magnification SEM images of characteristic wear scar features for: (a) untreated CP-titanium, (b) run 4 (75 mm/s nitriding speed), (c) run 3 (60 mm/s nitriding speed), and (d) run 2 (45 mm/s nitriding speed), where (b)-(d) were all remelted at a speed of 20 mm/s......................................................158
LIST OF TABLES

Table 1-1. Comparison between titanium, 304 stainless steel, and aluminum .................. 1

Table 2-1. Fine polishing procedure .................................................................................. 30

Table 2-2. Values of constants used in Equation 2-11 ......................................................... 40

Table 3-1. List of nitriding experiments .............................................................................. 46

Table 3-2. Trail widths with and without LSP ..................................................................... 49

Table 3-3. Peak temperature on the back face of the substrate for three different experiments .......................................................................................................................... 51

Table 3-4. Weight increase with and without LSP. ............................................................. 58

Table 4-1. List of experimental runs performed ................................................................. 64

Table 5-1. List of nitriding-remelting experiments ............................................................ 88

Table 5-2. Predicted and measured values of nitrogen intake, Δw ..................................... 94

Table 5-3. Nitrogen content of microstructural features at 30 mm/s nitriding speed ......... 95

Table 5-4. Effect of varying nitriding speed on at. % N and average case hardness for a constant remelting speed of 10 mm/s .............................................................. 105

Table 6-1. List of experimental runs ................................................................................. 115

Table 6-2. Wear coefficients for different samples ............................................................. 129
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Chapter 1

Introduction

1.1 Titanium: benefits and drawbacks

Titanium and its alloys have been widely studied in the past few decades, mainly as potential replacements for steel, aluminum, and superalloys. Titanium possesses a high strength-to-weight ratio; it is 40% less dense than steel and nickel-base superalloys, and has a tensile strength that is higher than aluminum and comparable to martensitic stainless steel [1]. Titanium components can withstand higher operating temperatures than aluminum [2]. Due to the formation of a thin, passive oxide on the surface, titanium has excellent corrosion resistance, making it a suitable candidate for harsh reactive environments [3] including the human body [4]. These properties have led to titanium being referred to as a ‘wonder metal’ [5], with current and future applications in the aerospace, chemical, automotive, and biomedical industries, among others. However, the widespread use of titanium in the industry has been hampered by the high costs incurred during extraction, processing, and machining, making titanium more expensive than steel or aluminum [6]. Table 1-1 compares titanium, 304 stainless steel, and aluminum, with respect to processing energy and costs.

Table 1-1. Comparison between titanium, 304 stainless steel, and aluminum

<table>
<thead>
<tr>
<th>Property</th>
<th>Titanium</th>
<th>304 Stainless Steel</th>
<th>Aluminum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strength-to-Weight ratio (kNm/kg) [7]</td>
<td>120</td>
<td>77</td>
<td>130</td>
</tr>
<tr>
<td>Maximum operating temperature (°C) [2,8]</td>
<td>540</td>
<td>899</td>
<td>130</td>
</tr>
<tr>
<td>Processing energy (kWhr/kg) [7]</td>
<td>100</td>
<td>21</td>
<td>56</td>
</tr>
<tr>
<td>Domestic production cost ($/kg) [7]</td>
<td>9</td>
<td>2.4</td>
<td>2</td>
</tr>
</tbody>
</table>
The potential cost-saving benefits of using titanium, for example as a structural material in aerospace [9] and automotive applications [10,11] in order to reduce fuel consumption, have spurred government and industry funded research programs [12,13] aimed at finding cost-effective and energy-efficient methods of extracting, processing, and machining titanium. The ARPA-E METALS program [7], for instance, targets a cost reduction in titanium stock from the current $9/kg to less than $4/kg to make titanium cost-competitive with stainless steel.

Apart from this economic disadvantage, titanium suffers from a serious engineering drawback, namely, its poor tribological properties. Titanium is notorious for exhibiting high coefficients of friction, high wear rates, and poor abrasion and fretting resistance when sliding against itself or other materials [14–17]. At room temperature, titanium has a hexagonal close-packed (hcp) crystal structure (known as α-Ti) with a $c/a$ ratio of 1.587 that is less than the ideal value of 1.633 [18]. This makes it prone to slip along the prismatic plane $\{10\overline{1}0\}$ rather than the base plane $\{0001\}$, leading to an increase in friction coefficient [19] and galling tendency [18].

Titanium’s metallic bond has a lower $d$-bond character compared to other transition metals, enhancing its surface chemical activity and increasing its tendency to form strong interfacial bonds with other mating surfaces. Buckley et al. [20] observed a relation between this low $d$-bond character of titanium and its high coefficients of friction with itself and with other materials. Miyoshi et al. [21] correlated the low theoretical tensile and shear strengths of titanium to high tendencies of material transfer and the resulting high friction coefficients; they reported friction coefficient values as high as 60 for titanium sliding against itself in vacuum, making titanium especially vulnerable to galling and seizing [15]. Molinari et al. [22] provided a metallurgical basis for the low wear resistance of the Ti-6Al-6V alloy. They recognized two distinct speed-dependent wear regimes: at high sliding speeds, the titanium alloy was found to wear by delamination attributed to the low plastic shear strength and low work hardening behavior of titanium; on the other hand, at low sliding speeds, surface oxides formed and were easily worn by spalling and
microfragmentation, leading to oxidative wear [22]. The preceding discussion makes it clear that the surfaces of titanium components need to be modified to improve their wear resistance before they can be used in tribo-applications such as precision gears, orthopedic implants, bolts and fasteners, and so on. Some common surface engineering treatments to enhance the tribological properties of titanium surfaces are briefly described in the following section.

### 1.2 Surface engineering of titanium

Surface engineering can be defined as a “treatment of the surface and near-surface regions of a material to allow the surface to perform functions that are distinct from those functions demanded from the bulk of the material” [23]. In the context of this dissertation, the functions that the surface engineering treatment must perform are to harden the surface and enhance the wear resistance of titanium. Surface engineering in tribology can be either surface coating or surface modification techniques [24]. In surface coating methods, thin-film coatings of harder materials (such as TiN) are deposited on titanium to improve its wear resistance, using techniques such as physical vapor deposition (PVD) and chemical vapor deposition (CVD) [25,26]. PVD processes further include ion plating, plasma spray, thermal evaporation, and sputtering [27]. Surface coating methods can achieve high hardness at the surface, but are characterized by low deposition rates, poor adhesion to the substrate (especially in evaporation processes), complex equipment, and low film thicknesses (1-10 µm) [28]; as such, PVD and CVD are incapable of producing a deep and hard case that is required in high contact stress tribosystems such as gears and bearings [25,29].

Surface modification of titanium is implemented by thermochemical processes such as boronizing [30–32], carburizing [33], nitriding [29,34–43], and oxidizing [44–48]. The neutral atomic radii of the oxygen (0.6 Å), nitrogen (0.71 Å), and carbon (0.77 Å) atoms are about half or less than half that of titanium (1.5 Å); consequently, O, N, and C atoms readily diffuse through the
titanium lattice and can occupy the interstitial octahedral sites (0.61 Å radius) in the HCP structure of α-Ti [49]. The N and O atoms exhibit high interstitial solid solubility in the α-Ti phase, as seen in the phase diagrams of Figures 1-1a and b, causing a significant solid solution hardening effect [50]. Further, the interstitial O, N, and C atoms also increase the $c/a$ ratio of the α-Ti HCP structure, which changes the slip plane from the prismatic {10\bar{1}0} to the basal {0001} plane, increasing the galling resistance of titanium [19]. In addition, B, C, N, and O atoms also strengthen the titanium matrix by precipitation hardening, forming the hard ceramic phases TiB/TiB$_2$, TiC, TiN/Ti$_2$N, and TiO$_2$/TiO respectively within the titanium matrix. As nitrogen has the highest hardening effect of all these interstitial atoms [50], nitriding is a widely used and well-investigated thermochemical method of hardening titanium surfaces.

![Figure 1-1. a) Ti-N phase diagram [51], and b) Ti-O phase diagram [52].](image)

Nitriding of titanium may be effected by ion implantation, diffusion, or laser/electron beam processes [53], each method differing in the mechanism of impregnating the titanium substrate with nitrogen. In ion implantation, nitrogen ions are accelerated into the titanium substrate through a voltage difference [53]; however, this method can only produce a compound nitride layer having a thickness of about 25-250 atomic layers [54]. The diffusion method, as the name suggests, relies upon the diffusion of nitrogen atoms into the titanium surface at elevated temperatures. Nitrogen
diffusion into the titanium substrate can be brought about either by heating the substrate to a high
temperature in a nitrogen or ammonia gas atmosphere (gas nitriding) [34–36], or by exposing the
substrate to a nitrogen plasma (plasma nitriding) that simultaneously heats the surface and provides
nitrogen ions to it [38–41,55]. Plasma nitriding has the added advantage of an inherent sputtering
phenomenon that also cleans the substrate and reduces impurities in the nitrided sample [55]. Both
the gas nitriding and plasma nitriding processes are capable of forming functionally graded cases
comprising a compound layer (TiN, Ti2N) at the top and a diffusion zone containing a solid solution
of nitrogen in titanium, α-Ti(N), deeper in the titanium substrate [26]. The hardness and depth of
the resulting nitride cases depend upon the temperature and duration of the process; compound
layer depths up to 50 µm (plasma nitriding) and 15 µm (gas nitriding) have been recorded, with
total depths (including the diffusion layer) achieved up to 200-300 µm [34]. However, since
diffusion takes place in the solid state, gas and plasma nitriding are slow processes, typically
requiring 1-100 hours [26]. Further, since the whole substrate experiences a high temperature (400-
950 °C for plasma nitriding and 650-1000 °C for gas nitriding [26]) for long durations during the
process, the bulk microstructure is affected along with the surface; thus, gas and plasma nitriding
are not true ‘surface engineering’ methods according to the definition mentioned at the beginning
of Section 1.2. Plasma and gas nitriding methods have also been found to reduce the fatigue strength
of titanium alloys, especially at high processing temperatures [29]. Nitriding titanium using high
energy density sources, such as a laser beam or an electron beam, circumvent these shortcomings
while introducing new ones. Laser nitriding of titanium will be discussed in the next section.
1.3 Laser nitriding of titanium

1.3.1 Background

Lasers are characterized by their monochromatic, coherent, polarized, narrow, and low-divergence beams. Focused laser beams can deliver large quantities of energy (kilowatts) to a narrow spot (usually a fraction of a millimeter) on the surface of the substrate, leading to high energy intensities of the order of $10^{10}$-$10^{12}$ W/m² during welding (compared to $10^6$-$10^8$ W/m² for flux-shielded or gas-shielded arcs [56]). Further, this energy is absorbed within the first few atomic layers of the substrate, making the laser ideally and uniquely suited to surface engineering applications [57] such as nitriding of titanium. Laser nitriding of titanium has been extensively researched for more than three decades. A typical laser nitriding process can be described as follows:

i. The titanium substrate, usually in the form of a test coupon, is scanned under a laser beam at or near its focal plane in the presence of pure or diluted nitrogen gas flow (Figure 1-2a). The laser beam can be operated in the pulsed or continuous-wave (CW) mode. The nitrogen gas issues through a nozzle that is either coaxial (coaxial nozzle) or at an angle to the laser beam (side nozzle). The process is usually conducted in a controlled environment containing pure or diluted nitrogen to avoid oxidation of the titanium substrate.

ii. Due to the high energy density of the laser beam at or near focus, the irradiated area of the titanium substrate melts* to a depth of hundreds of microns and incorporates nitrogen at its molten surface. The nitrogen-rich titanium melt is transported deeper into the melt pool by convection currents within the melt pool. The main driving force for convection is the so-

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*If the laser energy density is high enough, the irradiated area can also vaporize, causing plasma formation near the surface of the substrate. This phenomenon will be covered in greater detail in Section 1.3.2.2.
called Marangoni force arising out of surface tension gradients; since the surface tension for a liquid metal decreases with increasing temperature, the center region of the free surface of the melt pool has lower surface tension than at the edges, driving fluid flow from the center to the edges (Figure 1-2b). Since nitrogen transport occurs in the liquid phase, the laser nitriding process is much faster than solid-state diffusion processes such as gas nitriding and plasma nitriding.

iii. When the laser beam moves away from the area under consideration (e.g. Y-Y in Figure 1-2b), the nitrogen-rich melt experiences rapid and non-equilibrium solidification due to a ‘self-quenching’ effect whereby the surface rapidly loses heat to the bulk via conduction. This results in the precipitation of phases such as stoichiometric or near-stoichiometric TiN, a solid solution of nitrogen in titanium, $\alpha$-Ti(N), and martensitic titanium, $\alpha'$-Ti. The TiN phase is gold-colored and hence easily identified on the surface of the treated sample. The TiN and $\alpha$-Ti(N) phases form a strong metallurgical bond with the substrate, thereby enhancing the hardness and wear resistance of the treated substrate. The microstructure of the resulting nitrided layer can be controlled by varying processing parameters such as laser power, spot size (off-focal distance), scan speed, and the nitrogen gas flow rate. On the other hand, rapid solidification makes the brittle nitrided layer susceptible to cracking and porosity, and causes an increase in surface roughness. Studies in the laser nitriding literature usually focus on overcoming these disadvantages (especially surface cracking). A detailed review of the laser nitriding literature is presented in Section 1.3.2.
1.3.2 Literature review

1.3.2.1 Chronological development of laser nitriding process

The use of lasers to nitride titanium and its alloys was first demonstrated in 1984 by Katayama et al. [58], who used pulsed and continuous-wave (CW) CO₂ and Nd:YAG lasers to harden the surface of titanium up to 700 HV. In the 1980’s and 1990’s, research focused on understanding and characterizing the laser nitriding process and finding optimal processing conditions to produce crack-free nitrided surfaces on CP-Ti and Ti-6Al-4V substrates. Bell et al. [29] used the laser nitriding technique with a view to improving the wear resistance and load bearing capacity of titanium for applications such as gears and bearings. Using a CO₂ laser in both the pulsed and CW modes, they were able to produce 0.5 mm deep nitrided cases on CP-Ti...
substrates. Two types of dendrites were observed in the microstructure: large dendrites near the surface, exhibiting cubic symmetry and hardness values close to 1500 HV; and dendrites near the melted-unmelted region interface showing hexagonal symmetry and having a hardness of 600 HV†. The cubic dendrites were identified as the compound TiN, while the hexagonal dendrites (which appeared to be hollow after deep etching) were identified as a solid solution of nitrogen in α-titanium, α-Ti(N). Morton et al. [59] reported an improvement in the wear behavior of laser-nitried titanium during lubricated rolling and sliding at high Hertzian contact stresses; they used a CO₂ laser to nitride the Ti-6Al-4V (henceforth Ti64) alloy using a side nozzle arrangement. Morton et al. [59] found that the angle of the nozzle needed to be at least 30 degrees and that the nitrogen flow had to cover at least thrice the melt pool width to avoid oxygen contamination. They also reported that low scan speeds (less than 16 mm/s) lead to embrittlement and high surface roughness, while high speeds (more than 48 mm/s) made the nitrided layer inhomogeneous. Diluting the nitrogen gas flow with argon (up to 60% dilution) and preheating the substrate up to 300 °C were found to reduce crack formation. No cracks were observed at surface hardness values of 600 HV or lower, although elsewhere [60] the threshold surface hardness value for crack formation was reported as 650 HV by the same authors. Roughness of the nitried layer was attributed to the high viscosity of the TiN-rich melt, whereas the waviness of the nitrided layer was due to convective flow. Jianglong et al. [61] nitrided Ti64 using a CO₂ laser and studied the general characteristics of the nitriding process. They noted that TiN formation depended upon a threshold energy density of 5 x 10⁸ W/m², below which no nitride formation was observed irrespective of the scan speed. They proposed the following mechanism for the laser nitriding process, where the [] sign refers to a melt and (N) represents N in the titanium structure [61]:

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†The Vickers hardness values of untreated CP-Ti and Ti-6Al-4V alloys are 140-200 HV and 327-370 HV respectively [1].
i. Surface absorption \[\text{[Ti]} + \text{N}_2 \rightarrow \text{[Ti]} + \text{[N]_2}\]
ii. Nitrogen decomposition \[\text{[N]_2} \rightarrow \text{[2N]}\]
iii. Nitrogen transfer \[\text{[N]_{\text{surface}}} \rightarrow \text{[N]_{\text{inside}}}\]
iv. TiN precipitation \[\text{[Ti(N)]} \rightarrow \text{TiN} + \text{[Ti(N)]}\]
v. Melt solidification \[\text{[Ti(N)]} \rightarrow \text{TiN} + \alpha\text{-Ti(N)}\]

According to Kloosterman et al. [62] who nitrided CP-Ti using a CO2 laser in the presence of pure N2 flow, the threshold laser energy density to form TiN was $2.5 \times 10^9$ W/m² or higher. They noted that apart from the mechanism proposed by Jianglong et al. [61], TiN could also form by the exothermic reaction $\text{Ti} + 0.5\text{N}_2 \rightarrow \text{TiN}$. Kloosterman et al. [62] further differentiated between two types of cracks in the nitrided layer: microcracks that were confined to the top 2-10 μm, and macrocracks that penetrated deeper into the solidified layer. The microstructure near the surface of the nitrided layer comprised a thin TiN layer (1-3 μm) and TiN dendrites that grew from the thin layer and were surrounded by nitrogen-rich Ti. Needle-like particles (560 HV hardness), coarse structures (300 HV hardness), and groups of TiN dendrites (swept away by convection currents) were observed by them deeper in the melt pool. Mriddha and Baker [63] used a 1.35 kW CO2 laser to nitride CP-Ti in a controlled pure-N2 environment, and reported rippling, cracking, and pores at the surface; the cracks were seen to originate at the pores. The melt pool was inhomogeneous due to capillary flow of the melt. In a subsequent publication in which a parametric study of the process was conducted, Mriddha and Baker [64] found that low gas flow rates and high speeds were essential to reduce surface crack formation on CP-Ti substrates in a pure-N2 gas flow. Moreover, they reported that crack-free nitried surfaces formed when the N2 gas flow was diluted with either Ar or He gases. Although nitrogen dilution eliminated crack formation, the TiN dendrites produced by the pure N2 flow were absent when the N2 flow was diluted. The crack-free nitried layers had depths up to 550 μm. Weerasinghe et al. [65] also found that diluting the nitrogen gas flow resulted in crack-free nitried surfaces in CP-Ti substrates; however, the TiN dendrites were found to be confined to the top 25 μm of the solidified layer. Weerasinghe et al. [65] also explored the effects
of a post-nitriding laser-remelting run in argon gas flow, and found that it increased the homogeneity and reduced the surface roughness of the nitrided layer. Hu and Baker [66] reported that the laser-nitrided Ti64 sample had a lower tendency to crack when preheated to about 300 °C (agreeing with Morton et al.’s [59] result) using a laser glazing run in argon gas flow. Xue et al. [67] found that preheating reduced the macrocracking tendency, while N2 flow dilution eliminated microcracks on the surface of a pulsed Nd:YAG laser-nitrided Ti64 sample. Further, Xue et al. [68] measured residual stresses in the nitrided layer to be tensile (950 MPa in the scan direction and 800 MPa perpendicular to the scan direction); preheating reduced these tensile stresses and hence the tendency to form macrocracks. Xue et al. [68] also detected minor oxygen contamination on the nitrided surface (but none deeper in the nitrided layer), and concluded that oxidation did not contribute towards cracking.

Hu et al. [69] identified the ‘thick needle’ phase (also referred to as ‘laths with rounded ends’ [70], ‘plates’ [71], or simply ‘dendrites’ [72] in the laser nitriding literature) in laser-nitrided CP-Ti and Ti64 specimens as being hexagonal TiN0.3. Xin et al. [70] analyzed the microstructure of Ti64 specimens nitrided using a CO2 laser in an 80% N2 flow and identified two distinct zones: zone I, about 50 µm from the surface, consisted of cubic TiN0.8 dendrites, metastable hexagonal TiN0.3, and martensitic α’-Ti; whereas zone II consisted primarily of nitrogen-rich martensitic α’-Ti. The atomic percentage of the nitrogen solute in the α’-Ti phase was found to be 3-4% at the boundary of zones I and II, while it was less than 1% at the bottom of zone II. Nwobu et al. [72] used quantitative microanalysis to identify two types of dendrites in the microstructure of nitrided CP-Ti: δ-TiN dendrites with nitrogen content greater than 30 at.%; and α-TiN0.3 dendrites containing 18-22 at. % nitrogen, produced by the peritectic reaction L + δ-TiN \( \rightarrow \) α (Figure 1-1a)\(^1\). Because of the measured composition of 18-22 at. %, they referred to this phase as α-TiN0.25

\(^1\)L = liquid, δ = fcc, α = hcp, β = bcc in the crystallography of Ti. The crystal structures of δ-TiN, α-Ti, and β-Ti, therefore, are fcc, hcp, and bcc respectively.
instead of $\alpha$-TiN$_{0.3}$. The effect of laser nitriding on the wear properties of titanium was studied by Yerramareddy and Bahadur [73], Xin et al. [74], Man et al. [75], and Ettaqi et al. [76], who reported an improvement in erosion and dry sliding wear resistance, abrasive resistance, cavitation erosion resistance, and a reduction in the coefficient of friction respectively.

In the 2000’s, the process development of laser nitriding continued with a focus on reducing oxidation on the laser-nitrided surface and conducting more wear resistance tests on the laser-nitrided titanium samples. Chen et al. [77] used a specially designed nozzle to avoid oxidation during pulsed Nd:YAG laser nitriding of Ti64 in an uncontrolled atmosphere. They concluded that oxygen-free nitriding was possible when the nitrogen gas flow was sufficiently low to maintain laminar flow conditions; high flow rates promoted oxygen contamination of the flow through turbulent mixing and led to oxide formation at the surface. Abboud et al. [78], who used a gas-shielding device to avoid oxidation during CO$_2$ laser nitriding of Ti64, agreed with Chen et al. [77] that turbulent gas flows should be avoided to ensure oxide-free nitrided layers. Raaif et al. [79] and Kaspar et al. [71] used a bell-shaped inert gas cover to maintain an oxygen-free atmosphere during CO$_2$ laser nitriding of CP-Ti and Ti64 respectively.

Several researchers also discussed the effect of the laser nitriding treatment on the wear and corrosion properties of titanium, the latter being especially important in biomedical applications where good corrosion fatigue resistance is required [80]. Geetha et al. [81], who nitrided the biomedical Ti-13Nb-13Zr alloy using a pulsed Nd:YAG laser and reported improved corrosion resistance compared to the base alloy, argued that the surface roughness inherent to the laser nitriding process (especially when carried out in a pure-N$_2$ environment) can be used advantageously for osseointegration. Vadiraj et al. [82] nitrided a biomedical Ti alloy with a pulsed CO$_2$ laser and found a reduction in fretting wear rate. Sathish et al. [83], Zhang et al. [84], Majumdar [85], and more recently Dahotre et al. [86], also reported an improvement in the wear resistance, corrosion resistance, and osseointegration of laser-nitrided biomedical titanium alloys.
Kaspar et al. [71] used a CO\textsubscript{2} laser to nitride Ti64 in dilute N\textsubscript{2} environments and found that increasing the hardness to a value of 550 HV was enough to significantly increase the cavitation erosion wear resistance, which is important in applications such as pumps, impellers, and steam turbine blades. Recently, the use of Ti64 in automotive applications was explored by Duraiselvam et al. [87]. They used a CW diode laser with a rectangular beam profile to produce a 120 µm-thick nitrided layer with a hardness of 760 HV on Ti64 specimens; the nitrided sample performed better than grey cast iron at the same wear testing conditions, prompting the authors to patent their technique [88] as a viable process of producing wear-resistant Ti64 specimens that can replace grey cast iron in disk brake rotor applications.

Apart from CO\textsubscript{2} and Nd:YAG lasers, researchers in recent times have also used free electron lasers (FEL) [89,90], diode lasers [85,87,91], and Ytterbium lasers [86] to perform nitriding of titanium. Lisiecki [91] lists higher absorption and more uniform heating as some of the main advantages of using a diode laser with a rectangular beam mode over more conventional laser sources such as the CO\textsubscript{2} laser with a Gaussian beam mode. Finally, two-dimensional (2D) finite element models of the heat and mass transfer occurring during laser nitriding were developed by Kuznetsov and Nagornova [92], Dahotre et al. [93], and Höche et al. [89]; while the first two papers neglected fluid flow, Höche et al. [89] considered both convection and diffusion in their model, and calculated several important dimensionless numbers such as the Peclet number (ratio of convective heat transfer to conductive heat transfer, value close to 10), Reynolds number (ratio of inertial forces to viscous forces, value close to 500), and the Marangoni number (ratio of the Marangoni surface tension gradient forces to the viscous forces, value close to 5000) in the melt pool. Using their 2D model, Höche et al. [89] were able to predict surface deformation due to Marangoni flow, and recognized the tradeoff between high melt depths and low surface roughness, since the convective effects responsible for transporting nitrogen deeper into the melt pool were also responsible for deforming the surface and reducing surface quality.
1.3.2.2 The role of near-surface plasma in laser nitriding of titanium

If the laser energy density is high enough (of the order of $10^{10}$ W/m$^2$ [94]), the irradiated area of the substrate melts and vaporizes, leading to the formation of a plasma plume near the surface. A simplified description of the formation of such a laser-induced plasma is presented below [95]:

i. In a metal where the first ionization potential is typically low, the metal vapor is easily ionized by the high intensity of the laser beam, giving rise to primary free electrons near the surface. Free electrons can also be generated by thermionic emission and the photoelectric effect [96].

ii. These primary free electrons gain energy by absorbing the laser radiation through a process called inverse bremsstrahlung. The energetic free electrons then collide with the neutral atoms and molecules of the processing gas, causing dissociation and ionization and producing secondary free electrons and ions in the process. This triggers a cascade ionization process in the gas, leading to gas breakdown and plasma formation. Gas breakdown is said to have occurred when the free electron density is of the order of $10^{24}$/m$^3$ [97]. The presence of the primary free electrons reduces the threshold intensity required to cause optical breakdown of the processing gas by about four orders of magnitude [98], as well as the effective ionization potential of the processing gas [95]. According to Grigoryants [95], the threshold power density for a CO$_2$ laser to cause optical breakdown is approximately $6 \times 10^9$ W/m$^2$.

iii. The absorption of the laser energy by the plasma increases with the degree of ionization (i.e. the free electron density); if the laser is operated in the CW mode, a steady state can

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$^3$For N$_2$ gas, the dissociation energy for the N$_2 \rightarrow$ 2N reaction is 9.8 eV, the first ionization potential to produce an N$_2^+$ radical is 15.6 eV, and the dissociative ionization potential to produce an N$^+$ radical is 23.4 eV [131]. These values can be compared to the first ionization potential of Ti, which is 6.8 eV [96].
be reached when the absorbed laser energy is balanced by energy losses due to plasma re-radiation. In the steady state, the laser energy can sustain the plasma in a coaxial flow of the processing gas even when the original source of free electrons, the metal substrate, is removed from the laser beam path. Such a plasma has been referred to as a ‘continuous optical discharge’ (COD) plasma [99] or a ‘laser-sustained plasma’ (LSP) [100] in the literature; the latter terminology will be used in this dissertation.

iv. Peak temperatures in the range of 15000 – 17000 K have been measured at the core of steady-state argon LSP’s [100,101]. Although it is more difficult to characterize a nitrogen LSP, its peak temperature is expected to be the same order of magnitude. This makes the LSP an interesting tool from the standpoint of high-temperature materials processing.

