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Modification of Ion Nitriding of Ti-6Al-4V for Simultaneous Improvement of Wear and Fatigue Properties

Khorameh Farokhzadeh

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Modification of Ion Nitriding of Ti–6Al–4V for Simultaneous Improvement of Wear and Fatigue Properties

By

Khorameh Farokhzadeh

A Dissertation
Submitted to the Faculty of Graduate Studies through the Department of Mechanical, Automotive and Materials Engineering in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy at the University of Windsor

Windsor, Ontario, Canada

2014

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DECLARATION OF CO-AUTHORSHIP / PREVIOUS PUBLICATION

I. Co-Authorship Declaration

I hereby certify that this dissertation, and the research to which it refers, is the outcome of my own work, except where due recognition has been given. The plasma (ion) nitriding treatments were conducted at Exactatherm Ltd., located at 2381 Anson Drive, Mississauga, ON, as covered in Chapter 3, Section 3.1.1 of the dissertation.

I am aware of the University of Windsor Senate Policy on Authorship and I certify that I have properly acknowledged the contribution of other researchers to my dissertation.

II. Declaration of Previous Publication

This dissertation includes three original papers that have been previously published/submitted for publication in peer reviewed journals, as follows:

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I declare that this is a true copy of my dissertation, including any final revisions, as approved by my dissertation committee and the Graduate Studies office, and that this dissertation has not been submitted for a higher degree to any other University or Institution.
Extensive application of titanium alloys in the aerospace sector is restricted due to their poor tribological properties especially when contact of surfaces is inevitable. Over the past few decades, many coating deposition and thermochemical treatments have been developed to improve the wear resistance of titanium alloys such as plasma (ion-) nitriding. A typical ion nitried microstructure in titanium alloys consists of a thin surface layer composed of TiN and Ti$_2$N titanium nitrides (compound layer), a region of nitrogen-stabilized α titanium (α-case), and a nitrogen diffusion zone. However, similar to other nitriding processes, the ion nitriding treatment involves high temperatures (750-1100°C) and results in brittle surface features and substrate microstructural changes that lead to deterioration of fatigue strength. In this research, a modified plasma nitriding treatment was developed to achieve simultaneous improvements of wear resistance and fatigue strength by optimization of the microstructure. The findings revealed that utilizing a low temperature of 600°C during the nitriding treatment inhibited the formation of brittle surface features (α-case) and bulk microstructural changes and increased the resistance of ion nitried surfaces to surface crack initiation and propagation. The nitried alloys exhibited a higher fatigue strength compared with those reported in the literature. Furthermore, at least 48% reduction in the coefficient of friction compared to the untreated alloy and considerable improvements in wear resistance were obtained by the formation of a thin (< 2 µm) compound layer on the surface supported by a 40 µm deep nitrogen diffusion zone. It was found that further improvements in wear resistance can be achieved by alteration of the surface microstructure prior to the plasma nitriding
treatment. As such, a novel pretreatment step was developed to increase the nitriding kinetics at low temperatures via introducing a severe plastic deformation (SPD) surface layer and subsurface microstructural defects, such as twins, in the near-surface region. This pretreatment step resulted in a 50% deeper diffusion zone and the formation of a nanocrystalline TiN surface layer after plasma nitriding. Overall, the research performed in this dissertation provides a new insight into the microstructural evolution during plasma nitriding of titanium alloys.
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TABLE OF CONTENTS

DECLARATION OF CO-AUTHORSHIP / PREVIOUS PUBLICATION .......... ii
ABSTRACT ...................................................................................................................... iv
ACKNOWLEDGEMENTS .......................................................................................... vi
LIST OF TABLES ........................................................................................................ x
LIST OF FIGURES ...................................................................................................... xii
LIST OF ABBREVIATIONS/SYMBOLS .................................................................... xxxvii

CHAPTER 1: INTRODUCTION .............................................................................. 1
  1.1 Background and Motivation .............................................................................. 1
  1.2 Objectives .......................................................................................................... 2
  1.3 Scope .................................................................................................................. 3

CHAPTER 2: LITERATURE SURVEY .................................................................. 5
  2.1 Titanium Alloys .................................................................................................. 5
  2.2 Ti-6Al-4V Alloy ................................................................................................ 7
      2.2.1 Microstructural Development in Ti-6Al-4V Alloy ........................................ 7
  2.3 Fatigue Behaviour of Titanium Alloys ............................................................... 12
  2.4 Tribological Behaviour of Titanium Alloys ...................................................... 15
  2.5 Surface Treatments for Enhancing Tribological Properties of Titanium Alloys .. 21
      2.5.1 Coating Deposition Techniques ................................................................... 22
      2.5.2 Thermochemical Treatments ....................................................................... 23
      2.5.3 Diffusion Treatments ................................................................................. 25
      2.5.4 Duplex treatments ...................................................................................... 28
  2.6 Plasma Nitriding of Titanium Alloys ............................................................... 29
      2.6.1 Fundamentals of Plasma Nitriding .............................................................. 29
      2.6.2 The Effect of Plasma Nitriding on Microstructure of Titanium Alloys .......... 31
      2.6.3 The Effect of Plasma Nitriding on Tribological Behaviour of Titanium Alloys .... 35
      2.6.4 The Effect of Plasma Nitriding on Fatigue Behaviour of Titanium Alloys ....... 40
  2.7 The Combined Effect of Cold Working and Diffusion Treatments ............... 45

CHAPTER 3: MATERIALS AND EXPERIMENTAL DETAILS ............................... 60
  3.1 Plasma Nitriding of Ti-6Al-4V Alloy ............................................................... 61
      3.1.1 Process Optimization ............................................................................... 63
      3.1.2 Shot Peening Pretreatment and Fabrication of SPD Surface Layer ............ 66
  3.2 Mechanical Testing Methods .......................................................................... 67
      3.2.1 Uniaxial Tensile Tests .............................................................................. 67
      3.2.2 Rotation Bending Fatigue Tests ................................................................. 68
  3.3 Evaluation of Tribological Properties ............................................................. 68
      3.3.1 Ball-on-disk Tests ..................................................................................... 68
      3.3.2 Microscratch Tests ................................................................................... 71
  3.4 Characterization Methods ............................................................................... 72
      3.4.1 Surface Topography and Fractographic Studies ........................................... 72
      3.4.2 Cross-sectional Investigation of Microstructures ......................................... 73
      3.4.3 Cryogenic Fracture analysis ...................................................................... 74
      3.4.4 Examination of Wear Tracks, Scratch Tracks, and Wear Debris Particles ....... 75
      3.4.5 Surface Profile Measurements by Optical Interferometry ......................... 75
      3.4.6 Surface Topography Imaging by Atomic Force Microscopy ....................... 77
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.4.7 Compositional Analysis by X-ray Diffraction Method</td>
<td>78</td>
</tr>
<tr>
<td>3.4.8 Elemental Analysis by Optical Emission and X-Ray Spectroscopic Methods</td>
<td>78</td>
</tr>
<tr>
<td>3.4.9 Residual Stress Measurements by X-ray Diffraction</td>
<td>79</td>
</tr>
<tr>
<td>3.4.10 Focused Ion Beam Technique</td>
<td>80</td>
</tr>
<tr>
<td>3.4.11 Analytical Transmission Electron Microscopy</td>
<td>81</td>
</tr>
<tr>
<td>3.4.12 Microhardness Measurements</td>
<td>84</td>
</tr>
<tr>
<td>CHAPTER 4: RESULTS</td>
<td>97</td>
</tr>
<tr>
<td>4.1 Mechanical Properties of Ti-6Al-4V Alloy</td>
<td>98</td>
</tr>
<tr>
<td>4.1.1 Tensile Tests</td>
<td>98</td>
</tr>
<tr>
<td>4.1.2 Fatigue Tests</td>
<td>99</td>
</tr>
<tr>
<td>4.2 Tribological Properties of Ti-6Al-4V Alloy</td>
<td>101</td>
</tr>
<tr>
<td>4.2.1 Wear Rate</td>
<td>101</td>
</tr>
<tr>
<td>4.2.2 Friction Behaviour</td>
<td>101</td>
</tr>
<tr>
<td>4.2.3 SEM Observations of Worn Surfaces and Wear Debris Particles</td>
<td>102</td>
</tr>
<tr>
<td>4.3 Optimization of the Plasma Nitriding Treatment</td>
<td>106</td>
</tr>
<tr>
<td>4.3.1 Nitriding Duration</td>
<td>107</td>
</tr>
<tr>
<td>4.3.2 Nitriding Atmosphere (Pressure and Composition)</td>
<td>111</td>
</tr>
<tr>
<td>4.3.3 Nitriding Temperature</td>
<td>115</td>
</tr>
<tr>
<td>4.4 Analytical Microscopy Studies and Characterization of Plasma Nitrided Ti-6Al-4V Alloy</td>
<td>122</td>
</tr>
<tr>
<td>4.4.1 TEM/EELS Analysis</td>
<td>122</td>
</tr>
<tr>
<td>4.4.2 XPS Analysis</td>
<td>124</td>
</tr>
<tr>
<td>4.4.3 Glow Discharge Spectroscopy</td>
<td>125</td>
</tr>
<tr>
<td>4.5 Residual Stress Measurement</td>
<td>127</td>
</tr>
<tr>
<td>4.6 Mechanical Properties of Plasma Nitrided Ti-6Al-4V Alloy</td>
<td>128</td>
</tr>
<tr>
<td>4.6.1 Tensile Tests</td>
<td>128</td>
</tr>
<tr>
<td>4.6.2 Cryogenic Fracture Tests</td>
<td>129</td>
</tr>
<tr>
<td>4.6.3 Fatigue Tests</td>
<td>130</td>
</tr>
<tr>
<td>4.7 Tribological Properties of Plasma Nitrided Ti-6Al-4V Alloy</td>
<td>131</td>
</tr>
<tr>
<td>4.7.1 Microscratch Tests</td>
<td>131</td>
</tr>
<tr>
<td>4.7.2 Ball-on-disk Wear Tests</td>
<td>135</td>
</tr>
<tr>
<td>4.8 Shot Peening Pretreatment</td>
<td>143</td>
</tr>
<tr>
<td>4.8.1 Microstructural Characterization of Ti-6Al-4V Alloy Subjected to Shot Peening Pretreatment</td>
<td>143</td>
</tr>
<tr>
<td>4.8.2 Microstructural Characterization of Ti-6Al-4V Alloy with the Shot Peening Pretreatment Subjected to Plasma Nitriding</td>
<td>145</td>
</tr>
<tr>
<td>4.8.3 Sliding Performance of Plasma Nitrided Ti-6Al-4V Surface Subjected to the Shot Peening Pretreatment</td>
<td>148</td>
</tr>
<tr>
<td>CHAPTER 5: DISCUSSION OF THE RESULTS</td>
<td>262</td>
</tr>
<tr>
<td>5.1 The Effect of Plasma Nitriding Microstructure on the Sliding Performance of Ti-6Al-4V Alloy</td>
<td>262</td>
</tr>
<tr>
<td>5.2 The Effect of Plasma Nitriding on the Tensile Properties and Fatigue Behaviour of Ti-6Al-4V Alloy</td>
<td>268</td>
</tr>
<tr>
<td>5.3 The Effect of Shot Peening Pretreatment on Plasma Nitriding of Ti-6Al-4V Alloy</td>
<td>282</td>
</tr>
<tr>
<td>CHAPTER 6: CONCLUSIONS</td>
<td>295</td>
</tr>
<tr>
<td>CHAPTER 7: FUTURE DIRECTIONS</td>
<td>298</td>
</tr>
<tr>
<td>BIBLIOGRAPHY</td>
<td>300</td>
</tr>
<tr>
<td>LIST OF PUBLICATIONS AND CONFERENCE PRESENTATIONS RESULTING FROM THIS WORK</td>
<td>321</td>
</tr>
<tr>
<td>APPENDIX A: COPYRIGHT RELEASES FROM PUBLICATIONS</td>
<td>322</td>
</tr>
</tbody>
</table>
### LIST OF TABLES

Table 2.1 Summary of common heat treatments for Ti-6Al-4V alloy [9].......................... 11

Table 2.2 The plasma nitriding conditions in the study by Yildiz et al. and the corresponding properties and wear rates [158]................................................................. 39

Table 3.1 Elemental analysis of the as-received Ti-6Al-4V material used in this research .................................................................................................................. 61

Table 3.2 The plasma nitriding conditions tried in this research................................. 64

Table 3.3 The average surface roughness and some of the mechanical properties of counterface materials ............................................................................................................. 69

Table 4.1 Tensile properties of the mill-annealed Ti-6Al-4V alloy used in this research 98

Table 4.2 Surface roughness measurement results obtained by optical profilometry measured over a surface area of 450 µm × 600 µm................................................................. 107

Table 4.3 Results obtained from measurement of microstructural features for 600°C plasma nitriding treatments for different durations measured using an image analysis software based on cross-sectional SEM micrographs ......................................................... 109

Table 4.4 Average α grain size measurement results in the substrate; measured using an image analyzing software based on cross-sectional SEM micrographs (at least 300 grains) ........................................................................................................................................... 109

Table 4.5 Plasma nitriding conditions selected for investigating the effect of nitriding temperature ........................................................................................................... 111
Table 4. 6 Surface roughness measurement results obtained by optical profilometry measured over a surface area of 450 µm × 600 µm. Each reported value is the average of at least three measurements.

Table 4. 7 Results obtained from measurement of microstructural features for 600°C plasma nitriding treatments for different durations measured using an image analysis software based on cross-sectional SEM micrographs.

Table 4. 8 Average α grain size measurement results in the substrate; measured using an image analyzing software based on cross-sectional SEM micrographs.

Table 4. 9 Plasma nitriding conditions selected for investigating the effect of nitriding temperature.

Table 4. 10 Surface roughness measurement results obtained by optical profilometry.

Table 4. 11 Results obtained from measurement of microstructural features for 24-hour plasma nitriding treatments at different temperatures measured using an image analysis software based on cross-sectional SEM micrographs.

Table 4. 12 Average α grain size measurement results in the substrate; measured using an image analyzing software based on cross-sectional SEM micrographs.

Table 4. 13 The binding energies of the Ti (2p₁, 2p₃), N (1s), and O (1s).

Table 4. 14 The obtained results from residual stress measurements on the surface of plasma nitrided Ti-6Al-4V alloy.

Table 4. 15 Tensile data obtained from uniaxial tensile tests on untreated Ti-6Al-4V alloy and plasma nitrided alloy at 600°C and 900°C.

Table 5. 1 The obtained results of the quantitative fatigue crack propagation analysis.

Table 5. 2 Physical properties of Ti-6Al-4V alloy and TiN.
LIST OF FIGURES

Figure 1. 1 The research methodology flowchart illustrating the different steps that were followed to optimize the plasma nitriding treatment for simultaneous improvements in the fatigue strength and wear resistance of Ti-6Al-4V alloy ........................................ 4

Figure 2. 1 A schematic representation of slip planes and slip directions in HCP α titanium [1]........................................................................................................................................................................ 49

Figure 2. 2 The effect of annealing temperature and rate of cooling on microstructure of Ti-6Al-4V alloy. (a) α’ martensite, (b) primary α+α’ martensite+retained β, (c) primary α+α’ martensite+retained β, (d) primary α+metastable β, (e) acicular α + β, (f) primary α and acicular α+β, (g) primary α and acicular α + β, (h) primary α and β, (i) plate-like α and β, (j) equiaxed α and intergranular β, (k equiaxed α and intergranular β, (l) equiaxed α and intergranular β [9]. ........................................................................................................ 49

Figure 2. 3 Optical micrographs showing the effect of cooling rate from the β phase field on the microstructure of Ti-6Al-4V alloy. (a) Furnace cooling (1˚C/min) results in the formation of plate-like α within the β grains and at the β grain boundaries. (b) Typical commercial cooling (100˚C/min) results in the formation of a Widmanstätten type of microstructure consisting of colonies of acicular α in a matrix of β and α layers at prior β grain boundaries (basket-weave structure). (c) Water quenching of relatively thin sections (800˚C/min) resulting in the formation of needle-like α’ martensite [190]. ...................... 50

Figure 2. 4 Variation of yield strength and tensile elongation with the cooling rate from the β phase field for the lamellar microstructures in Ti-6Al-4V and other α+β titanium alloys [190]. ........................................................................................................ 50

Figure 2. 5 An optical micrograph from bimodal (duplex) microstructure in Ti-6Al-4V alloy. The microstructure consists of equiaxed primary α grains in a matrix of transformed β [191]. ........................................................................................................ 51

Figure 2. 6 Typical crack front profiles observed in Ti-6Al-4V alloy in (a) bimodal and (b) fully lamellar microstructures (R = 0.1, da/dN ~ 10^{-10} m/cycle). The significantly rougher crack front profile in the fully lamellar microstructure is responsible for its superior fatigue crack growth properties. The arrows show the direction of crack propagation [19]........................................................................................................ 51
Figure 2. 7 The effect of d-valence character of metallic bonding of several metals on their coefficient of friction when sliding against (a) themselves and (b) SiC single crystal under vacuum at low load and sliding velocity [37]............................................................................ 52

Figure 2. 8 The relationship between coefficient of friction (COF) and the ideal tensile strength for metals in contact with themselves. The tests were conducted at room temperature at a sliding velocity is 0.7 mm/min and an applied load of 0.01 N under vacuum. Due to its lower theoretical cohesive strength, the stress required to separate Ti planes apart (cohesive force) during sliding contact is lower and thus extensive material transfer and adhesion takes place during sliding action of Ti surfaces [38]....................... 52

Figure 2. 9 Cross-sectional images of Ti-6Al-4V after wear tests against AISI M2 counterface. (a) The formation of surface oxide scales and oxidative wear mechanism at low sliding speeds (0.3 m/s), (b) The formation and delamination of mechanically mixed layer (MML) accompanied by subsurface plastic deformation characteristics of delamination wear mechanism at high sliding speeds (0.8 m/s) [25].......................... 53

Figure 2. 10 A schematic wear map showing different wear mechanisms for the Ti-6Al-6V-2Sn alloy sliding against AISI steel counterface [60]. ......................................................... 53

Figure 2. 11 Electrical characteristics of a glow discharge plasma [135]. ................. 54

Figure 2. 12 Ti-N binary phase diagram [192]. ..................................................... 54

Figure 2. 13 Schematic illustration of the plasma nitrided microstructure in titanium alloys [192] ......................................................................................................................... 55

Figure 2. 14 (a) Microhardness-depth profiles of the surface of plasma nitrided titanium alloys, (1) commercially pure titanium and (2) VT5 alloy (containing 5.4% Al). The addition of aluminum (α stabilizing element) decreased the diffusion rate of nitrogen atoms. (b) The effect of β phase on the depth of nitrogen diffusion during plasma nitriding of titanium alloys at (1) 550°C and (2) 600°C [152]........................................... 55

Figure 2. 15 Optical micrographs of Ti-6Al-4V alloy after plasma nitriding in nitrogen for 3 hours at 1000°C showing the formation of an α-case underneath the compound layer at (a) low magnification and (b) high magnification [81]......................................................... 56

Figure 2. 16 An optical micrograph showing the formation of an α-case in commercially pure (CP) titanium plasma nitrided in a 95% N₂ - 5% H₂ atmosphere at 1000°C for 16
hours. The $\alpha$-case is distinguished due to absence of hydride precipitation in this phase while extensive precipitation occurred in the substrate [81].

Figure 2. 17 (a) A cross-sectional backscattered electron (BSE) image of the plasma nitrided Ti-6Al-4V and (b) the corresponding auger electron spectroscopy (AES) map of the aluminum distribution confirming the presence of an aluminum-rich layer underneath the compound layer [158].

Figure 2. 18 Wear test results on plasma nitrided TiAl-6V after a 12-hour treatment at 850°C in a nitrogen atmosphere. The wear tests were performed against AISI 1137 steel counterface using SAE 30 oil as a lubricant [81].

Figure 2. 19 Wear test results for untreated and plasma nitrided Ti-6Al-4V alloys. The limited improvement of wear resistance with an 8-h treatment was attributed to insufficient depth of hardening and thus lack of support for the compound layer resulted in delamination of this layer. A longer nitriding treatment (24 h), on the other hand, promoted a deeper diffusion zone and resulted in better sustainment of the compound layer on the surface [24].

Figure 2. 20 The S-N curve obtained by rotating bending test ($R = -1$) for Ti-6Al-4V alloy, STA: solution treated at 950°C for 1 hour and aged at 540°C for 4 hours, A4 and N4 were annealed and nitried at 850°C for 4 hours and A15, N15 were annealed and nitrided at 850°C for 15 hours, respectively [172].

Figure 2. 21 (a) Fracture surface of nitrided Ti-6Al-4V alloy (900°C for 1 hour) after low cycle fatigue test under $\pm 5 \times 10^{-3}$ cyclic strains. (b) The fatigue crack initiated by transgranular brittle fracture at the nitrided surface layer [178].

Figure 2. 22 A cross-sectional polarized micrograph of mechanical twins in the subsurface of an $\alpha$-titanium alloy after shot peening [187].

Figure 3. 1 (a) A secondary electron SEM image showing the microstructure of as-received Ti-6Al-4V (ELI grade) used in this research, the microstructure consisted of equiaxed $\alpha$ grains, retained $\beta$ particles at $\alpha$ grain boundaries, and fine recrystallized $\beta$ particles inside the $\alpha$ grains. (b) A higher magnification SEI showing that the $\alpha$ grains were delineated by different orientation of fine recrystallized $\beta$ particles (etched in glycerol + HF (1:1) solution).
Figure 3. 2 (a) A schematic presentation of the plasma nitriding facility; no external heating source was used, (b) the titanium coupons were placed on titanium stands inside a cathodic cage that was also made from a titanium alloy to minimize contamination. (c) Schematic illustration of plasma nitriding set up for tensile and fatigue samples. The samples were hung inside the cathodic cage using titanium wire in order to ensure the uniform formation of plasma surrounding the samples. .................................................. 87

Figure 3. 3 (a) The plasma nitriding unit located at Exactatherm Ltd. used in this research. (b) A titanium cage was used to intensify the glow discharge. (c) The test coupons were placed in the geometric center of the titanium cage. ......................... 88

Figure 3. 4 Schematic representations showing the dimensions of (a) tensile and (b) fatigue samples.......................................................... 89

Figure 3. 5 MTS Criterion-43 electromechanical universal testing equipment used to perform tensile test in this research, (b) a clip-on axial extensometer was used to measure the strain values....................................................... 89

Figure 3. 6 (a) Bruker’s Universal Mechanical Tester (UMT) tribometer used for wear tests wear tests in this research, the enclosed area is where the image of shown in “b” was taken. (b) The lower rotational drive used for ball-on-disk tests and the friction/force sensor on the upper drive. The enclosed area is the location where the image shown in “c” was taken. (c) The ball-on-disk test set-up showing the suspension springs, upper sample holder (ball holder) and lower sample holder (test coupon holder). ................. 90

Figure 3. 7 CSM Instruments Micro-Combi Tester with the microscratch test set-up showing the automated stage, optical microscope and the diamond Rockwell indenter. 91

Figure 3. 8 An optical surface profilometer (Veeco, Wyko) was used in this research to measure the surface roughness after nitriding treatments.......................................................... 92

Figure 3. 9 (a) Three-dimensional (3D) and (b) two-dimensional (2D) optical profilometry images of the wear tracks used for measuring the worn area and wear rates after the wear tests in this investigation......................................................... 92

Figure 3. 10 (a) A typical three-dimensional optical surface profile of the wear track on plasma nitrided Ti-6Al-4V tested against AISI 52100 steel counterface, (b) height histogram obtained from the profile shown in “a” based on which the average height of transferred material was estimated, (c) two-dimensional optical surface profile from “a”, (d) calculation of accumulated area using an image analyzer software................................. 93
Figure 3.11 Scanning electron micrographs illustrating the procedure of focused ion beam (FIB) milling to study the cross section of scratch paths and wear tracks in this investigation. (a) Deposition of a platinum layer on the selected area using a gas injection system prior to milling to prevent surface features from damage during the milling process. (b) Cutting a trench normal to the deposited platinum layer, using gallium (Ga) ions at an accelerating voltage of 30 kV and beam current of 10 nA (rough milling). (c) Polishing the milled cross section with progressively decreasing ion beam currents from 200 to 80 pA.

Figure 3.12 The focused ion beam (FIB)/SEM were used for in depth site-specific cross-sectional analysis of wear tracks and scratch paths in this research. Imaging from the ion-milled trenches was performed using the electron beam at an angle of 54°.

Figure 3.13 SEM images illustrating the procedure of TEM sample preparation using the focused ion beam (FIB) milling lift-out technique. An approximately 1 µm thick layer of tungsten (W) was deposited on the region of interest to protect surface features from the milling damage. (a) Two trenches were cut on either side of the tungsten layer using a Ga ion beam, (b) a frame cut was made on the bottom of the TEM sample, (c) frame cuts were also made on the left side and a portion of the right side of the TEM sample and the TEM sample was attached to a micromanipulator by deposition of a tungsten layer, (d) the TEM sample was cut free from the bulk, (e) TEM sample was lifted out by the micromanipulator and carried to a copper grid, (f) TEM sample was joined to the copper grid using a layer of tungsten and the micromanipulator was detached, (g) further milling continued on both sides of the TEM sample, (h) electron transparency was achieved.

Figure 4.1 Engineering stress-strain curves for mill-annealed Ti-6Al-4V alloy used in this research (loading rate: 0.5 mm/min).

Figure 4.2 A typical stereo micrograph from the fracture surface of Ti-6Al-4V alloy after uniaxial tensile test showing a ductile “cup and cone” type of failure.

Figure 4.3 Typical secondary electron SEM images of the fracture morphology of Ti-6Al-4V alloy after tensile tests. (a) Ductile type of failure consisting of a dimpled region at the center surrounded by shear lip, the enclosed areas are the locations where higher magnification images were taken. (b) A higher magnification view of the equiaxed dimples in the middle region.

Figure 4.4 Secondary electron SEM image from the tensile fracture morphology of Ti-6Al-4V alloy (shear lip region) after being immersed in Kroll’s reagent showing
homogenous deformation of the α phase and β particles under tensile loads. The light grey particles marked on the image are β particles in the dark grey background which is the α phase.

Figure 4.5 The S-N curve obtained from rotation bending fatigue tests on Ti-6Al-4V alloy.

Figure 4.6 (a) A secondary electron SEM micrograph from fatigue fracture at 769 MPa ($N_f = 1.1 \times 10^5$ cycles, high cycle fatigue region). Only one origin of fatigue crack initiation was observed which was located close to the surface of the sample. Fatigue crack propagated with two different morphologies in Regions I and II leading to the final rupture. (b) A higher magnification view of the fatigue crack initiation site which shows signs of distortion and plastic deformation. (c) A higher magnification view of crack propagation in Region I, relatively smooth surfaces with microcracks and striations perpendicular to the crack growth direction. (d) A higher magnification view of crack propagation in Region II consisting of ripple marks and microcracks perpendicular to the propagation direction. (e) Striations in the crack propagation Region I. (f) Dimples in the final rupture region indicating a ductile type of failure.

Figure 4.7 (a) A secondary electron SEM image of the fatigue fracture at 816 MPa ($N_f = 4.3 \times 10^4$ cycles, low cycle fatigue region). The fatigue crack initiated at one location close to the surface and propagated with two different morphologies in Regions I and II leading to the final rupture. The arrows show the crack propagation direction. (b) A higher magnification view of the fatigue crack initiation site. (c) A higher magnification view of the crack propagation in Region I showing relatively smooth surfaces. (d) Striations in the enclosed area marked in (c) within the crack propagation Region I. (e) A higher magnification view of crack propagation in Region II consisting of ripple marks and microcracks perpendicular to the propagation direction. (f) Dimples in the final rupture region indicating a ductile type of failure.

Figure 4.8 The variation of wear rate as a function of applied load during ball-on-disk wear tests on Ti-6Al-4V alloy determined based on (a) mass loss measurements, (b) volumetric wear measured using optical profilometry compared with those calculated from mass loss measurements. The wear tests were carried out against AISI 52100 steel counterface at 0.1 m/s sliding speed for a total sliding distance of 200 m (5000 cycles).