Although plasma formation is a commonly encountered phenomenon in laser materials processing [94,102], it has received limited attention in the laser nitriding literature. Morton et al. [59], probably drawing an analogy from laser welding processes, differentiated between two regimes of melting during laser nitriding: ‘normal melting’ below laser power densities of $10^9$ W/m$^2$ where energy transfer occurred through photons impinging upon the surface with an efficiency of less than 50 %, and ‘keyhole melting’ above power densities of $10^9$ W/m$^2$ where plasma formation resulted in energy transfer efficiencies close to 100 %. Although higher melt depths were achieved within the keyhole melting regime, it was fraught with problems such as high surface roughness, specimen distortion, and crack formation, and was thus deemed undesirable by the authors [59]. Thomann et al. [98] studied the laser-induced plasma that formed during pulsed CO$_2$ and XeCl laser nitriding of CP-Ti substrates; they found that the CO$_2$ laser-induced plasma occurred due to gas breakdown and was rich in ionic and atomic nitrogen species. They concluded that near-surface plasma formation enabled better energy coupling between the laser and the substrate and was hence necessary for the nitriding process [98]. Geetha et al. [81] observed near-surface plasma formation
in their pulsed Nd:YAG laser nitriding experiments in both pure and dilute nitrogen atmospheres; they noted that nitrogen dissociation in the plasma led to greater nitrogen diffusion rates into the melt pool. Moreover, they also reported that in an argon-diluted nitrogen atmosphere, ionic argon in the Ar-N₂ plasma hindered the diffusion of nitrogen, leading to a dendrite-free microstructure; as noted earlier, this effect has been observed before in the laser nitriding literature [64,65,74], albeit in the absence (or without the mention) of plasma formation. Höche et al. [103] and Ohtsu et al. [104] also argued that plasma formation aided the nitrogen dissociation process leading to the formation of nitrogen radicals that can diffuse faster into the titanium melt pool; plasma formation was thus dubbed beneficial to the laser nitriding process. Yu and Sun [105] conducted laser nitriding of titanium using a CO₂ laser in the presence and absence of a nitrogen plasma struck and sustained using an independent plasma gun. They found that at the same laser power density (10⁹ W/m²), the presence of the nitrogen plasma significantly enhanced the nitriding efficiency; this was attributed to the greater nitrogen intake occurring due to the presence of ionic and atomic nitrogen in the plasma.

On the other hand, Abboud et al. [78] took precautions to avoid plasma formation in their CO₂ laser nitriding experiments of Ti64, because the plasma (a) absorbed the laser radiation and hence reduced laser absorption on the titanium substrate, and (b) occasionally caused the focusing lens to break. Chen et al. [77] reported that the titanium-rich plasma pushed the nitrogen gas flow away from the titanium substrate and hence acted as a barrier between the nitrogen flow and the titanium substrate; consequently, they recommended that the laser power density be maintained at low values to prevent metal evaporation and subsequent plasma formation. However, Ohtsu et al. [106] recently found that the titanium-rich plasma could be confined to the substrate by maintaining a high enough pressure of nitrogen gas (100 kPa); at such high pressures, nitrogen radicals could effectively interact with the melt, leading to efficient coupling between the nitrogen gas flow and the substrate and, as a consequence, thicker nitrided layers.
1.3.2.3 Laser-sustained plasma (LSP) nitriding of titanium

Recently, the role played by near-surface plasma during CW CO₂ laser nitriding of CP-Ti in open and uncontrolled atmosphere was investigated in great detail by Nassar et al. [107] and Black et al. [108]. Using a combination of charge-couple device (CCD) imaging and optical spectroscopy, Nassar et al. [107] characterized the near-surface plasma formed during the laser nitriding process as a function of scanning speed and off-focal distance. They found three main processing regimes pertinent to plasma formation:

I. At low scanning speeds and small off-focal distances (i.e. conditions favoring higher power densities and longer beam-substrate interaction times), a Ti-rich plasma formed near the surface and did not allow the nitrogen gas flow to interact with the substrate, resulting in surface oxidation; Chen et al. [77] made a similar observation and argued against plasma formation since they believed that the Ti-rich plasma baffled the contact between nitrogen and the titanium substrate.

II. At intermediate scan speeds and off-focal distances, the near-surface plasma was richer in nitrogen species such as N and N⁺; this ensured sufficient interaction between the gas and the substrate and resulted in near-stoichiometric titanium nitride layers on the substrate. This regime can be thought of as similar to the one studied by researchers such as Thomann et al. [98] who concluded that plasma formation was necessary for efficient laser nitriding, as mentioned earlier.

III. Finally, at high scan speeds and/or large off-focal distances, near-surface plasma was not observed.

Nassar et al. [107] thus found a processing window of scan speeds and off-focal distances (Regime II) where a nitrogen-rich near-surface plasma struck during laser nitriding CP-Ti. Further, Nassar et al. [107] observed that nitriding in the presence of nitrogen-rich plasma (Regime II) in
an open and uncontrolled atmosphere reduced surface oxidation in the nitrided layers; this was attributed to the gettering action of the plasma whereby the active nitrogen species reacted with atmospheric oxygen. Also, microstructural characterization of the nitrided layers revealed no evidence of energy attenuation of the laser beam in the presence of plasma; this was because the laser energy absorbed by the LSP was transferred to the substrate via two mechanisms: (a) energetic nitrogen species in the plasma colliding with the substrate, and (b) low-wavelength ultraviolet re-radiation by the LSP that is absorbed more efficiently by the titanium substrate compared to the CO₂ laser radiation (10.64 µm wavelength) [107]. The presence of nitrogen-rich plasma was thus found to be beneficial for the laser nitriding process. Further, to reap the benefits of nitriding in the presence of nitrogen-rich plasma beyond the processing conditions of Regime II, Nassar et al. [107] conducted nitriding experiments in the presence of a pre-struck laser-sustained plasma (LSP) in coaxial nitrogen gas flow (Figure 1-3a). Laser-sustained plasma (LSP) is plasma that is generated and sustained near the focal plane of a laser beam in a gaseous atmosphere away from any potentially interacting surface [108]. A freestanding nitrogen LSP had a tear-drop shape with dimensions of approximately 15 mm in the axial direction and 5 mm in the radial direction (Figure 1-3b). This approach, henceforth referred to as LSP nitriding, allowed them to access the high scan speed/large off-focal distance processing conditions of Regime III in the presence of nitrogen-rich plasma. Nassar et al. [107] thus developed the LSP nitriding method that enabled them to conduct laser nitriding of CP-Ti in open and uncontrolled atmosphere in the presence of nitrogen-rich plasma over a broad processing window of scan speeds and off-focal distances (Regimes II and III). As part of his doctoral dissertation, Nassar [109] also demonstrated the utility of using an N₂-Ar LSP (50% N₂ by volume) to form hard and crack-free layers on CP-Ti substrates.

Black et al. [108] studied the interaction between a nitrogen LSP and a CP-Ti substrate by maintaining the CP-Ti substrate parallel to the axis of the CO₂ laser beam (Figure 1-3c); these experiments differed from Nassar et al.’s [107] experiments (Figure 1-3a) where the substrate was
normal to the laser beam. In Black et al.’s [108] configuration, the nitrogen LSP was the sole heating source since the laser beam did not irradiate the substrate. When the axis of the nitrogen LSP was brought within 2.5 mm of the CP-Ti substrate and maintained there for 5 seconds, the substrate melted and incorporated nitrogen from the plasma, resulting in the synthesis of TiN layers up to 300 µm in thickness on the substrate. Such rapid growth of TiN crystals on the CP-Ti substrate without any direct radiation from the CO₂ laser beam demonstrated the utility of the nitrogen LSP as a high-energy source of active nitrogen species.

Figure 1-3. (a) Schematic of Nassar et al.’s [107] LSP nitriding process with the substrate perpendicular to the laser beam, (b) CCD image of freestanding nitrogen LSP, and (c) schematic of Black et al.’s [108] LSP nitriding process with the substrate parallel to the laser beam. Images (a) and (b) reproduced from Ref. [107], and image (c) reproduced from Ref. [108].

1.3.2.4 Summary of literature review

An extensive survey of the literature on the laser nitriding technique as a means to improve the surface hardness and wear characteristics of titanium and its alloys was conducted. It was found
that the main advantages of the laser nitriding process over other competing processes are: (a) a significant reduction in processing times, (b) the formation of a strong metallurgical bond between the substrate and the hardened layer, (c) an ability to selectively harden the surface without affecting the bulk, and (d) an ability to achieve deep nitrided layers. The main drawbacks of the laser nitriding method are crack formation, surface roughness, and inhomogeneity in the hardened layer at high scan speeds. To prevent crack formation, the processing nitrogen gas is usually diluted with an inert gas such as argon or helium; although this approach is effective in forming crack-free nitrided surfaces, it is found to limit the TiN dendrite concentration in the hardened layer, resulting in microstructures that comprise a thin (3-5 µm) TiN layer at the top, TiN dendrites that grow from the thin layer to depths of around 50 µm, and a dendrite-free region deeper in the nitrided layer. Thus, elimination of surface cracks appears to come at the expense of reduced control over the microstructure, limiting the case depth and hardness to low values. The literature review also revealed considerable confusion regarding the role and utility of near-surface plasma formation during laser nitriding of titanium. However, the recent works of Nassar [109] and Black [110] conclusively showed that under the right processing conditions, nitrogen-rich near-surface plasma could be formed; further, if laser nitriding of CP-Ti was conducted in the presence of such a nitrogen-rich plasma, either struck at the surface or pre-struck and sustained by the power of the laser beam, surface oxidation could be eliminated without any energy attenuation of the laser beam. The laser-sustained plasma (LSP) nitriding process thus showed sufficient promise to merit further investigation, which will be the focus of this dissertation.
1.4 Dissertation overview

1.4.1 Problem statements

The work described in this dissertation will focus on developing the LSP processing method as a viable technique to develop deep, hard, and crack-free cases on CP-titanium. Apropos of the literature survey described in Section 1.3.2, the following research questions were identified and will be addressed in this dissertation:

1. How does the presence of laser-sustained plasma (LSP) affect the heat and mass transfer during laser nitriding at different processing conditions? (Chapter 3)

2. How do processing conditions such as off-focal distance, scan speed, and N₂:Ar gas flow ratio affect the microstructure during the LSP nitriding process? In particular, what effect does argon addition to the gas flow have on the microstructure? (Chapter 4)

3. Is it possible to form hard, deep, crack-free, nitrided cases on CP-Ti substrates with a better control over the microstructure than that afforded by the currently favored approach of nitrogen dilution? (Chapter 5)

4. Finally, can the wear resistance of CP-Ti be improved using the LSP processing method? (Chapter 6)

1.4.2 Organization of dissertation

In Chapter 2, the materials and the high-power CO₂ laser system used for the nitriding experiments are described. Details of the various material characterization techniques employed on the nitrided CP-Ti samples are provided. In addition, a three-dimensional heat conduction solution for a moving heat source [111] that was used to model the heat transfer occurring during the LSP nitriding process is also described.
In Chapter 3, laser nitriding experiments conducted at three different processing conditions in the presence and absence of a nitrogen LSP are described. The LSP nitriding and conventional laser nitriding processes are compared with respect to energy transfer, mass transfer, and surface oxidation tendencies. The work described in this Chapter was published in Ref. [112].

In Chapter 4, the results of LSP nitriding experiments conducted at different off-focal distances, scan speeds, and N$_2$:Ar gas flow ratios, are reported. Through weight measurements and microstructural characterization, a drastic reduction in nitrogen intake in the presence of argon is observed; this is attributed to a change in melt pool dynamics from convection-dominated (in pure nitrogen flow) to diffusion-dominated (in diluted nitrogen flow). The work described in this Chapter was published in Ref. [113].

In Chapter 5, a two-step method is developed that consists of laser nitriding (in a pure N$_2$ LSP) in the first step followed by laser remelting (in a pure Ar LSP) in the second step to perform deep-case hardening of CP-Ti substrates. Nitrogen intake is determined by the nitriding speed in the first step, while microstructure refinement is dictated by the remelting speed of the second step; thus, a greater control over the microstructure is demonstrated compared to the nitrogen-dilution approach commonly adopted in the laser nitriding literature. The remelting scan is shown to improve the homogeneity of the nitrided layer and to eliminate crack formation. The work described in this Chapter has been submitted to a journal [114] and is currently under review.

In Chapter 6, the two-step method developed in Chapter 5 is used to deposit multiple overlapping nitrided trails at four different nitriding speeds. Reciprocating ball-on-plate wear testing is conducted on the treated samples and the results are compared to the base metal, CP-Ti. A significant improvement in the wear properties of CP-Ti is reported due to the nitriding-remelting treatment. The work described in this Chapter is in preparation for submission to a journal.

Finally, in Chapter 7, conclusions are drawn and recommendations for future work are made.
Chapter 2

Experimental details and heat transfer model

2.1 Introduction

As noted at the end of Chapter 1, this dissertation will explore the applicability of the LSP nitriding method towards developing deep and hard cases on CP-Ti substrates, thereby improving their wear resistance. Details of the materials, experimental procedures, and theoretical analysis are presented in this Chapter.

2.2 Experimental details

2.2.1 Specimen preparation (pre-processing)

Commercially-pure (99% purity) grade 2 titanium ordered from McMaster-Carr was used in the nitriding experiments. The stock was ordered in the form of 3.175 mm (1/8 in.) thick plates that were machined into rectangular test coupons having final dimensions of 25.4 mm (1 in.) x 50.8 mm (2 in.) x 3.175 mm (1/8 in.). Prior to the laser nitriding experiments, the test coupons were successively ground using sandpaper of grit sizes 120, 240, 400, and 600. This maintained consistency and removed the passive oxide layer from the substrate before nitriding. The substrate was then cleaned using acetone and isopropyl alcohol.
2.2.2 Experimental setup

2.2.2.1 Laser system

A PRC STS 5000 CO₂ laser, operating in the continuous-wave (CW) mode at a wavelength (λ) of 10.6 µm, was used for the laser nitriding experiments. The collimated laser beam had a 1/e² diameter (defined as the diameter where the beam intensity drops to 1/e² = 13.5% of its maximum value), D_{coll}, of 22 mm and a ‘quadramode (Q-mode)’ intensity distribution, which was a superposition of four fundamental transverse electromagnetic (TEM) modes: TEM₀₀ (14 %), TEM₁₀ (14 %), TEM₀₁* (36 %), and TEM₀₂* (36 %). The theoretical intensity distribution of the Q-mode laser beam as a superposition of four fundamental TEM modes is plotted against radial distance in Figure 2-1 for a laser power of 3.5 kW and a 1/e² radius of 200 µm. The beam quality factor (M²), which is the ratio of actual beam divergence to the theoretical beam divergence of a Gaussian beam, was 3.2.

![Q-mode of the PRC 5000 laser beam](image)

Figure 2-1. Theoretical intensity profile of the Q-mode CO₂ laser beam shown as a superposition of four fundamental TEM modes.
2.2.2.2 Beam path and optics

The collimated laser beam produced by the PRC laser was guided to the processing chamber by four copper mirrors and a quarter-wave plate which imparted circular polarization to the laser beam. The beam path was sealed and a positive pressure was maintained using compressed air to minimize contamination due to dust and moisture. In the processing chamber, the laser beam was focused using a zinc selenide (ZnSe) plano-convex lens having a focal length, $f$, of 127 mm (5 in). The $1/e^2$ spot diameter at focus, $d_{\text{focus}}$, was calculated to be 0.25 mm using Equation 2-1 [94]:

$$d_{\text{focus}} = \frac{4M^2f\lambda}{\pi D_{\text{coll}}}$$  \hspace{1cm} (2-1)

Preventive maintenance of the laser system was carried out by the manufacturer twice a year to ensure that the beam mode remained consistent. The optics were cleaned and the laser beam was aligned periodically as needed.

2.2.2.3 Processing chamber

The nitriding experiments in this research were carried out in processing chamber open to the atmosphere. The processing chamber was enclosed by windows that were impervious to the CO$_2$ laser wavelength of 10.6 µm. High-purity nitrogen (99.999 % pure) and/or argon (99.997 % pure) gases were used for processing, and their flow rates were controlled individually using Omega rotameters; the processing gases flowed into the Precitec laser head independently and issued out of a copper nozzle, which was coaxial with the laser beam and 10 mm in diameter. The focal plane of the ZnSe lens was 13 mm below the copper nozzle. The CP-Ti coupon was clamped on its shorter edge (25.4 mm, 1 in.) to an Aerotech stage that translated in the horizontal X-Y plane, while the laser head translated along the vertical Z direction, giving a total of three degrees of freedom. The Z-position of the laser head determined the focal plane of the beam, and the Z-position needed for
the focal plane to coincide with the surface of the coupon was determined beforehand. The laser power, X-Y translation of the stage, Z-translation of the laser head, and scan speed were controlled by a Labview program that interfaced with both the PRC laser and the Aerotech stage, while the gas flow rates were manually adjusted on the rotameter before each experiment. The complete experimental set up is shown in Figure 2-2a, with a schematic of the LSP nitriding process in Figure 2-2b and a CCD image of a freestanding nitrogen LSP in Figure 2-2c.

Figure 2-2. a) Experimental setup, b) Schematic of LSP nitriding process, c) CCD image of a freestanding nitrogen LSP (green arrow points in the direction of the laser beam).

2.2.3 Laser-sustained plasma processing

2.2.3.1 Methodology

All the experiments in this dissertation were conducted at a laser power of 3.5 kW unless otherwise noted. Prior to the experiments, the laser power was checked on a Coherent calorimeter placed in the processing chamber at the end of the beam path (i.e. after the ZnSe focusing lens) to determine the input laser power needed to be produced by the PRC laser to obtain an output power of 3.5 kW at the calorimeter. The LSP processing experiments proceeded as follows:
i. The nitrogen and/or argon gas flow was manually adjusted to the desired flow rate, measured in standard liters per minute (slpm), using the rotameter.

ii. The laser head position along the Z-axis was adjusted to obtain the required off-focal distance (OFD), and the ignition coupon (CP-Ti, labeled in Figure 2-2a) clamped to the Aerotech stage was translated to the desired starting position.

iii. The beam was then turned on and the ignition coupon was translated under the laser beam at the desired scan speed. The OFD and scan speed needed to ignite and sustain the plasma were determined from the processing conditions given in Nassar et al. [107]. It must be noted here that an argon plasma could be struck at much lower powers (~2 kW) than a nitrogen plasma (~3.1 kW). The ignition coupon served as a source of free electrons to initiate plasma formation, as discussed in Section 1.3.2.2. Once initiated, the nitrogen and/or argon plasma could be sustained by the energy of the laser beam indefinitely near its focal plane after the ignition coupon was removed from the beam path. The laser-sustained plasma (LSP) was allowed to stabilize for about 5 seconds. A CCD image of a freestanding nitrogen LSP is shown in Figure 2-2c.

iv. The test coupon was then scanned underneath the LSP at the desired processing conditions (OFD, scan speed, and laser power). The LSP was extinguished by turning the laser beam off at the end of the experiment.

Steps ii-iv above were realized by a pre-written program that was read and executed by the Labview interface.

2.2.3.2 In situ temperature monitoring

During some experiments, the temperature at the back of the substrate was monitored using one or more K-type Omega thermocouples. The thermocouples were spot-welded to the substrate
to ensure good thermal contact between the thermocouple bead and the substrate; the thermocouples were welded near the center region (to avoid edge effects) of the back surface (to shield the thermocouple bead from the LSP radiation). The temperatures were logged at a sampling rate of 100 measurements per second using a separate Labview program and a National Instruments data acquisition system (NI-DAQ).

2.2.4 Characterization techniques (post-processing)

2.2.4.1 Weight measurement

Weight measurements were conducted on the treated samples to quantify the nitrogen intake into the melt pool. Five or more identical runs were conducted at a given set of processing conditions on a single coupon to reduce statistical error; the coupons were weighed before and after processing, and the average weight increase per nitrided trail was recorded. The weight measurement runs were conducted on slightly larger coupons having dimensions of 50.8 mm (2 in.) x 50.8 mm (2 in.) x 3.175 mm (1/8 in.). The weighing machine had a scale interval of $10^{-4}$ grams.

2.2.4.2 Optical metallography

Metallography is an important step in evaluating the merits of a given processing technique and optimizing the processing parameters. The ASM Handbook [115] defines metallography as “… the scientific discipline of examining and determining the constitution and the underlying structure of (or spatial relationships between) the constituents in metals, alloys and materials”.
The purpose of the metallographic investigation conducted in this dissertation was to impart a fine polish and etch to the transverse cross sections of the nitrided trails so they could be observed under optical and scanning electron microscopes, thus allowing a study of the effect of the LSP nitriding treatment on the transverse cross-sectional microstructure (grain morphologies, grain boundaries, phases, defects, melt pool depths etc.) of the nitrided case. Metallography entailed the following steps:

**Sectioning and mounting:**
The nitrided sample was sectioned at a feed rate of 0.075 mm/s using a silicon carbide (SiC) abrasive cut-off wheel rotating at 3000 rpm in the presence of a flow of distilled water. The sectioning was conducted at the center of the trail to avoid edge effects. The sectioned piece was mounted in bakelite in a hot mounting press.

**Rough polishing:**
The transverse cross-section of the mounted sample was polished using sandpaper of grit sizes of 120, 240, 400, 600, 800, and 1200, in that order. The sandpaper was fixed to a rotating wheel while the mounted sample was manually held on the rotating sandpaper applying moderate pressure in the presence of the flow of distilled water.

**Fine polishing:**
The sample was subjected to finer polishing using the procedure outlined in Table 2-1. The fine polishing steps were performed on a machine that achieved counter rotation between the sample and the cloth automatically, the latter rotating at 150 rpm. The times given in Table 2-1 are approximate; the final colloidal silica polishing step was allowed to continue till the sample had a mirror-like finish with no scratches.
Table 2-1. Fine polishing procedure

<table>
<thead>
<tr>
<th>Polishing compound</th>
<th>Cloth (Leco Corp.)</th>
<th>Force (N)</th>
<th>Time (min.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 µm diamond suspension</td>
<td>Ultra Silk</td>
<td>20-25</td>
<td>6</td>
</tr>
<tr>
<td>1 µm diamond suspension</td>
<td>Ultra Silk</td>
<td>20-25</td>
<td>6</td>
</tr>
<tr>
<td>Colloidal silica solution (nominal particle size 0.08 µm)</td>
<td>Imperial</td>
<td>15-20</td>
<td>10</td>
</tr>
</tbody>
</table>

**Etching:**

The polished sample was etched using a stronger version of Kroll’s reagent containing 85-90 mL distilled water, 5 mL hydrofluoric acid, and 5 mL nitric acid. The sample was etched for 5 seconds before being washed with distilled water.

**Optical microscopy:**

The polished and etched transverse cross-section was observed under an optical microscope (Nikon Epiphot 300) at magnifications of 50x, 100x, and 200x. Analyses of optical micrographs and determination of dendrite volume fractions in the melt pool were conducted using the image processing software, ImageJ [116].

**Microhardness testing:**

Vickers microhardness testing (Leco MHT 200) was conducted on the polished and etched transverse cross-sections. Each hardness indentation was made using a load of 30 grams for 15 seconds. Hardness indents were made at different depths in the solidified melt pool, with 3-5 indents per depth, to generate a hardness depth profile. Average case hardness values were calculated from a minimum of nine hardness measurements taken near the center region of the solidified melt pool.
2.2.4.3 Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS)

Scanning electron microscopy (Philips XL30 ESEM) was conducted on the transverse cross sections when higher magnification was desired. SEM was also used on the top surface of the nitrided layer to observe surface morphology and to detect defects such as cracks and pores. Semi-quantitative energy dispersive spectroscopy (FEI Quanta 200 Environmental SEM) was used to determine elemental composition in some cases. The EDS spectra were analyzed using Oxford Instruments’ AZtecEnergy software, which used Ti and BN as factory standards to identify titanium and nitrogen respectively.

2.2.4.4 X-ray diffraction (XRD)

X-ray diffraction (PANalytical XPert Pro MPD operated in the Bragg Brentano geometry) was performed on the top surface of the nitrided layers for phase identification. The X-rays were generated (40 kV, 40 mA) using a Cu anode having a K$\alpha$ wavelength of 1.5406 Å. The continuous scans were conducted within a 2θ-range of 25° to 70° using a step size of 0.026°. The MDI JADE software, equipped with a database of powder diffraction files (PDF’s), was used to identify peaks.

2.2.4.5 Optical profilometry

Three-dimensional (3D) optical profilometry (Zygo NewView 7300) was conducted on the top surface of the processed specimens to study the effect of varying processing parameters on surface roughness. Zygo’s Mx™ was used as the post-processing software to determine quantities such as root mean square (RMS) roughness, peak-to-valley height, etc. from the 3D surface profiles.
2.2.5 Wear testing

Linear reciprocating ball-on-flat sliding wear tests were conducted to evaluate the change in wear resistance due to the LSP treatment. In this test, a ball reciprocates linearly over a sample for a fixed number of cycles under a normal load, thereby causing it to wear; the volumes of the wear scar on the ball and the sample are then used to compare the wear resistance of different materials under similar testing conditions. Reciprocating wear tests were conducted on the processed and unprocessed samples in accordance with ‘Procedure A’ of the ASTM G133-05 standard [117] using a Plint tribometer at laboratory conditions of 24 °C and 45% relative humidity (RH). An alumina ball, 9.525 mm (3/8 in.) in diameter, slid back and forth on top of the sample with a reciprocating frequency of 5 Hz and a stroke length of 10 mm. A normal force of 25 N was applied between the ball and the sample. The test was run for a duration of 16 minutes and 40 seconds which led to a total sliding distance of 100 m. No lubrication was used. A schematic of this test is shown in Figure 2-3.

![Schematic of a linear reciprocating ball-on-flat wear test](image)

Figure 2-3. Schematic of a linear reciprocating ball-on-flat wear test. Image reproduced from the ASTM G133-05 standard [117].

Frictional force was monitored throughout the test using a data acquisition system (IOtech WaveBook/512H™) at a sampling rate of 250 Hz. Optical profilometry was performed on the wear
scars on the flat samples; wear volumes and wear profiles along the transverse and longitudinal directions were calculated using the Zygo Mx™ software. The wear scars were also observed at high magnification under the SEM to gain more insight into wear mechanisms.

2.2 Heat transfer model

2.2.1 Background

The LSP nitriding and remelting processes are complicated to model due to a variety of physical effects that include: plasma-melt pool interaction; fluid flow in the melt pool; material properties (specific heat, thermal conductivity, surface tension etc.) that are functions of both temperature and solute (nitrogen) concentration; advection of nitrogen in the melt pool; and solidification of TiNx phases, among others. In this work, melt depths and melt pool lifetimes were of primary interest; hence, an analytical heat conduction solution valid for a moving heat source, developed by Cline and Anthony [111], was used to model the heat transfer occurring in the substrate during LSP processing **. The solution allows a calculation of the steady-state three-dimensional temperature field in a semi-infinite substrate due to a moving Gaussian heat source such as a laser beam. A brief derivation of the Cline and Anthony solution [111] is presented in the following section.

**A comprehensive overview of modeling techniques in laser materials processing is available in reference books by Steen and Majumdar [151] and Dowden [119].
2.2.2 Heat conduction due to moving heat source

Consider a laser heat source, $Q$ (W/m$^3$), moving with velocity $v$ in the positive $X$-direction over a semi-infinite substrate defined by $z > 0$, as shown in Figure 2-4. The intensity profile of the volumetric heat source, assumed to be Gaussian in the $X$-$Y$ plane, is given by:

$$Q = \frac{P}{2\pi R^2} \exp \left( -\frac{[(x-vt)^2+y^2]}{2R^2} \right) \frac{h(z)}{\lambda}$$  \hspace{1cm} (2-2)

where $P$ is the laser power (W), $R$ is the spot radius (m) containing all the laser power, $v$ is the velocity (m/s) of the heat source moving along the $X$-direction, $t$ is the time (s), $\lambda$ is the penetration depth (m), making $h(z) = 1$ for $0 < z \leq \lambda$ and $h(z) = 0$ for $z > \lambda$, and $x$, $y$, and $z$ denote co-ordinates (m) along the $X$, $Y$, and $Z$ axes respectively. The Cartesian co-ordinate system is as indicated in Figure 2-4. The heat generated at the top of the semi-infinite substrate is conducted into the bulk; this heat conduction is governed by the well-known Equation 2-3:

$$\frac{\partial T}{\partial t} - \nabla^2 T = \frac{Q}{\rho C_p}$$  \hspace{1cm} (2-3)

where $\nabla^2$ denotes the Laplace operator, $T$ is the temperature ($^\circ$C), $\rho$ and $C_p$ are the substrate material’s density (kg/m$^3$) and specific heat (J kg$^{-1}$ $^\circ$C$^{-1}$) respectively. The initial temperature of the
substrate is uniform and equal to zero. Since the substrate is semi-infinite, its boundaries are assumed to be far enough from the top surface \((z = 0)\) not to be affected by the heat generation; in other words, the temperature at all faces barring the top surface remains equal to zero. The boundary condition at the top surface is assumed to be adiabatic. Thus,

\[ T(x, y, z) = 0 \text{ at } t = 0 \]

\[ T = 0 \text{ as } x, y, z \rightarrow \infty, \text{ and as } x, y \rightarrow -\infty \quad (2-4) \]

\[ \frac{\partial T}{\partial z} = 0 \text{ at } z = 0 \]

The problem at hand can be formally stated as follows: what temperature distribution in the substrate, \(T(x, y, z)\), satisfies Equation 2-3 subject to the initial and boundary conditions given by Equation 2-4, where the volumetric heat source is given by Equation 2-2?