Figure 4.9 (a) Variation of coefficient of friction with the sliding distance during ball-on-disk wear tests at different applied loads of 0.8 N, 1.2 N, 2 N, 3.5 N, and 5 N. (b) The average value of coefficient of friction in the steady state region decreased with the applied normal load.
Figure 4.10 (a) Three-dimensional and (b) two-dimensional optical profilometry images from the wear track at 0.8 N applied load. (Sliding speed: 0.1 m/s, sliding distance: 200 m, AISI 52100 steel counterface).

Figure 4.11 A back-scattered electron SEM image showing the typical morphology of wear track on Ti-6Al-4V alloy surface tested against AISI 52100 steel counterface at 0.8 N normal load, 0.1 m/s sliding speed after 200 m. The enclosed area is the location where higher magnification images in Figure 4.12 were taken.

Figure 4.12 Back-scattered SEM micrographs of the wear track on the surface of Ti-6Al-4V alloy at the applied load of 0.8 N. (a) The wear track consisted of dark grey patches of accumulated material (flat plateaus) as well as ploughing grooves. (b) A higher magnification view of location “I” showing the morphology of wear debris particles surrounding the plateaus. (c) A higher magnification view of location “II” showing the microcracks frequently observed within the plateaus. (d) A higher magnification view of location “III” showing the abrasive grooves on the wear track and some fine debris particles embedded inside the grooves. (Sliding speed: 0.1 m/s, sliding distance: 200 m, counterface material: AISI 52100 steel).

Figure 4.13 EDS analysis of the dark grey plateau marked as “c” on the SEM image shown in Figure 4.12-a showing the presence of oxygen and iron in this region in addition to titanium, aluminum and vanadium elements of the Ti-6Al-4V alloy.

Figure 4.14 (a) Back-scattered electron SEM image (BSI) showing the wear scar on the steel counterface after sliding against Ti-6Al-4V at an applied load of 0.8 N (Sliding speed: 0.1 m/s, sliding distance: 200 m). The enclosed area is the location where higher magnification image in “b” was taken. (b) The accumulated material on one side of the worn surface on the counterface.

Figure 4.15 (a) Secondary electron SEM image of (a) the platelet debris which were approximately 20 µm long and 10 µm wide, (b) the fine equiaxed debris particles ranging from 0.3 µm to 3 µm in diameter, both generated during wear tests at an applied normal load of 0.8 N. (c) A typical EDS spectrum of the wear debris particles showing the presence of titanium, aluminum and vanadium as well as iron and oxygen. (Sliding speed: 0.1 m/s, sliding distance: 200 m, AISI 52100 steel counterface).

Figure 4.16 (a) Three-dimensional and (b) two-dimensional optical profilometry images of the wear track at 5 N applied load. (Sliding speed: 0.1 m/s, sliding distance: 200 m, AISI 52100 steel counterface).
Figure 4.17 A back-scattered electron SEM image showing the typical morphology of wear track on Ti-6Al-4V alloy surface tested against AISI 52100 steel counterface at the 5 N normal load, 0.1 m/s sliding speed after 200 m. The enclosed area is the location where higher magnification images shown in Figure 4.18 were taken.......................... 166

Figure 4.18 Back-scattered SEM micrographs of the wear track on the surface of Ti-6Al-4V alloy at the applied load of 5 N. (a) The wear track consisted of dark grey patches of accumulated material as well as ploughing grooves. (b) A higher magnification view of location “I’’ showing the abrasion grooves on the wear track and some fine debris particles scattered on the grooves. (c) A higher magnification view of location “II” showing the fragmentation of the plateaus. (Sliding speed: 0.1 m/s, sliding distance: 200 m, counterface material: AISI 52100 steel). .......................................................... 167

Figure 4.19 EDS analysis of the region marked as “c” on the SEM image shown in Figure 4.18-a showing the presence of oxygen and iron in this region in addition to titanium, aluminum and vanadium elements of the Ti-6Al-4V alloy. A higher intensity peak of iron was observed at this loading condition (5 N) compared to lower loads (0.8 N).......... 168

Figure 4.20 (a) Secondary electron SEM image (SEI) of the cutting chip-like debris, (b) SEI of the platelet debris with sliding marks, (c) SEI of the loose fine debris particulates, all generated during wear tests at 5 N applied load. The enclosed areas are the locations where EDS analyses were performed. (d) EDS analysis of the enclosed area shown in “a’’ indicating that the cutting chip-like was composed of the same elements as the Ti-6Al-4V alloy, (e) EDS analysis of the enclosed area shown in “b’’ indicating that the wear debris was composed of the same elements as the Ti-6Al-4V alloy in addition to oxygen and iron. (Sliding speed: 0.1 m/s, sliding distance: 200 m, AISI 52100 steel counterface). 168

Figure 4.21 (a) Back scattered electron SEM image (BSI) of the wear scar on the steel counterface after wear test at 5 N against Ti-6Al-4V alloy (Sliding speed: 0.1 m/s, sliding distance: 200 m). The enclosed area is the location where the higher magnification image shown in “b’’ was taken. (b) Formation and fragmentation of the mechanically mixed layer (MML) on the worn surface of the counterface...................................................... 169

Figure 4.22 Back-scattered SEM micrographs showing the focused ion beam (FIB) milling location on the wear track of Ti-6Al-4V alloy after the ball-on-disk wear test at 0.8 N applied load. (a) A plateau on the wear track where FIB trench was milled, the enclosed area is the location where EDS analysis was performed. (b) A high magnification view of the image shown in (a). (Sliding speed: 0.1 m/s, sliding distance: 200 m, counterface material: AISI 52100 steel). ...................................................... 170

Figure 4.23 EDS spectrum obtained from the enclosed area in Figure 4.22-a showing presence of oxygen and iron in addition to titanium, vanadium and aluminum on the wear
track. (Applied normal load: 0.8 N, sliding speed: 0.1 m/s, sliding distance: 200 m, counterface material: AISI 52100 steel).

Figure 4.24 Back-scattered SEM images showing the ion milled cross section of worn surfaces of Ti-6Al-4V alloy at 0.8 N applied load. (a) General view of the subsurface region showing the mechanically mixed layer (MML) and the subsurface region. The enclosed areas are the locations where higher magnification images in (b), (c) were taken. (b) A high magnification view of the enclosed area in (a) showing that MML layer consisted of agglomerated particles, and (c) a high magnification view of the enclosed area in (a) showing that delamination occurred within the MML layer.

Figure 4.25 (a) A back-scattered electron SEM image from the ion milled cross section of wear track showing the mechanically mixed layer (MML) and the location where EDS mapping was performed. The distribution of (b) oxygen, (c) aluminum, (d) titanium, (e) vanadium, (f) iron obtained by EDS elemental analysis. (Applied normal load: 0.8 N, sliding speed: 0.1 m/s, sliding distance: 200 m, counterface material: AISI 52100 steel).

Figure 4.26 Back-scattered electron SEM images showing the location of FIB milling on the wear track of Ti-6Al-4V alloy after the ball-on-disk wear test at 5 N applied load. (a) A plateau on the wear track before ion milling, (b) the location of FIB trench on the plateau, (c) a high magnification view of the image shown in (a), and (d) a high magnification view of the location where FIB milling for cross-sectional analysis of the wear track was performed. (Sliding speed: 0.1 m/s, sliding distance: 200 m, counterface material: AISI 52100 steel).

Figure 4.27 Back-scattered SEM images showing the ion milled cross section of worn surfaces of Ti-6Al-4V alloy at 5 N applied load. (a) General view of the subsurface region showing the mechanically mixed layer (MML) and the subsurface region. Occasional white streaks where observed in the MML layer as marked by the arrows. The enclosed area marks the location observed at higher magnification in (b). (b) A high magnification view of the enclosed area in (a) showing the white streaks inside the mechanically mixed layer, and (c) a higher magnification image showing plastic deformation in the subsurface region evidenced by the elongation of grains parallel to the sliding direction (as indicated by the arrows).

Figure 4.28 A back-scattered electron SEM image from the ion milled cross section of wear track showing the mechanically mixed layer (MML) and the location where EDS mapping was performed. The distribution of (b) oxygen, (c) aluminum, (d) titanium, (e) vanadium, (f) iron obtained by EDS elemental analysis. It was observed that the white streaks in the MML were rich in iron. (Applied normal load: 5 N, sliding speed: 0.1 m/s, sliding distance: 200 m, counterface material: AISI 52100 steel).
Figure 4.29 XRD spectra of the plasma nitrided surfaces after 24- and 45-h treatments at 600°C............. 176

Figure 4.30 Secondary electron SEM images of the cross section of plasma nitrided Ti-6Al-4V alloy at 600°C for (a) 24 h and (b) 45 h.............................................. 177

Figure 4.31 Microhardness-depth profiles in the near-surface region of plasma nitrided samples at 600°C for 24- and 45-h durations indicating a deeper diffusion zone after 45 hours of nitriding................................................. 178

Figure 4.32 The variation of coefficient of friction with sliding distance during microscratch tests on untreated and plasma nitrided Ti-6Al-4V alloy at 600°C for 24 and 45 hours. The microscratch tests were performed under constant loading conditions (a) 5 N, (b) 20 N........................................................................ 179

Figure 4.33 XRD pattern of the plasma nitrided surface treated in an atmosphere containing 3% and 6% N₂-balance H₂ for 24 hours at 600°C................................. 180

Figure 4.34 XRD pattern of the plasma nitrided surface treated in an atmosphere containing 3% N₂-balance Ar for 24 hours at 600°C........................................... 181

Figure 4.35 Scanning electron SEM images of the cross section of plasma nitrided alloy at a total pressure of 400 Pa, (a) overall view in the near-surface region, (b) an image acquired at a higher magnification indicating the formation of compound layer and α-case...................................................... 182

Figure 4.36 Scanning electron SEM image of the cross section of plasma nitrided alloy treated in a 3%N₂-balance Ar atmosphere, the presence of microvoids underneath the compound layer is likely due to the sputtering effect of heavy Ar atoms in the plasma. 183

Figure 4.37 Scanning electron SEM image of the cross section of plasma nitrided alloy treated in a 6%N₂-balance H₂ atmosphere................................................. 183

Figure 4.38 Microhardness-depth profiles for plasma nitrided alloy in nitriding atmospheres containing 3% and 6% N₂ showing that increasing the nitrogen content inversely affected the hardness and depth of nitrogen diffusion........................................... 184

Figure 4.39 Microhardness-depth profiles for plasma nitrided alloy treated in nitriding atmospheres containing H₂ and Ar as carrier gas......................................... 184
Figure 4.40 Microhardness-depth profiles for plasma nitrided alloy treated in nitriding atmospheres with different pressures (67 Pa, 400 Pa). ................................................................. 185

Figure 4.41 (a) Secondary electron SEM image from the surface topography of plasma nitrided Ti-6Al-4V after a 24-hour treatment at 500°C, (b) a higher magnification view of the image shown in (a). (Tilt angle: 45˚) ................................................................. 185

Figure 4.42 (a) Secondary electron SEM image from the surface topography of plasma nitrided Ti-6Al-4V after a 24 hr treatment at 600˚C, (b) a higher magnification view of the image shown in (a). (Tilt angle: 45˚) ................................................................. 186

Figure 4.43 An atomic force microscopy (AFM) image from the surface of plasma nitrided Ti-6Al-4V after a 24-hour treatment at 600°C ................................................................. 186

Figure 4.44 (a) Secondary electron SEM image from the surface topography of plasma nitrided Ti-6Al-4V after a 24 hr treatment at 900˚C, (b) a higher magnification view of the image shown in (a). (Tilt angle: 45˚) ................................................................. 187

Figure 4.45 The XRD spectra of the plasma nitrided Ti-6Al-4V surfaces treated at (a) 500°C showing presence of Ti$_2$N, TiN$_{0.3}$ and traces of TiN in the compound layer, (b) 600°C showing abundance of TiN and Ti$_2$N and TiN$_{0.3}$ in the compound layer, (c) 900˚C showing the abundance of TiN and presence of Ti$_2$N in the compound layer. A higher contribution of α-Ti peaks (reflections from the substrate) in the XRD spectrum of the plasma nitrided alloy at 500°C and fewer number of titanium nitride peaks indicated the thin nature of the compound layer formed at this temperature. ................................................................. 188

Figure 4.46 A typical secondary electron SEM image of the cross section of plasma nitrided Ti-6Al-4V alloy at 500°C for 24 hours showing the formation of a thin compound layer and a shallow diffusion zone. The diffusion zone was differentiated by dissolution of fine recrystallized β particles inside the α grains. ................................................................. 189

Figure 4.47 (a) A typical secondary electron SEM image of the cross section of plasma nitrided Ti-6Al-4V alloy at 600°C for 24 hours showing the formation of a thin compound layer and a deep diffusion zone. The diffusion zone was differentiated by the dissolution of fine recrystallized β particles inside the α grains. (b) A higher magnification view from the near-surface microstructure showing a well-bonded interface between the compound layer and the diffusion zone. (c) A higher magnification view of the substrate. ........................................................................................................................................ 189

Figure 4.48 A back-scattered electron SEM image (BSI) of the FIB-milled cross section of the plasma nitrided microstructure (600°C, 24 hours). The compound layer/diffusion
zone interface was not clearly distinguished indicating a well-bonded interface between the compound layer and diffusion zone. A layer of Pt was deposited on the surface prior to the milling as a protection layer to avoid the ion milling damage.

Figure 4.49 (a) A typical secondary electron SEM image of the cross section of plasma nitrided Ti-6Al-4V alloy at 900˚C for 24 hours showing the formation of a thin compound layer, an α-case (β-free zone), and a deep diffusion zone. The diffusion zone was differentiated by dissolution of fine recrystallized β particles inside the α grains. (b) A higher magnification view showing the presence of an α-case at the interface between the compound layer and the diffusion zone. (c) A higher magnification view of the α-case region showing the presence of a distinct layer underneath the compound layer, according to the EDS line-scans this layer had a high concentration of aluminum and it is thus called the “Al-rich” layer.

Figure 4.50 EDS analysis showing the distribution of N, O, Al, Ti, and V elements in the region underneath the compound layer in the plasma nitrided Ti-6Al-4V alloy at 900˚C for 24 hours. The white line is the location where the EDS line scan was performed. A higher concentration of Al was found in the region underneath the compound layer (Al-rich layer).

Figure 4.51 A back-scattered electron SEM image showing the ion milled cross section of plasma nitrided Ti-6Al-4V alloy at 900˚C. A platinum layer was deposited on the surface to protect surface features from milling damage. Grains (approximately 1-3 µm in size) that were differentiated on account of their different contrasts were TiN grains according to the XRD results. (Tilt angle: 54˚)

Figure 4.52 Secondary electron SEM images of the substrate microstructure after plasma nitriding treatment at 900˚C (for 24 hours). (a) Substantial grain growth, (b) microstructural transformation from equiaxed mill-annealed microstructure to bimodal microstructure consisting of equiaxed α grains and grains composed of α/β lamellae.

Figure 4.53 Microhardness-depth profile for plasma nitrided Ti-6Al-4V at different temperatures. The depth of diffusion zone was estimated at the distance from the compound layer interface where the hardness value reached that of the substrate.

Figure 4.54 (a) Scanning TEM (STEM) image of the cross section of plasma nitrided Ti-6Al-4V alloy showing the locations where the electron energy loss spectroscopy (EELS) analyses were performed. (b) EELS spectrum collected from locations marked as “1” in (a) falls within the compound layer and contains a nitrogen peak at 401 eV as well as two α-titanium peaks at 456 eV and 461 eV. (c) The grain marked as “2” in (a) falls within the diffusion zone and only shows α-titanium peaks. (d) EELS line scan confirming that the thickness of compound layer was around 2 µm.
Figure 4.55 Bright-field TEM image of cross section of plasma nitrided Ti-6Al-4V alloy (600°C for 24 hours). The enclosed areas are the locations where closer observation at higher magnifications was performed................................................................. 194

Figure 4.56 Higher magnification bright-field TEM images of locations marked as “a” and “b” in Figure 4.55 showing a distinct grain structure in the compound layer within the size range of 480 ± 20 nm, easy to distinguish from that of the diffusion zone whose grain size was around 4 µm. A 5-6 nm thick layer was also revealed on the surface which was characterized by x-ray photoelectron spectroscopy (XPS) analysis....................... 195

Figure 4.57 Bright-field TEM image of the location marked as “c” in Figure 4.55 showing a couple of grains in the compound layer and the corresponding selected area electron diffraction pattern (SAD) indicating presence of TiN (Fm-3m) in the marked region. .............................................................. ................................................... 196

Figure 4.58 A bright-field TEM image of the surface vicinity of the plasma nitrided Ti-6Al-4V alloy and the corresponding selected area electron diffraction pattern (SAD) indicating presence of Ti₂N (P4_2/mmm) in the marked region........................................... ................................................... 196

Figure 4.59 (a) a typical high resolution TEM (HRTEM) image obtained from the compound layer, the enclosed areas are the locations where fast Fourier transform (FFT) patterns were derived. (b), (c) FFT diffraction patterns showing the presence of Ti₂N (P4_2/mmm) in the marked regions. ........................................................................................................ 197

Figure 4.60 A typical bright-field TEM image of the region marked as “d” in Figure 4.55, showing a well bonded compound layer/diffusion zone interface that could not be clearly delineated. ..................................................................................................................... 198

Figure 4.61 Bright-field TEM image of the region marked s “e” in Figure 4.55 and corresponding electron diffraction pattern of α-Ti crystal structure (P63/mmm). .......... 198

Figure 4.62 XPS survey scan with a wide energy range of 0-1100 eV acquired from the plasma nitrided Ti-6Al-4V surface. ..................................................................................................................... 199

Figure 4.63 Glow discharge optical emission spectroscopy (GDOES) atomic concentration profile obtained on plasma nitrided Ti-6Al-4V after a 24 hour treatment at 600°C in a dilute nitrogen atmosphere (3% N₂) showing a high concentration of nitrogen in the compound layer and a slightly higher amount of aluminum at the interface between the compound layer and the diffusion zone. ..................................................................................................................... 199
Figure 4.64 Stress-strain curves of the plasma nitrided and untreated alloys comparing the tensile properties before and after plasma nitriding treatments at two different temperatures of 600˚C and 900˚C. The yield strength (0.2% offset yield) was obtained based on the slope of the elastic region. It was found that the tensile and yield strength of the alloy were not affected by plasma nitriding at 600˚C, however, the ductility (tensile elongation, %) decreased from 13.9 to 7.8. Conversely, plasma nitriding at 900˚C resulted in substantial degradation of strength and ductility of the alloy. ...................... 200

Figure 4.65 Secondary electron images showing the fracture surface of the plasma nitrided Ti-6Al-4V alloy, (a) general morphology showing a cup and cone type of failure, the enclosed areas are the locations where higher magnification images in (b) and (d) were taken, (b) a brittle type of fracture in the surface vicinity, the enclose area is where a higher magnification image in (c) was taken, (c) cleavage surfaces and the formation of microcracks close to the surface, (d) dimpled rupture area indicated in (a). .................. 201

Figure 4.66 (a) Secondary electron image showing circumferential (secondary) cracks on the surface of plasma nitrided alloy (marked by the arrows), the enclosed area is where the higher magnification image in (b) was taken, (b) a higher magnification SEI from the location indicated in (a) showing that the secondary cracks were connected at a 45˚ angle. .......................................................... ................................................... ................................... 202

Figure 4.67 (a) A typical secondary electron SEM image of the cryogenic fracture microstructure of plasma nitrided Ti-6Al-4V (600˚C, 24 hours). The enclosed area is the location where higher magnification image shown in “b” was taken. (b) A secondary electron fractograph revealing the brittle fracture of the compound layer and the presence of lateral microcracks underneath the compound layer. The microcracks propagated parallel to the surface into the diffusion zone. These microcracks were deflected (c) or stopped (d) at β particles in the diffusion zone. ............................................. 204

Figure 4.68 S-N curves illustrating the fatigue behaviour of Ti-6Al-4V alloy before and after plasma nitriding treatment at two different temperatures of 600˚C and 900˚C. The high cycle and low cycle fatigue regions were designated based on 10^5 cycles of loading and the fatigue endurance limit was determined at 10^7 cycles. ................................. 205

Figure 4.69 (a) A secondary electron SEM images (SEI) of the fatigue fracture surface of plasma nitrided alloy at 600˚C tested at 569 MPa, the enclosed areas show the locations where higher magnification images were taken. The fracture surface consisted of a crack initiation site, a smooth area of crack propagation (Region I) followed by a rough propagation area (Region II) and the final rupture. (b) The fatigue crack initiation site on the surface associated with fragmentation and crack formation in the compound layer, (c) higher magnification image of the enclosed area in Figure 4.69-b illustrating striations and signs of plastic deformation in the compound layer, (d) fatigue crack propagation at the location indicated in Figure 4.69-a; a relatively smooth area with striations and
microcracks perpendicular to the crack propagation direction, (e) a higher magnification view of striations at the location indicated in Figure 4.69-d, (f) the dimpled morphology observed in Region II prior to the final rupture.................................206

Figure 4.70 Acoustic emission (AE) signal recorded during the microscratch test was used to study failure phenomena (angular, tensile and transverse cracks) as each and cracking event on the scratch path has an acoustic emission peak associated with it. Angular cracks initiated close to the edges of scratch path at 0.75 N, the tensile cracks formed a second critical normal load of 8 N, and at 15. N angular and tensile cracks combined into semi-circular cracks.................................................................207

Figure 4.71 (a) Variation of the coefficient of friction (COF) with sliding distance for untreated and plasma nitrided Ti-6Al-4V at 600˚C for 24 h. (b) The average COF value for plasma nitrided and untreated Ti-6Al-4V alloy at different applied normal loads.. 208

Figure 4.72 Back-scattered electron SEM images of the scratch track on the surface of plasma nitrided alloy at 600˚C under 0.5 N applied load showing (a) a general view of the scratch track, (b) a high magnification micrograph of a flattened asperity located in the area enclosed in (a) where FIB milling was carried out for cross-sectional analysis. .... 209

Figure 4.73 Back-scattered electron SEM images of the FIB-milled cross section of scratch track at 0.5 N load at the location indicated in Figure 4.72. (a) A general view of the cross section, (b) a high magnification image of the area enclosed in (a) showing the formation of microvoids in the surface vicinity within the compound layer likely at grain boundaries.................................................................210

Figure 4.74 Back-scattered electron images of the scratch track on the surface of plasma nitrided alloy at 600˚C under 1 N applied load showing (a) a general view of the scratch track, (b) a high magnification micrograph of a flattened asperity located in the area enclosed in (a) where FIB milling was carried out for cross-sectional analysis............ 211

Figure 4.75 Back-scattered electron SEM images of the FIB-milled cross section of scratch track at 1 N load at the location indicated in Figure 4.79 showing that the microcracks that initiated from the surface or subsurface microvoids appear to have grown intergranularly in the Compound Layer.................................................................212

Figure 4.76 Back-scattered electron images of the scratch track on the surface of plasma nitrided alloy at 600˚C under 10 N applied load showing (a) a general view of the scratch track, (b) a high magnification micrograph of the area enclosed in (a) where FIB milling was carried out for cross-sectional analysis. The tensile cracks within the scratch track have been marked by arrows........................................................................213
Figure 4.77 Back-scattered electron SEM images of the FIB-milled cross section of scratch track at 10 N load at the location indicated in Figure 4.78. (a) A general view of the cross section, (b) a high magnification image of the area enclosed in (a) showing the propagation of microcracks within the compound layer and into the diffusion zone..... 214

Figure 4.78 Back-scattered electron images of the scratch track on the surface of plasma nitrided alloy at 600°C under 20 N applied load showing (a) a general view of the scratch track, (b) a high magnification micrograph of the area enclosed in (a) where FIB milling was carried out for cross-sectional analysis. The semi-circular cracks within the scratch track have been marked by arrows.............................. 215

Figure 4.79 SEM observations from surface and FIB-milled cross section showed that even at the highest applied load of 20 N in microscratch tests, plasma nitrided Ti-64 surface at 600°C did not experience any spallation. The cracks were stopped at β particles in the diffusion zone........................................................................................................... 216

Figure 4.80 Acoustic emission (AE) output combined with SEM observations of the scratch track on the plasma nitrided surface (900°C, 24 h) showing the onset of asperity fracture at 0.4 N, the formation of tensile cracks at 1.5 N, and buckling at 5.5. N ....... 217

Figure 4.81 Comparison of coefficient vs. sliding distance curves during microscratch tests performed at a constant normal load of 5 N on surfaces that were plasma nitrided at 600°C and 900°C. It can be observed that higher nitriding temperature resulted in higher coefficient of friction value with larger fluctuations. The average coefficient of friction values were 0.05 ± 0.005 and 0.06 ± 0.02 and for 600°C and 900°C treatments, respectively. .................................................................................................................................. 218

Figure 4.82 Back-scattered electron images of the scratch track on the surface of plasma nitrided alloy at 900°C under 1 N applied load showing (a) a general view of the scratch track, (b) a high magnification micrograph of the area enclosed in (a) where FIB milling was carried out for cross-sectional analysis. The microcracks on the surface asperities have been marked by arrows. (Tilt angle: 54°) ................................................................. 219

Figure 4.83 SEM observations of the FIB-milled cross section at the location indicated in Figure 4.82 showing the formation of microcracks parallel to the sliding direction in the compound layer (tilt angle: 54°). .......................................................... 220

Figure 4.84 Back-scattered electron SEM images of the scratch track on the surface of plasma nitrided Ti-6Al-4V alloy at 900°C after a microscratch test at an applied load of 20 N......................................................................................................................... 221
Figure 4.85 SEM observations of the FIB-milled cross section at the location indicated in Figure 4.84 showing the propagation of microcracks perpendicular to the sliding direction in the compound layer likely along grain boundaries (tilt angle: 54˚) ........................................ 222

Figure 4.86 Secondary electron SEM images from wear evolution as the applied normal load was increased: (a) 0.5 N, (b) 1 N, (c) 2 N, and (d) 3 N. Sliding direction and width of wear tracks are marked by arrows in the micrographs. (Sliding velocity: 0.1 m/s, sliding distance: 200 m, tilt angle: 50˚) ................................................................. 223

Figure 4.87 Secondary electron SEM image of the wear track on the surface plasma nitrided coupon after a couple of hundreds of cycles (10 m) at 0.5 N. The insert shows the overall view of the wear track developed (Tilt angle: 50˚) ................................................................. 224

Figure 4.88 Three-dimensional optical profilometry image showing severe deformation and smearing of transferred material from the steel counterface to the plasma nitrided surface .................................................................................................................. 224

Figure 4.89 Cutting chip-like wear debris particles found around the wear track of 0.5 N wear test after 10 m. According to EDS analysis these particles were rich in Fe and Cr. ................................................................................................................................. 225

Figure 4.90 Secondary electron SEM images showing examples of (a) severe deformation as evidenced by abrasion grooves, (b) spallation of the transfer layers formed on the surface of plasma nitrided Ti-6Al-4V alloy during wear tests against AISI 52100 steel counterface at 0.5 N after 200 m. (Sliding speed: 0.1 m/s, tilt angle: 50˚) ................. 225

Figure 4.91 (a) Secondary electron SEM image showing patches of transferred material on the surface of plasma-treated sample after wear test under an applied load of 2 N (tilt angle: 50˚). (b) Typical EDS analysis taken from the transferred layers showing that Fe and O were the main constituents of the transfer layers. .................................................................................................................. 226

Figure 4.92 Back-scattered electron SEM images of (a) cutting chip-like debris, (b) platelets and fine debris particles generated during wear tests at 2 N. (sliding speed: 0.1 m/s) ................................................................................................................................. 226

Figure 4.93 Secondary electron SEM images of (a) the oxide layers accumulated on the plasma nitrided surface at 3 N, (b) fine wear debris particles surrounding the oxide plateaus, (c) severe abrasion and fragmentation of the oxide plateaus. (The sliding direction (SD) is marked by an arrow) ................................................................. 227
Figure 4.94 (a) Three-dimensional optical profilometry image of a patch of oxide layer on the wear track of the plasma nitrided alloy tested at 2 N, (b) shows the same area after immersing the coupon in an aqueous solution containing hydrochloric acid. (c), (d) show secondary electron SEM images taken from the same locations shown in (a) and (b). (e) High magnification views of the locations shown in (c) and (d) indicating that most of the oxide layer was dissolved in the hydrochloric acid solution and the plasma nitrided surface underneath was unaffected by the sliding contact except for minor polishing of the asperity tips. (Sliding speed: 0.1 N, sliding distance: 200 m, tilt angle: 40°) ........... 228