Cline and Anthony [111] solved this problem using the Green’s function approach. The Green’s function \((m^3)\), \(G(x', y', z', t' | x, y, z, t)\), is an integral kernel that can be physically thought of as the system response at point \((x, y, z)\) in the substrate at time \(t\), caused by an instantaneous release of unit energy at time \(t'\) by a point heat source located at co-ordinates \((x', y', z')\). Green’s functions pertaining to heat conduction have been calculated for a variety of geometries and boundary conditions [118]. For an infinite substrate with boundary conditions given by Equation 2-4, the Green’s function for the heat conduction equation (Equation 2-2) is [118], \(G_1\), is:

\[ G_1 = \frac{\exp\left[\frac{-(x-x')^2 + (y-y')^2 + (z-z')^2}{2D(t-t')}\right]}{8\pi D(t-t')^{3/2}} \quad (2-5) \]

where \(D\) \((m^2 s^{-1})\) is the thermal diffusivity of the substrate material. For a semi-infinite substrate \((z \geq 0)\) with a point heat source at the top surface \((z' = 0)\), all the heat generated goes into the half-space defined by \(z > 0\), as opposed to the infinite substrate where heat flows equally into the two half spaces defined by \(z > 0\) and \(z < 0\). Moreover, if no heat losses from the surface \(z = 0\) are assumed, the condition \(\frac{\partial T}{\partial z}|_{z=0}\) is true for both the infinite and semi-infinite substrates. From these
arguments, it is clear that the Green’s function, $G$, for the semi-infinite substrate is simply twice the expression for $G_1$ [119]:

$$G = \frac{\exp \left[ -\frac{[(x-x')^2 + (y-y')^2 + (z-z')^2]}{4\pi D(t-t')} \right]}{4\pi^2 D(t-t')}$$ (2-6)

where $z' = 0$ at the surface. The steady-state temperature field due to the continuous Gaussian heat source given by Equation 2-2 is then obtained by: i) multiplying the Green’s function, $G$ (m$^{-3}$), by $Q/(\rho C_p)$ (°C m$^{-3}$s$^{-1}$), and then ii) integrating this product along $x'$, $y'$, $z'$, and $t'$ till a time of $t = 0$. In other words, the temperature at $(x, y, z, t)$ is found by superimposing the effects of individual Gaussian heat sources centered at $(x', y', z' = 0)$ at all times $t'$ such that $t' \leq 0$ [111]:

$$T(x, y, z) = \int_{t' = 0}^{t' = \infty} \int_{x' = -\infty}^{x' = \infty} \int_{y' = -\infty}^{y' = \infty} \int_{z' = -\infty}^{z' = \infty} \frac{Q(x', y', z', t')}{\rho C_p} G(x', y', z', t' | x, y, z, t) \, dz' \, dy' \, dx' \, dt'$$ (2-7)

Substituting for $Q$ and $G$ using Equations 2-2 and 2-6, the integrals over $x'$ and $y'$ can be solved analytically, while the integral over $z'$ is simply equal to unity. Cline and Anthony [111] calculated the integral in Equation 2-7 to be:

$$T(x, y, z) = \frac{P}{\rho C_p} \int_{0}^{\infty} \frac{\exp \left[ -\frac{[(x+\sigma \mu^2)^2 + y^2 + z^2]}{2R^2 + 4Dt'} \right]}{(2\pi^3Dt')^{3/2}} \, d\mu$$ (2-8)

which is concisely expressed using dimensionless numbers to be:

$$T(x, y, z) = \frac{P}{\rho C_p DR} \int_{0}^{\infty} \frac{\exp (-H)}{(2\pi^3)^{3/2}(1+\mu^2)} \, d\mu$$ (2-9)

where$^{\dagger\dagger}$:

$$H = \frac{(X+\sigma \mu^2)^2 + Y^2}{2(1+\mu^2)} + \frac{Z^2}{2\mu^2}, \quad \sigma = \frac{Rv}{D}, \quad X = \frac{x}{R}, \quad Y = \frac{y}{R}, \quad Z = \frac{z}{R}$$ (2-10)

In equation 2-10, $\mu$ denotes dimensionless time, $\sigma$ denotes dimensionless scan speed, and $X$, $Y$, and $Z$ denote dimensionless Cartesian co-ordinates. The steady-state temperature field in the semi-

$^{\dagger\dagger}$Some typographical errors were detected in Cline and Anthony’s original article [111] by the present author – these have been rectified in Equation 2-10.
infinite substrate, \( T(x, y, z) \), is thus easily computed through a numerical calculation of the definite integral given in Equation 2-9 using the dimensionless number definitions given in Equation 2-10. Moreover, using the transformation \( \Delta x = \nu \Delta t \), the temperature of any point \((y, z)\) in a given transverse cross-section (i.e. \( x = \) constant plane) can be calculated as a function of time, \( t \). It is important to note that unlike a moving point heat source solution (e.g. Rosenthal’s solution [120]), Cline and Anthony’s solution (Equation 2-8 or 2-9) for a Gaussian heat source does not predict infinite temperature at the origin \((x = y = z = 0)\) i.e. underneath the beam axis. Furthermore, the effects of different laser beam profile shapes (Gaussian or otherwise) can be incorporated into the heat transfer model – this will be discussed in the next section.

2.2.3 Application to LSP processing

A slightly modified form of Cline and Anthony’s solution (Equation 2-9) can be used to model the heat transfer in the titanium substrate during LSP processing:

\[
T(x, y, z) = T_{room} + \frac{\eta}{\rho c_p DR} \int_0^\infty \frac{\exp(-H)}{(2\pi^3)^{1/4} (1+\mu^2)} d\mu \tag{2-11}
\]

where \( T_{room} \) is the room temperature (25 °C) and \( \eta \) is the fraction of the laser energy absorbed by the titanium substrate, subject to some simplifying assumptions about the system.

2.2.3.1 Simplifying assumptions

- Constant material properties of the substrate were assumed i.e. temperature and solute concentration dependence of properties such as specific heat, thermal conductivity, and density, was neglected.
• A semi-infinite substrate was assumed, according to the requirements of Cline and Anthony’s [111] solution. From Equation 2-10, the characteristic length scale for the system, $L_{\text{char}}$, can be chosen to be either the beam radius ($R$) or the quotient of thermal diffusivity and the scan velocity ($D/v$), the latter being more relevant to the moving heat source problem. For a thermal diffusivity of $D = 7 \times 10^{-6} \text{ m}^2/\text{s}$ [121] and a typical scan speed of $v = 45 \text{ mm/s}$, the characteristic length scale is calculated to be $L_{\text{char}} \sim 0.15 \text{ mm}$, which is an order-of-magnitude less than the coupon thickness, which was 3.175 mm (Section 2.2.1). Thus, it was concluded that the bottom face of the finite-sized coupons did not affect the temperature calculations appreciably [119]; in other words, the coupons were thick enough to allow for a semi-infinite substrate assumption.

• Convective and radiative losses from the top surface were neglected because of the presence of the high-temperature plasma above the melt trail.

• Latent heats of melting and solidification, and the heat of formation of the exothermic Ti + 0.5N$_2$ $\rightarrow$ TiN reaction were neglected. These effects can be incorporated into the model by an appropriate choice of the energy absorption efficiency, $\eta$ [72], which was measured experimentally for both the LSP nitriding and remelting processes (Section 2.2.3.3).

• Heat conduction was considered to be the only mechanism of heat transfer in the substrate, and convective heat transfer due to fluid flow in the melt pool was neglected.

• It was assumed that the intensity profile of the energy incident upon the substrate, due to the combination of the laser beam and the LSP, was the same (quadramode) as that of the laser beam. Nassar et al. [107] observed identical melt pool shapes when they nitrided CP-Ti substrates with and without a nitrogen LSP under similar conditions, which suggested that the intensity profile of the incident energy did not vary significantly in the presence of plasma.
2.2.3.2 Q-mode of the PRC laser beam

The temperature distribution of Equation 2-11 assumes a Gaussian intensity profile given by Equation 2-2 as the heat source. Since the solution given by Equation 2-11 is linear with respect to the heat source, the temperature distribution due to a non-Gaussian heat source (such as the Q-mode intensity profile shown in Figure 2-1) could be calculated by expressing the non-Gaussian heat source as a linear superposition of two or more Gaussian heat sources, and then summing the temperature distributions due to each of these Gaussian sources. It was found that the non-dimensional quadramode intensity profile ($I_{Q\text{-mode}}^*$) of the PRC laser beam as a function of the non-dimensional radial co-ordinate ($r^*$) could be accurately expressed as a sum of three non-dimensional Gaussian profiles as:

$$I_{Q\text{-mode}}^* = \sum_{i=1}^{3} a_i \exp\left[-\left(\frac{r^*}{b_i}\right)^2\right]$$  \hspace{1cm} (2-12)

where $a_i$ and $b_i$ are fitting parameters that control the height and width of the individual Gaussians respectively. The optimized values of the fitting parameters were found to be:

$$(a_1, a_2, a_3) = (70.5516, 76.8708, -147.142)$$
$$(b_1, b_2, b_3) = (0.683714, 0.730346, 0.706686)$$ \hspace{1cm} (2-13)

It should be noted that the negative value of $a_3$ indicates that the third Gaussian used in the fit acted as a heat sink – while this was physically unrealistic, it mathematically allowed the Q-mode intensity profile to be fit to a sum of three Gaussians with high accuracy.

An individual stationary Gaussian heat source, $Q_i$, has a functional form given by:

$$Q_i = \frac{P_i}{2\pi R_i^2} \exp\left(-\frac{r^2}{2R_i^2}\right)$$ \hspace{1cm} (2-14)

which is similar to Equation 2-2 (with $v = 0$ for a stationary beam) that was used in Cline and Anthony’s solution. $Q_i$ is thus uniquely defined by a combination of the variables $P_i$ (that determines its height) and $R_i$ (that determines its width). For a PRC laser operating at a power of
$P_0$ (Watts) and a spot radius of $r_0$ (m) at the substrate, $P_i$ (Watts) and $R_i$ (m) of the individual Gaussians can be calculated by dimensionalizing $a_i$ and $b_i$:

$$R_i = \frac{b_ir_0}{\sqrt{2}} \quad \text{and} \quad P_i = 4a_iP_0 \left(\frac{R_i}{r_0}\right)^2 = 2a_i b_i^2 P_0$$

(2-15)

where the spot radius at the substrate, $r_0$, varies with the off-focal distance (OFD) as [94]:

$$r_0^2 = \left(\frac{d_{\text{focus}}}{2}\right)^2 \left[1 + \left(\frac{4\lambda M^2 \text{OFD}}{\pi d_{\text{focus}}^2}\right)^2\right]$$

(2-16)

Using Equations 2-13, 2-15, and 2-16, it was thus possible to accurately express the Q-mode intensity profile of the PRC laser beam, at a given laser power and off-focal distance, using a sum of three Gaussian profiles with optimized values of $P_i$ and $R_i$ ($i = 1$ to 3). As an example, the Q-mode intensity distribution of Figure 2-1 (plotted for a laser power of $P_0 = 3500$ W and a $1/e^2$ radius of $r_0 = 200 \times 10^{-6}$ m) has been fitted to a sum of the three Gaussians (shown as the dashed line in Figure 2-1) having $(P_i, R_i)_{i=1 \text{ to } 3}$ values of $(230862$ W, 58 x $10^{-6}$ m), $(287023$ W, 62 x $10^{-6}$ m), and $( -514385$ W, 60 x $10^{-6}$ m) respectively. As expected, $P_1$, $P_2$, and $P_3$ added up to 3500 W, which was the operating power of the Q-mode laser beam. The temperature contributions from the three individual Gaussian heat sources defined by $(P_i, R_i)_{i=1 \text{ to } 3}$ were then added to obtain the temperature field due to the quadrarmode PRC laser beam at a given power, off-focal distance, and scan speed. In this way, Cline and Anthony’s solution methodology was slightly modified to calculate temperature fields due to a moving non-Gaussian Q-mode laser beam.

Table 2-2. Values of constants used in Equation 2-11.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific heat, $C_p$ (J/kg °C)</td>
<td>528 [121]</td>
</tr>
<tr>
<td>Density, $\rho$ (kg/m$^3$)</td>
<td>4500 [121]</td>
</tr>
<tr>
<td>Thermal diffusivity, $D$ (m$^2$/s)</td>
<td>$7 \times 10^{-6}$ [121]</td>
</tr>
<tr>
<td>Energy absorption efficiency, $\eta$</td>
<td>0.14 (nitriding) and 0.1 (remelting)</td>
</tr>
<tr>
<td>Room temperature, $T_{\text{room}}$ (°C)</td>
<td>25</td>
</tr>
</tbody>
</table>
2.2.3.3 Calculation of temperature field

The definite integral in Equation 2-11 was estimated using numerical quadrature implemented by the QAGI subroutine in the QUADPACK [122] library in FORTRAN. Thermal properties of titanium at room temperature [121] were used for the calculations, and are given in Table 2-2. Sample FORTRAN scripts written to calculate the width and depth of three isotherms (1670 °C, 2350 °C, and 3290 °C) as a function of time, and to calculate the x-z co-ordinates of isotherms in the transverse cross-section, can be found in the Appendices A and B respectively. The code was verified by successfully replicating the temperature plot given in Figure 7b of Cline and Anthony’s original article [111] at identical simulation conditions.

The efficiency of energy absorption ($\eta$) was used as a tuning parameter to fit the melt width calculated by the model to the experimentally observed melt widths for the LSP nitriding and melting processes. CP-Ti substrates were scanned under a prestruck pure-nitrogen LSP (8 mm off-focal distance) at speeds of 30, 45, and 60 mm/s, and under a prestruck pure-argon LSP (7 mm off-focal distance) at speeds of 20, 25, and 30 mm/s at a laser power of 3.5 kW. The melt pool width was measured in all cases and the value of $\eta$ was adjusted so that the calculated width of the melt isotherm for titanium (1670 °C) was within ±5% of the experimentally measured trail width for all the scan speeds. The values of $\eta$ for the LSP nitriding and melting processes were found to be 0.14 and 0.1, respectively, as shown in Figure 2-5. As expected, the value of $\eta$ for LSP nitriding was higher due to the exothermicity of TiN formation in the melt pool.

---

‡‡In the LSP nitriding runs, the surface microstructure showed a ‘zipper-like’ structure at the trail edges, believed to have formed due to melt overflow (explained in Section 4.3.1.3). In this dissertation, the melt width is defined and measured as the width of the nitrided trail excluding the zipper-like regions.
Figure 2-5. Determination of the energy absorption efficiency ($\eta$) for a) argon LSP melting (7 mm off-focal distance) and b) LSP nitriding (8 mm off-focal distance) experiments. The error bars indicate a range of ±5% around the measured widths.

Figure 2-6. a) Melt isotherm (shown in red) plotted using Equation 2-11, superimposed upon transverse cross-section of melt pool obtained by LSP nitriding at a speed of 30 mm/s and off-focal distance of 8 mm, b) corresponding width and depth of the melt pool as a function of time.

The heat transfer model served mainly to calculate isotherm dimensions and lifetimes, where lifetime is defined as the time for which a given isotherm in the substrate has non-zero dimensions; these concepts will be extensively used in Chapter 6. As an example, the melt isotherm for titanium (1670 °C) during LSP nitriding at 30 mm/s scan speed, 8 mm off-focal distance, and 3.5 kW power, is shown as the red line superimposed upon the transverse cross-section of the melt pool in Figure 2-6a. The corresponding melt pool lifetime calculation is shown in Figure 2-6b,
where the width and depth of the melt isotherm are plotted as a function of time; the melt pool lifetime for this case was calculated to be 0.119 seconds.

### 2.3 Chapter summary

In this chapter, the experimental and analytical techniques used in this dissertation were described. Common details pertaining to the materials, the high-power PRC CO₂ laser system, beam delivery optics, LSP processing methodology, and the post-processing material characterization techniques were provided. An analytical heat conduction solution [111] pertaining to a moving heat source was used to model heat transfer during the LSP processing of titanium. Since this solution was valid for Gaussian beams, the quadramode beam profile of the PRC laser was fitted to the sum of three Gaussian heat sources. The efficiency of energy absorption at the substrate, $\eta$, was experimentally determined for both the LSP nitriding ($\eta = 0.14$) and LSP remelting ($\eta = 0.1$) processes by ensuring that the calculated melt widths were within ±5% of the measured trail widths at three scan speeds each. In conclusion, the groundwork for the experiments of Chapters 3-7 was established in this Chapter.
Chapter 3

Comparison between LSP nitriding and conventional laser nitriding

3.1 Introduction

The desirability of the presence of near-surface plasma during laser nitriding of titanium has been debated in the literature, as discussed in detail in Section 1.3.2.2. Some researchers [81,98,103–105] have argued that the presence of atomic and ionic nitrogen species aided the laser nitriding process and increased the nitriding efficiency, while others [59,77,78] have claimed that the plasma absorbed the laser energy and acted as a baffle between the titanium substrate and the nitrogen gas flow. Nassar et al. [107] noticed that at processing conditions of 3.5 kW laser power, 8 mm off-focal distance (OFD), 90 mm/s scan speed, and 16 standard liters per minute (slpm) of pure-nitrogen gas flow, the melt pool of the nitrided layer looked identical with or without LSP in cross-sectional optical micrographs suggesting no energy attenuation of the laser beam; moreover, they reported a reduction in surface oxidation in the presence of plasma at this set of conditions.

In this Chapter, the work of Nassar et al. [107] will be expanded by systematically studying and quantifying the effect of LSP on the heat and mass transfer of the nitriding process. Three experimental conditions were chosen using combinations of scan speeds and off-focal distances chosen from the processing window of Nassar et al. [107] as shown in Figure 3-1, and nitriding experiments were conducted with and without LSP. The conditions were chosen such that when the experiment was conducted without a pre-struck plasma (i.e. only with the laser beam), no surface-struck plasma was observed. This was important in order to isolate the effect of LSP from that of a laser-only nitriding process. The samples nitrided with and without the LSP were
characterized using a variety of techniques and the results were compared, thus allowing the unique effects of LSP on the nitriding process to be isolated, studied, and quantified. This methodology thus allowed for a direct comparison of the LSP nitriding process and conventional laser nitriding processes.

![Figure 3-1](image)

Figure 3-1. Experimental conditions studied (denoted by triangles) to quantify the effect of LSP in nitriding. The conditions are overlaid on a LSP nitriding processing window plot, reproduced from Nassar et al. [21] with minor modifications.

### 3.2 Methodology

All the experiments were performed using the CO₂ laser and the experimental setup described in Section 2.2.2. The CP-Ti coupons were 50.8 mm x 50.8 mm x 3.175 mm in dimension, unless otherwise noted. High-purity nitrogen gas was used in all the experiments. The laser power (3.5 kW) and nitrogen gas flow (16 slpm) were held constant, while speed and OFD were varied as shown in Table 3-1. It must be noted that when the OFD decreases, the laser spot size decreases,
which increases the incident energy density and aids in the formation of a surface-struck plasma. Hence, the scan speed was increased to counter the increased energy density by decreasing the net energy deposited on the surface.

Table 3-1. List of nitriding experiments.

<table>
<thead>
<tr>
<th>Run#</th>
<th>Scan speed (mm/s)</th>
<th>OFD (mm)</th>
<th>LSP / No LSP</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>60</td>
<td>9</td>
<td>No LSP</td>
</tr>
<tr>
<td>2</td>
<td>60</td>
<td>9</td>
<td>LSP</td>
</tr>
<tr>
<td>3</td>
<td>90</td>
<td>8</td>
<td>No LSP</td>
</tr>
<tr>
<td>4</td>
<td>90</td>
<td>8</td>
<td>LSP</td>
</tr>
<tr>
<td>5</td>
<td>180</td>
<td>7</td>
<td>No LSP</td>
</tr>
<tr>
<td>6</td>
<td>180</td>
<td>7</td>
<td>LSP</td>
</tr>
</tbody>
</table>

Scanning electron microscopy (SEM) and optical profilometry were used to characterize the surface of the nitrided layer. To measure the nitrogen intake into the melt pool, the samples were weighed before and after treatment, and the weight gain per unit trail length was noted. Optical metallography was used to observe microstructure in the transverse cross-section. Surface oxidation was observed by visual inspection. Temperature measurements were obtained from the back of the substrate to study the energy flux at the surface qualitatively in the following two configurations:

Axis of laser beam and LSP perpendicular to substrate (Figure 2-2b): One thermocouple was directly beneath the nitrided trail, while the other was 13 mm away from the trail. The temperature measurements were performed for only one set of processing conditions – 8 mm OFD, 90 mm/s scan speed, 3.5 kW power and 16 slpm nitrogen gas flow. At these conditions, the following three experiments were conducted to compare their respective heat fluxes: nitriding with laser beam only (i.e. without LSP, run 3 in Table 3-1), nitriding with LSP (run 4 in Table 3-1), and a laser melting run with argon gas flow at 16 slpm with no near-surface plasma.

Axis of laser beam and LSP parallel to substrate (Figure 3-2): In this configuration, the axis of the nitrogen LSP was parallel to the face of the substrate, similar to the setup used by Black [123] in
her dissertation (Figure 1-3c). The nitrogen LSP was maintained at the center of the front face of the substrate for 5 seconds at different distances, \( d \), away from the front face of the substrate. Two thermocouples recorded the temperature at the back face of the substrate as shown in Figure 3-2. The distances between the laser axis and the substrate, \( d \), were 15, 12, 10, 9, 8, 7, 6, and 5 mm, in that order. The LSP was extinguished at the end of 5 seconds and the substrate was allowed to cool down to room temperature before \( d \) was varied to the next value. The substrate had dimensions of 25.4 mm x 50.8 mm x 3.175 mm, and the shorter edge (25.4 mm) was parallel to the LSP axis.

![Diagram of temperature measurement](image)

Figure 3-2. Schematic of temperature measurement in parallel configuration with location of the thermocouples.

### 3.3 Results and discussion

#### 3.3.1 Effect of LSP on surface morphology

SEM conducted on the top surface of the nitrided layers revealed small volcano-like pores in the presence of LSP (Figure 3-3), but none in its absence. Optical profilometry (Figure 3-4) was performed for runs 3 and 4, which confirmed that these features were extrusions on the nitrided
surface. A likely reason for this is increased incorporation of nitrogen in molten titanium in the presence of plasma due to the presence of active species such as N atoms and N\(^+\) ions – a phenomenon that has been reported in fusion welding [124]. For instance, Bandopadhyay et al. [125] observed enhanced nitrogen solubility in tantalum and niobium at high temperatures in the presence of nitrogen plasma, and attributed it to the presence of atomic species of nitrogen present in the plasma. In LSP nitriding, due to increased nitrogen incorporation in the presence of plasma, the liquid titanium was oversaturated with nitrogen. When liquid titanium cooled, the solubility limit of nitrogen in titanium was lowered, causing the nitrogen atoms to recombine and bubble out of the surface and giving rise to the porous features seen in Figure 3-3. When the gas bubbled out of the liquid, it expelled liquid titanium which solidified forming ridges in a direction opposite to that of the laser beam velocity (i.e. on the cooler region of the substrate). The formation of similar features has been observed in fusion welding by Deyev et al. [126]. In the laser nitriding literature, Mridha and Baker [63] observed the formation of pores on the surface and attributed it to the surplus nitrogen in the melt pool; however, they operated in the absence of plasma, and the pores on the surfaces of their trails were not accompanied by liquid expulsion as seen in this work. In Figure 3-3, it was also observed that these features almost disappeared at the high speed of 180 mm/s. This was attributed to the reduced interaction time of the nitrogen species with molten titanium. Surface ripples were observed in all cases. Epitaxial grain growth of titanium nitride can be seen to start from the edges and proceed along the direction of highest heat loss. Three distinct zones were identified: nitrided surface (N), transition zone (T), and the CP-titanium substrate (S), as labeled in Figure 3-3a. The surface microstructure will be discussed in greater detail in Section 4.3 of Chapter 4.
Figure 3-3. SEM images of nitrided surfaces for all the six conditions listed in Table 3-1. List of nitriding experiments. The scale marker (500 μm) is the same for a given OFD/speed combination with and without LSP, but is different for different conditions. The white arrow in (c) points in the direction of the laser beam velocity relative to the substrate, and applies to all micrographs. The nitrided zone (N), the transition zone (T), and the substrate (S) have been labeled in (a).

Figure 3-4. Optical profilometry of nitrided surface at processing conditions of 8 mm OFD and 90 mm/s speed from Table 3-1 for (a) no LSP (run 3) and (b) LSP (run 4).

Table 3-2. Trail widths with and without LSP.

<table>
<thead>
<tr>
<th>OFD / Scan speed</th>
<th>Trail width (mm)</th>
<th>Difference in trail width</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>No LSP</td>
<td>LSP</td>
</tr>
<tr>
<td>9 mm, 60 mm/s</td>
<td>1.44</td>
<td>1.50</td>
</tr>
<tr>
<td>8 mm, 90 mm/s</td>
<td>1.26</td>
<td>1.37</td>
</tr>
<tr>
<td>7 mm, 180 mm/s</td>
<td>0.842</td>
<td>1.13</td>
</tr>
</tbody>
</table>
3.3.2 Effect of LSP on energy transfer to substrate

3.3.2.1 Perpendicular configuration

The trail widths of the nitrided surface were measured for each of the six cases and are marked in Figure 3-3. The results are reported in Table 3-2. It was seen that the LSP widened the nitrided trail, with the effect being most pronounced at the highest speed and lowest OFD. Increasing the OFD moved the laser focal plane away from the substrate, which also moved the LSP up by the same amount. The nitrogen LSP consists of active species (N, N+) that need to interact with the melt pool as closely as possible for efficient nitriding. Calorimetric measurements showed that the nitrogen LSP absorbed about 38% of the laser power; yet, the transverse cross-sections with and without LSP looked identical with respect to the melt pool depth and distribution of TiN dendrites (Section 3.3.4), suggesting that energy transfer to the substrate wasn’t compromised due to the presence of the plasma. This indicated that 38% of laser energy absorbed by the LSP was transferred to the titanium plate during nitriding by other mechanisms such as (a) re-radiation of energy by the plasma at smaller wavelengths which is absorbed more efficiently by the titanium substrate, and (b) collisions of the high-energy particles (such as neutral atoms and ions) in the plasma with the titanium surface [107]. The second mechanism is responsible for both heat and mass transfer. Every collision of a gas particle (neutral atom, ionized atom or molecule) with the molten titanium surface can be either reflective (leading to energy transfer depending upon the elasticity of the collision) or absorptive (leading to incorporation of nitrogen into the melt pool), depending upon the sticking coefficient. For both mechanisms, especially for the second one, it is imperative that the titanium surface be exposed to the core of the plasma to enable efficient energy transfer from the plasma to the substrate. These mechanisms might broaden the energy profile of the LSP (compared with the laser beam). To study this, temperatures were measured at the back of
the 3.175 mm-thick substrate at two points: directly underneath the beam, and 13 mm away from
the beam. The peak temperatures recorded by the thermocouples are shown in Table 3-3 for three
different experiments: nitriding without LSP, nitriding with LSP, and laser melting in the presence
of argon. The last run was conducted to observe the extent of exothermicity of the formation of
titanium nitride phase change. The gas flow was maintained at 16 slpm (nitrogen for the first two
runs and argon for the third).