Figure 4.95 Optical micrographs of the wear scars on steel counterface balls tested against plasma nitrided Ti-6Al-4V alloy at (a) 0.5 N, (b) 1 N, (c) 2 N, and (d) 3 N. (sliding distance: 200 m, sliding speed: 0.1 m/s) ........................................................................................................ 229

Figure 4.96 Area of wear scar on steel counterface balls as a function of applied load during wear tests of plasma nitrided Ti-6Al-4V alloy. (Sliding distance: 200 m, sliding speed: 0.1 m/s) ........................................................................................................ 229

Figure 4.97 Variation of volumetric wear (volume of transferred material to the plasma nitrided surfaces during sliding) with applied load during wear tests. (Sliding speed: 0.1 m/s, sliding distance: 200 m) ........................................................................................................ 230

Figure 4.98 Variation of the coefficient of friction with the sliding distance at different applied loads for the plasma nitrided surfaces (600°C, 24 h) tested against AISI 52100 steel counterface balls at 0.1 m/s. ........................................................................................................ 230

Figure 4.99 Variation in coefficient of friction with sliding distance for untreated and plasma nitrided Ti-6Al-4V alloy (600°C, 24 h) tested against AISI 52100 steel counterface balls at 2 N, 0.1 m/s. ........................................................................................................ 231

Figure 4.100 Comparison of average coefficient of friction values in the steady state condition for untreated and plasma nitrided Ti-6Al-4V alloy (600°C, 24 h) tested against AISI 52100 steel counterface under different applied loads at 0.1 m/s. ......................... 231

Figure 4.101 Back-scattered electron SEM micrographs of the worn surface of plasma nitrided Ti-6Al-4V tested against alumina counterface balls at 2 N, 0.01 m/s for 200 m. (a) General morphology of the wear track, (b) a high magnification view showing that the worn surface consisted of dark grey patches in a light grey background and the formation of cracks perpendicular to the sliding direction. The EDS analysis indicated that presence of Al, Ti, N and O elements on the worn surfaces, however, the dark grey regions were richer in Al and O. ........................................................................................................ 232
Figure 4.102 (a) Back-scattered and (b) secondary electron SEM micrographs of the wear track on the surface of plasma nitrided Ti-6Al-4V tested against alumina counterface balls at 10 N, 0.01 m/s for 200 m. The enclosed areas marked as “1” and “2” are the location were higher magnification images were taken................................................. 233

Figure 4.103 Secondary electron SEM micrographs showing different features on the wear tracks of plasma nitrided Ti-6Al-4V tested at 10 N against alumina counterface. (a) Severe plastic deformation and abrasion in the region marked as “2” in Figure 4.102. (b) The formation and removal of plateaus on the surface in the region marked as “1” in Figure 4.102. (c) The formation of microcracks perpendicular to the sliding direction on the plateaus in the region marked as “1” in Figure 4.102................................................................. 234

Figure 4.104 Secondary electron SEM micrographs of the different wear debris morphologies generated after wear tests of plasma nitrided Ti-6Al-4V against alumina at 10 N, 0.01 m/s. (a) Platelet debris, (b) cutting chip-like and fine debris......................... 234

Figure 4.105 (a) Secondary and (b) back-scattered electron SEM micrographs of the wear track on the surface of untreated Ti-6Al-4V tested against alumina counterface balls at 10 N, 0.01 m/s for 200 m. The enclosed areas marked as “1” and “2” are the location were higher magnification images were taken................................................................. 235

Figure 4.106 Secondary electron SEM micrographs showing different features on the wear tracks of untreated Ti-6Al-4V tested at 10 N against alumina counterface. (a) Severe plastic deformation and abrasion in the region marked as “1” in Figure 4.105. (b) High magnification view of the enclosed area in (a) showing the formation of microcrack perpendicular to the sliding direction as well as fracture and removal of part of the surface. (c) The formation of plateaus on the surface in the region marked as “2” in Figure 4.105................................................................. 236

Figure 4.107 Secondary electron SEM micrographs showing different wear debris morphologies generated after wear tests of untreated Ti-6Al-4V against alumina at 10 N, 0.01 m/s. (a) Platelet debris, (b) cutting chip-like and fine debris................................. 236

Figure 4.108 Typical (a) Three-dimensional and (b) two-dimensional optical surface profilometry images of the worn surfaces on plasma nitrided Ti-6Al-4V tested at 5 N showing flattening and polishing wear of the surface asperities. ......................... 237

Figure 4.109 Typical (a) Three-dimensional and (b) two-dimensional optical surface profilometry images of the worn surfaces on plasma nitrided Ti-6Al-4V tested at 10 N showing removal of the compound layer and some part of the diffusion zone. .............. 237
Figure 4.110 Typical two-dimensional profiles of the worn surfaces on plasma nitrided and untreated Ti-6Al-4V tested at 10 N showing a deeper and wider wear track on the surface of the untreated alloy. .................................................. 238

Figure 4.111 Variation of coefficient of friction (COF) with sliding distance during ball-on-disk wear tests on plasma nitrided surfaces against sapphire counterface at 0.01 m/s. .................................................. 238

Figure 4.112 Variation of coefficient of friction (COF) with sliding distance during ball-on-disk wear tests on plasma nitrided and untreated Ti-6Al-4V surfaces against alumina counterface at 10 N and 0.01 m/s.................. 239

Figure 4.113 Secondary electron SEM micrographs of the cross section of wear track on plasma nitrided Ti-6Al-4V alloy tested at 10 N. (a) A general view of the cross section, (b) a higher magnification view of the location shown in (a) exhibiting the formation of a mechanically mixed layer (MML) on the surface after the wear test and severe plastic deformation underneath the MML as evidenced by the elongation of $\beta$ particles.......... 239

Figure 4.114 A secondary electron SEM micrograph of the cross section of the wear track on the plasma nitrided Ti-6Al-4V tested at 10 N. A mechanically mixed layer (MML) was formed on the surface after the wear tests. Underneath the MML, the Ti-6Al-4V substrate was severely deformed as evidenced by the elongation of the beta particles. Another notable feature are the microvoids nucleation and coalescence in the subsurface region likely evidence of the formation of shear bands during the wear test. .................. 240

Figure 4.115 Secondary electron images (SEI) from the surface of a Ti-6Al-4V coupon (a) before and (b) after shot peening. (a) The as-received microstructure contains equiaxed $\alpha$ grains with fine recrystallized $\beta$ particles and retained $\beta$ particles at grain boundaries (marked by the arrows). The $\alpha$ grains can be differentiated by the different orientation of recrystallized $\beta$ particles inside each grain. (b) The surface of shot peened samples after polishing contained no remnant oxide phases or contaminants. The severe plastic deformation was evidenced by the abundance of deformation bands and twins inside the $\alpha$ grains as marked by the arrows (Etched in glycerol + HF (1:1) solution). . 241

Figure 4.116 The distribution of $\alpha$ grain size on the surface of Ti-6Al-4V coupons before and after shot peening. The measurements were made based on SEM observations. .... 241

Figure 4.117 (a) Cross-sectional secondary electron image (SEI) of the shot-peened alloy. The severe plastic deformation (SPD) and twinning regions have been marked in the image. The bulk microstructure consisted of equiaxed $\alpha$ grains with fine recrystallized $\beta$ particles and retained $\beta$ particles at grain boundaries. The enclosed areas are the locations
where higher magnification images in (b)-(d) have been taken. (b) Extensive plastic deformation in the SPD layer (~ 5 µm thick) was evidenced by elongation of the intergranular β particles parallel to the shot peened surface. (c) Below the SPD layer, plastic deformation was dominated by multiple twinning to a depth of ~ 20 µm. (d) Farther from the surface only single-system twinning was observed.

Figure 4.118 A secondary electron image (SEI) from surface morphology of untreated Ti-6Al-4V coupon after plasma nitriding (600°C, 24 h, 6% N₂-balance H₂). Conical features were developed on the surface after the nitriding treatment (tilt angle: 45°).

Figure 4.119 Cross-sectional secondary electron images (SEI) images after plasma nitriding at 600°C, for 24 h in a 6%N₂-balance H₂ atmosphere (a) with the shot peening pretreatment and (b) without the shot peening pretreatment. A compound layer was formed on top of a diffusion zone by the nitriding treatment. The diffusion zone was delineated by the dissolution of fine recrystallized β particles inside the α grains. A deeper DZ was formed in the SP-PN sample and the mechanical twins were also observed in this sample. An electroless Ni coating was applied to protect the surface features from mechanical damage during the metallographic preparation of cross sections.

Figure 4.120 Microhardness-depth profiles for the plasma nitrided Ti-6Al-4V with the shot peening pretreatment (SP-PN) and without the shot peening pretreatment (PN). A deeper diffusion zone with higher hardness values in the SP-PN sample indicated that shot peening pretreatment resulted in enhanced diffusion of nitrogen interstitial atoms. The microhardness values were obtained by microindentations made at a maximum normal load of 245 mN using a diamond Vickers indenter.

Figure 4.121 (a) A cross-sectional bright field (BF) TEM micrograph showing the near-surface microstructure of plasma nitrided Ti-6Al-4V alloy with the shot peening pretreatment. The enclosed area shows the region where high magnification TEM images in have been taken. (b) A cross-sectional scanning transmission electron micrograph (STEM) from the same location in (a) showing the compound layer/diffusion zone interface. The compound layer was distinguished by its distinctive texture and finer grain size.

Figure 4.122 (a) Across-sectional bright field (BF) TEM micrograph showing subgrains and dislocations in the diffusion zone of the pretrated plasma nitrided alloy. The grain marked by “x” is the location where selected area electron diffraction pattern (SAD) was taken. (b) SAD pattern from the marked region in (a) indicating reflections from the α-Ti structure. (c) BF TEM micrograph from micro-twinning inside one of the grains in the diffusion zone. The images were taken from approximately 5 µm below the nitrided surface.
Figure 4.123 (a) A cross-sectional bright field (BF) TEM micrograph from the near surface of pretreated plasma nitrided alloy; the marked regions show the locations where higher magnification images were taken, (b) grain morphology of the compound layer inner layer, (c) nanograins in the compound layer outer layer, (d) a selected area electron diffraction (SAD) pattern corresponding to tetragonal Ti2N phase in the compound layer inner layer shown in (b), (e) SAD pattern corresponding to the FCC rings of TiN structure in the compound layer outer layer shown in (c) ............................................ 248

Figure 4.124 A cross-sectional bright field (BF) TEM micrograph illustrating the grain morphology of the compound layer and diffusion zone in the plasma nitrided alloy without shot peening pretreatment (PN sample). The compound layer/diffusion zone interface has been delineated based on corresponding electron energy loss spectroscopy (EELS) maps. The present phases were identified by electron diffraction patterns from the marked location. (b) A selected area electron diffraction pattern from the marked region in (a) showing reflections from both TiN and Ti2N crystals. .............................. 249

Figure 4.125 X-ray diffraction (XRD) spectra from the plasma nitrided surfaces with the shot peening pretreatment (SP-PN) and without the pretreatment (PN). A higher contribution of Ti2N and α-Ti phases was observed in the SP-PN sample. The lower intensity of TiN peaks may be due to their nano-scale grain size. ................................................. 250

Figure 4.126 Two dimensional optical profiles from scratch tracks on the plasma nitrided Ti-6Al-4V surface with the shot peening pretreatment (SP-PN) and without the pretreatment (PN) after single-pass microscratch tests at 10 N. Wider and deeper scratches were formed on the plasma nitrided surfaces without the pretreatment (PN) under the same testing conditions. ................................................................. 251

Figure 4.127 Scratch hardness values for plasma nitrided surfaces with the shot peening pretreatment (SP-PN) and without the pretreatment (PN) as a function of applied load measured by microscratch tests. The results are based on single-pass microscratch tests performed at 5 N, 10 N, and 20 N at a loading rate of 10 N/min and sliding speed of 1 mm/min. The shot peening pretreatment resulted in higher scratch hardness values especially at lower loads (e.g., 5 N) where the contribution of subsurface deformation on the hardness value is minimal................................................................. 251

Figure 4.128 Acoustic emission signals plotted against sliding distance during the microscratch tests on (a) plasma nitrided surface without the shot peening pretreatment (PN), (b) plasma nitrided surface with the shot peening pretreatment (SP-PN). The large pulses of acoustic emission that are observed in the PN sample after two sliding passes indicate damage to the coating and coating failure. The results are based on multiple pass (five sliding passes) microscratch tests performed at 20 N at a loading rate of 10 N/min and sliding speed of 1 mm/min................................................................. 252
Figure 4.129 (a) A secondary electron image (SEI) from the scratch track on the surface of plasma nitrided alloy with the shot peening pretreatment (SP-PN) after multiple-pass (five sliding passes) microscratch test at 20 N. Angular and transverse microcracks were the only failures observed and no delamination was detected. The marked regions at the rim and in the middle of the scratch track are the locations where higher magnification images were taken, (b) a SEI from angular cracks at the rim of the scratch track at the location indicated in (a), (c) a SEI from transverse cracks in the middle of the scratch track at the location indicated in (a). ................................................................. 253

Figure 4.130 (a) A secondary electron image (SEI) from the scratch track on the surface of plasma nitrided alloy without the pretreatment (PN) after multiple-pass (five sliding passes) microscratch test at 20 N. In addition to angular and transverse microcracks, occasional chipping of the compound layer was detected around the scratch track rims. The marked regions are the locations where higher magnification images were taken, (b) a SEI showing cracks in the compound layer in the direction parallel to the scratch direction at the location indicated in (a), (c) a SEI from chipping of the compound layer at the scratch track rim at the location indicated in (a). ........................................... ....... 254

Figure 4.131 (a) A typical back-scattered electron SEM image of the wear track on the surface of plasma nitrided Ti-6Al-4V alloy at 2 N, 0.005 m/s showing generation of patches of material on the surface, (b) A high magnification image of one of these patches at the location marked on (a), (c) energy dispersive spectroscopy (EDS) pattern obtained from the location marked on (c) showing the presence of Al, O, Ti, and N elements. ................................................................. ................. 255

Figure 4.132 (a) Back-scattered electron SEM micrograph of the wear track on the surface of SP-PN sample (plasma nitrided with the shot peening pretreatment) tested against alumina counterface at 5 N, 0.005 m/s for 10 m (2000 cycles), the enclosed area is the location where higher magnification image was taken, (b) a higher magnification view of the area marked in (a) showing the occasional formation of microcracks inside the wear tracks (Tilt angle: 45˚). (c) Energy dispersive x-ray spectroscopy (EDS) spectrum obtained from the location marked as “1” in (b) showing that the light grey areas on the wear track consisted of Ti, N and Al elements. (d) EDS spectrum obtained from the location marked as “2” in (b) showing the abundance of O in the dark grey areas on the wear track in addition to Ti, N and Al elements. .............................................. ... 256

Figure 4.133 A secondary electron SEM micrograph showing the debris generated on the surface of SP-PN sample (plasma nitrided with the shot peening pretreatment) during wear test against alumina counterface at 5 N, 0.005 m/s for 10 m (2000 cycles) (Tilt angle: 45˚). The debris particles were infrequently observed after the wear test and the EDS analysis showed presence of Ti, Al, N and O elements in these particles. ........... 257
Figure 4.134 (a) Secondary electron, (b) back-scattered electron SEM micrographs of the wear track on the surface of PN sample (plasma nitrided without the shot peening pretreatment) tested against alumina counterface at 5 N, 0.005 m/s for 10 m (2000 cycles). The enclosed areas are the locations were higher magnification images were taken. (Tilt angle: 45˚) ............................................................ 257

Figure 4.135 Secondary electron SEM micrographs of the locations marked in Figure 4.134-a showing (a) the delamination of the mechanically mixed layer and (b) the abrasion grooves on the worn surface of PN (plasma nitrided without shot peening) sample tested against alumina counterface at 5 N, 0.005 m/s for 10 m (2000 cycles)(Tilt angle: 45˚). ........................................ ............................. 258

Figure 4.136 (a) A secondary electron SEM micrograph of the worn surface on the PN (plasma nitrided without the shot peening pretreatment) sample tested against alumina counterface at 5 N, 0.01 m/s for 10 m (2000 cycles). (b) The abrasion grooves (marked by arrows) and wear debris particles (enclosed area) on the worn surface (Tilt angle: 45˚). (c) Energy dispersive x-ray spectroscopy (EDS) pattern obtained from wear debris showing presence of N, O, Ti and V elements. .......................................................... 259

Figure 4.137 (a) A typical secondary electron SEM micrograph of the worn surface on the SP-PN (plasma nitrided with the shot peening pretreatment) surface tested against alumina counterface at 5 N applied load, 0.01 m/s sliding distance for 10 m (2000 cycles). (b) A back-scattered electron SEM micrograph of the wear track at a higher magnification showing existence of a mechanically mixed layer. The enclosed area is the location where the energy dispersive x-ray spectroscopy (EDS) pattern shown in “c” was taken. (c) The EDS pattern obtained from the enclosed area in “b” indicating a high contribution of O and the presence of N, Ti and V elements. .................................................. 260

Figure 4.138 Variation of coefficient of friction (COF) with applied load obtained by ball-on-disk wear tests on plasma nitrided Ti-6Al-4V alloy with and without shot peening pretreatment against alumina counterface balls (3 mm diameter) at 0.005 m/s. ........... 261

Figure 5. 1 A schematic illustration indicated estimated nitrogen concentration in the surface vicinity based on the Fick’s law and microhardness measurements. ................. 288

Figure 5. 2 A FIB cross-sectional view of a tensile crack formed on the surface of plasma nitrided Ti-10V-2Fe-3Al alloy (a near-β titanium alloy) during microscratch test at 10 N applied load. (b) Corresponding EDS maps used to identify the different phases present in “a”; the β particles were differentiated by abundance of vanadium and the compound
layer by the absence of aluminum. The plasma nitriding was performed at 600°C for 24 h in an atmosphere of 3% N₂-balance H₂ ................................................................. 289

Figure 5. 3 Stress-life (S-N) curves showing the effect of plasma nitriding on fatigue behaviour of Ti–6Al–4V alloy. It was also found that the fatigue data of nitried samples fell into the S-N curve of untreated Ti–6Al–4V alloy after polishing the surfaces ....... 290

Figure 5. 4 Secondary electron SEM images (SEI) showing (a) a general view of the fatigue fracture surface (tested at 728 MPa) of the plasma nitrided alloy after the compound layer was partially polished. (b) No evidence of cleavage facets or brittle failure of the compound layer were observed at the crack initiation site originating from the surface. The enclosed regions show the presence of slip steps inside the grains close to the crack initiation site. Crack propagation was accompanied by the formation of (c) striations and microcracks perpendicular to the crack growth direction which gradually transformed to (d) dimples close to the final rupture region. ........................................ 291

Figure 5. 5 Comparison of fatigue data obtained for plasma nitried Ti–6Al–4V alloy in this investigation compared to the conventional plasma and gas nitriding of the alloy by several researchers [161, 261-263]. .................................................. 292

Figure 5. 6 Secondary electron SEM micrographs of the fracture surface of Ti-6Al-4V alloy plasma nitrided at 900°C. (a) General morphology of the fracture surface, (b) brittle fracture and fragmentation of the compound layer at the crack initiation site, (c) farspaced striations in the diffusion zone revealing fast crack propagation in this region, (d) striations in different orientations and planes indicating rapid fatigue crack growth due to large grain size, (e) dimples observed in the middle area indicating that the cracks initiated circumferentially and propagated towards the center. ...................................... 293

Figure 5. 7 Coefficient of friction variation with distance at the initial stage of sliding. Ball-on-disk tests on Ti-6Al-4V against AISI 52100 steel at different applied normal loads ..... 294

xxxvi
LIST OF ABBREVIATIONS/SYMBOLS

AC  Air cooled
AES Auger electron spectroscopy
AFM Atomic Force Microscopy
BCC Body centered cubic
BSE Backscattered electron
BSI Backscattered electron scanning electron microscopy image
COF Coefficient of friction
CP Commercially pure
EDM Electrical discharge machine
EDS Energy dispersive x-ray spectroscopy
EELS Electron energy loss spectroscopy
ELI Extra low interstitial
FC Furnace cooled
FCC Face centered cubic
FFT Fast Fourier transform
FIB Focused ion beam
GDOES Glow discharge optical emission spectroscopy
HCF High cycle fatigue
HCP Hexagonal close packed
HV-TPN High voltage triode plasma nitriding
LCF Low cycle fatigue
LV-TPN Low voltage triode plasma nitriding
MML Mechanically mixed layer
N Number of cycles to failure
PSI Phase shift interference
PVD Physical vapor deposition
R_\text{a} Average roughness
R_\text{q} Root mean square roughness
R_\text{t} Maximum peak to valley height
R_\text{v} Average valley depth
RMS Root mean square roughness
RPM Revolutions per minute
SAD Selected area electron diffraction
SEI Secondary electron scanning electron microscopy image
SE Secondary electron
SEM Scanning electron microscopy
SPD Severe plastic deformation
STA Solution treated and aged
STEM Scanning transmission electron microscopy
TEM Transmission electron microscopy
TTS Tribologically transformed structure
VSI Vertical shift interference
WQ Water quenched
XPS X-ray photoelectron spectroscopy
XRD X-ray diffraction
CHAPTER 1: INTRODUCTION

1.1 Background and Motivation

In the history of replacing steels with lightweight materials in aerospace, automotive and biomedical sectors, titanium alloys have received considerable attention. These alloys exhibit a high strength-to-weight ratio, corrosion/oxidation resistance, stability at elevated temperatures, and fatigue resistance. Nevertheless, poor wear resistance restricts their application for components subjected to sliding contact. Unfortunately, the surface engineering techniques that are in place to improve the tribological properties of Ti alloys, e.g., nitriding, adversely influence other mechanical properties such as the fatigue endurance limit. Nitriding improves friction and wear resistance of Ti alloys by the formation of a thin layer composed of TiN and Ti$_2$N titanium nitrides, i.e., a compound layer, on the surface. The nitried microstructure also consists of a region of nitrogen-stabilized α titanium, the α-case, and a nitrogen diffusion zone underneath the compound layer. The brittle nature of the compound layer and α-case and the high stiffness gradient at the interface with the Ti substrate, promote premature failures commencing from the surface. Moreover, since conventional nitriding treatments are carried out at elevated temperatures (750-1100°C), they are usually accompanied by grain growth and microstructural transformations in the substrate, which have a seriously deleterious effect on the mechanical properties especially the fatigue strength.
Until recently, no controlled studies have been found for the modification of nitriding treatments for titanium alloys with the aim of simultaneous wear resistance and fatigue strength improvements. Therefore, this investigation sets out to design a surface treatment for Ti-6Al-4V, the most widely-used titanium alloy, based on plasma nitriding treatment to improve its performance under sliding contact and cyclic loading conditions. Thus, this study provides a major contribution to research in the field of surface engineering of titanium alloys by providing an insight into the microstructure-property relationship of the plasma nitrided alloys.

1.2 Objectives

The general objectives of this thesis were to:

- Improve the fatigue performance of the plasma nitrided Ti-6Al-4V alloy by optimization of the nitriding treatment parameters while maintaining enhanced tribological properties (wear rate and coefficient of friction).
- Investigate the effect of plasma nitriding parameters (duration, temperature, gas composition and pressure, etc.) on the microstructure.
- Understand the micromechanisms of crack initiation and propagation in the plasma nitrided microstructures under sliding contact (wear) and cyclic loading (fatigue) conditions.
- Study the microstructure-property relationship in plasma nitrided Ti-6Al-4V in order to find new approaches to improve the fatigue strength of the nitrided alloy and reduce its wear and coefficient of friction by tailoring the microstructure.
The methodology that was adopted in order to achieve these objectives is shown in Figure 1.1.

1.3 Scope

The overall structure of the study takes the form of seven chapters, including the Introduction. The second chapter includes a review of the literature on the tribological and fatigue properties of titanium alloys, especially Ti-6Al-4V alloy. The surface engineering techniques for reduction of wear rate and coefficient of friction of titanium alloys and the fundamentals of plasma nitriding are reviewed. Subsequently, the effect of nitriding treatments, with a special focus on plasma nitriding, on the microstructure, mechanical properties and tribological behaviour of titanium alloys are discussed; and the controversy over the effect of nitriding on fatigue properties is covered.

Chapter 3 is concerned with the adopted methodology and testing methods used for this study. The fourth chapter presents the experimental results of the research on microstructural analyses, sliding tests (microscratch and wear tests) and mechanical properties (tensile and fatigue). Chapter 5 discusses the results and Chapter 6 presents a brief summary of the findings. Finally, Chapter 7 points out some future research directions.
Figure 1. The research methodology flowchart illustrating the different steps that were followed to optimize the plasma nitriding treatment for simultaneous improvements in the fatigue strength and wear resistance of Ti-6Al-4V alloy.
CHAPTER 2: LITERATURE SURVEY

2.1 Titanium Alloys

Titanium is a lightweight element — with a density of 4.6 g/cm$^3$ that is between 40-50% lower than that of iron and nickel — that can be strengthened through additions of alloying elements and deformation processing routes. Pure titanium has two allotropic forms of body-centered cubic (β phase) and hexagonal close-packed (α phase) crystal structures. The β phase which is stable at higher temperatures has an allotropic phase transformation to the α phase at 882˚C. The allotropic transformation in titanium is strongly influenced by alloying elements; elements like aluminum, boron, oxygen, and nitrogen increase the β-transus temperature and are referred to as α stabilizing elements. Conversely, β stabilizing elements decrease the β-transus temperature and stabilize the β phase at room temperature either by eutectoid transformations (iron, and hydrogen) or by the formation of solid solutions (vanadium, molybdenum, and niobium). Elements such as zirconium, hafnium and tin have insignificant effects on the α/β transformation and are generally considered as neutral elements in titanium.

The unit cell parameters of the α phase are a=0.295 nm and c=0.468 nm resulting in a c/a ratio of 1.5871 which is smaller than the ideal value of 1.633 for HCP crystal structures. The main plastic deformation modes of the α phase are slip of dislocations and deformation twinning. In α phase titanium slip deformation occurs along a total of 12 slip systems in $\langle 0002 \rangle$ basal plane, $\{10\bar{1}0\}$ prismatic planes, $\{10\bar{1}1\}$ pyramidal planes along $\langle 11\bar{2}0 \rangle$ densely-packed directions (Figure 2.1). The β titanium crystal structure has a
lattice parameter of 0.3306 nm at 900°C. The deformation slip systems in β titanium are similar to all BCC metals, namely \{110\}, \{112\} and \{123\} with \{111\} Burgers vector.

Titanium alloys are classified as α, β and α+β alloys based on the alloying elements and phases present in their microstructure. The family of α and near-α titanium alloys are single-phase α alloys and may contain a small β phase content (2-5 vol.%). These alloys are known for their high temperature stability and corrosion resistance; however, their microstructures cannot be modified by heat treatments. Commercially pure (CP) titanium, Ti-5Al-2.5Sn, Ti-3Al-2.5Sn, Ti-8Al-1Mo-1V, and Ti-6Al-2Sn-4Zr-2Mo are some of the commercial alloys in this group.

The family of α+β titanium alloys contain a combination of α and β stabilizing elements and can be heat-treated to achieve a wide range of microstructures and properties. Ti-6Al-4V, the most widely used titanium alloy, Ti-3Al-2.5V, Ti-6Al-2Sn-4Zr-6Mo, Ti-6Al-6V-2Sn, and Ti-4Al-4Mo-4Sn-0.5Si are some α+β alloys in this group.