Table 3-3. Peak temperature on the back face of the substrate for three different experiments

<table>
<thead>
<tr>
<th>Thermocouple location (back face of substrate)</th>
<th>Peak temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitriding without LSP</td>
<td>Nitriding with LSP</td>
</tr>
<tr>
<td>Under beam</td>
<td>170.6</td>
</tr>
<tr>
<td>13 mm away from beam</td>
<td>56.2</td>
</tr>
</tbody>
</table>

The peak temperatures recorded directly beneath the laser beam with and without LSP were
similar, suggesting that the laser energy absorbed by the plasma was deposited to the substrate via
re-radiation and high-energy particle collision as mentioned above. Also, the thermocouple located
13 mm away from the laser beam (on the back side of the substrate) recorded a higher peak
temperature for nitriding with LSP than without, showing that the plasma expanded the heat flux
profile. The temperature recorded in the glazing run was significantly lower than in the laser
nitriding case, both scans being comparable due to the absence of near-surface plasma. This
indicated that the heat released from the surface alloying process was not negligible and needs to
be accounted for in a nitriding model; this exothermic release of heat can be estimated as follows.
If \( W_N \) (g/mm) is the mass of nitrogen incorporated per unit nitrided length, \( \Delta H_f \) (kJ/mol) is the
standard heat of formation of TiN, \( M_N \) (g/mol) is the molar mass of atomic nitrogen, and \( L_N \) (mm)
is the length of the nitrided trail, then the heat released due to the formation of TiN in the melt pool
during laser nitriding, \( Q_{TN} \) (J), can be estimated as:
\[ Q_{TiN} = \frac{1000 \Delta H_f W_{N-L-N}}{M_N} = 49.4 \text{ J} \]  

(3-1)

where \( \Delta H_f = -337.65 \text{ kJ/mol} \) [127], \( M_N = 14 \text{ g/mol} \), \( L_N = 50.8 \text{ mm} \), and \( W_N = 4.033 \times 10^{-5} \text{ g/mm} \) (from weight measurement data for laser nitriding at 8 mm OFD and 90 mm/s speed, Table 3-4). Equation 3-1 assumes that all the nitrogen incorporated into the melt pool resides in the TiN phase, and \( Q_{TiN} \) thus gives the upper limit of the energy released in the melt trail during nitriding. If the laser power is \( P_0 \) (W) and the scan speed is \( v_{scan} \) (mm/s), the total heat input during to the laser beam scan, \( Q_{laser} \) (J), can be calculated as:

\[ Q_{laser} = \frac{P_0 L_N}{v_{scan}} = 1975 \text{ J} \]  

(3-2)

where \( P_0 = 3500 \text{ W} \), \( v_{scan} = 90 \text{ mm/s} \), and \( L_N = 50.8 \text{ mm} \) as before. From Equations 3-1 and 3-2:

\[ \frac{Q_{TiN}}{Q_{laser}} = 0.025 \]  

(3-3)

i.e. the heat released due to TiN formation is about 2.5% of the heat incident due to laser irradiation on the substrate. It was shown in Section 2.2.3.3 that the absorption efficiencies of the nitriding and melting processes were 14% and 10% respectively, suggesting that the nitriding process contributed an additional 4% energy to the melt pool; this increase in energy can thus be attributed to the exothermicity of the formation of TiN based on the above calculations.

3.3.2.2 Parallel configuration

The energy coupling between the nitrogen LSP and the substrate was also studied by measuring the temperature at the back face of the substrate when the laser beam did not interact directly with the substrate i.e. when the LSP axis was parallel to the substrate (Figure 3-2). In this configuration, the substrate was not directly irradiated by the laser beam, which allowed for a study of energy transfer between the nitrogen LSP and the substrate excluding direct absorption of the laser beam energy. The temperature rise recorded by the thermocouples TC1 and TC2 at the end of
5 seconds for each value of $d$ is shown in Figure 3-5. In the absence of direct radiation by the laser beam, the LSP transferred energy to the substrate by re-radiation and by energetic collisions of high-temperature nitrogen species with the substrate.

![Figure 3-5](image)

**Temperature rise in 5 seconds**

Figure 3-5. Temperature rise, $\Delta T$ ($^\circ$C), recorded by two thermocouples TC$_1$ and TC$_2$ at the end of 5 seconds. The location of the thermocouples can be found in Figure 3-2.

As a first approximation, the titanium substrate can be modeled using the lumped capacitance method that neglects temperature gradients within the substrate [128]. From Figure 3-5, it is evident that this is a good assumption for values of $d \geq 9$ mm since the temperatures recorded by the two thermocouples were almost equal. The energy absorbed by the titanium coupon, $Q_{abs}$ (W), increases the temperature of the coupon according to:

$$
Q_{abs} = \rho V C_p \frac{\Delta T}{t}
$$

(3-4)

where $\rho$ is the density of titanium (4500 kgm$^{-3}$ [121]), $C_p$ is the specific heat capacity of titanium (528 Jkg$^{-1}$C$^{-1}$ [121]), $V$ is the volume of the titanium coupon ($4.09 \times 10^{-6}$ m$^3$), $\Delta T$ ($^\circ$C) is the temperature rise of the substrate during time $t$, the duration of the experiment (5 seconds). Assuming the nitrogen LSP to be a sphere radiating energy at the rate of $Q_{source}$ (W), the incident radiation upon the titanium substrate, $Q_{inc}$ (W), can be expressed as:
\[
\frac{Q_{\text{inc}}}{Q_{\text{source}}} = F \tag{3-5}
\]

where \( F \) is the view factor for the sphere-rectangle geometry (Figure 3-6a) and is given by [129]:

\[
F = \frac{1}{2\pi} \left\{ \sin^{-1} \left[ \frac{2B_2^2 - (1-B_1^2)(B_1^2 + B_2^2)}{(1+B_1^2)(B_1^2 + B_2^2)} \right] + \sin^{-1} \left[ \frac{2B_1^2 - (1-B_2^2)(B_1^2 + B_2^2)}{(1+B_2^2)(B_1^2 + B_2^2)} \right] \right\} \tag{3-6}
\]

\( B_1 = \frac{L_1}{d} \) and \( B_2 = \frac{L_2}{d} \)

Here, \( L_1 = 50.8 \text{ mm} \) and \( L_2 = 25.4 \text{ mm} \) are the dimensions of the rectangular face of the coupon and \( d \) is the distance between the LSP and the coupon (Figure 3-6a). The radiation incident upon the substrate, \( Q_{\text{inc}} \), is only partially absorbed by the titanium substrate. Assuming an absorption coefficient of \( \eta_{\text{rad}} = 0.5 \) [130] (typical for titanium in the optical emission spectrum of a freestanding nitrogen LSP [109]), the heat absorbed by the coupon can be written as:

\[
Q_{\text{abs}} = \eta_{\text{rad}} Q_{\text{inc}} \tag{3-7}
\]

Equation 3-7 assumes that the temperature rise of the substrate is solely due to uniform heating by the incident radiation from the plasma. Combining Equations 3-4, 3-5, and 3-7:

\[
Q_{\text{source}} = \frac{Q_{\text{inc}}}{F} = \frac{\rho V C_p \Delta T(d)}{\eta_{\text{rad}} F(d)} \text{ for } d \geq 9 \text{ mm} \tag{3-8}
\]

Figure 3-6. a) Schematic of the sphere-plate geometry for view factor calculation, b) \( \frac{Q_{\text{inc}}}{F} \) plotted for distances \( d \geq 9 \text{ mm} \). The vertical error bars denote a range of ±10% around the respective data points.
Equation 3-8 suggests that \( Q_{\text{source}} \), the energy of the radiating LSP, can be found by computing the ratio \( \frac{Q_{\text{inc}}}{P} \), where \( F \) is calculated from Equation 3-6 for distances \( d \geq 9 \text{ mm} \). Further, if the assumption that the substrate is heated uniformly by the incident plasma radiation is true, then the computed value of \( Q_{\text{source}} \) must be the same for all distances \( d \). Figure 3-6b shows the ratio \( \frac{Q_{\text{inc}}}{F} \) plotted for distances \( d \geq 9 \text{ mm} \). It can be seen that a constant value of \( Q_{\text{source}} = 998 \text{ W} \) was obtained within an error bar of ±10%. Since the plasma absorbed about 38% (1.33 kW) of the 3.5 kW laser power sustaining it, it is concluded that the LSP re-radiated around 75% of the power that it absorbed. The remaining 25% of the absorbed energy (332 W) is used to heat the nitrogen gas that exits the freestanding LSP after recombination. Treating the LSP as a control volume, the temperature of the exiting molecular \( \text{N}_2 \) gas was estimated to be around 1000 °C from tabulated values of enthalpy for nitrogen [131].

In general, the radiative heat transfer from the LSP to the substrate is expected to vary spatially. For the idealized case of heat transfer from a point source to a large plate, the theoretical irradiance profile, \( I_{\text{point}}(d,r) \) (W/m²), obeys Lambert’s cosine law and is given by [132]:

\[
I_{\text{point}}(d,r) = \frac{Q_{\text{source}}}{4\pi d^2} \left( \frac{d}{\sqrt{d^2 + r^2}} \right)^3
\]

(3-9)

where \( d \) is the distance from the point source to the plate and \( r \) is the radial distance in the plane of the substrate face. \( I_{\text{point}}(d,r) \) is plotted in Figure 3-7 for a source power of 998 W and the distances \( d \) considered in this study. The intensity profile shows a strong radial variation for shorter distances, while for larger distances, the profile could be approximated to be uniform, explaining why the thermocouples TC1 and TC2 recorded similar temperatures. For smaller distances of \( d < 9 \text{ mm} \), the radial variation in intensity led to the divergence of the \( \Delta T \) curves recorded by the two thermocouples in Figure 3-5, rendering the lumped capacitance model inapplicable. In addition to this, energy transfer due to collisions with energetic nitrogen species was also expected for values of \( d < 9 \text{ mm} \), since the plate was effectively within the plasma (Figure 2-2c) for these distances.
The intensity profile of the total energy transfer to the substrate can, in principle, be estimated from the temperature-time history recorded by the two thermocouples; this entails solving the inverse heat conduction problem, and is a possible direction for future work in characterizing the nitrogen LSP.

![Irradiance profiles for point source](image)

**Figure 3-7.** Theoretical irradiance profiles for an ideal case of a point source radiating energy on to a large plate for various distances $d$. The point source was assumed to radiate energy at the rate of 998 W.

### 3.3.3 Effect of LSP on surface oxidation

Since all the nitriding experiments were conducted in a processing chamber open to the atmosphere with a high-power laser beam, the CP-titanium substrate was susceptible to oxidation during or after the nitriding run due to the high temperatures reached on the surface [1]. Figure 3-8 shows the nitried trails for the six experimental conditions listed in Table 3-1. Each of the six substrates shown contains six identical trails. It can be seen that while all the trails are gold-colored (color of near-stoichiometric TiN), runs 1 and 3 showed blue and purple discolorations, indicating oxide formation on titanium [133]. No such discoloration was observed when nitriding was
conducted in the presence of LSP. The reduction in surface oxidation in the presence of LSP was attributed to the gettering of atmospheric oxygen by the nitrogen plasma by Nassar et al. [107], who also reported the formation of NO$_x$ gases due to chemical reactions between the excited nitrogen species in the LSP and atmospheric oxygen. The high-pressure high-temperature core of the plasma also pushes the oxygen out, thus effectively protecting the substrate from any oxygen interaction. It can be seen from Figure 3-8 that the propensity to form oxides at the surface increased at lower speeds and greater OFD’s, due to higher surface temperatures reached at lower speeds and a decrease in the gettering effect of the LSP at higher OFD’s.

Figure 3-8. Nitrided samples for the experiments listed in Table 3-1. The numerical labels indicate the run # for the respective coupon from Table 3-1.
3.3.4 Effect of LSP on the nitrogen intake into the melt pool

Nitrogen intake into the melt pool during the nitriding process can be determined by measuring the weight of the CP-titanium substrate before and after the treatment. Weight change can be taken to be an indicator of nitrogen intake into the melt pool, since oxygen incorporation, if any, is confined to the surface [68]. This approach can be used to compare nitriding efficiencies with and without the LSP. The weight change per unit nitrided length is shown in Table 3-4. It can be seen that the LSP facilitated nitrogen intake by enhancing nitrogen incorporation in liquid titanium, as discussed in Section 3.3.1.

Table 3-4. Weight increase with and without LSP.

<table>
<thead>
<tr>
<th>OFD, Speed</th>
<th>Weight increase per unit nitrided length ((10^{-5} \text{ g/mm}))</th>
<th>Difference in weight increase</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>No LSP</td>
<td>LSP</td>
</tr>
<tr>
<td>9 mm, 60 mm/s</td>
<td>6.86</td>
<td>8.86</td>
</tr>
<tr>
<td>8 mm, 90 mm/s</td>
<td>4.03</td>
<td>5.26</td>
</tr>
<tr>
<td>7 mm, 180 mm/s</td>
<td>1.23</td>
<td>1.90</td>
</tr>
</tbody>
</table>

During laser and LSP nitriding, nitrogen was first incorporated into the surface of the melt pool, from where it was transported by convection and diffusion deeper into the melt pool. Marangoni convection is the primary driving force for nitrogen transport in the melt pool [89,107]. The surface tension of liquid titanium decreases with an increase in temperature [134]. Thus, there was a surface tension gradient on the liquid surface with surface tension being highest at the edges (regions of lower temperature) and lowest at the center of the melt pool (region of highest temperature). This gradient drove the nitrogen-rich liquid away from the center towards the edges, resulting in a nitrided surface layer that was deeper at the edges than at the center. This arose because the nitrogen-rich liquid driven to the melt pool sides solidified before it could circulate back to the center of the melt pool. The optical micrographs of Figure 3-9 show the Marangoni effect clearly, together with microstructural features of the nitrided layer, such as dendrites, needle-like structures,
and the heat affected zone in the CP-titanium substrate. The cross-sectional micrographs also provided qualitative evidence for the claim made in Section 3.3.2.1, namely that laser energy absorbed by the plasma was transferred to the substrate with minimal attenuation. The weight change results of Table 3-4 also indicated that enhancement of nitrogen intake into the melt pool was most prominent at the highest speed / lowest OFD combination.

<table>
<thead>
<tr>
<th>OFD and scan speed</th>
<th>9 mm and 60 mm/s</th>
<th>8 mm and 90 mm/s</th>
<th>7 mm and 180 mm/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>No LSP</td>
<td><img src="image1" alt="a) Run 1" /></td>
<td><img src="image2" alt="c) Run 3" /></td>
<td><img src="image3" alt="e) Run 5" /></td>
</tr>
<tr>
<td>LSP</td>
<td><img src="image4" alt="b) Run 2" /></td>
<td><img src="image5" alt="d) Run 4" /></td>
<td><img src="image6" alt="f) Run 6" /></td>
</tr>
</tbody>
</table>

Figure 3-9. Optical micrographs of transverse cross-sections of all six nitrided samples listed in Table 3-1. The scale marker for each pair of micrographs is indicated in the bottom figure.

### 3.4 Chapter summary

A high-power CO₂ laser was used to strike and sustain a nitrogen plasma away from the substrate in open atmosphere. Laser-nitriding of commercially-pure titanium was conducted in the presence and absence of this laser-sustained plasma for three sets of experimental conditions, by varying the off-focal distance (OFD) and scan speed (9 mm OFD and 60 mm/s, 8 mm OFD and 90 mm/s, 7 mm OFD and 180 mm/s), keeping the laser power (3.5 kW) and nitrogen gas flow (16 slpm) constant. The effect of LSP on the nitriding process was characterized by scanning electron and optical microscopy, optical profilometry, temperature and weight measurements. The main findings were as follows:

- Weight measurements of the substrates provided quantitative evidence, for the first time, of enhanced nitrogen intake into the melt pool when nitriding was performed in the presence of
pre-struck nitrogen laser-sustained plasma. Nitrogen intake into the melt pool was 54% more with LSP than with only the laser beam at 7 mm OFD and 180 mm/s speed.

- LSP nitriding produced rougher porous features on the surface at lower speeds. Due to oversaturation of molten titanium with nitrogen, the excess nitrogen recombined and bubbled out of the melt pool surface, forming pores. These rough features were negligible at the highest speed. No such pores were observed when nitriding was performed in the absence of the LSP.

- Nitriding with LSP reduced the oxygen concentration at the surface compared to nitriding with only the laser beam, at 9 mm OFD and 60 mm/s speed. Without LSP, oxidation was visually evident at low speeds, whereas the high-speed runs (180 mm/s) gave gold-colored layers without oxide formation both with and without LSP.

- In a configuration where the substrate was perpendicular to the axis of the laser beam, the LSP was not found to attenuate energy transfer to the substrate. It appeared to broaden the energy flux on the substrate. At 7 mm OFD and 180 mm/s speed, the width of the nitrided trail was found to be 34% more with the LSP compared to nitriding with only the laser beam.

- In a configuration where the substrate was parallel to the axis of the LSP, energy transfer occurred between the LSP and the substrate primarily by radiation when the distance between the LSP axis and the substrate was greater than or equal to 9 mm. At distances less than 9 mm, both radiation and collisions with energetic nitrogen species are expected to transfer energy to the substrate. Using a lumped capacitance model for the titanium substrate to estimate the radiation intensity, the nitrogen LSP was found to re-radiate 998 Watts of the 3.5 kW laser power that was used to sustain it.

- Marangoni effect was evident in the transverse cross-sectional micrographs at all the experimental conditions, with and without LSP.

- LSP nitriding was thus found to have potential to form TiN-rich surface layers on CP-titanium in open atmosphere. The maximum benefits (i.e. smooth surfaces, wider trails, and higher
nitrogen intake) were observed at lower off-focal distances and higher speeds. At these conditions, LSP nitriding can be a faster and more effective way of nitriding titanium compared to conventional laser-nitriding.
Chapter 4

Effect of processing parameters on microstructure

4.1 Introduction

A knowledge of processing-structure-property relationships enables a user to optimize processing parameters to achieve the desired properties of a given material. The LSP nitriding technique involves many processing parameters including laser power, off-focal distance (which determines the beam spot size at the substrate), scan speed, and nitrogen gas flow rate. The nitrogen gas flow may be diluted with argon \[59,64,65,67,71\] to mitigate crack formation, adding the process variable N\(_2\):Ar flow ratio. In Chapter 3, it was shown that nitriding in the presence of a prestruck LSP can complement the laser nitriding process by reducing surface oxidation, enhancing nitrogen intake, and increasing surface coverage without attenuating energy transfer to the substrate. The objective of this Chapter is to investigate the LSP nitriding method further by studying the microstructure of the nitrided layer as a function of specimen scan speed, off-focal distance, and N\(_2\):Ar gas flow ratio. In this investigation, single nitrided trails were deposited on commercially pure titanium by varying scan speed, off-focal distance, and N\(_2\):Ar ratio. The nitriding experiments conducted in this Chapter differed from typical laser nitriding experiments in two ways: one, these experiments were conducted in the presence of LSP in open atmosphere, unlike most laser nitriding experiments which are conducted in controlled nitrogen (with or without argon) environments; and two, these experiments were conducted at higher power densities compared to typical nitriding experiments. This comparison is shown in Figure 4-1, where ‘C’ denotes a controlled environment (nitrogen with or without argon) and ‘O’ denotes open
atmosphere. A variety of characterization techniques were used to study the effect of processing parameters on the microstructure.

![Laser nitriding processing conditions (from the literature)](image)

Figure 4-1. Processing conditions from the literature [62,65,69,72,78,79,135] and this work. 'C' denotes controlled environment and 'O' denotes open atmosphere.

**4.2 Methodology**

All the experiments were performed using the experimental setup described in Section 2.2.2. A total of 21 LSP nitriding experiments were conducted by varying the scan speed, off-focal distance (OFD), and N₂:Ar ratios, also shown in Table 4-1. All runs were carried out at a laser power of 3.5 kW and a nitrogen gas flow rate of 16 standard liters per minute (slpm). To study the effect of argon dilution, the nitrogen gas flow was kept the same (16 slpm), and argon was added to the flow in steps of 1 slpm. Microstructure at the surface and in the transverse cross section was studied as a function of the processing parameters using optical and scanning electron microscopy. Optical profilometry was used to observe surface topography. Weight measurements of the nitrided
CP-Ti substrates were performed to study the nitrogen intake into the melt pool as a function of argon dilution. X-ray diffraction (XRD) was used to identify phases on the surface of the nitrided layer. Energy dispersive spectroscopy (EDS) was used to estimate the N:Ti atomic ratio in several microstructural features observed on the surface; each EDS reading was based on an average of three measurements on the same microstructural feature.

Table 4-1. List of experimental runs performed.

<table>
<thead>
<tr>
<th>Run #</th>
<th>Scan speed (mm/s)</th>
<th>OFD / Beam diameter (mm)</th>
<th>N₂:Ar (slpm:slpm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>135</td>
<td>8 / 1.34</td>
<td>16:0</td>
</tr>
<tr>
<td>2</td>
<td>180</td>
<td>8 / 1.34</td>
<td>16:0</td>
</tr>
<tr>
<td>3</td>
<td>225</td>
<td>8 / 1.34</td>
<td>16:0</td>
</tr>
<tr>
<td>4</td>
<td>270</td>
<td>8 / 1.34</td>
<td>16:0</td>
</tr>
<tr>
<td>5</td>
<td>300</td>
<td>8 / 1.34</td>
<td>16:0</td>
</tr>
<tr>
<td>6</td>
<td>90</td>
<td>8 / 1.34</td>
<td>16:0</td>
</tr>
<tr>
<td>7</td>
<td>90</td>
<td>10 / 1.68</td>
<td>16:0</td>
</tr>
<tr>
<td>8</td>
<td>90</td>
<td>12 / 2.02</td>
<td>16:0</td>
</tr>
<tr>
<td>9</td>
<td>90</td>
<td>14 / 2.34</td>
<td>16:0</td>
</tr>
<tr>
<td>10</td>
<td>50</td>
<td>8 / 1.34</td>
<td>16:0</td>
</tr>
<tr>
<td>11</td>
<td>70</td>
<td>8 / 1.34</td>
<td>16:0</td>
</tr>
<tr>
<td>12</td>
<td>90</td>
<td>8 / 1.34</td>
<td>16:0</td>
</tr>
<tr>
<td>13</td>
<td>50</td>
<td>8 / 1.34</td>
<td>16:1</td>
</tr>
<tr>
<td>14</td>
<td>70</td>
<td>8 / 1.34</td>
<td>16:1</td>
</tr>
<tr>
<td>15</td>
<td>90</td>
<td>8 / 1.34</td>
<td>16:1</td>
</tr>
<tr>
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<td>50</td>
<td>8 / 1.34</td>
<td>16:2</td>
</tr>
<tr>
<td>17</td>
<td>70</td>
<td>8 / 1.34</td>
<td>16:2</td>
</tr>
<tr>
<td>18</td>
<td>90</td>
<td>8 / 1.34</td>
<td>16:2</td>
</tr>
<tr>
<td>19</td>
<td>50</td>
<td>8 / 1.34</td>
<td>16:3</td>
</tr>
<tr>
<td>20</td>
<td>70</td>
<td>8 / 1.34</td>
<td>16:3</td>
</tr>
<tr>
<td>21</td>
<td>90</td>
<td>8 / 1.34</td>
<td>16:3</td>
</tr>
</tbody>
</table>
4.3 Results and discussion

4.3.1 Nitriding with a pure nitrogen LSP

4.3.1.1 Effects of varying off-focal distance

Since the LSP is located near the focal plane of the CO₂ laser beam, the distance between the LSP and the substrate can be adjusted by moving the laser head vertically. From their study of laser-sustained argon plasma, Akarapu et al. [101] found that the hottest region of the LSP (and hence the highest concentration of excited species) is at its core. Thus, the core of the plasma needs to be in close contact with the titanium substrate to ensure efficient nitriding. This effect can be observed in Figures 4-2a-d, which show optical micrographs for OFD’s of 8, 10, 12, and 14 mm (corresponding to beam diameters of 1.34, 1.68, 2.02, and 2.34 mm respectively at the test coupon) at a scan speed of 90 mm/s (runs 6-9 in Table 4-1). The condition of 8 mm OFD – 90 mm/s scan speed (run 6) was chosen from Nassar et al. [107], and the OFD was increased in steps of 2 mm keeping the other conditions constant. Figure 4-2a exhibits regions which appear as black patches. These corresponded to areas with surface orientations that reflected the illumination away from the camera optics and are discussed in detail in Section 4.3.1.2. To the naked eye, the entire surface of Figure 4-2a was actually a uniform bright gold color. It can be seen that the quality of the nitried layer decreased with increasing OFD, and the surface color changed from gold-colored to a duller shade. There are at least three possible causes for this. First, increasing the OFD defocused the laser beam further, thus decreasing the laser beam intensity that reached the surface. Second, the excited nitrogen species in the LSP gettered the atmospheric oxygen and hence prevented surface oxidation; this gettering effect became less effective as the LSP moved further away from the substrate, thus resulting in more oxygen incorporation into the melt pool forming dull-colored
oxynitrides on the surface. And third, increasing the OFD moved the LSP away from the surface reducing other mechanisms of energy transfer such as re-radiation at shorter wavelengths and collisions of energetic nitrogen species with the substrate, which, as was shown in Chapter 2, are important contributors to energy transfer at smaller OFD’s.

Figure 4-2. Effect of off-focal distance on surface morphology: a) 8 mm OFD b) 10 mm OFD c) 12 mm OFD d) 14 mm OFD at processing conditions of 3.5 kW power, 90 mm/s speed, 16 slpm N₂. Laser scan direction is from top to bottom. Some black patches in (a) are arrowed and labeled. Scale marker of 1 mm shown on the bottom right is common for all micrographs.

4.3.1.2 Effects of varying scan speed

The scan speed was varied from 135 mm/s to 300 mm/s (runs 1 to 5 in Table 4-1), keeping the remaining parameters constant (8 mm OFD, 16 slpm N₂ flow). The optical micrographs of the top surfaces are shown in Figures 4-3a-e. The effect of increasing speed was twofold: one, it decreased the energy per unit length deposited on the surface, and two, it decreased the interaction time of the alloying gas with molten titanium. Both these effects could account for the width of the
nitrided trail shrinking from 1.13 mm in Figure 4-3a to 0.74 mm in Figure 4-3e. At all speeds, cracks were visible on the surface at a low magnification of 50x. These cracks were mostly perpendicular to beam scan direction, and were believed to form because of the high temperature gradients in the direction of the laser beam scan. They originated at the edges and arrested near the center, although some of them crossed the entire trail width. From the micrographs, it was apparent that the crack density increased with speed. This observation cannot be generalized over the whole range of nitriding speeds possible, from 1.1 mm/s [72] to 250 mm/s [62]. For instance, the scan speeds in these experimental runs were as high as those of Kloosterman et al. [12], who also observed that crack density increased with speed in this range; alternatively, Mridha and Baker [64] and Abboud et al. [78] reported an increase in crack formation with decreasing speed for the scanning speed range of approximately 5 to 50 mm/s. This discrepancy possibly arises because the tendency of crack formation depends upon at least two factors: the tendency to form macrocracks (discussed in Chapter 6) increases with an increase in the volume fraction of TiN dendrites in the δ-Ti matrix (which increases with decreasing speed), and the tendency to form microcracks (observed in Figure 4-3) increases with the rate of solidification (which increases with increasing speed).

A rudimentary analysis can be conducted by considering the idealized case of an infinite TiN plate having thickness $a$, thermal diffusivity $D$, thermal coefficient of expansion $\alpha$, Young’s modulus $E$, and Poisson’s ratio $\nu$. The tensile stress developed in the plate, $\sigma_t$, when the surface is cooled at the rate of $\dot{T}$ is given by [136]:

$$\sigma_t = \frac{E\alpha a^2}{3(1-\nu)D}$$  \hspace{1cm} (4-1)

Equation 4-1 shows that the tensile stress induced by the cooling is directly proportional to both the cooling rate at the surface and the square of the plate thickness. Substituting the mechanical and thermal properties of TiN at 1000 °C [137] and assuming the plate thickness $a$ to be 300 μm (a
typical value for the nitrided layer thickness at the edges) and the cooling rate $T$ as $2 \times 10^5$ °C/s (a typical value for the cooling rate at the surface calculated using the heat transfer model described in Chapter 2), the value of $\sigma_{t}$ was obtained as 6894 MPa, which is more than an order of magnitude greater than the modulus of rupture for TiN (234 MPa [137]). Moreover, the weaker porous regions found on the edges of the nitrided trails (discussed in Section 4.3.1.3) provide crack initiation sites, which further lowers the rupture modulus of the LSP nitrided layer.