The class of meta-stable β titanium alloys contain sufficient β stabilizing elements to retain a fully β phase microstructure at room temperature. These alloys exhibit excellent hardenability, formability and their microstructures can be tailored to achieve high levels of strength and ductility. Ti-13V-11Cr-3Al, Ti-10V-2Fe-3Al, Ti-11.5Mo-6Zr-4.5Sn (Beta III), and Ti-3Al-8V-6Cr-4Zr-4Mo (Beta-C) are some commonly used alloys in this group.
2.2 Ti-6Al-4V Alloy

Many titanium alloys have been designed and developed. However, to date Ti–6Al–4V is the most popular titanium alloy due to a combination of outstanding properties and ease of fabrication [1]. Ti–6Al–4V has a high specific strength, good fatigue and corrosion resistance and biocompatibility and is stable at temperatures up to 400°C. The extra low interstitial (ELI) grade of Ti–6Al–4V is fabricated with low concentrations of oxygen and iron for applications where higher fracture toughness and damage tolerance especially at cryogenic temperatures are needed [2]. The aluminum and vanadium contents in the chemical composition may reach 6.75% and 4.5%, respectively. However, it should be noted that although higher contents of aluminum result in higher strength levels, they tend to decrease the ductility, fracture toughness and stress corrosion resistance especially by precipitation of coherent fine Ti₃Al (α₂) particles (with an ordered hexagonal DO₁₉ structure) within the α phase.

The aerospace applications of Ti–6Al–4V include engine and airframe components, e.g., blades, discs, wheels, etc. [3]. In automotive industry it is mainly used in high-performance cars for engine parts, boy parts and fittings, e.g., valves, valve springs, connecting rods, rocker arms [4]. This alloy is also extensively used in surgical implants, sonar equipment, hydrofoils, water-jet inducers, seawater ball valves for nuclear submarines.

2.2.1 Microstructural Development in Ti-6Al-4V Alloy

A wide range of properties can be achieved in Ti-6Al-4V alloy by tailoring its microstructure through various heat treatments and thermo-mechanical processing routes.
[5, 6]. Similar to other $\alpha+\beta$ titanium alloys, three different microstructures of fully lamellar, fully equiaxed, and bimodal (duplex) can be obtained in Ti-6Al-4V alloy. The evolution of microstructural features depends on prior deformation history of the alloy (degree, time and temperature), annealing time and temperature, cooling rate and ageing conditions [7, 8]. The effect of annealing time, temperature and cooling rate are schematically shown in the pseudo-binary phase diagram in Figure 2.2.

2.2.1.1 Lamellar Microstructures

Lamellar ($\beta$-annealed) microstructures develop upon cooling from temperatures above the $\beta$-transus temperature (995°C for Ti-6Al-4V, 975°C for Ti-6Al-4V, ELI grade). To have a better control over the $\beta$ grain size, alloys are kept 30-50°C above the $\beta$-transus temperature. The cooling rate from the $\beta$ phase field determines the size of $\alpha$ colonies, width of $\alpha$ lamellae and thickness of $\alpha$ layers at grain boundaries.

Lamellar microstructures form by a nucleation and growth mechanism and their structure varies from a colony of crystallographically-aligned $\alpha$ laths (Figure 2.3-a) to basket-weave arrangements (Figure 2.3-b) upon increasing the cooling rate. At cooling rates less than a critical value (~1000°C/min), the $\beta$ phase undergoes a martensite transformation resulting in the formation of a needle-like microstructure (Figure 2.3-c). The mechanical properties of $\beta$-annealed microstructures are strongly related to the $\alpha$ colony size because it determines the effective slip length. Although each colony is composed of $\alpha$ laths (HCP crystal structure) in a matrix of $\beta$ phase (BCC crystal structure), slip transfers across the $\alpha/\beta$ interface in colonies with common prior $\beta$ grain origin since the slip systems are either parallel or closely related to each other [9].
The β-annealed microstructures generally exhibit a high damage tolerance, and with increasing the cooling rate from the β phase field the yield strength increases and the ductility decreased due to decreased slip length. However, significantly high yield strengths and low levels of ductility at cooling rates exceeding 800°C/min correspond to martensite microstructures in which the effective slip length is equal to the width of an individual α plate. It should also be noted that the maximum ductility is associated with the change in fracture mode from a ductile transcry stalline type of fracture at low cooling rates to a ductile inter-crystalline along α/β grain boundaries at higher cooling rates (Figure 2.4).

2.2.1.2 Bimodal microstructures

Bimodal (duplex) microstructures result from recrystallization in the α+β phase field, prior to which a deformation stage in the dual phase region is necessary. This microstructure consists of equiaxed primary α grains (α_p) in a matrix of transformed β (Figure 2.5). When the volume fraction of α_p is high (>50 vol.%) these grains start to interconnect. The most influential processing parameters for these microstructures are the recrystallization temperature (between 800-850°C for Ti-6Al-4V) and cooling rate which determine the volume fraction of equiaxed primary α grains and the morphology of transformed β matrix [10]. Mechanical properties of bimodal microstructures are dominated by the grain size and alloying element partitioning. Generally since the α colony size of bimodal structures and hence their effective slip length is much smaller than the lamellar structures, they exhibit higher ductility and yield strength at a constant cooling rate. Alloying element partitioning increases with volume fraction of α_p and
reduces the strength of lamellar regions compared to a fully lamellar structure. At low volume fractions of $\alpha_p$ (10-20 vol.%) and high temperatures (~600°C), $\alpha$ colony size has a greater influence and at large volume fractions of $\alpha_p$, alloying element partitioning effect is dominant. Overall, bimodal microstructures show improved ductility and yield stress compared to fully lamellar microstructure due to the pronounced effect of reduced slip length.

### 2.2.1.3 Equiaxed microstructures

Bimodal structures containing more than 50 vol. % of $\alpha_p$ develop interconnected $\alpha$ phase regions with $\beta$ particles at grain boundary triple points and are referred to as equiaxed microstructures. One of the proposed mechanisms for the formation of fully equiaxed microstructures states that during recrystallization annealing at low temperatures (800-850°C), the $\alpha$ phase penetrates through the and $\beta/\beta$ grain boundaries, resulting in a microstructure composed of incompletely recrystallized $\alpha$ and a small volume fraction of fine globular $\beta$ particles. Another possible processing route is when the cooling rate from the $\alpha+\beta$ recrystallization temperature is sufficiently low that instead of $\alpha$ lamellae, $\alpha_p$ grains form inside the $\beta$ grains. A general-purpose treatment given to Ti-6Al-4V alloy is mill annealing; which results in the formation of an equiaxed microstructure. This treatment consists of a hot working step in the $\alpha+\beta$ temperature region, followed by annealing at 700°C for 30 min to several hours and air cooling. Since this is not a full anneal, the structure may contain traces of the deformation step [1]. Details of typical commercial heat treatment procedures for Ti-6Al-4V alloy are tabulated in Table 2.1.
Medical and biomedical sectors have greatly appreciated biocompatibility, corrosion resistance and low modulus of elasticity of titanium alloys in surgical implants and artificial body components, e.g., components of dental, knee and hip replacements, heart valve stents, etc. [11, 12]. In automotive industry, considerable reduction in weight and fuel consumption can be achieved by replacing steels with titanium alloys, however, challenges are encountered in mass-produced vehicles due to considerable costs of raw material and fabrication. Titanium alloys have also found applications in sporting goods and consumer products such as eyeglasses frames, cameras, jewelry, etc. [13, 14].
2.3 Fatigue Behaviour of Titanium Alloys

The nucleation and propagation of fatigue cracks in titanium alloys are highly dependent on their microstructural features [15]. Since the focus of this research is Ti-6Al-4V alloy, this section summarizes the fatigue behaviour of α+β titanium alloys with respect to the microstructural effects.

In lamellar microstructures, microcracks nucleate from the slip bands in the α colonies, or at the intersection of the slip bands and prior β boundaries. In martensite microstructures, fatigue cracks may initiate α plates with higher width or length. Microcracks grow along persistent slip bands and extend over a few grain diameters before the long fatigue crack growth stage. As the crack size increases, the propagation rate slows down because the crack front will encounter more and stronger microstructural obstacles. Thus, the propagation rate is function of in-plane obstacles and crack front profile and is different for coarse and fine structures [16].

When the crack front encounters two adjacent areas with different crystallographic orientations, e.g., two α colonies or two individual martensite plates, it can locally deviate from its propagation plane in the directions of different slip planes in the two adjacent areas. Thus, the crack front becomes bifurcated and local crack tips are separated by a distance which is proportional to the α colony size or width of the martensite plate. Further movement of the bifurcated crack front requires propagation of the two local cracks in unfavourable directions along unfavourably oriented crystallographic planes and the coarser the microstructure the larger the strength of this obstacle.

For α+β titanium alloys at high stress ratios (R=0.7), the crack front geometry overshadows the “ductility” term in describing the microcrack propagation behaviour.
With increasing slip length (α colony size), the crack front roughness increases, crack growth is delayed and $\Delta K_{th}$ is increased. At low stress ratios (R=0.1), crack closure results in higher $\Delta K_{th}$ values and increases with increasing roughness of the fracture surface. Both of these increase with increasing slip length (α colony size) and therefore, for macrocracks at low R-ratios the propagation rate is further lowered [17-19]. In coarse lamellar microstructures microcracks grow rapidly within the slip bands and change paths at colony boundaries and/or β grain boundaries. In fine lamellar structures, a higher density of colony boundaries decreases the propagation rate. In martensite microstructures, each individual martensite plate act as an obstacle and decreases the crack growth rate further.

In the bimodal microstructures fatigue cracks initiate from the lamellar regions at low stress amplitudes since the alloying element partitioning has a more significant effect than the small α colony size. This has been confirmed by experimental results at elevated temperatures (more than 600°C) where bimodal microstructures have an equal or even higher high cycle fatigue strength (HCF) than the fully lamellar microstructures. An intermediate annealing treatment between the bimodal recrystallization and the final aging treatment can eliminate the negative effect of alloying element partitioning. This would give the α-stabilizing elements such as Al and O sufficient time to diffuse from the primary α phase into the lamellar regions. The microcrack propagation rate is slower in bimodal structures compared to fully lamellar structures due to the positive contribution of small α colony size. On the contrary, macrocrack propagation shows an opposite behaviour on account of a rougher crack front profile in fully lamellar structures (Figure 2.6) [18-20].
The fatigue behaviour of fully equiaxed Ti-6Al-4V alloy is dominated by the average α grain size since it determines the effective slip length. Fully equiaxed microstructures possess lower resistance to fatigue crack nucleation and short fatigue crack propagation (HCF strength) compared to bimodal microstructures. The reason is that the fatigue crack nucleates within the α grains in the equiaxed microstructure and propagates through areas of interconnected α grains. Although crystallographic texture is the same for both structures, the slip length is larger in the equiaxed structure due to the interconnected α grains. The long fatigue crack propagation behaviour of the equiaxed and bimodal microstructures follows a similar trend.

Compared to a fully lamellar microstructure\(^1\), the equiaxed microstructure possesses higher resistance to fatigue crack initiation due to the smaller effective slip length and strong influence of the crystallographic texture. The macrocrack front profile is quite smooth in fully equiaxed microstructures and increasing the α grain size results in slower macrocrack propagation rates at both high and low stress ratios [1, 21]. It should be noted that when comparing the HCF behaviour of different α+β titanium alloys, the feasibility of obtaining these microstructures in commercial practice must also be considered. For commercial application, the 6 μm grain size in fully equiaxed condition is very attractive because its HCF strength (around 650 MPa) cannot be easily obtained for fully lamellar or bimodal microstructures.

\(^1\) When the thickness of α plates in lamellar microstructure are equal to the α grain size in equiaxed microstructure.
2.4 Tribological Behaviour of Titanium Alloys

Titanium alloys are renowned for their poor tribological characteristics [22, 23]; their strong tendency to seize and gall under sliding, high and unstable coefficient of friction and high wear rates [24-27]. Severe galling and metal transfer occurs when Ti alloys slide against themselves and other alloys\(^2\), ceramics or even polymers [28-31]. This behaviour is attributed to their low resistance to work hardening and plastic shearing, inability of surface oxides to protect the underlying metal and possibility of microstructural embrittlement by dissolved oxygen [25, 32-34].

One of the fundamental properties that contributes to the strong adhesion tendency and high coefficient of friction of titanium is its electron configuration. The d-valence electron occupation in titanium, like other transition metals, affects many of the physical and chemical properties such as cohesive energy, shear modulus, chemical stability and magnetic properties. Due to its high degree of d-bond unsaturation and thus low value of d-valence character, titanium shows a strong tendency to bond with mating contact surfaces, e.g., metal and non-metal (Figure 2.7) [35-37].

According to Miyoshi et al. [38] there is a strong correlation between the ideal tensile strength of metals, a function of their Young’s modulus, surface energy and interplanar spacing according to \( \sigma_{\text{max}} = \sqrt{\frac{E \gamma}{d}} \), and their adhesion and friction behaviour in contact with non-metals and themselves. Accordingly metals with higher ideal tensile strength tend to have lower coefficients of friction and lower tendency for adhesion.

\(^2\) Except Ag-10Cu alloy and Babbitt metal (grade 2) that showed mild scoring and no galling sliding against Ti-4Al-4Mn alloy.
Titanium has a low elastic modulus and ideal tensile strength and experiences extensive metal transfer and high friction forces under sliding conditions (Figure 2.8).

Crystal structure is another factor which promotes junction growth and poor frictional behaviour of sliding Ti surfaces. As mentioned in section 1, \(\alpha\)-Ti has an HCP structure with three independent slip planes and c/a ratio of 1.588 which is less than the ideal value for closest packing. The low c/a ratio results in activation of non-basal slip planes and the increase in the number of active slip systems promotes extensive plastic deformation and junction growth under sliding contact [39, 40].

The role of surface oxides have on the tribological behaviour of titanium alloys has been investigated extensively in the literature. Oxidation happens almost instantaneously when Ti surfaces are exposed to air but the oxide layer cannot prevent galling and seizure [41]. In fact, the inherent titanium oxide layer is also responsible for impaired adhesion of ordinary lubricants and poor adhesion of electroplated metallic coatings to Ti surfaces [28, 40]. Rabinowicz [42] showed that most of the common lubricants are ineffective when applied to titanium since the bonding between the lubricants and Ti surface is not strong enough to hold the lubricant on the surface. Only halogenated compounds brought a considerable decrease in the friction of titanium, especially those with straight-chained hydrocarbons in which halogen atoms were distributed along the molecular chain rather than the cyclic molecules. Among the halogenated compounds those containing fluorine proved to be more effective probably due to their penetration through the oxide layer and chemical reaction with titanium atoms that held the lubricant on the surface. Unfortunately at heavy loads all the tested lubricants failed to inhibit direct metal-to-metal contact.
Moreover, according to the oxidation-dominated wear theory [43-45], oxide films that form at asperity tips due to frictional heating inhibit direct metal-to-metal contact and adhesion and contribute to mild wear by acting as a boundary lubricant. However, the tribo-oxides that form on the surface of titanium during sliding do not generally provide any adhesion resistance due to their thin (5-10 nm) and brittle nature [36, 46] and the internal stresses that build up in these layers due to volumetric difference and thermal expansion mismatch between the titanium substrate and the oxides [47]. Moreover, the titanium substrate has a low resistance to plastic shearing and work hardening and cannot provide sufficient mechanical support for the thin and weak titanium oxide layer [48, 49].