![Figure 4-3. Effect of scan speed on surface morphology: a) 135 mm/s b) 180 mm/s c) 225 mm/s d) 270 mm/s e) 300 mm/s at processing conditions of 3.5 kW power, 8 mm OFD, 16 slpm N$_2$ flow. Some cracks, black patches, and longitudinal ridges have been arrowed and labeled. Scale marker of 1mm shown on the bottom right is common for all micrographs.](image)

Figures 4-3a-e also capture an interesting trend: there are a number of black patches that are visible on the top surface at the lowest speed (135 mm/s), which gradually decrease as the speed is increased, until they vanish completely at the highest speed (300 mm/s). Similar black patches were observed in Figure 4-2a at a speed of 90 mm/s. These black patches were an artefact of the optical microscope, since they were not visible to the naked eye, despite being big enough to be visible were they actually present. SEM images (Figure 4-4a) of the black patches showed that they corresponded to rough areas on the surface which reflected light away from the objective lens,
unlike the smoother gold-colored regions. From Figures 4-3a-e, it can be inferred that the presence of these features depended upon the interaction time of nitrogen with the surface of the melt pool. The black patches corresponded to porous expulsion sites (discussed in Section 3.3.1) that formed when nitrogen gas bubbled out of the melt surface. The surface topography images acquired by optical profilometry showed that these rough features were narrow peaks of the order of 35 microns (Figure 4-4b).

![SEM image and profilometry image](image_url)

Figure 4-4. a) SEM image (20x) of the top surface of run 1 at 135 mm/s scan speed. Inset image shows a magnified image (200x) of one of the rough 'black spot' regions in the optical micrographs of Figure 4-3. Black arrow indicates the direction of the laser beam scan. b) Optical profilometry images show surface topography in 2 and 3 dimensions. The vertical scale ranges from -19.6 to 45.2 µm.

The liquid that was expelled in the wake of the beam scan direction solidified immediately in a direction normal to the isotherms i.e. in the direction of greatest negative temperature gradient. Figures 4-7a, e, and i show SEM images of LSP-nitrided surfaces at lower speeds of 90, 70, and 50 mm/s respectively. It can be seen that such features (arrowed in the micrograph) dominated the surface morphology at these speeds. The smoother regions observed at higher speeds (Figure 4-3e) were absent at lower speeds, since the nitrogen plasma interacted for longer with the melt pool.
Finally, in the optical micrographs of Figure 4-3, longitudinal ridges were observed, and were considered to be plasma-etched boundaries.

4.3.1.3 Surface features

As a basis for comparing the changes in surface features with addition of argon in Section 4.3.2, a representative case, run 12 from Table 4-1 (90 mm/s speed and 16:0 N₂:Ar ratio) is shown in Figures 4-5a and 4-5b, with different morphologies labeled as A, B and C. A is the transition region near the fusion line between the base metal and the nitrided trail, B represents the ‘wavy’ features on the surface, and C represents the smooth portion of the trail. Under the naked eye with normal illumination, A, B and C appeared gold-colored, C being the shiniest.

When titanium melted under the laser beam, its volume increased. This effect, combined with Marangoni convection, caused liquid to spill over the trail edges onto the cooler CP-Ti substrate. The spilled liquid titanium solidified when it came into contact with the cooler un-melted substrate. The solidification front had a cellular appearance; these cellular features (labelled ‘A’ in Figure 4-5a) were seen to contain micropores when viewed under high magnification (Figure 4-5b). Optical profilometry (Figure 4-5a) showed that the region corresponding to ‘A’ exhibited a series of crests and troughs; this phenomenon was true of all runs, with or without argon. Energy-dispersive spectroscopy (EDS) performed on two ‘crest’ regions and one ‘trough’ region revealed that the crests corresponded to nitrogen-rich TiN cells (atomic N:Ti = 0.84), while the troughs corresponded to titanium-rich intercellular regions (N:Ti = 0.07 - 0.15). Figure 4-5a also shows a melt isotherm§§ (1670 °C for titanium) representing the trailing boundary at the surface of the melt.

§§Since the model was fitted against trail widths at lower nitriding speeds (30, 45, and 60 mm/s) in Chapter 2, the model overestimated the melt trail width at higher speeds such as 90 mm/s, as seen in Figure 4-5a.
pool, estimated using the moving heat source model described in Chapter 2, superposed upon the SE micrograph.

Figure 4-5. a) Surface (scanning electron micrograph) and transverse cross section (optical micrograph) of run 12 in Table 4-1 (90 mm/s speed, 16:0 N₂:Ar gas flow ratio, 3.5 kW power and 8 mm OFD). A, B and C represent different surface morphologies. Surface topography contours obtained from optical profilometry are shown at the top, with the height scale ranging from -35.5 to 43.6 µm shown on the bottom left of the profilometry image. A melt isotherm (drawn in red) of the trailing side of the melt pool has been superposed on the SEM image. The topography contour plot, the melt isotherm, and both the scanning electron and optical micrographs are drawn to the same scale (500 µm scale shown at the bottom). The arrow shows the beam scan direction. b) Higher magnification scanning electron micrograph of the cellular features of region A and the transition from A to B. The scale marker is 50 µm and is shown at the top. The arrow shows the beam scan direction.
Region B corresponded to the ‘wavy’ features on the surface of the nitrided trail, including the porous regions described in Section 4.3.1.2. They originated at the A/B boundary (Figure 4-5b) at an angle to the scan direction, and arrested near the centerline, where they became parallel to the scan direction. Like the cells in region A, they grew perpendicular to the melt isotherm at the surface in the direction of maximum negative temperature gradient. It was evident that region B comprised TiN surface dendrites growing from the TiN cells (peaks) of region A. Indeed, EDS showed that the atomic N:Ti ratio in this region was 1.12. Interestingly, multiple solidifying TiN grains following the direction of maximum temperature gradient sometimes converged, leading to pore formation due to supersaturation of nitrogen in the melt pool. Solidification modes depend upon the thermal gradient $G$ and the solidification rate $R$; the ratio $G/R$ determines the degree of constitutional undercooling [138], and low values of $G/R$ cause instability in solidification fronts. $G/R$ ratios are lowest at the center of the melt pool and highest near the edge. Hence, the cellular grain growth of region A transformed into dendritic growth in region B moving closer to the center of the melt pool, where solidification rates $R$ were high and thermal gradients $G$ were low. The TiN dendrites were more abundant at low speed and undiluted nitrogen gas flow, since these conditions provided the greatest interaction time of the melt pool with the nitrogen plasma. The dendrites were thus able to incorporate more nitrogen from the plasma and continue to solidify towards the center line. The dendrites could be removed when the surface was manually ground with 200 grit sandpaper for about 15 seconds, as shown in Figures 4-6a and 4-6b. This was expected due to their elevation (about 30-40 μm relative to the untreated substrate) evident from the topographical image (Figure 4-5a). The intercellular features (blue regions) of region A, labeled in Figure 4-6b, survived the grinding because they were at a lower elevation than the dendritic features.
Region C in Figure 4-5a is the smooth region between the surface dendrites of region B. It appeared shiny under normal illumination because of its low roughness and was depressed by about 40 μm compared to the untreated substrate with a similar elevation to that of the intercellular regions. The difference in elevation between regions B and C is believed to be a consequence of rippling induced by surface tension gradients [139]. EDS performed in region C indicated a N:Ti atomic ratio of approximately 0.78.

4.3.2 Nitriding with a N₂-Ar LSP

LSP nitriding experiments conducted with nitrogen plasma revealed surface cracks. Previous investigations have shown that one way to reduce crack formation and improve surface
quality is to dilute the nitrogen gas flow with an inert gas such as argon [59,64,65,67,71,109]. To study the effect of argon dilution, measurements were carried out where the nitrogen gas flow was kept constant at 16 slpm, and argon was added to the flow in steps of 1 slpm. The surfaces and transverse cross sections of single trails were studied.

Figure 4-7 shows SEM images of the nitrided surface for a matrix of runs conducted at different N₂:Ar gas flow ratios and speeds, representing runs 10 through 21 in Table 4-1. The expulsion sites (Figure 4-4), sometimes associated with pores, can be seen to increase with decreasing translation speed for a N₂:Ar ratio of 16:0; however, they were not observed in the specimens nitrided with the N₂-Ar mixtures. The cellular transition region, Region A in Figure 4-5, was found at all N₂:Ar ratios and translation speeds. The wavy region, Region B in Figure 4-5a, decreased with increasing argon flow and increasing translation speed. The flat region, Region C in Figure 4-5a, dominated the central region of the trails at N₂:Ar ratios of 16:2 and 16:3. Figure 4-8 shows transverse cross sections of the same runs. It should be noted that the tendency towards surface oxidation was reduced with addition of argon to the nitrogen gas flow. This permitted the scan speed to be reduced when conducting experiments with nitrogen diluted with argon, compared to the nitrogen-only experiments, which showed significant surface oxidation at lower speeds (i.e. equal to or less than 50 mm/s).
Figure 4-7. SEM images of nitrided surfaces at N\textsubscript{2}:Ar ratios of 16:0 to 16:3 and speeds of 90, 70, and 50 mm/s corresponding to runs 10 through 21 in Table 4-1 (3.5 kW power, 8 mm OFD). Laser scan direction is from right to left as indicated by the white arrow in (e). All micrographs were obtained at the same magnification, and the scale marker on each micrograph is 1 mm.
Figure 4-8. Optical micrographs of transverse cross sections at N₂:Ar ratios of 16:0 to 16:3 and speeds of 90, 70, and 50 mm/s, corresponding to runs 10 through 21 in Table 4-1 (3.5 kW power, 8 mm OFD). Scale marker of 500μm shown below the images is common for all micrographs.
The optical micrographs of the transverse cross sections shown in Figure 4-8 provided important information about the transport mechanisms of nitrogen in the melt pool. With no argon in the gas flow, Marangoni convection dominated melt pool dynamics. The gradient of surface tension of liquid titanium with respect to temperature is negative [134], which meant that the surface tension was greater at the edges of the melt pool than at the center. This provided a driving surface force that pulled the liquid from the melt pool center towards the edges, setting up convection currents in the melt pool. This mechanism transported nitrogen from the center to the outer edges, from where the nitrogen was swept deeper into the melt pool by the convection current. Cooling occurred first at the edges which were rich in nitrogen swept there by Marangoni convection, explaining why the surface titanium nitrided dendrites of region B originated there. At speeds of 70 and 90 mm/s, the liquid did not have sufficient time to recirculate. The transverse cross sections in the absence of argon were thus seen to contain titanium nitride dendrites deep in the melt pool, more so at the sides than underneath the center, leading to a non-uniform dendrite distribution. It will be shown in Chapter 5 that this trend changes at low speeds (e.g. 30 mm/s) where the melt has sufficient time to recirculate before solidifying, forming a more uniform layer containing titanium nitride dendrites***.

As argon was introduced into the gas flow, the transport mechanism of heat and mass (i.e. nitrogen) changed from convection-dominated to diffusion-dominated (Figures 4-8a-d). Addition of 1 slpm of argon flow significantly reduced the amount of TiN dendrites in the melt pool (Figure 4-8b, 4-8f, and 4-8j). Two slpm of argon flow limited the dendrites to a thin (~20 µm) surface layer, suggesting a diffusion-layer of titanium nitride at the top, which solidified in a planar manner for the first 5 µm or so, before developing a dendritic morphology (Figure 4-8c). When the trails were

***The uniformity in the nitrided layer processed at low speeds such as 30 mm/s with a pure N\textsubscript{2} LSP, however, comes at the cost of excessive cracking and oxidation at the surface.
weighed to determine the weight of nitrogen incorporated into the melt pool, it was found that the weight decreased by about 70% when the nitrogen concentration was decreased by 11% (by volume), as shown in Figure 4-9.

Figure 4-9. Weight change per unit nitrided length of substrate as a function of argon flow in 16 slpm nitrogen flow (runs 12, 15, and 18 from Table 4-1) at processing conditions of 3.5 kW power, 8 mm OFD, and 90 mm/s scan speed. The corresponding transverse cross-sectional micrographs are shown as inset images.

Argon thus had a strong influence on nitrogen intake. The reduced concentration of nitrogen at the melt pool surface decreased surface tension gradients and reduced Marangoni convection. This limited nitrogen incorporation only to diffusion, since the TiN diffusion layer acted as a barrier by preventing fresh nitrogen from the plasma from being incorporated into the melt pool. In a Marangoni convection-dominated melt flow, the nitrogen-rich liquid Ti is replenished by pure liquid Ti from the bottom of the melt pool, thus allowing more liquid to interact with and incorporate the nitrogen from the plasma. The reduction in Marangoni convection was also evident from the transverse cross-sectional surface profiles of Figure 4-10. In a flow dominated
by surface tension gradients, the center region immediately beneath the beam axis was depressed compared to the edges, where humps formed [139]; it can be observed in Figures 4-10a-d that in a nitrogen-only experiment (Figure 4-10a), these features dominated, whereas when argon was introduced into the flow, the surface became flatter, and at a ratio of 16:2 (Figure 4-10c), the surface was more or less flat at all speeds. All this suggests the suppression of Marangoni convection and surface tension effects when argon is introduced into the gas flow.

Figure 4-10. Three-dimensional surface topography images obtained using optical profilometry for four different N\textsubscript{2}:Ar ratios: a) 16:0 b) 16:1 c) 16:2 and d) 16:3 slpm:slpm. The smoothing effect of argon gas flow on the nitrided surface can be clearly seen. Sa is the (arithmetic) mean surface roughness, Sq is the root mean square (RMS) roughness and Sz is the height difference between the highest and the lowest points on the measured surface. The roughness profile (in microns) for representative transverse cross-sectional planes is shown below each three-dimensional surface profile.
Another interesting microstructural feature was the thin (~5 µm) TiN surface layer formed when nitrogen was diluted with argon (Figure 4-11). This thin layer was observed even with argon gas flow as high as 25 slpm in 16 slpm of nitrogen. To observe the near-surface features in more detail, a high magnification scanning electron micrograph of one case (run 13 in Table 1: 50 mm/s speed and 16:1 N₂:Ar gas flow ratio) was obtained (Figure 4-11b). The scanning electron micrograph shows the thin TiN layer on top (arrowed). The planar-to-dendritic transition in solidification morphology of the TiN layer occurred because the thermal gradient $G$ (and hence $G/R$) was the highest at the melt pool surface (favoring planar solidification), and decreased deeper
into the melt pool (favoring dendritic solidification). Also, the concentration of nitrogen decreased with increasing distance from the surface. This explanation contrasted with Nassar’s [109] hypothesis that the TiN layer was due to vapor deposition of TiN. At the same time, another solidification front proceeded from the bottom of the melt pool towards the surface. This second solidification front was not as rich in nitrogen, and hence solidified mainly as a solid solution of nitrogen in titanium. XRD conducted on the top surface of run 13 (N\(_2\):Ar gas flow ratio of 16:1 and speed 90 mm/s) indicated the presence of \(\alpha\)-Ti, TiN, and TiN\(_{0.3}\) phases in the nitrided layer (Figure 4-12).

![X-ray diffraction analysis](image)

Figure 4-12. X-ray diffraction analysis conducted at the top surface of run 13 in Table 4-1 (N\(_2\):Ar 16:1, speed 90 mm/s, 3.5 kW power and 8 mm OFD).

The SEM image in Figure 4-11b shows that the microstructure consisted of thick dendrites (likely to be TiN) in a matrix of a solid solution of nitrogen in titanium, \(\alpha\)-Ti(N), and long slender needle-like structures (likely to be nitrogen-rich acicular martensitic titanium). A discussion on the metastable TiN\(_{0.3}\) phase, along with a detailed phase identification of the mentioned microstructural features using EDS, and will be presented in Chapter 5.
Finally, it can be observed that nitriding with a N\textsubscript{2}-Ar LSP reduced the tendency towards surface cracking on the nitrided layer (Figure 4-7); this was because the more ductile $\alpha$-titanium matrix underneath the thin TiN surface layer allowed the TiN layer to contract and relax its residual tensile stresses upon cooling. As discussed in the idealized case of an infinite ceramic plate (Equation 4-1), the tensile residual stress developed at the surface is proportional to the square of the plate thickness. Since nitriding with a diluted nitrogen LSP drastically reduced the thickness of the nitrided layer, the tensile stresses induced at the surface also reduced proportionally. Cracks were also not observed in the transverse cross sections. It is likely that the surface cracks were limited to the thin TiN layer on the top. Crack elimination was thus achieved with dilution of nitrogen gas, in agreement with the literature [59,64,65,67,71,109]; however, this appeared to come at the cost of a significant reduction of nitrogen intake into the melt pool. In Chapter 5, a new two-step method of eliminating crack formation without limiting nitrogen intake during the nitriding process will be presented and developed.

### 4.4 Chapter summary

Investigation of the laser-sustained plasma (LSP) nitriding method as a function of off-focal distance, scan speed, and N\textsubscript{2}:Ar gas flow ratio determined the following:

- Surface quality was influenced by the off-focal distance (OFD) during LSP nitriding. The LSP nitriding method required a close interaction between the excited species (N, N+) at the core of the plasma and the melt pool. At a scan speed of 90 mm/s, a maximum OFD of 8 mm ensured sufficient interaction of the active species in the plasma with the CP-Ti substrate and efficient heat and mass transfer.
• For speeds ranging from 135 – 300 mm/s, the density of cracks was observed to increase with an increase in scan speed. The cracks originated in the porous trail edge and were perpendicular to the scan direction. Porous expulsion sites (which resembled black patches in the optical micrograph) were observed at the melt surface. These sites increased in number with decreasing speed, and their formation was attributed to the surplus gas escaping the liquid surface due to saturation at lower speeds and/or high nitrogen concentration. The LSP was thus found to enhance nitrogen incorporation during nitriding.

• The addition of argon to the nitrogen gas flow in the plasma significantly decreased nitrogen intake into the melt pool. Reduction of nitrogen concentration by 11 % (by volume) caused the nitrogen intake to decrease by over 70%. Compared to the nitrogen-only cases, addition of argon to the gas flow significantly reduced crack formation on the surface.

• Surface dendrites of TiN were observed to increase with decreasing speed and increasing \( \text{N}_2: \text{Ar} \) ratio. Argon addition reduced the surface roughness by reducing surface tension gradients at the surface of the melt pool. Marangoni convective effects were found to diminish at \( \text{N}_2: \text{Ar} \) ratios of 16:2 and 16.3. This prevented the sub-surface Ti-rich liquid from being exposed to the nitrogen atmosphere, hence limiting the nitrogen intake to diffusion rather than a combination of convection and diffusion.

• A thin 5 µm coating of TiN was observed at all \( \text{N}_2: \text{Ar} \) ratios, even at high Ar flows of 25 slpm. SEM images showed that this was a layer which solidified in planar fashion from the surface down into the melt pool, before dendrites and needle-like structures formed. TiN, TiN\(_{0.3}\), and \( \alpha \)-Ti phases were detected on the surface of the nitrided layer from XRD.

• Nitriding with a \( \text{N}_2: \text{Ar} \) LSP showed potential to form crack-free surfaces. However, due to reduced nitrogen intake, the resulting microstructure comprised a thin TiN layer confined to the surface with little or no dendrites observed deeper in the melt pool at Ar flows of 2
slpm and higher in 16 slpm flow of N₂. The nitrogen dilution approach to crack prevention was thus seen to come at the cost of a reduced control over the microstructure.
Chapter 5

A two-step method to perform deep-case hardening of CP-titanium

5.1 Introduction

It was shown in Chapter 4 that LSP nitriding in a pure-N₂ gas flow produced non-uniform nitrided layers containing surface cracks. Adding argon to the nitrogen gas flow greatly reduced the tendency towards surface cracking in single LSP-nitrided trails and made the melt pool more uniform. However, dilution of the nitrogen gas flow led to microstructures consisting of a thin (~5 μm) TiN layer at the top, with a dendrite-free, nitrogen-rich, martensitic titanium region deeper in the melt pool. Thus, reduced surface cracking was achieved at the cost of lower nitrogen intake in the melt pool and reduced control over the microstructure. A possible way of eliminating cracking on the laser-nitrided surface without limiting nitrogen intake into the melt pool is by laser-remelting the nitrided layer in argon gas flow. The benefits of such a post-nitriding remelting run have been investigated previously by Weerasinghe et al. [65]. They used a 2 kW CW CO₂ laser beam, defocused to a spot diameter of 1-2 mm, to perform laser nitriding on IMI829 (Ti-5Al-3.5Sn-3Zr-1Nb-0.3Si) and CP-Ti substrates, and then laser-remelted the nitrided layers in argon gas flow. They performed two such experiments (one for IMI829 and the other for CP-Ti), and reported that the remelting scan smoothed the nitrided layer and reduced the scatter in hardness values (i.e. made the layer more homogenous). However, Weerasinghe et al. [65] did not discuss the effect of remelting on surface cracking and did not follow up their exploratory work with future experiments.

In this Chapter, it is hypothesized that laser-remelting the nitrided layer in the presence of an argon LSP can reduce or eliminate surface cracks. A two-step method is proposed to produce uniform, nitrogen-rich, crack-free, hard, and deep cases on CP-titanium using LSP processing:
i. In the first step, a nitrided layer is deposited on a titanium substrate in the presence of a prestruck, pure-nitrogen LSP, with the laser beam oriented normal to the substrate surface, as described in Chapters 3 and 4. This nitrided layer has the following microstructure: a thin, 5 μm TiN surface film, containing transverse surface cracks; TiN dendrites growing from the surface layer into an α-Ti(N) matrix; and fine, acicular, martensitic α’-Ti further from the surface. Single nitrided trails exhibit high surface roughness and are characteristically inhomogeneous, as shown in Chapter 4. The trails are deeper at the edges than at the center, due to the effect of Marangoni convection, which also causes nitrogen buildup (and subsequent nitride formation) at the edges.

ii. In the second step, the nitrided layer is remelted under a prestruck pure-argon LSP at speeds low enough to partially or fully melt the dendrites. Decreasing the remelting speed increases time for which the melt pool is molten, and is thus expected to eliminate surface cracks, reduce surface roughness, and homogenize the surface layer.

Consequently, the amount of nitrogen intake is controlled by the nitriding step, and the extent of microstructural refinement and surface crack elimination is controlled by the remelting step. Unlike the nitrogen dilution method of reducing crack formation, the proposed remelting method does not suffer from the drawback of limited nitrogen intake into the melt pool. This allows the microstructure and depth of the hard case to be tailored by varying the nitriding and/or remelting speeds.

To test this hypothesis, LSP nitriding-remelting experiments were conducted by varying both the nitriding and remelting speeds. The treated layers were analyzed using a variety of characterization techniques. The moving heat source solution described in Chapter 2 was used to model the heat transfer in the melt pool. From these data, the effects of processing parameters
(nitriding and remelting speeds) on the microstructure, hardness, and case depth of the nitrided layers were determined.

5.2 Methodology

All the experiments were conducted using the materials and the experimental setup described in Sections 2.2.1 and 2.2.2. The LSP nitriding runs were conducted according to the procedure detailed in Section 2.2.3.1, using a nitrogen gas flow of 16 slpm. After pausing for a sufficient time (~5 minutes) to allow the coupon to cool down to room temperature, remelting was conducted in the same direction under a prestruck pure-argon LSP, with an argon gas flow of 25 slpm. A schematic of this two-step processes is shown in Figure 5-1.

![Figure 5-1. Schematic for LSP nitriding and remelting experiments.](image)

Nitriding was conducted at scan speeds of 30, 45, 60, and 75 mm/s, while remelting was conducted at scan speeds of 10, 15, 20, and 25 mm/s. The nitriding experiments were conducted at an off-focal distance (OFD) of 8 mm (1.34 mm beam diameter at the substrate), and the remelting
experiments at an OFD of 7 mm (1.18 mm beam diameter at the substrate). All the experiments were conducted at a power of 3.5 kW. A complete list of the twenty experimental runs is shown in Table 5-1.

Table 5-1. List of nitriding-remelting experiments.

<table>
<thead>
<tr>
<th>Run #</th>
<th>Nitriding speed (mm/s) (8 mm OFD)</th>
<th>Remelting speed (mm/s) (7 mm OFD)</th>
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<tr>
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<td>75</td>
<td>10</td>
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</table>

The weight of each sample was measured before and after the two-step treatment to estimate nitrogen intake. Scanning electron and optical microscopy were used to observe the microstructure of the top surface and the transverse cross section. Analyses of optical micrographs and determinations of dendrite volume fractions in the melt pool were conducted using the image processing software, ImageJ. Vickers hardness tests were conducted on the transverse cross-sections of the treated layers; hardness indentations were made at different depths in the center region of the solidified melt pool, with three measurements taken at each depth. XRD and optical profilometry were conducted on the top surface to study the effect of remelting on phase change and surface topography, respectively. EDS was conducted in the spot mode for runs 1-5 (Table 5-1).
for phase identification of microstructural features deeper in the melt pool, based on an average of three readings taken on a given microstructural feature. EDS line scans were conducted along the centerline of the transverse cross-sections of the solidified melt pool for runs 2 and 5 (Table 5-1) to obtain a qualitative depth profile of nitrogen. The noisy line scan signal was averaged over depth intervals of 100-150 μm to smooth the nitrogen depth profile.

5.3 Calculations

The heat transfer model of Section 2.2 was used to calculate isotherm dimensions and lifetimes, where lifetime is defined as the time for which a given isotherm in the substrate has non-zero dimensions. Three isotherms were of interest in this study: the melting point of CP-Ti (1670 °C); the peritectic isotherm for the Liquid + TiN $\rightarrow$ α-Ti reaction (2350 °C); and the melting point of stoichiometric TiN (3290 °C). The temperature values were taken from Ref. [51]. As explained in Section 2.2.3.3, the dimensions of a given isotherm in the CP-Ti substrate can be calculated as a function of time for different laser processing conditions. An example was shown in Chapter 2 (Figure 2-6b), where the width and depth of the melt isotherm were plotted as a function of time for a nitriding scan speed of 30 mm/s (run 1 in Table 5-1). The melt pool lifetime for this case was calculated to be 0.119 seconds. The values of isotherm lifetimes for four LSP nitriding speeds (30, 45, 60, and 75 mm/s) using $\eta = 0.14$ and $r_0 = 0.677 \times 10^{-3}$ m, and four remelting speeds (10, 15, 20, and 25 mm/s) using $\eta = 0.1$ and $r_0 = 0.595 \times 10^{-3}$ m, were calculated using the procedure (and notations) of Section 2.2.3.3, and are shown in Figures 5-2a and 5-2b. The predicted isotherm lifetimes were found to vary linearly with the inverse of scan speed. The relation between the melt pool lifetime $t_{\text{melt}}$ (s) and the LSP nitriding scan speed $v$ (mm/s) can be expressed as a linear equation ($R^2 = 1$):

\[
t_{\text{melt}} = \frac{4}{v} - 0.0147 \tag{5-1}
\]
5.4 Results and discussion

5.4.1 LSP nitriding

Figure 5-3 shows the transverse cross-sections of all 20 experimental cases listed in Table 5-1. Let us first consider the nitrided trails which were not remelted in the argon LSP i.e. runs 1, 6, 11, and 16. As the nitriding speed was reduced from 75 mm/s to 30 mm/s, the nitrided layer became deeper and more rounded in shape. During LSP nitriding, Marangoni convection occurred at the surface owing to the temperature and surface tension gradients between the center (higher temperature and lower surface tension region) and the edges (lower temperature and higher surface tension region). Surface tension gradient forces transported the melt from the center to the edges, thus setting up convection loops within the melt pool. At low speeds such as 30 mm/s, the melt pool was molten for longer (more than three times longer than at 75 mm/s), allowing the fluid flow in the melt pool to reach a quasi-steady state. In this situation, two counter-rotating convection loops were set up in each half of the symmetric melt pool, making the nitrided layer deeper at the center than at the edges [107,140], as seen in Figure 5-3a (run 1). The solidified melt pool boundary in run 1 of Figure 5-3a had two inflection points in each half, which is typical for flows with high Marangoni numbers.
(ratio of surface tension forces to viscous forces) and low Prandtl numbers (ratio of kinematic viscosity to thermal diffusivity) [140]. The convection currents swept large pieces of solidified TiN to the bottom of the melt pool.

<table>
<thead>
<tr>
<th>Nitriding speed (mm/s)</th>
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<table>
<thead>
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<th>1 mm</th>
</tr>
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<tbody>
<tr>
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<td>b) Run 2</td>
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<td>g) Run 7</td>
</tr>
<tr>
<td>k) Run 11</td>
<td>l) Run 12</td>
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<tr>
<td>p) Run 16</td>
<td>q) Run 17</td>
</tr>
<tr>
<td>b) Run 2</td>
<td>c) Run 3</td>
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<tr>
<td>g) Run 7</td>
<td>h) Run 8</td>
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<td>c) Run 3</td>
<td>d) Run 4</td>
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<tr>
<td>h) Run 8</td>
<td>i) Run 9</td>
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<tr>
<td>n) Run 15</td>
<td>p) Run 16</td>
</tr>
<tr>
<td>d) Run 4</td>
<td>e) Run 5</td>
</tr>
<tr>
<td>i) Run 9</td>
<td>q) Run 17</td>
</tr>
<tr>
<td>o) Run 15</td>
<td>r) Run 18</td>
</tr>
<tr>
<td>e) Run 5</td>
<td>j) Run 10</td>
</tr>
<tr>
<td>n) Run 15</td>
<td>s) Run 19</td>
</tr>
<tr>
<td>f) Run 6</td>
<td>o) Run 14</td>
</tr>
<tr>
<td>p) Run 16</td>
<td>t) Run 20</td>
</tr>
</tbody>
</table>

Figure 5-3. Optical micrographs of transverse cross-sections of all the experimental cases (with corresponding run #) listed in Table 5-1. Scale marker of 1 mm shown at the bottom is common for all micrographs.
For speeds greater than 30 mm/s, Marangoni forces transported the nitrogen-rich melt to the edges, while the low density titanium-rich melt near the center flowed up towards the surface, as discussed in Chapter 4. Due to the lower melt pool lifetimes associated with higher speeds, the melt pool solidified before the nitrogen-rich melt could flow back to the center of the trail, making the solidified nitrided layer non-uniform in appearance and shallower at the center, as seen in Figures 5-3f (run 6), 5-3k (run 11), and 5-3p (run 16). Figures 5-4a and 5-4b show higher magnification micrographs of runs 11 and 16 respectively, for coupons nitrided at 60 and 75 mm/s, respectively. The highly convective nature of nitrogen transport at higher nitriding speeds resulted in several regions in the melt pool that did not contain sufficient nitrogen to exhibit TiN dendrites, indicated by arrows in Figures 5-4a and 5-4b. The high Marangoni forces associated with the high-power LSP nitriding process also resulted in nitrogen build-up at the melt pool edges, forming TiN regions with Vickers hardness greater than 1000 HV0.3. Such non-uniformity made a post-nitriding remelting scan necessary in order to homogenize the nitrided layer.

![Figure 5-4. Higher magnification optical micrographs of LSP nitrided coupons at speeds of 60 mm/s (run 11) and 75 mm/s (run 16). The scale marker of 200 μm shown at the bottom is common for both micrographs. The regions that did not exhibit TiN dendrites are indicated by black arrows.](image)

The nitrogen intake into the melt pool was quantified by measuring the weight of the samples before and after the LSP nitriding treatment. The measured weight gain per unit length is plotted against the inverse of nitriding speed in Figure 5-5, with the data point for the nitriding
speed of 90 mm/s from Chapter 3 also included in the plot. As expected, the nitrogen content of the nitrided trails increased with decreasing scan speed due to the increased energy input to the substrate and consequently longer melt lifetimes.

Interestingly, similar to the isotherm lifetimes Figure 5-2 and described by Equation 5-1, the nitrogen intake per unit length, $\Delta w$ (g/mm), also appeared to be a linear function of the inverse of nitriding speed, with the linear fit ($R^2 = 0.99$) shown in Figure 5-5:

$$10^5 \Delta w = \frac{781}{v} - 3.35 \quad (5-2)$$

Equations 5-1 and 5-2 give the following linear relation between nitrogen intake and the melt pool lifetime $t_{melt}$ (s):

$$10^5 \Delta w = 195 t_{melt} - 0.42 \quad (5-3)$$

Equation 5-3 provides a quick way of estimating nitrogen intake at a given set of processing conditions; for a given laser power, OFD, and scan speed, the heat transfer model of Section 2.2 can be used to determine the melt pool lifetime, $t_{melt}$, which can then be substituted into Equation
5-3 to calculate the nitrogen intake. As an example, the measured (Table 3-4) and predicted (Equation 5-3) nitrogen intake in LSP nitriding experiments conducted at two different processing conditions (7 mm OFD, 180 mm/s speed; and 9 mm OFD and 60 mm/s speed; 3.5 kW power for both), are shown in Table 5-2. The measured and calculated values were within 8% of each other.

Table 5-2. Predicted and measured values of nitrogen intake, $\Delta w$.

<table>
<thead>
<tr>
<th>Processing conditions (OFD, Speed)</th>
<th>$t_{\text{melt}}$ (s)</th>
<th>Calculated $\Delta w$ ($10^{-5}$ gmm$^{-1}$)</th>
<th>Measured $\Delta w$ ($10^{-5}$ gmm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9 mm, 60 mm/s</td>
<td>0.0513</td>
<td>9.59</td>
<td>8.86</td>
</tr>
<tr>
<td>7 mm, 180 mm/s</td>
<td>0.0129</td>
<td>2.09</td>
<td>1.9</td>
</tr>
</tbody>
</table>

Nitrogen incorporation into a given region on the substrate only occurred as long as the region was molten. Taking the derivative of $\Delta w$ with respect to $t_{\text{melt}}$ and dividing by a typical melt pool width of 2 mm (as estimated from Figures 5-3a, 5-3f, 5-3k, and 5-3p), the average mass flux of nitrogen entering the titanium melt pool, $\Omega_{N,Ti}$, was estimated to be:

$$\Omega_{N,Ti} = \frac{1}{\text{width}} \left( \frac{d\Delta w}{dt_{\text{melt}}} \right) = 9.7 \times 10^{-4} \frac{g}{\text{mm}^2\text{s}}$$

(5-4)

During the LSP nitriding process, nitrogen gas flowed at the rate of 16 slpm through a 10 mm-diameter nozzle, giving a mass flux of nitrogen gas from the nozzle of $4.24 \times 10^{-3}$ gmm$^{-2}$s$^{-1}$. The efficiency of nitrogen intake, $\varepsilon$, defined as the ratio of nitrogen mass flux entering the melt pool to the ratio of nitrogen mass flux coming out of the nozzle, could be estimated as:

$$\varepsilon = \frac{9.7 \times 10^{-4}}{4.24 \times 10^{-3}} = 0.23$$

(5-5)

The mass flux of nitrogen into the melt pool (Equation 5-4) and the efficiency of nitrogen intake (Equation 5-5) were determined as they are expected to be important inputs to computational models of the LSP nitriding process.
5.4.2 LSP nitriding and remelting

5.4.2.1 Characteristic microstructural features

To observe the microstructural features in the transverse cross section more closely, higher magnification SEM images were obtained. Representative SEM images are shown in Figures 5-6a and 5-6b for run 4 (30 mm/s nitriding speed, 15 mm/s remelting speed) and run 1 (30 mm/s nitriding speed, no remelting), respectively. Five distinct microstructural features were identified and are labeled in Figure 5-6:

I. A continuous film (thickness ~5 μm) at the surface, observed only in the nitrided layers that were not remelted. It may be recalled that this thin film was also observed when nitriding was conducted with a diluted nitrogen gas flow in Chapter 4 (Figure 4-11).

II. Short (~50 μm length) columnar dendrites close to the surface.

III. Long (~150 μm length) columnar dendrites around 200 μm below the surface.

IV. Coarse (edge-to-edge dimension ~20 μm), equiaxed, dendrites at the bottom of the melt pool, some of which coalesced.

V. Thin (thickness < 1 μm), acicular needles in the interdendritic regions.

EDS was performed on the features in spot mode, with three measurements conducted per feature. The features were chosen from cases having differing remelting speeds and a common nitriding speed of 30 mm/s. Table 5-3 shows the nitrogen content of features I-V above.

Table 5-3. Nitrogen content of microstructural features at 30 mm/s nitriding speed.

<table>
<thead>
<tr>
<th>Feature</th>
<th>Remelting speed (run #)</th>
<th>Average N content (at. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>No remelting (run 1)</td>
<td>36.7</td>
</tr>
<tr>
<td>II</td>
<td>No remelting (run 1)</td>
<td>27.6</td>
</tr>
<tr>
<td>III</td>
<td>25 mm/s (run 2)</td>
<td>20.7</td>
</tr>
<tr>
<td>III</td>
<td>10 mm/s (run 5)</td>
<td>15.6</td>
</tr>
<tr>
<td>IV</td>
<td>25 mm/s (run 2)</td>
<td>23.1</td>
</tr>
<tr>
<td>V</td>
<td>10 mm/s (run 5)</td>
<td>Negligible</td>
</tr>
<tr>
<td>V</td>
<td>25 mm/s (run 2)</td>
<td>Negligible</td>
</tr>
</tbody>
</table>
Figure 5-6. SEM image (backscatter mode) of transverse cross section of (a) run 4 (30 mm/s nitriding speed, 15 mm/s remelting speed), and (b) run 1 (30 mm/s, no remelting) near the surface. The scale marker for (a) is 200 μm and for (b) is 20 μm. Five distinct microstructural features have been labeled in the micrographs.
The metastable $\alpha$-TiN$_{0.3}$ phase is labeled in red.

Using the Ti-N phase diagram of Figure 5-7, the solidification pathways corresponding to the nitrogen content determined by EDS can be estimated, which in turn can be used to identify the phases of the respective microstructural features of Figure 5-6:

\textbf{a) $N > 28$ at. %}

Liquid (L) with a nitrogen content greater than 28 at. % solidified as

$L \rightarrow L + \delta TiN \rightarrow \delta TiN,$

where the $\delta$ symbol indicates the face-centered cubic (FCC) structure of the TiN phase. The thin continuous surface film (feature I in Figure 5-6 and Table 5-3) solidified in this manner and was thus identified as a TiN film. The film solidified in a planar front for approximately 5 μm after which it branched into dendrites whose primary arm thickness was also close to 5 μm (Figure 5-6b). The planar growth of $\delta$-TiN at the surface was expected due to two reasons: one, because the thermal gradient at the surface was large due to the heat flux from the LSP; and two, because the slope of the liquidus line is small at nitrogen concentrations greater than 35 at. %, and becomes zero near stoichiometric ratios.
of δ-TiN (Figure 5-7); both these factors stabilized the planar solidification front according to the theory of constitutional supercooling [138]. The near-surface dendrites (feature II), with N content of almost 28 at. %, were also believed to form via this solidification path, the dendritic morphology arising as a result of the increased slope of the liquidus line at nitrogen concentrations around 28 at. % and below.

b) 20.5 at. % < N < 28 at. %

Liquid with a nitrogen content between 20.5 and 28 at. % solidified as

\[ L \rightarrow L + \delta TiN \rightarrow \delta TiN(N=28\%) + \alpha Ti(N)(N=20.5\%). \]

The peritectic transformation occurred at the surface of the δ-TiN dendrites formed during the first transformation, leading to the formation of the hexagonal close packed (HCP) α-Ti(N) phase on the surface of the δ-TiN dendrites. The coarse dendrites of feature IV solidified in this fashion. It is possible that these dendrites solidified at the nitrogen-rich edge of the melt surface and were swept to the bottom of the melt pool by Marangoni convection currents.

c) 15.2 at. % < N < 20.5 at. %

Liquid with a nitrogen content between 15.2 and 20.5 at. % solidified as

\[ L \rightarrow L + \delta TiN \rightarrow L(N=15.2\%) + \alpha Ti(N)(N=20.5\%) \rightarrow \alpha Ti(N). \]

As in case (b), the δ-TiN phase solidified from the melt first. At the peritectic isotherm, δ-TiN phase transformed into the α-Ti(N) phase in the presence of the liquid phase. The nitrogen contents of the long dendrites of feature III was 15.6 at. % at a remelting speed of 10 mm/s, and 20.7 at. % for a remelting speed of 25 mm/s, suggesting that they are α-Ti(N); moreover, the dendrites at the 10 mm/s remelting speed looked like thick needles and showed lesser secondary arm growth than those at 25 mm/s remelting speed.
d) \textbf{N < 4 at. %}

Liquid with a low nitrogen content of less than 4 at. % solidified as

\[ L \rightarrow L + \beta Ti \rightarrow \beta Ti \rightarrow \beta Ti + \alpha Ti \rightarrow \alpha' Ti + \alpha Ti, \]

where \( \alpha' \) indicates hexagonal close packed (HCP) martensitic titanium formed from body-centered cubic (BCC) \( \beta \)-Ti via a diffusionless transformation. The \( \alpha' \)-Ti phase solidified as acicular needles (feature V).

The effects of remelting the nitrided layers on the microstructural features are discussed in the following sections.

\textbf{5.4.2.2 Effect of remelting on microstructure}

The nitrided samples were remelted under a pure-argon LSP at scan speeds of 10, 15, 20, and 25 mm/s. The remelting scan speed determined the average melt pool temperature, cooling rate, and melt pool lifetime, which in turn affected dendrite refinement and melt pool dilution. For example, higher magnification optical micrographs of run 1 (30 mm/s nitriding speed, no remelting), run 2 (30 mm/s nitriding speed, 25 mm/s remelting speed), and run 5 (30 mm/s nitriding speed, 10 mm/s remelting speed) are shown in Figures 5-8b, 5-8c, and 5-8a, respectively. Isotherms for the melting point of titanium (1670 °C, red), peritectic isotherm (2350 °C, green), and the melting point of TiN (3290 °C, blue) for remelting speeds of 10 mm/s and 25 mm/s are superposed on Figures 5-8a and 5-8c, respectively. Since the isotherms varied with time, they were plotted at the instant when their width was maximum. The regions above the 3290 °C isotherm, between the 3290 °C and the 2350 °C isotherms, and between the 1670 °C and the 2350 °C isotherms, are labeled as zones I, II, and III, respectively. It should be noted that the model overestimated isotherm dimensions because it did not take into account the energy expended in overcoming the latent heat of melting of the dendrites.
Let us first consider the highest remelting speed of 25 mm/s (Figure 5-8c). Here, the dendrites in zone I dissolved completely, causing solute redistribution and homogenization of the microstructure near the surface. This nitrogen-rich liquid resolidified with finer dendrites compared to the original nitrided layer (Figure 5-8b). Long columnar dendrites were observed in zone I (Figure 5-8c). Zone II represented a region that melted only partially. The dendrite volume fraction in this region was visibly lower (47.8%) than that in zone I (55.5%), probably due to the unmelted, high-density, TiN dendrites being transported to the sides and the bottom of the melt pool by convection currents, thus reducing the average nitrogen concentration in zone II. This in turn caused a buildup of high-melting point nitrogen-rich regions in zone III, observed more clearly in the low magnification micrograph of run 2 (Figure 5-3b). As the depth of the melt isotherm for titanium (1670 °C, red line in Figure 5-8c) did not exceed the depth of the nitrided layer, the temperatures in zone III were too low to dissolve the TiN. Consequently, dilution of the nitrided Zone III could not occur. The average case hardness and standard deviation for run 2, computed from nine hardness measurements (three measurements each at three different melt depths) taken in the center region of the remelted layer, was measured to be 729±164 HV₀.₃.
Conversely, at the lowest remelting speed of 10 mm/s (Figure 5-8a), the isotherm dimensions increased due to the higher heat input. Now, the melt isotherm for titanium penetrated into the Ti substrate, introducing fresh, titanium liquid into the nitrided melt pool, where the longer melt pool lifetime resulted in more efficient convective mixing and a reduced dendrite volume fraction upon solidification. The higher melt pool temperatures also ensured that there was no buildup of hard material at the bottom, resulting in more homogenous microstructures. These effects can be observed in the hardness profiles of Figure 5-9a, plotted for remelting speeds of 25 mm/s (run 2) and 10 mm/s (run 5). Each hardness value represents the mean, and the error bars indicate the range of three hardness measurements taken at a given depth. A tradeoff between high hardness values and microstructural homogeneity is readily apparent. At a remelting speed of 25 mm/s, there was no appreciable dilution of the nitrided layer, resulting in higher hardness numbers. Moreover, the remelted layer, which had a case depth of 650 μm, was harder at a depth of 460 μm than at the top, and showed larger scatter in the individual data points. At a remelting speed of 10 mm/s, lower hardness values and smaller scatter in hardness values were observed, along with a more gradual decrease of hardness with depth for a case depth approaching 800 μm. The anomalous high scatter in hardness values at the bottom of the melt pool (namely at depths of 632 μm and 755 μm for remelting speeds of 25 mm/s and 10 mm/s respectively in Figure 5-9a) was due to the hemispherical shape of the melt pool, which caused the center indent to be within the nitrided-remelted region and the other two indents at the same depth to be in the base metal region.

Figure 5-9b shows the qualitative depth profile of nitrogen content in the melt pool measured by an EDS line scan along the center of the melt pool for the same two remelting speeds. Expectedly, the hardness profile correlated well with the nitrogen depth profile. The EDS scan provided further evidence of the melt pool dilution that occurred at the lowest remelting speed of 10 mm/s.
Figure 5-9. a) Hardness profile for sample nitrided at 30 mm/s and remelted at two different speeds of 25 mm/s (run 2) and 10 mm/s (run 5), and b) EDS line scan results showing qualitative depth profiles of nitrogen content (atomic %) in the melt pool.

Figure 5-10. Linear correlation between Vickers hardness number (VHN) and dendrite volume fraction (DVF).

The effect of nitrogen dilution and/or dendrite refinement on hardness was quantified by plotting Vickers hardness numbers (average of three measurements) against dendrite volume fractions, as shown in Figure 5-10. A total of 24 data points were computed at three different depths, for nitriding speeds of 30 and 45 mm/s and all remelting speeds (i.e. runs 2-5 and 7-10). These examples were selected because their microstructures showed appreciable quantities of dendrites.
The linear correlation between Vickers hardness numbers (VHN) and dendrite volume fractions (DVF) in the microstructures could be described using the linear fit \( R^2 = 0.84 \):

\[
VHN = 10.95DVF + 74
\]

At higher nitriding speeds of 60 and 75 mm/s, the remelting scans at all speeds became more effective in diluting the nitrided layer, as their lower dendrite contents dissolved more readily and solute macrosegregation was reduced more effectively. The effect of varying remelting speed on phase transformations in the melt pool for the highest nitriding speed of 75 mm/s can be seen in the XRD spectrum of Figure 5-11. For the nitriding-only case (no remelting, run 16), TiN, \( \alpha\)-TiN\(_{0.3} \), and \( \alpha\)-Ti phases were detected near the surface, similar to the XRD pattern shown in Chapter 4 (Figure 4-12) where nitriding was conducted with a N\(_2\)-Ar LSP.

![Figure 5-11. XRD data showing the effect of remelting on phase transformation in a sample nitrided at a speed of 75 mm/s.](image)

The \( \alpha\)-TiN\(_{0.3} \) phase does not appear in the phase diagram of the Ti-N system and merits further explanation. According to the ‘general comments’ section in the powder diffraction file (PDF) card...
41-1352 [141], Lengauer detected the so-called $\alpha$-TiN$_{0.3}$ phase near the nitrogen-rich phase boundary of a Ti-TiN mixture which was arc melted and annealed at 1127 °C; the probable location of this phase is marked in red on the phase diagram of Figure 5-7. Further, $\alpha$-TiN$_{0.3}$ has the same hexagonal crystal structure as $\alpha$-Ti with a slightly expanded lattice due to the presence of nitrogen, from which it can be inferred that $\alpha$-TiN$_{0.3}$ is a nitrogen-rich solid solution of N in $\alpha$-Ti and can be alternatively expressed as $\alpha$-Ti (N = 23 at. %). Because of this, the two-theta peaks of $\alpha$-TiN$_{0.3}$ and $\alpha$-Ti appear together in the XRD spectrum of a Ti-N system (e.g. the ‘no remelting’ spectrum of Figure 5-11), the $\alpha$-TiN$_{0.3}$ peaks being to the left of the $\alpha$-Ti peaks due to the increased d-spacing of the former according to Bragg’s law. Since laser and LSP nitriding are rapid processes involving non-equilibrium solidification, the peritectic product $\alpha$-Ti (N = 20.5 at. %) is expected to solidify at melt concentrations of 20.5 at. % < N < 28 at. % at 2350 °C, as discussed in Section 5.4.2.1. It must hence be noted that the peak labeled as $\alpha$-TiN$_{0.3}$ in this dissertation (and in the general laser nitriding literature [69–72,81]) refers to the nitrogen-rich solid solution, $\alpha$-Ti (N), and does not necessarily indicate a N:Ti ratio of 0.3 (i.e. 23 at. % N). Indeed, from the EDS data of Table 5-3, it is seen that the composition of different non-TiN microstructural features varied over a wide range of 15 – 23 at. % nitrogen.

Decreasing the remelting speed successively converted the TiN and $\alpha$-TiN$_{0.3}$ phases into $\alpha$-Ti(N), a solid solution of nitrogen in titanium. At the lowest remelting speed of 10 mm/s, the higher melt pool temperatures and longer melt pool lifetimes were sufficient to completely transform the TiNx phases into $\alpha$-Ti(N). Low remelting speeds of 15 and 10 mm/s also resulted in oxygen pickup leading to a small amount of rutile formation, which most likely occurred after the argon LSP had moved to a position where the argon flow no longer blanketed the surface.

At a constant remelting speed, more dendrite dissolution and refinement was seen at higher nitriding speeds, where the melt pool had a shallower depth and lower nitrogen content. For example, consider runs 5, 10, 15, and 20, nitrided at speeds of 30, 45, 60, and 75 mm/s, respectively,
and all remelted at the lowest speed of 10 mm/s. From the weight measurements of Figure 5-5, and calculating the melt pool areas using the ImageJ software, the average atomic percent (at. %) of nitrogen in the melt pool could be approximated as:

\[
\text{at. } \% \text{ } N = 100 \times \frac{\text{weight gain (gmm}^{-1})}{14 \text{(g mol}^{-1})} + \frac{0.0045 \text{(g mm}^{-2}) \times \text{melt pool area (mm}^2)}{48 \text{(g mol}^{-1})}
\]

(5-7)

where 0.0045 g mm\(^{-3}\) is the density of titanium, 14 g mol\(^{-1}\) is the atomic weight of nitrogen, and 48 g mol\(^{-1}\) is the atomic weight of titanium. The average nitrogen contents in the melt pool calculated from Equation 5-7 for different nitriding speeds and a constant remelting speed of 10 mm/s are shown in Table 5-4. Comparison with the Ti-N phase diagram (Figure 5-7) shows that these at. % values were lower than 15.2 %, the minimum required for TiN to precipitate. In contrast, optical micrographs of runs 5, 10, 15, and 20 in Figure 5-3 showed thick TiN dendrites at the lowest nitriding speed (30 mm/s, run 5) and thin dendritic networks at intermediate speeds (45 and 60 mm/s, runs 10 and 15, respectively), due to non-equilibrium solidification.

<table>
<thead>
<tr>
<th>Nitriding speed (mm/s)</th>
<th>Average at. % N</th>
<th>Average case hardness</th>
</tr>
</thead>
<tbody>
<tr>
<td>75 (run 20)</td>
<td>3.6</td>
<td>488±28</td>
</tr>
<tr>
<td>60 (run 15)</td>
<td>5.6</td>
<td>489±50</td>
</tr>
<tr>
<td>45 (run 10)</td>
<td>7.6</td>
<td>516±34</td>
</tr>
<tr>
<td>30 (run 5)</td>
<td>11.1</td>
<td>559±37</td>
</tr>
</tbody>
</table>

For the extreme case (highest nitriding speed of 75 mm/s and lowest remelting speed of 10 mm/s, run 20), the dendrites dissolved completely, resulting in a homogenous microstructure comprising a solid solution of nitrogen in α-Ti(N). This was attributed to the more pronounced mixing effect during remelting for the higher nitriding speeds, bringing the nitrogen-rich melt closer to its thermodynamic equilibrium state upon solidification. For nitriding speeds below 75 mm/s, the α-Ti(N) phase may be formed by remelting at speeds below 10 mm/s and/or remelting multiple times to reduce solute segregation. The effect of remelting multiple times using an argon
LSP is shown in Figure 5-12. A sample nitrided at 45 mm/s (Figure 5-12a) was remelted at 15 mm/s once (Figure 5-12b) and eight times (Figure 5-12c). Dendrite refinement accompanied by a noticeable reduction in dendrite volume fraction (from 41.8% for one remelt to 34.6% for eight remelts) was observed in the center region of the respective layers, and the hard, TiN regions at the melt pool edges dissolved completely.

Table 5-4 also compares the average case hardness and standard deviation with the average at. % N in the melt pool. The average case hardness for the highest nitriding speed and lowest remelting speed (run 20) was 488 HV0.3. Since the microstructure consisted solely of Ti(N), this increase in hardness was attributed to solid solution strengthening [50]. When compared by weight percent (wt. %), the solution strengthening effect of nitrogen is approximately twice that of oxygen [49]. The strengthening effect of nitrogen in titanium can be expressed by an empirical relation (slightly modified from [49] by substituting wt.% $O = 2\text{wt.}% N$) that relates the Vickers hardness number ($VHN$) to the nitrogen wt. %, $N$, in the solid solution:

$$VHN = 65 + 310\sqrt{2N}$$  \hspace{1cm} (5-8)  

For Run 20 (75 mm/s nitriding, 10 mm/s remelting), the calculated nitrogen concentration was 1.06 wt. % (3.6 at. %). Substituting into Equation 5-8, the predicted hardness for run 20 was 516 HV.
(an overestimate due to the presence of surface rutile lowering the melt pool nitrogen), which agreed well with the average case hardness of 488±28 HV$_{0.3}$ measured in this study.

Finally, the micrographs in Figure 5-3 show that remelting with an argon LSP made the nitrided layers more uniform and hemispherical, as the heat transfer mechanism in the melt pool changed from convection-dominated to diffusion-dominated. As shown in Chapter 4, the presence of argon above the melt surface reduced Marangoni convection during LSP processing by suppressing local surface tension gradients, which subsequently reduced the surface roughness of the solidified melt pool surface.

5.4.2.3 Effect of remelting on surface morphology

Nitriding in the presence of the pure-nitrogen LSP resulted in surface cracking, as discussed in Chapter 4. Remelting speeds (10-25 mm/s) were kept lower than the nitriding speeds (30-75 mm/s) in order to reduce cooling rates. More importantly, remelting at speeds of 20 and 10 mm/s diluted the nitrided layer, making the surface more ductile and reducing its propensity to crack. This is illustrated in the SEM images (50x mag.) of the melt pool surfaces shown in Figures 5-13a-f for three different cases (no remelting, remelting at 20 mm/s, remelting at 10 mm/s) and two different nitriding speeds (75 mm/s, 30 mm/s) i.e. runs 1, 3, 5, 16, 18, and 20. Cracks were observed in the nitrided-only cases, as shown and arrowed in Figures 5-13a and 5-13d (the reader is advised to zoom in to the images to see the cracks more clearly). At the lowest nitriding speed (30 mm/s), remelting at 20 mm/s did not significantly dilute the nitrided layer (as discussed in Section 5.4.2.2); rather, it coarsened the dendrites near the surface (dendrite volume fraction = 59.6 %) and did not reduce the near-surface hardness (701 HV$_{0.3}$). This rendered the surface brittle so that it cracked, as shown in Figure 5-13b. However, remelting at the lowest speed of 10 mm/s (Figure 5-13c) diluted the layer, reduced the dendrite volume fraction (47.2 %), and consequently
the hardness near the surface (596 HV\textsubscript{0.3}). This made the surface sufficiently ductile to solidify without cracking, as shown in Figure 5-13c. The threshold surface hardness value of 596 HV\textsubscript{0.3} agreed with the results of Morton et al. [59], who reported cracking in Ti-6Al-4V substrates at surface hardness values greater than 600 HV during laser nitriding in an Ar-N\textsubscript{2} gas flow without remelting. At the highest nitriding speed of 75 mm/s, remelting at 20 mm/s also made the surface sufficiently ductile (526 HV\textsubscript{0.3}) to eliminate crack formation (Figure 5-13e). This confirmed that at higher nitriding speeds (lower nitrogen contents), remelting was more effective in diluting the nitrided layer. As expected, remelting at 10 mm/s (Figure 5-13f) also produced a crack-free surface.

<table>
<thead>
<tr>
<th>Remelting speed (mm/s)</th>
<th>No remelting</th>
<th>20</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>a) Run 1</td>
<td>b) Run 3</td>
<td>c) Run 5</td>
</tr>
<tr>
<td>75</td>
<td>d) Run 16</td>
<td>e) Run 18</td>
<td>f) Run 20</td>
</tr>
</tbody>
</table>

Figure 5-13. SEM images (50x magnification) of the top surface of LSP nitrided-remelted samples for two nitriding conditions that were remelted using the following conditions: no remelting, remelting at speeds of 20 mm/s and 10 mm/s. Cracks are denoted by white arrows. Scale markers on all the micrographs indicate a length of 500 \(\mu\)m. The direction of laser beam scan was from left to right.

Figure 5-13 showed that remelting eliminated surface protrusions and reduced surface roughness, as confirmed by optical profilometry data for remelting speeds of 10 and 20 mm/s and a nitriding speed of 75 mm/s, shown in Figure 5-14. Remelting in the presence of an argon LSP
changed the surface roughness profile of the nitrided layer. A smoothed hump was observed in the
remelted layers of Figures 5-14b and 5-14c, due to solidification of the surface tension gradient-
induced ripples at the melt pool surface; the hump measured 55 µm in height and was close to the
value of 50 µm calculated by Anthony et al. [139] as representative for titanium. Remelting also
increased the width of the nitrided layer due to the increased heat input to the substrate. At the
lowest speed of 10 mm/s, the width doubled from the original 2 mm (Figure 5-14a) to
approximately 4 mm (Figure 5-14c).

Figure 5-14. 3D contours and corresponding surface profiles along a line across the width of
nitrided surface for: a) no remelting (run 16), b) remelting at 20 mm/s (run 18), and c) remelting at
10 mm/s (run 20) speed. The nitriding speed was 75 mm/s.

5.4.2.4 Comparison with nitrogen dilution method

In the two-step nitriding-remelting method developed in this Chapter, nitrogen intake into
the melt pool occurred uninhibited in the first step in the presence of a pure-nitrogen LSP. The two-
step method was thus able to eliminate surface cracking without suffering from the disadvantage
of reduced nitrogen intake. This can be contrasted with the nitrogen dilution approach of Chapter 4, where nitrogen intake was compromised to reduce surface cracking tendencies. Moreover, the two-step approach afforded greater control over the microstructure than the nitrogen dilution method, since nitrogen intake was controlled by the first step and microstructural refinement and dilution by the second remelting step. Thus, the two-step method developed in this Chapter is expected to achieve harder and deeper cases in the titanium substrate than the nitrogen dilution approach adopted in Chapter 4 and in the general laser nitriding literature [59,64,65,67,71,109], with a greater control over microstructural refinement.

5.5 Chapter summary

- A two-step LSP method was developed to form deep, hard, nitrided cases on commercially pure titanium. In the first step, a prestruck nitrogen laser-sustained plasma (LSP) was used to nitride the titanium substrate. In the second step, the nitrided layer formed in step one was remelted under a prestruck argon LSP. The nitrogen intake was controlled by varying the nitriding speed in the first step, and the extent of microstructure refinement by varying the remelting speed in the second step.

- Energy-dispersive spectroscopy (EDS) was used to estimate the nitrogen content of five distinct microstructural features in the solidified layer. Solidification pathways leading to the formation of these features were proposed, based on the Ti-N phase diagram and the measured nitrogen content.

- It was shown for the first time that remelting can eliminate the cracks formed on the surface of the nitrided layer. Maximum remelting speeds required for crack elimination, as a function of nitriding speed, were identified. Below a threshold surface hardness value of 596 HV0.3, no surface cracking was observed. This threshold value agreed well with that
determined by Morton et al. [59], who laser-nitrided Ti-6Al-4V using an Ar-N\textsubscript{2} gas flow with no remelting.

- Unlike the nitrogen dilution approach to prevent crack formation, the remelting method described in this work did not limit the nitrogen intake into the melt pool. This enabled microstructures comprising a uniform distribution of TiN dendrites to be produced in nitrided case depths up to 800 µm, which is not possible with the nitrogen dilution approach shown in Chapter 4.

- It was shown that the microstructure of the nitrided case could be tailored by optimizing the combination of nitriding and remelting speeds. The microstructure could be varied from a two-phase mixture of TiN\textsubscript{x} dendrites embedded in a titanium matrix, to a single-phase solid solution of nitrogen in titanium, α-Ti(N). For the two-phase dendritic microstructure, a linear relation between dendrite volume fraction and Vickers hardness was proposed. For the α-Ti(N) microstructure, the measured average case hardness values matched well with existing empirical relations describing the strengthening effect of nitrogen on titanium [49].

- The analytical heat conduction solution described in Section 2.2 was used to model both the LSP nitriding and remelting steps.

- A combination of weight measurements and melt pool lifetime calculations was used to quantify the nitrogen intake during the LSP nitriding step. The mass flux of nitrogen into the melt pool was estimated to be 9.7 x 10\textsuperscript{-4} g/mm\textsuperscript{2}s, while the nitrogen intake efficiency, defined as the fraction of nitrogen issuing out of the nozzle that was incorporated into the melt pool, was calculated to be 0.23. Mass flux and nitrogen intake efficiency are expected to be important inputs to computational models of LSP nitriding.

- Criteria for critical remelting speeds required to homogenize the nitrided layer were identified as a function of nitriding speed. At the critical remelting speed, the melt isotherm for titanium (1670 °C) was found to penetrate into the base metal, causing solute
redistribution and homogenization of the nitrided case through enhanced convective mixing. The increased homogeneity came at the cost of decreased average hardness of the nitrided case. Remelting also caused a significant decrease in surface roughness, as previously observed by Weerasinghe et al. [65].

- The two-step LSP nitriding-remelting process thus showed promise for creating deep, hard, nitrided cases on commercially pure titanium. Average case hardness values of 475 – 729 HV0.3 and case depths up to 0.8 mm were achieved in this study.

In Chapter 6, this two-step method will be extended to cover wider areas by depositing multiple overlapping trails. Further, the effects of this wide-area case hardening treatment on the wear resistance of commercially pure titanium will be evaluated.
Chapter 6

Effect of two-step treatment on wear resistance

6.1 Introduction

A two-step LSP nitriding-remelting method was developed in Chapter 5 to form deep, hard, and crack-free nitried cases on CP-titanium substrates. The method consisted of depositing a single nitried trail (~ 2 mm wide) using a pure-N₂ LSP, followed by remelting the nitried trail using a pure-Ar LSP. In practical applications, e.g. to perform case hardening of titanium gears or bearings, the nitried layer is required to span greater widths than those achieved by single trails. This can be achieved by depositing multiple trails, where each trail overlaps the preceding trail, to span the required area. In this Chapter, four processing conditions from Chapter 5 are chosen to deposit multiple overlapping trails and achieve wide-area coverage. Eight nitriding trails are deposited using a pure-N₂ LSP with an overlap of 0.8 mm. Following this, a pure-Ar LSP is used to remelt the nitried trails using the same overlapping distance. The deposited cases are analyzed using a variety of characterization techniques. The effect of the two-step treatment upon the wear resistance of CP-titanium is studied using a reciprocating ball-on-flat wear tester with alumina as the counterface.
6.2 Methodology

The materials and the CO$_2$ laser system described in Section 2.1 were used to perform all the experiments. The LSP nitriding-remelting method developed in Chapter 5 was modified to deposit multiple overlapping trails as follows:

i. The coupons were first nitrided using a pure-nitrogen LSP. The LSP was scanned over the CP-Ti substrate eight times, with a spacing of 0.8 mm between two successive trails. The coupon was allowed to cool down to room temperature before depositing the next overlapping trail. Eight such overlapping nitried trails were deposited. The direction of the LSP nitriding scan was the same for each trail. The off-focal distance (OFD) was maintained at 8 mm for all LSP nitriding runs, and the nitrogen gas flow was held constant at 16 standard liters per minute (slpm).

ii. Following the nitriding treatment, the substrate was allowed to cool down to room temperature, after which it was subjected to the LSP remelting treatment. The LSP remelting methodology was the same as that described in step one, except that it was conducted in a pure-argon LSP. The direction of the LSP remelting scans was the same for each trail, and the same as that of the LSP nitriding scans. The OFD for the LSP remelting scans was maintained at 7 mm, while the argon gas flow was 25 slpm.

All the LSP nitriding and remelting experiments were conducted at a laser power of 3.5 kW. Four experimental conditions were studied by varying the nitriding speed (30, 45, 60, and 75 mm/s) while maintaining a constant remelting speed (20 mm/s). The nitriding experiments were conducted at an off-focal distance (OFD) of 8 mm, and the remelting experiments at an off-focal distance of 7 mm. A nitriding-only run was also conducted at 90 mm/s with no remelting. The complete list of experimental runs is shown in Table 6-1. The percent overlap between successive trails, different
for each run due to the constant trail spacing of 0.8 mm used in this study, is also shown in Table 6-1.

Table 6-1. List of experimental runs.

<table>
<thead>
<tr>
<th>Run #</th>
<th>Nitriding speed (mm/s)</th>
<th>Remelting speed (mm/s)</th>
<th>Overlap (%) for nitriding run</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>30</td>
<td>20</td>
<td>64</td>
</tr>
<tr>
<td>2</td>
<td>45</td>
<td>20</td>
<td>62</td>
</tr>
<tr>
<td>3</td>
<td>60</td>
<td>20</td>
<td>58</td>
</tr>
<tr>
<td>4</td>
<td>75</td>
<td>20</td>
<td>54</td>
</tr>
<tr>
<td>5</td>
<td>90</td>
<td>No remelting</td>
<td>50</td>
</tr>
</tbody>
</table>

To characterize the microstructure of the treated samples, runs 1-4 in Table 6-1 were conducted by clamping the center of the shorter (25.4 mm, 1 in.) edge of the test coupon to the moveable stage. Characterization techniques such as weight measurement, x-ray diffraction (XRD), optical microscopy, and Vickers hardness testing were used as described in Chapter 5. For the hardness tests, five hardness indentations were made at each depth for three different depths, giving a total of fifteen case hardness measurements. The dendrite volume fractions and the dimensions of the hardened case were measured using ImageJ.

Due to relaxation of residual tensile stresses after the LSP nitriding-remelting treatment, some sample bending was observed when the samples were clamped only on one edge. Since wear testing required a flat surface, runs 2-4 in Table 6-1 were repeated by clamping both the short edges of the coupon to prevent sample deformation. Wear tests were also conducted on the untreated CP-Ti substrate and A2 tool steel for benchmarking purposes. Alumina balls, 4.76 mm (3/16 in.) in radius, were used as the counterface material in the sliding wear test. Prior to the wear tests, all the samples were sectioned into square blocks that had the following final dimensions: 25.4 mm (1 in.) x 25.4 mm (1 in.) x 3.175 mm (1/8 in.). 60 grit sandpaper was used to grind all the samples (treated CP-Ti i.e. runs 2-4 in Table I, untreated CP-Ti, and A2 tool steel) to remove surface protrusions from the treated samples. This achieved uniformity in surface roughness across all wear test
samples and reduced the dependence of surface topography on the wear test outputs. The samples and the alumina balls were cleaned using acetone and compressed air before each wear test. Wear tests were conducted according to the procedure detailed in Section 2.2.5. Scanning electron microscopy (SEM) was performed on the wear scar to gain insight into the wear mechanisms. Optical profilometry was performed on the worn surfaces, and the volume of the wear scars were measured using the post-processing software, Zygo Mx™.

6.3 Calculations

The moving heat source solution developed in Section 2.2 was used to model the heat transfer occurring during the LSP nitriding process. In Chapter 5, it was shown that the quantity of nitrogen intake per unit length into a given surface of the titanium substrate, $\Delta w$ (gmm$^{-1}$), is directly proportional to the time for which that surface remains molten i.e. the ‘melt pool lifetime’, $t$ (s), as:

$$10^5 \Delta w = 195t - 0.42$$

(6-1)

Figure 6-1. Schematic of transverse cross section of a) multiple overlapping trails (this Chapter), and b) a single trail (Chapter 5), during LSP nitriding. Region 1+2 represents the current trail in the process of being deposited, region 2+3 represents the last trail that was deposited, and region 2 represents the overlapping region between the successive trails. The direction of the laser beam scan is normal to the plane.
During LSP nitriding of multiple trails, successive trails overlapped, as shown in Figure 6-1: region 1+2 represents the trail in the process of being deposited, region 2+3 represents the previously deposited trail, and region 2 is the overlap between the two successive trails. Unlike the single trail experiments conducted in Chapter 5 (Figure 6-1b), different regions of the melt pool had different melt pool lifetimes for the multiple overlapping trails conducted in this Chapter. Region 1, the newly melted base material, had a lower melting point and hence stayed molten for a longer time. On the other hand, region 2, the overlapping area between successive trails, was richer in nitrogen due to the previous nitriding trail, and hence had a higher melting point that reduced the time for which it was molten. If \( o \) is the fraction of overlap between successive trails, the effective melt pool lifetime for the current trail, \( t_{1+2} \), can be approximated as a weighted average of melt pool lifetimes for region 1, \( t_1 \) (lifetime of melt isotherm for titanium, 1670 °C), and region 2, \( t_2 \) (lifetime of peritectic isotherm for the Ti-N system, 2350 °C), as:

\[
t_{1+2} = (1 - o)t_1 + ot_2
\]  

(6-2)

The fraction of overlap, \( o \), is calculated as:

\[
o = 1 - \frac{\text{trail offset}}{\text{trail width}}
\]  

(6-3)

It must be noted that since the overlapping distance was maintained the same for all experiments, the value of \( o \) increased with a decrease in nitriding speed due to greater trail widths, as shown in Table 6-1. Using the trail widths for nitriding speeds of 30, 45, 60, and 75 mm/s from the single trail results of Chapter 5 (Figures 5-3a, 5-3f, 5-3k, and 5-3p respectively), and the values of \( t_1 \) and \( t_2 \) calculated in Figure 5-2 for the lifetimes of the melting (1670 °C) and peritectic (2350 °C) isotherms respectively, the effective melt pool lifetime during LSP nitriding with overlapping trails, \( t_{1+2} \), was calculated for nitriding speeds of 30, 45, 60, and 75 mm/s using Equations 6-2 and 6-3. The calculated value of \( t_{1+2} \) was then substituted into Equation 6-1 to estimate the nitrogen intake per trail during multiple overlapping nitrided trails.
6.4 Results and discussion

6.4.1 Nitrogen intake during multiple overlapping trails

The weight gain of the samples after the nitriding-remelting treatment was found to vary linearly with the inverse of nitriding speed. This was consistent with the findings of the single trail LSP nitriding experiments of Chapter 5. When the weight gain measured after depositing multiple overlapping trails was divided by the total number of trails i.e. 8, it was found that the nitrogen intake per nitrided trail was lower for the multiple overlapping experiments than for the single trail experiments conducted of Chapter 5 by about 14-20%. This was because of the reduction in effective melt pool lifetimes occurring in multiple overlapping trails compared to single trails, as explained in Section 6.3.

Figure 6-2. Variation of nitrogen intake per nitrided trail with inverse of nitriding speed, shown for single trail measurements (Chapter 5), multiple overlapping trail measurements (present Chapter), and multiple overlapping trail calculations.

Figure 6-2 compares the nitrogen intake per trail measured for multiple overlapping trails (present Chapter) and single trails deposited at similar conditions in Chapter 5, at four different nitriding speeds. Figure 6-2 also shows the nitrogen intake per trail calculated using the semi-
empirical model discussed in Section 6.3. The calculated values of the nitrogen intake per trail for multiple overlapping trails were within 10% of the measured values, the agreement being better at higher nitriding speeds.

6.4.2 Microstructure

Optical micrographs of the transverse cross-section of the nitrided cases deposited using runs 1-4 in Table 6-1 are shown in Figures 6-3a-d. A dendritic microstructure was observed at all nitriding speeds. Remelting the nitrided trails in an argon LSP resulted in solute redistribution, the extent of which depended upon the depth and nitrogen content of the LSP-nitrided layer, as discussed in Chapter 5. For a constant remelting speed (20 mm/s in this case), the solute redistribution during remelting was most pronounced for the layer nitrided at the highest speed of 75 mm/s (run 4). Solute redistribution homogenized the nitrided case and reduced the variance in hardness values. The remelting-induced homogenization effect can also be observed in Figures 6-3a-d: the waviness of the melt pool boundary (Figures 6-3a and 6-3b) decreased with increasing nitriding speeds, resulting in a flat-bottomed melt pool at the highest nitriding speed of 75 mm/s (Figure 6-3d). The maximum case depths for nitriding speeds of 30, 45, 60, and 75 mm/s were measured to be 880, 660, 600, and 550 μm respectively.
Figure 6-3. Optical micrographs of the transverse cross-sections of runs 1-5 in Table 6-1. The scale marker shown in (d) is 2 mm and is common to all micrographs. Hot tearing cracks in (a) and (e) are indicated by white arrows.

The homogenization effect of remelting came at the cost of a reduction in the average case hardness values, as seen in Figure 6-4a. Knowing the measured weight gain and the area of the nitrided layer (measured using ImageJ), the average atomic percent of nitrogen in the melt pool was calculated (using Equation 5-7 in Chapter 5) and is also shown in Figure 6-4a.
Figure 6-4. (a) Average case hardness (with standard deviation) and nitrogen content (at. %) in the melt pool as a function of nitriding speeds; optical micrographs taken near the center of the melt pool for (b) run 1, (c) run 2, (d) run 3, and (e) run 4 from Table 6-1. The scale marker of 280 μm shown at the top is common to all the micrographs.

As the nitriding speed increased, the LSP remelting scan caused a successive refinement of the dendritic structure. This can be seen in the optical micrographs of Figures 6-4b-e, which show the center of the cross-sections of the nitrided trails of runs 1-4 respectively. The gold-colored regions represent hard TiN\textsubscript{x} phases, while the dark regions represent the interdendritic nitrogen-rich titanium that was etched out. The average case hardness dropped from 1050±197 HV\textsubscript{0.3} (TiN\textsubscript{x} volume fraction = 86.8%) for the lowest nitriding speed (30 mm/s) to 564±64 HV\textsubscript{0.3} (TiN\textsubscript{x} volume fraction = 29.4%) for the highest nitriding speed (75 mm/s). XRD spectra (Figure 6-5) showed that the surface microstructure at the lowest nitriding speed of 30 mm/s (run 1) consisted predominantly of the TiN phase. At higher nitriding speeds, the remelting scan was more efficient in dissolving the TiN dendrites and diluting the microstructure by introducing fresh titanium into the melt pool, as shown in Chapter 5. This made TiN\textsubscript{0.3} the dominant phase at higher nitriding speeds (runs 2, 3, and 4 in Figure 6-5). Interestingly, the α-TiN\textsubscript{0.3} peak was stronger than the α-Ti peak in all the spectra. Finally, rutile formation was observed in the XRD spectra of all the runs due to overheating of the sample after the LSP had passed over it, because of titanium’s affinity to oxygen at temperatures in excess of 600 °C [1].
At the lowest nitriding speed of 30 mm/s, the TiN\textsubscript{x} volume fraction was high enough (86.8\%) to cause dendrite coalescence. This prevented the interdendritic titanium-rich liquid from feeding the additional volume created by tensile strains (resulting from the nitriding-remelting treatment) and solidification shrinkage, causing intergranular ‘hot tearing’ macrocracks [142], as labeled in Figures 6-3a and 6-3e. The hot tears (~60-80 μm wide) initiated at grain boundaries and propagated along the depth of the nitrided layer. Macrocracks were also visible when the substrate was nitrided at the highest speed (90 mm/s) without remelting (Figure 6-3e). Moreover, it may be recalled that such macrocracks were not detected in the cross-sectional micrographs of the single trail nitriding studies conducted in Chapters 4 and 5, suggesting that the formation of macrocracks is related to the multiple overlapping trail process conducted in a pure-N\textsubscript{2} LSP. This can be attributed to a step-wise build-up of tensile stresses, with each laser pass, on the surface of the nitrided layer in a direction perpendicular to the beam scan direction. Figures 6-3b, 6-3c, and 6-3d show that remelting was successful in eliminating the hot tearing cracks for nitriding speeds of 45,
60, and 75 mm/s by reducing the volume fraction of dendrites. Also, a comparison of Figures 6-3d and 6-3e suggests that the multiple overlapping remelting scans made the nitrided layer more uniform, similar to the results of the single trail experiments of Chapter 5.

6.4.3 Wear testing

Since macrocracks penetrating through the depth of the nitrided case were detected at the lowest nitriding speed (30 mm/s), this specimen (run 1) was deemed undesirable from the point of view of practical application, and wear tests were not conducted for this case. The dry reciprocating wear tests were conducted on the untreated CP-titanium substrate, and runs 2-4 from Table 6-1 using an alumina ball as the counterface. After all the test specimens were ground with a 60-grit sandpaper prior to the wear tests (to ensure comparable starting surface roughness), it was revealed that the surface of run 2 (45 mm/s nitriding speed) had a network of microcracks that were visible with the naked eye. The wear tests produced a wear scar that was visible with the naked eye in all cases, suggesting severe wear [24] occurred at the test conditions. The region of the alumina ball in contact with the substrate suffered discoloration and appeared black with the naked eye; however, the ball suffered negligible wear in comparison to the substrate. All the wear analysis was hence focused on the wear of the substrate. Low and high magnification SEM images of the wear scars for the four mentioned specimens are shown in Figures 6-6a-d and Figures 6-7a-d respectively.
Figure 6-6. Low magnification SEM images of wear scar for: (a) untreated CP-titanium, (b) run 4 (75 mm/s nitriding speed), (c) run 3 (60 mm/s nitriding speed), and (d) run 2 (45 mm/s nitriding speed), where (b)-(d) were all remelted at a speed of 20 mm/s.
Figure 6-7. High magnification SEM images taken at the middle of the wear scar for: (a) untreated CP-titanium, (b) run 4 (75 mm/s nitriding speed), (c) run 3 (60 mm/s nitriding speed), and (d) run 2 (45 mm/s nitriding speed), where (b)-(d) were all remelted at a speed of 20 mm/s.

6.4.3.1 Untreated CP-titanium substrate

The wear characteristics of titanium and its alloys (mainly Ti-6Al-4V) have been well-studied in the tribology literature [14,16,17,22,143,144]. Hong and Winer [17] attributed the wear of CP-titanium to the formation of black-colored TiO, a product of the tribooxidation reaction, that destroyed the protective TiO$_2$ layer on titanium and increased friction between titanium and the alumina disk against which it was sliding. Dong and Bell [143] and Qu et al. [16] opined that the low thermal conductivity of Ti64 led to high temperatures at the alumina-Ti64 sliding interface, favoring tribochemical reactions that led to the formation of titanium aluminides (e.g. Ti$_3$Al) and subsequently an increase in wear rates. The reciprocating wear tests conducted in this Chapter
differed from the sliding wear tests mentioned above in that the wear debris generated in the former is trapped between the two reciprocating bodies and is hence expected to contribute to the wear of the substrate via three-body abrasion [24]. The wear debris observed in the SEM images of Figures 6-6a and 6-7a was likely to be TiO fragments [17,22]. At the low speed (0.1 m/s) and load (25 N) of the tests conducted in this Chapter, oxidative wear was likely to be the dominant mechanism of wear [22,40]. The black discoloration of the alumina counterface was thought to be due to transfer of TiO fragments from the worn substrate. Parallel grooves were observed in the wear scar of the untreated CP-Ti substrate (Figures 6-6a and 6-7a) due to plastic flow in the ductile titanium substrate caused by the abrasive effect of the TiO wear debris. Moreover, the plowing effect of the reciprocating alumina ball resulted in pile-up of material at the edges of the wear scar for the untreated substrate as labeled in Figure 6-6a.

6.4.3.2 Nitrided-remelted substrates

The wear scars of the substrates treated using the nitriding-remelting process at nitriding speeds of 75, 60, and 45 mm/s are shown in Figures 6-6b-d and Figures 6-7b-d respectively. It is observed that the TiO wear debris decreased with a reduction in nitriding speed, due to the reduced tendency of the TiN-rich surface to oxidize. Moreover, the resistance to three-body abrasion also improved due to surface hardening, as seen from the absence of the parallel grooves when compared to the wear scar of CP-titanium. At low nitriding speeds, the surface hardness increased, so that the surface resembled a ceramic and showed evidence of microspalling. Failures via plastic detachment (visible at the highest nitriding speed of 75 mm/s where the surface was still soft) and via microspalling (visible at the lowest nitriding speed of 45 mm/s where the surface was harder) are shown in Figures 6-7b and 6-7d respectively. Henceforth, the term ‘base’ will refer to the base CP-Ti substrate, and ‘N75’, ‘N60’, and ‘N45’ will refer to the nitrided-remelted samples that were
nitrided at 75 mm/s (run 4), 60 mm/s (run 3), and 45 mm/s (run 2) respectively and remelted at a speed of 20 mm/s. Higher magnification SEM images of some surface features of the wear scars can be found in Appendix C.

6.4.3.3 Effect of nitriding-remelting treatment on wear resistance

The wear resistance of different materials can be quantified and compared by measuring the volumes of their wear scars under similar wear testing conditions. In the context of this Chapter, the respective wear resistances of the untreated CP-Ti sample and of runs 2-4 were compared using optical profilometry to measure the volumes of the wear scars shown in Figure 6-6. The wear test was also conducted on A2 tool steel (a known wear-resistant material) and its wear scar volume was measured for comparison. Figure 6-8 presents a summary of the wear test results. The measured wear scar volumes for the above specimens are shown in Figure 6-8a. The frictional force between the reciprocating ball and the substrate was monitored in situ throughout the duration of the test, which lasted 16 minutes and 40 seconds; average values for the coefficient of friction for each minute of the test are shown in Figure 6-8b. The longitudinal and transverse profiles of the wear scars for the treated and untreated titanium samples are shown in Figures 6-8c and 6-8d respectively.

Figure 6-8a shows that the wear volume of the substrate reduced after the nitriding-remelting treatment. It is seen that the wear resistance of the base substrate was enhanced by 70%, 72%, and 80% when the substrate was nitrided at speeds of 75, 60, and 45 mm/s respectively, followed by remelting at 20 mm/s in all cases.
For both adhesive and abrasive wear (due to plastic deformation), a simple model [24] predicts that the wear volume, $Q$ (mm$^3$/m), is inversely proportional to the surface Vickers hardness, $H$ (kgf/mm$^2$), as:

$$Q = \frac{KWL}{H}$$

(6-1)

where $L$ (m) is the total sliding distance, $W$ (N) is the normal load, and $K$ is a proportionality constant known as the dimensionless wear coefficient. The value of $K$ denotes the severity of wear and is constant within a given wear regime. In engineering applications, a dimensional wear coefficient, $k$ (mm$^3$/N-m), which denotes the wear volume lost per unit sliding distance per unit normal load, is often reported:

$$k = \frac{K}{H} = \frac{Q}{WL}$$

(6-2)
Substituting \( W = 25 \text{ N}, L = 100 \text{ m} \) (Section 2.2.5), and the values of \( H \) (measured from the average of five hardness indents approximately 50 \( \mu \text{m} \) below the surface and shown in Table 6-2), and \( Q \) from Figure 6-8a, \( K \) and \( k \) were calculated for the base, N75, N60, and N45 substrates, and are shown in Table 6-2. The values of \( K \) were found to be in the range that is typical for three-body abrasive wear (0.5–5 \( \times 10^{-3} \)) [24].

Table 6-2. Wear coefficients for different samples.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Surface hardness, ( H ) (VHN or kgf/mm(^2))</th>
<th>( K )</th>
<th>( k ) (mm(^3)/N-m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base</td>
<td>160</td>
<td>1.25( \times 10^{-3} )</td>
<td>7.96( \times 10^{-5} )</td>
</tr>
<tr>
<td>N75</td>
<td>547</td>
<td>1.30( \times 10^{-3} )</td>
<td>2.43( \times 10^{-5} )</td>
</tr>
<tr>
<td>N60</td>
<td>621</td>
<td>1.37( \times 10^{-3} )</td>
<td>2.25( \times 10^{-5} )</td>
</tr>
<tr>
<td>N45</td>
<td>870</td>
<td>1.36( \times 10^{-3} )</td>
<td>1.60( \times 10^{-5} )</td>
</tr>
</tbody>
</table>

The treated samples resisted wear by: a) resisting oxidative wear of titanium and hence the formation and material transfer of TiO debris to the alumina ball, and b) resisting plastic deformation occurring due to three-body abrasive wear by the TiO debris because of their increased surface hardness. However, the increase in surface hardness reduced the fracture toughness of the treated specimens, making them prone to failure via microspalling (Figure 6-7d) induced by brittle fracture at the surface; microspalling was not observed in the untreated base specimen (Figure 6-7a). This may be why the values of \( K \) were slightly greater for the treated surfaces (N45, N60, and N75) compared to the base metal by up to 8% - due to the additional failure mechanism of brittle fracture leading to microspalling as discussed above. Surprisingly, the N45 specimen showed the greatest wear resistance despite the presence of surface cracks (Figure 6-6d), probably because of the relatively low normal loads (25 N) used in this study. The surface cracks are expected to play an important role at higher normal loads by aiding failure via delamination wear. The N45 specimen showed a similar wear resistance to the wear-resistant A2 tool steel specimen that was tested under similar conditions (Figure 6-8a).
The variation of the coefficient of friction (CoF) with time (Figure 6-8b) can provide clues about the wear rates; for instance, the CoF for the base specimen remained approximately constant (0.22) throughout the test suggesting a steady wear rate, while the CoF for the treated specimens (N75, N60, and N45) increased with time, implying an increasing wear rate. The CoF for the N75 specimen was less than that for the base specimen due to reduced material transfer between the specimen and the counterface. The wear profiles of Figures 6-8c and 6-8d showed that the wear scar on the untreated specimen showed higher roughness than the scars for the treated specimens (N75, N60, and N45) – this may be viewed as visual proof of a reduction in the tendency towards material transfer in the treated specimens. However, somewhat counterintuitively, the CoF’s for the lower nitriding speeds (N60 and N45) were the highest of all four specimens. This was believed to be due to kinks (Figure 6-8d) in the transverse wear profile that were found to extend throughout the length of the wear profile and offered resistance to the motion of the reciprocating alumina ball, thus increasing the CoF. The kinks in the N60 and N45 specimens formed due to the higher variation of hardness at low nitriding speeds (Figure 6-4a) that led to uneven wear in the specimen. For instance, it is possible that the kinks represent harder pieces of TiN that did not dissolve during the remelting scans. Finally, it may be remarked from the wear profiles (Figures 6-8c and 6-8d) and the transverse cross-sectional micrographs (Figure 6-3) that the depths of the wear scars of the treated specimens were on the order of 40-60 μm i.e. approximately 6-10% of the case depth.

A direct comparison of the results of this study with wear testing data in the laser nitriding literature is complicated by the variety of wear testing geometries (e.g. ball-on-flat [79,84,145,146], pin-on-disk [74,87,135], disk-on-disk [147], sand-rubber wheel abrasion [73,148] etc.), counterface materials (e.g. hardened steel [73,145], titanium [146], abrasive sandpaper [74,149] etc.), and test conditions (normal load and sliding speed) employed in the literature. Sathish et al. [83] used a pulsed Nd:YAG laser in a pure-N₂ atmosphere to conduct laser nitriding on CP-Ti substrates; further, they performed reciprocating wear tests with an alumina ball as the counterface in Hank’s
solution at 37 °C, at testing conditions of 10 N load, 2 Hz reciprocating frequency, and 15 mm stroke length. These conditions were closest to the testing conditions of this Chapter. Sathish et al. [83] reported an improvement in wear resistance of 17% after laser nitriding, which was lower than the improvement of 70-80% that reported in this study.

### 6.5 Chapter summary

Multiple overlapping trails were deposited using the two-step nitriding-remelting treatment developed in Chapter 5 to form deep nitrided cases on CP-titanium substrates. The nitrogen content of the nitrided cases was varied by varying the nitriding speed (30, 45, 60, and 75 mm/s) and the remelting speed was kept the same (20 mm/s) for all the experiments. Reciprocating ball-on-flat wear tests were conducted for the untreated CP-titanium specimen, three treated specimens (nitrided at 45, 60, and 75 mm/s and all remelted at 20 mm/s), and wear-resistant A2 tool steel, using alumina as the counterface material. The findings of the study were as follows:

- The nitrogen intake per trail in the multiple overlapping trail experiments was lower than that for the single trail experiments of Chapter 5 at similar processing conditions. The difference was attributed to the lower melt pool lifetimes in the former.
- A semi-empirical model, based on the results of the single trail experiments of Chapter 5, was used to calculate the nitrogen intake per trail during multiple overlapping trails, and the calculated values were found to be within 10% of the measured values.
- Microstructural characterization revealed greater homogeneity and lower case hardness values at higher nitriding speeds, consistent with the results of Chapter 5. At the lowest nitriding speed of 30 mm/s, hot tearing macrocracks were observed. These cracks were related to the multiple overlapping process since they were not observed in single trail experiments performed at similar conditions. The macrocracks (~60-80 μm) were wider.
than the microcracks (~1-3 μm) seen in Chapters 4 and 5, and penetrated through the depth of the nitrided layer unlike the microcracks which were confined to the thin (~5 μm) TiN layer at the top. The macrocracks were also seen in a layer nitrided at a high speed of 90 mm/s with no remelting. Remelting at 20 mm/s was seen to eliminate the macrocracks for nitriding speeds of 45 mm/s and higher.

- The two-step process improved the wear resistance of the base CP-titanium substrate by 70-80 %. Based on values of the dimensionless wear coefficient ($K \sim 1.3 \times 10^{-3}$), three-body abrasion due to TiO debris was determined to be the dominant wear mechanism. The nitriding-remelting treatment reduced the tendency for oxidative wear of the titanium substrate, decreased the quantity of TiO debris, and provided more resistance to plastic deformation due to increased surface hardness; however, failure by microspalling induced by brittle fracture became prominent at low nitriding speeds. The specimen nitrided at 45 mm/s showed the greatest wear resistance, comparable to the wear resistance of A2 tool steel despite the presence of surface microcracks in the former.

- The specimens nitrided at 60 and 75 mm/s and remelted at 20 mm/s produced uniform and crack-free nitrided cases that had average case hardness values of 641±86 and 564±64 HV$_{0.3}$ respectively, case depths of 600 and 550 μm respectively, and showed an improvement of 70% in wear resistance compared to the untreated base CP-titanium substrate. The sample nitrided at 75 mm/s showed the lowest coefficient of friction of all the cases.
Chapter 7

Summary and future work

7.1 Summary

7.1.1 Motivation and objectives

This dissertation explored the feasibility of performing deep-case hardening of commercially-pure titanium using laser-sustained plasma (LSP) processing, with the objective of enhancing the surface hardness and wear resistance of titanium. An extensive review of the laser nitriding literature revealed that while laser nitriding has several advantages (faster processing times, potential for localized treatment, strong metallurgical bond between the nitrided layer and the substrate etc.) over other surface hardening techniques, the laser-nitrided layer suffers from problems such as crack formation, porosity, surface roughness, and inhomogeneity when formed in a pure-nitrogen atmosphere. These disadvantages are mitigated by performing the laser nitriding experiment in a dilute nitrogen atmosphere, where the nitrogen gas is usually diluted with an inert gas such as argon. While this approach (referred to in this dissertation as the ‘nitrogen dilution’ approach) is able to eliminate crack formation, it limits the thickness of the nitrided layer. A typical microstructure obtained from the nitrogen dilution method has a thin, continuous, 5 μm TiN film at the top, a TiN-dendritic region extending up to 50 μm below the film, and a dendrite-free region below. Moreover, due to the affinity of titanium towards oxygen, the laser nitriding experiments are usually conducted in controlled, oxygen-free, processing chambers to prevent surface oxidation. Apart from the microstructural limitations, the literature survey also revealed considerable
confusion among researchers regarding the role of near-surface plasma during laser nitriding. In light of the above issues, the aims of this dissertation were three-fold:

1. to elucidate the role of near-surface plasma on heat and mass transfer to the substrate (Chapter 3),
2. to study the effect of processing parameters (especially the N₂:Ar flow ratio) on the microstructure of the nitried layer during the LSP nitriding process (Chapter 4), and
3. to develop a new LSP processing method to form deep, crack-free, nitried cases on titanium to improve its wear resistance while enabling better control over the microstructure than that afforded by the nitrogen dilution approach (Chapters 5 and 6).

The key findings of this study are recapitulated in the following section; the reader is referred to the ‘Chapter summary’ sections of Chapters 3-6 for a more detailed description of the results.

### 7.1.2 Key findings

#### 7.1.2.1 Effects of near-surface nitrogen plasma (Chapter 3)

Laser nitriding experiments, conducted in a processing chamber open to the atmosphere at three combinations of off-focal distance and scan speed, each with and without a pre-struck laser-sustained nitrogen plasma, revealed that the laser-sustained nitrogen plasma did not attenuate energy to the substrate. The nitrogen LSP was found to re-radiate approximately 75 % of the laser energy it absorbed. Further, the presence of LSP increased the width of the nitried trails and reduced surface oxidation. Porous expulsion sites were observed on the surface of the LSP-nitried trails and were believed to form due to oversaturation of liquid titanium with nitrogen that subsequently caused nitrogen gas to be expelled out. This hypothesis was supported by weight
measurements indicating that the nitrogen LSP enhanced nitrogen intake into the melt pool for each set of conditions. The above beneficial effects (increased width, reduced surface oxidation, increased nitrogen intake) were most pronounced at conditions of lowest off-focal distance (7 mm) and highest scanning speed (180 mm/s).

7.1.2.2 Effects of processing parameters on microstructure during LSP nitriding (Chapter 4)

LSP nitriding experiments were conducted with a pre-struck LSP by varying the OFD, scanning speed, and the N₂:Ar gas flow ratio. Surface microcracks were observed for all the nitriding experiments conducted with a pure-N₂ LSP; the microcracks were perpendicular to the laser scan direction and increased with increasing scan speed. The porous features mentioned in Section 7.2.1 were found to decrease in number when the scan speed increased and/or the N₂:Ar ratio decreased, due to reduced interaction with the nitrogen species in the plasma. Increasing the Ar gas flow reduced the number of surface cracks. However, weight measurements and microstructural characterization revealed that the introduction of argon into the gas flow had a significant impact on nitrogen intake – an 11% dilution by volume of nitrogen in the LSP reduced the nitrogen intake into the melt pool by 70% – due to reduced Marangoni convection in the melt pool. A thin (~5 μm) and continuous film of TiN was observed at the surface when nitrogen gas flow was diluted with argon. The nitrogen dilution approach thus limited nitrogen intake into the melt pool and reduced control over the microstructure.

7.1.2.3 Two-step nitriding-remelting treatment for deep-case nitriding (Chapters 5-6)

To overcome the shortcomings of the nitrogen dilution approach, a two-step method was developed: in the first step, LSP nitriding was conducted in a pure-N₂ LSP, and in the second step,
the nitrided layer from the first step was remelted in a pure-Ar LSP. The nitrided layer formed in the first step displayed inhomogeneity (being thicker at the edges than at the center), surface roughness, and microcracks at the surface. At sufficiently low speeds (that depended upon the nitriding speed from the first step), the remelting scan eliminated the surface cracks, reduced surface roughness, and homogenized the nitrided layer, at the cost of a reduction in maximum hardness. By conducting experiments at varying nitriding and remelting speeds, the ability to apply the two-step method to tailor the microstructure from a two-phase mixture of TiN₅ dendrites in an α-Ti matrix to a uniform solid-solution of nitrogen in titanium, α-Ti (N), was shown. Compared to the nitrogen dilution approach, the two-step method was found to offer more control over the microstructure while still ensuring a crack-free surface.

The two-step method was then used to deposit multiple overlapping trails to increase surface coverage. The multiple overlapping trails gave rise to hot tearing macrocracks that penetrated the depth of the nitrided layer. The remelting scan was shown to eliminate macrocracks formed at all but the lowest nitriding speed. Reciprocating wear tests were conducted on the treated and untreated specimens using alumina as the counterface. Scanning electron microscopy of the wear scar showed that the two-step method resisted oxidative wear and hence reduced the formation of TiO debris, which decreased the intensity of three-body abrasive wear. The surface hardening effect of the nitriding-remelting treatment reduced wear due to plastic deformation but increased the tendency towards micropalling due to brittle fracture. Overall, the two-step treatment was able to improve the wear resistance of the base CP-titanium substrate by 70-80%.

7.1.3 Conclusions

The LSP nitriding-remelting method was found to be a viable technique to perform deep-case hardening of CP-titanium. The two-step method was found capable of eliminating both
microcracks and macrocracks in the nitrided layer, producing crack-free, uniform, nitrided cases having average case hardness values of up to 641±86 HV0.3 and case depths of up to 600 μm. The case hardness and case depth values could be tailored by optimizing the nitriding and remelting speeds. The two-step method enhanced the wear resistance of the CP-titanium substrate by up to 80 %. The presence of plasma minimized surface oxidation and thus allowed the experiments to be conducted in a processing chamber open to the atmosphere.

### 7.2 Recommendations for future work

The work described in this dissertation can be expanded upon in a number of ways. Some future directions are suggested below.

#### 7.2.1 Inverse heat conduction to determine energy flux from LSP

In Chapter 3, temperature measurements were obtained at the back of the titanium coupon in parallel and perpendicular configurations. In the parallel configuration, the lumped capacitance approximation was used to estimate the heat flux due to LSP radiation at LSP-substrate distances greater than or equal to 9 mm. For shorter distances, the spatially varying energy flux from the plasma, expected to be a contribution from both radiation and conduction of heat within the plasma, can be estimated by solving the inverse heat conduction problem where, given the temperature-time profile, the heat flux can be solved for. This approach can shed further light on the LSP as a source of energy.
7.2.2 Atomistic-scale modeling of nitrogen-titanium interface

Since the LSP-melt pool involves interaction between energetic nitrogen species and the titanium melt pool, atomistic modeling techniques such as reactive ReaxFF-based molecular dynamics (MD) [150] can be good candidates to model the energy transfer occurring due to collisions between atomic nitrogen and liquid titanium. ReaxFF MD simulations can help estimate accommodation and sticking coefficients between nitrogen atoms and liquid titanium at different temperatures and shed light on the kinetics of nitrogen incorporation in the laser and LSP nitriding cases (the former involves dissociation at the surface of the melt pool and was experimentally shown to be slower than LSP nitriding in Chapter 3). Further, qualitative estimates of the surface tension of liquid titanium as a function of nitrogen and argon concentration at the surface, a difficult experimental task, can be made using MD simulations.

7.2.3 Additional wear testing and rolling contact fatigue testing

The two-step multiple overlapping trail method needs to be characterized further using a variety of wear tests at different loads and speeds. Further, the method can be used to perform case hardening of cylindrical specimens and rolling contact fatigue testing can be conducted on the treated specimens – this will be especially necessary for high contact stress applications such as gears and bearings.

7.2.4 Addition of TiN thin film after two-step method

The two-step method developed in Chapter 5 can achieve the desired microstructure and case depth; however, the remelting scan was shown to reduce surface hardness values. An interesting approach would be to add a third step that can form a thin TiN film at the surface, which
will be supported by the hard case deposited by the two-step method before. The envisaged methodology would resemble the following steps:

i. Perform case hardening using the two-step method described in Chapter 5

ii. Grind or mill the surface to remove the post-remelting hump (Figure 5-14c)

iii. Perform LSP nitriding using a N₂-Ar LSP at a high speed to form a thin (~5 μm), crack-free, TiN film at the top.

This approach could potentially yield a transverse cross-sectional microstructure comprising a thin, hard, and crack-free TiN film at the surface that is supported by a deep nitrided case underneath.

The above recommendations may lead to the two-step LSP nitriding-remelting method described in this dissertation being further developed as a viable commercial process for case hardening of titanium.
References


Appendix A

FORTRAN script to calculate melt pool lifetimes

!this is a sample script that outputs melt pool width and depth as a function of time for three different isotherms: 1670 deg C, 2350 deg C, and 3290 deg C
!it can be used to calculate melt pool lifetimes for a desired laser power, energy absorption efficiency, scan speed, and off-focal distance, all of which are provided by the user

program main

implicit none

real, parameter :: a = 0.0E+00
real abserr
real, parameter :: epsabs = 0.0E+00
real, parameter :: epsrel = 0.001E+00
real, external :: f05
integer ier
integer, parameter :: inf = 1
integer neval
real, parameter :: pi = 3.141592653589793D+00
real, parameter :: Cp=2.376,D=0.07,T_room=25.0 !properties for titanium all units in CGS
real, parameter :: w0 = 0.12,lambda=0.0106,M_2=3.2 !laser parameters, lengths in mm
real, parameter :: afit(4)=(/70.5516,76.8708,-147.142,0.29644/),b(4)=(/0.683714,0.730346,0.706686,1.39561/) !fit parameters; fitting gaussian function f(x) = sigma[ai*exp(-(x/bi)**2)]. a4 and b4 refer to the PRC laser fitted to a single TEM00 mode
real T,Tmax,T_single,mult_fact,w,P(3),R(3),I0 !P and R are the parameters that define the gaussian in the form that cline/anthony use. these values are fed into the integral
real result
real true
integer i
real eX,Y,Z,V,x_real,y_real,z_real,v_scan,P0,alpha,off_focus,width(3),depth(3),scantime
common eX,Y,Z,V
open(unit=20,file='Tmax.txt')
open(unit=30,file='wd1.txt')
open(unit=40,file='wd2.txt')
open(unit=50,file='wd3.txt')

write(*,*) 'Enter P(W), alpha, OFD (mm), v (cm/s):'
read(*,*) P0,alpha,off_focus,v_scan
w = (w0**2)*(1 + ((lambda*off_focus*M_2)/(pi*w0**2))**2)
w = sqrt(w)
write(*,*) 'Spot size (mm):',w
w = 0.1*w !converting to cm

do i=1,3
R(i) = b(i)*w/(sqrt(2.0))
P(i) = afit(i)*4.0*P0*(R(i)/w)**2
write(90,*) P(i),R(i)
end do

P(4) = P0
R(4) = w

do x_real=0.2,-0.5,-0.001
scantime = (-x_real + 0.5)/v_scan
width = 0.0
depth = 0.0
z_real = 0.0
do y_real=-0.0,0.2,0.00001
T = 0.0
do i=1,3
V = R(i)*v_scan/D
eX = x_real/R(i)
Y = y_real/R(i)
Z = z_real/R(i)
call qagi (f05, a, inf, epsabs, epsrel, result, abserr, neval, ier )
mult_fact = alpha*P(i)/(Cp*D*R(i)*sqrt(2*pi**3))
T = T + result*mult_fact
end do
T = T + T_room
if(y_real.eq.0.0) Tmax = T
if(T.lt.1670.5.and.T.gt.1669.5) width(1)= 2.0*y_real*10000.0
if(T.lt.2350.5.and.T.gt.2349.5) width(2)= 2.0*y_real*10000.0
if(T.lt.3290.5.and.T.gt.3289.5) width(3)= 2.0*y_real*10000.0
end do
y_real = 0.0
do z_real=0.0,0.1,0.00001
T = 0.0
do i=1,3
V = R(i)*v_scan/D
eX = x_real/R(i)
Y = y_real/R(i)
Z = z_real/R(i)
call qagi (f05, a, inf, epsabs, epsrel, result, abserr, neval, ier )
mult_fact = alpha*P(i)/(Cp*D*R(i)*sqrt(2*pi**3))
T = T + result*mult_fact
end do
T = T + T_room
if(T.lt.1670.5.and.T.gt.1669.5) depth(1)= z_real*10000.0
if(T.lt.2350.5.and.T.gt.2349.5) depth(2)= z_real*10000.0
if(T.lt.3290.5.and.T.gt.3289.5) depth(3)= z_real*10000.0
end do
write(20,*) scantime,Tmax
write(30,*) scantime,width(1),depth(1)
write(40,*) scantime,width(2),depth(2)
write(50,*) scantime,width(3),depth(3)
end do

write ( *, '(a,i8)' ) ' Number of function evaluations, NEVAL = ', neval
write ( *, '(a,i8)' ) ' Error return code IER = ', ier
end program main

function f05 ( x )

    real f05
    real x
    common eX,Y,Z,V

    f05 = (exp(-(((eX + 0.5*V*x**2)**2 + Y**2)/(2*(1+x**2)) + 0.5*(Z**2)/x**2)))/(1+x**2)
    return

end function f05

!in the interest of saving space, the qagi subroutine is not included here. the user is advised to
!download the source code from the quadpack library available online:
! https://people.sc.fsu.edu/~jburkardt/f_src/quadpack/quadpack.f90
Appendix B

FORTRAN script to calculate shape of isotherms

!this is a sample script that outputs the x-z co-ordinates of three different isotherms
!it can be used to plot isotherm shapes for a desired laser power, energy absorption efficiency,
!scan speed, and off-focal distance, isotherm values, and the instant in time for which the values
!are desired, all of which are provided by the user

program main
implicit none
real, parameter :: a = 0.0E+00
real abserr
real, parameter :: epsabs = 0.0E+00
real, parameter :: epsrel = 0.001E+00
real, external :: f05
integer ier
integer, parameter :: inf = 1
integer neval
real, parameter :: pi = 3.141592653589793D+00
real, parameter :: Cp=2.3587,D=0.0695,T_room=25.0 !all units in CGS
real, parameter :: w0 = 0.12,lambda=0.0106,M_2=3.2 !laser parameters, lengths in mm
real, parameter :: afit(4)=(/70.5516,76.8708,-147.142,0.29644/),b(4)=(/0.683714,0.730346,0.706686,1.39561/) !fit parameters; fitting gaussian
function f(x) = sigma[ai*exp(-(x/bi)**2)]. a4 and b4 refer to the PRC laser fitted to a single TEM00 mode
real T,Tiso1,Tiso2,Tiso3,T_single,mult_fact,w,P(3),R(3),I0  !P and R are the parameters that
define the gaussian in the form that cline/anthony use. these values are fed into the integral
real result
real true
integer i
real eX,Y,Z,V,x_real,y_real,z_real,v_scan,P0,alpha,off_focus,width(3),depth(3),scantime
common eX,Y,Z,V
open(unit=20,file='isotherm1.txt')
open(unit=30,file='isotherm2.txt')
open(unit=40,file='isotherm3.txt')

! D = K/(rho*C)
! Cp = rho*C`

write(*,*) 'Enter P(W),alpha,OFD (mm),v (cm/s),Isotherm1 2 3 (deg C),scantime(s):'
read(*,*) P0,alpha,off_focus,v_scan,Tiso1,Tiso2,Tiso3,scantime
w = (w0**2)*(1 + ((lambda*off_focus*M_2)/(pi*w0**2))**2)
w = sqrt(w)
write(*,*) 'Spot size (mm):',w
w = 0.1*w !converting to cm

do i=1,3
R(i) = b(i)*w/(sqrt(2.0))
P(i) = afit(i)*4.0*P0*(R(i)/w)**2
write(90,*) P(i),R(i)
end do

P(4) = P0
R(4) = w

! do y_real=-0.2,0.2,0.00001
! do z_real=0.0,0.06,0.0001
! x_real=-0.03700025
  x_real = 0.5 - scantime*v_scan
  width = 0.0
  depth = 0.0
  z_real = 0.0
  do y_real=0.0,0.15,0.00005
  do z_real=0.0,0.8,0.00005
    T = 0.0
    do i=1,3
      V = R(i)*v_scan/D
      eX = x_real/R(i)
      Y = y_real/R(i)
      Z = z_real/R(i)
      call qagi (f05, a, inf, epsabs, epsrel, result, abserr, neval, ier )
      mult_fact = alpha*P(i)/(Cp*D*R(i)*sqrt(2*pi**3))
      T = T + result*mult_fact
    end do
    T = T + T_room
    if(T.lt.Tiso1+1.0.and.T.gt.Tiso1-1.0) then
      write(20,*) y_real*10000.0,-z_real*10000.0
      write(20,*) -y_real*10000.0,-z_real*10000.0
    end if
    if(T.lt.Tiso2+1.0.and.T.gt.Tiso2-1.0) then
      write(30,*) y_real*10000.0,-z_real*10000.0
      write(30,*) -y_real*10000.0,-z_real*10000.0
    end if
    if(T.lt.Tiso3+1.0.and.T.gt.Tiso3-1.0) then
      write(40,*) y_real*10000.0,-z_real*10000.0
      write(40,*) -y_real*10000.0,-z_real*10000.0
    end if
  end do
end do
end do

! end do
! end do

! write(*,* ) mult_fact
write ( *, '(a,i8)') ' Number of function evaluations, NEVAL = ', neval
write ( *, '(a,i8)') ' Error return code IER = ', ier

end program main

function f05 ( x )
real f05
real x
common eX,Y,Z,V

f05 = (exp(-(((eX + 0.5*V*x**2)**2 + Y**2)/(2*(1+x**2)) + 0.5*(Z**2)/x**2)))/(1+x**2)

! f05 = x*(eX+Y+Z+V)
return

end function f05

! In the interest of saving space, the qagi subroutine is not included here. The user is advised to
! download the source code from the quadpack library available online:
! https://people.sc.fsu.edu/~jburkardt/f_src/quadpack/quadpack.f90
Appendix C

High magnification (2000x) SEM images of wear scar features

Figure C-1. High magnification SEM images of characteristic wear scar features for: (a) untreated CP-titanium, (b) run 4 (75 mm/s nitriding speed), (c) run 3 (60 mm/s nitriding speed), and (d) run 2 (45 mm/s nitriding speed), where (b)-(d) were all remelted at a speed of 20 mm/s.
VITA

Amar M. Kamat

Amar M. Kamat was born and raised in Dombivli, a suburb of Mumbai, India. He obtained his Bachelor of Engineering (BE) degree in Mechanical Engineering from the University of Mumbai in 2008, and his Master of Science (MS) degree in Mechanical Engineering from Penn State University in 2011. For his MS thesis, he worked with Prof. Adri van Duin to develop reactive ReaxFF-based molecular dynamics models of soot and coal combustion. During his MS program, he also attended the inaugural CEFRC Combustion Summer School at Princeton University in the summer of 2010. Amar is currently a doctoral candidate in the Department of Engineering Science and Mechanics at Penn State, and is advised by Profs. Judith Todd and Stephen Copley. For his PhD dissertation, he has developed a two-step laser-sustained plasma processing method to form deep, crack-free, nitrided cases on titanium to improve its wear resistance. His graduate research has been published and presented in several international journals and conferences respectively. He has also been the recipient of various awards, scholarships, and travel grants during the course of his graduate studies.

Amar worked at Intel Corporation in the summer of 2014, where he developed CFD models using ANSYS Fluent to optimize the performance of reliability testing processes. In the summer of 2015, he was awarded the RISE-professional scholarship by DAAD (German Foreign Exchange Service) to perform research at BASF SE in Ludwigshafen, Germany. At BASF, he modeled the chemical kinetics of the polymerization of polyurethane using the Predici 11 software. Following his graduation in Dec 2016, Amar will work at the Center for Innovative Materials Processing through Direct Digital Deposition (CIMP-3D) at Penn State as a postdoctoral fellow in the field of metal additive manufacturing, and will conduct experimental and computational research to model the laser beam-powder interaction occurring during the powder bed fusion process.