A more recent investigation by Cui et al. [50] showed that the tribo-oxides that form at higher temperatures (400°C) are thicker and possess higher hardness values compared to those formed in the temperatures range of 20 to 200°C. These oxides in fact exhibited a protective effect during sliding and promoted an oxidation-dominated mild wear regime upon decreasing wear rate and coefficient of friction values.

Molinari et al. [51] performed a series of dry sliding tests on Ti-6Al-4V self-mating surfaces at different applied loads and sliding velocities. They found that hard surface scales were formed on top of plastically-deformed subsurface layers after sliding and the thickness of the layers was affected by the applied load and not the sliding speed. The oxide scale had low activation energy and a very low critical thickness and oxidative wear was dominant at low sliding speeds. Higher loads and sliding speeds increased the surface temperature resulting in dynamic recrystallization and thermal softening of the subsurface and reduction of its yield strength. Subsequently, plate-like debris particles
were formed by nucleation of lateral cracks and propagation parallel to the surface which made delamination wear the predominant mechanism.

In another investigation by Straffelini and Molinari [52], the mechanisms of oxidative and delamination wear were elucidated. They suggested that oxidative wear occurs when surface oxides continuously form and detach at contact asperities, the detached particles consequently compact together and sinter to form oxide scales on the surface. This layer is not tribologically-protective because it is very brittle and not well-supported by the substrate. Therefore, it tends to fragment easily and contribute to high wear rates (Figure 2.9-a). Delamination wear occurs by the formation and removal of hard surface layers also known as mechanically mixed layers (MML) that form under the combined action of intermixing of oxide particles and substrate strain hardening. Underneath the layers a region of plastic deformation extends to around 40 µm (Figure 2.9-b).

Chelliah et al. [53] reported that the oxide layer removal during sliding is facilitated by the formation of adiabatic shear bands at the oxide/metal interface especially at lower sliding speeds. The adiabatic shear banding, localized plastic deformation along certain directions, promotes cracking and delamination of the oxide layers. The effective role of adiabatic shear bands in this wear regime were also previously reported by Kailas et al. [54]. At higher sliding velocities, however, the deleterious effect of adiabatic shear bands was reduced due to higher surface and subsurface temperatures and uniform deformation of the titanium substrate. They found that upon increasing the sliding speed, the wear rate was first decreased and then raised as a result of extensive adhesive and abrasive wear.
The microstructural evolution in the surface layers of Ti-6Al-4V after sliding were studied by Liu et al. [55] and Nutt [56] under vacuum and ambient conditions. Their experimental results showed that severely deformed layers with fine equiaxed grains (50-100 nm) were formed on the surface followed by regions of high dislocation density and micro-twins. Faure et al. [57] showed that frictional heating can raise the surface layer temperature to the $\beta$-transus temperature and result in microstructural phase transformations (Widmanstätten or martensite transformations) in the surface vicinity. They also stated that the rise in surface temperature due to sliding is amplified by the low heat conductivity of titanium alloys. Cryogenic wear experiments by Jain et al. [58] on titanium revealed that the process of surface thermal softening was postponed and a higher density of twins were observed in the subsurface region compared to the room temperature.

The counterface material also plays an important role in the dry sliding wear mechanisms in titanium alloys. Evaluation of the dry sliding wear behaviour of Ti-6Al-4V alloy against AISI M2 steel counterface showed increased wear rates compared to self-mating surfaces at low loads and sliding speeds due to the abrasive action of hard carbides and their role in facilitating the spallation and fragmentation of brittle surface scales. At higher sliding speeds wear rate was lower compared to self-mating surfaces due to the higher thermal conductivity of the steel counterface. Similar observations were reported by Liu et al. [59]. Poletti et al. [60] also investigated the wear and friction behaviour of Ti-6Al-6V-2Sn alloy against AISI 52100 steel counterface at different loads and sliding speeds. They found that the main wear mechanism was adhesion (Figure 2.10). A mild oxidational wear regime was dominant at low loads, however, these oxides
cannot withstand high pressures and their delamination leads to abrasion, high wear rates and high coefficient of friction.

Different wear mechanisms have been detected for Ti-6Al-4V/alumina sliding pairs by Dong et al. [29]. They found that tribochemical wear was predominant at low sliding speeds and applied loads (less than 0.25 m/s, 20 N). They suggested that under these condition the reduction of alumina and the formation of intermetallics such as Ti$_3$Al results in the formation of tribolayer on the surface of alumina. Upon further sliding the tribolayer becomes thicker followed by occurrence of microcracks and partial spallations. At higher loads and sliding speeds, however, the oxidation kinetics of titanium becomes sufficiently high to form titanium oxide layers that act as diffusion barriers between alumina and titanium. Consequently, a wear transition is observed and the wear rate of alumina counterpart is decreased. Another study by Hong et al. [26] on titanium surfaces sliding against alumina revealed that when the tests were carried out at 400°C rutile (TiO$_2$) titanium oxide formed during wear and coefficient of friction was reduced. However, when the tests were carried out at room temperature, the oxide layer, mainly consisting of TiO, was easily detached during wear and contributed to high coefficient of friction.

Ultra high molecular weight polyethylene (UHMWPE) is another non-metal that has been extensively studied as a counterpart for titanium surfaces due to its application in biomedical sector [12, 31, 61, 62]. It has been found that titanium wear rate is strongly related to the surface roughness of the counterface, increasing substantially with the counterface roughness. The titanium oxide surface layer breaks down with the applied load and the exposed titanium adheres to the polymer surface (adhesive wear).
Furthermore, the detached oxide particles either become embedded in the polymer matrix or generate wear debris particles and contribute to abrasive wear [61].

The effect of microstructure on tribological behaviour of titanium alloys has been investigated by several researchers. Takeda et al. [63] investigated the effect of annealing temperature in the $\alpha+\beta$ region on fretting fatigue and sliding wear of workable Ti-4.5Al-3V-2Mo-2Fe alloy. Annealing at temperatures higher than 830°C resulted in precipitation of acicular $\alpha$ particles in $\beta$ phase that grew coarser upon increasing the annealing temperature. Meanwhile hardness increases with the annealing temperature up to 850°C, above which grain growth of $\beta$ phase and coarsening of acicular $\alpha$ result in hardness reduction. Wear rate and coefficient of friction were reported to be higher for alloys annealed at 830°C and 870°C (with lower hardness values) probably due to their soft nature and lower shear strength. Similar results were obtained by Feng et al. [64].

2.5 Surface Treatments for Enhancing Tribological Properties of Titanium Alloys

In order to overcome the poor performance of titanium alloys in sliding conditions, with metallic and non-metallic surfaces, many surface engineering techniques have been attempted and developed. The surface engineering techniques can be broadly classified as coating deposition techniques in which discrete coatings are overlaid on titanium surfaces and thermochemical treatments that involve modifying the surface and subsurface properties by diffusion, heat treatments and chemical reactions [65, 66]. Both classes will be discussed briefly in this section; however, special attention will be given to plasma nitriding treatment that is the main focus of this investigation.
2.5.1 Coating Deposition Techniques

2.5.1.1 Thermal Spray Coatings

Thermal spray coatings are applied by partial or complete melting of a solid rod or powder of metal and/or ceramic and their resolidification on the substrate surface. Plasma spraying, detonation gun, high velocity oxyfuel (HVOF) and vacuum plasma spraying have all been used in deposition of coatings on titanium substrates. For wear protection and resistance against galling and adhesion hard materials such as WC-Co, Mo, Cr-Ni are usually sprayed on titanium substrates. Moreover, the inherent porosity of sprayed coatings has been proven beneficial because it helps retain lubricants and increase service life [67-70].

2.5.1.2 Electroplating and Electroless Plating

A variety of soft and hard metals such as Ag, Cu, Cr, and Ni and their composites with particulate reinforcements and carbon nanotubes have been coated on titanium substrates with electroplating and electroless plating techniques. The inherent oxide film on the surface of titanium alloys is a major challenge in plating since it tends to passivate the surface and a strong interfacial bonding cannot be formed between the coating and substrate. Therefore pretreatment procedures play a critical role and should be followed with due care prior to electro- and electroless plating treatments such as several stages degreasing, abrasive blasting, and surface activations like Wood’s or copper strike [71-76].

22
2.5.1.3 Physical and Chemical Vapour Deposition

Physical vapour deposition (PVD) technique is extensively used to deposit metals, alloys, compounds and other materials on a wide range of substrates. However, higher temperatures may be needed to remove the inherent titanium oxide film from the surface of titanium alloys and establish a good interfacial bonding. Electron beam source and arc source reactive sputtering have been used to deposit TiN films on titanium substrates to improve their tribological properties. Diamond-like carbon (DLC), amorphous diamond-like carbon (ADLC), hydrogenated carbon films (a-C:H) and MoS\textsubscript{2} coatings have also been deposited on titanium substrates for enhanced wear resistance and reduce coefficient of friction. However, it has been established that in order to provide a good coating/substrate adhesion and inhibit premature coating delamination, the substrate should be hardened (e.g., by diffusion treatments) to support the deposited coatings [67, 77-84].

2.5.2 Thermochemical Treatments

Thermochemical processes are used for the modification of surface/subsurface properties and are based on heat treatments, diffusion of interstitial elements, and chemical reactions. The resulting surface microstructure generally consists of hard surface compounds, e.g., oxide, nitride, carbide, etc. and an extended diffusion zone. From the practical point of view, these treatments are divided into two categories of conventional and plasma processes. Conventional treatments are based on mass transfer in solid, liquid or gaseous media whereas in plasma (ion-assisted) treatments the energetic nature of ions, electrons, radicals, and activated species changes the surface
microstructure. The main plasma-based surface treatments are plasma-assisted deposition techniques such as plasma enhanced chemical deposition (CVD), ion beam techniques such as ion implantation and ion beam enhanced deposition, and plasma thermochemical processes such as plasma nitriding, plasma carburizing, etc. Some of the thermochemical treatments extensively used in the manufacturing and machining industries will be discussed here.

2.5.2.1 Ion Implantation

Ion implantation is a line-of-sight treatment based on accelerating ions in an electric field towards a substrate. The collision of high-velocity energetic ions with the atoms on the surface of the substrate knocks them away and they in turn collide with other atoms (collision cascade). This process of ion bombardment creates a layer of lattice damage and a layer rich in the implanted material both having Gaussian distributions. Nitrogen and carbon are the most implanted elements for titanium substrates and the hard implanted surfaces prevent plastic deformation and severe adhesive wear and reduce friction. The ion-induced damage, solid solution hardening and precipitation hardening are proposed to contribute to the hardening effect of ion implantation. The high energy collision of implanted ions with substrate increases dislocation density and atomic-scale disorder (similar to work hardening and shot peening), destroys grain boundaries and induces compressive residual stresses. Nitrogen implantation increases the hardness significantly at 50-200 nanometres in titanium substrates resulting in a microstructure of finely dispersed TiN precipitates in a deformed nitrogen-rich matrix. The fatigue strength, high cycle fatigue endurance limit and fretting
fatigue strength have been improved in addition to tribological properties with ion implantation. However, due to the limited depth of penetration by this technique, significant improvement of wear is only limited to moderate loads and mild sliding conditions [67, 85-91].

2.5.2.2 Laser Surface Alloying

Laser surface alloying (LSA) is a surface treatment that results in microstructural transformation and enrichment of the near-surface layers with alloying elements and is based on melting and rapid solidification as a high power laser scans over the surface. Laser surface remelting, laser surface melting and laser gas nitriding are different techniques studied in the same category. Both solid-state lasers (e.g., ruby) and gas lasers (e.g., CO2, Ar) in pulsed and continuous wave conditions have been employed for the treatments. Laser gas nitriding is a promising technique in surface hardening that has proven satisfactory in wear enhancement of titanium alloys. This treatment is based on laser surface alloying in a nitrogen atmosphere and results in a gradient composite microstructure reinforced with fine TiN dendrites [66, 92-95].

2.5.3 Diffusion Treatments

The interstitial elements of nitrogen, oxygen, carbon and boron have been introduced to the surface of titanium alloys through various thermochemical treatments. The surface layers form according to the phase equilibrium between the titanium and the interstitial element; generally consisting of solid solution diffusion zones beneath hard compound layers (TiC, TiB/TiB2, TiN/Ti2N, and TiO2). The modified microstructures
offer superior tribological performance, reduced wear loss and low coefficient of friction [85, 91, 96-101]. Since oxidizing and nitriding lead to deeper and more efficient surface hardening effects in titanium alloys, they will be explained further in this section.

2.5.3.1 Oxidizing

Oxygen has a high diffusion rate and solubility limit in α-Ti and can significantly strengthen titanium alloys by solid solution hardening. The titanium oxide layer (Rutile TiO$_2$) that forms on top of the oxygen diffusion zone has a high hardness and contributes to reduced coefficient of friction and wear resistance under sliding conditions. However, the brittle nature of the oxide scales and reduction of ductility by incorporation of oxygen atoms in the titanium structure create several adverse effects on mechanical properties such as degradation of fatigue and fracture toughness. Controlled oxidizing of titanium alloys has been conducted by several techniques such as Tifran process, oxygen diffusion hardening, plasma oxidation, and thermal oxidation [35, 82, 85, 102-106].

Dong et al. [103] introduced the thermal oxidation (TO) as a relatively simple and cost-effective method to improve the tribological properties of titanium alloys. The process involves isothermal oxidation inside an air furnace and variations in treatment parameters result in the formation of different surface microstructural features and depth of oxygen diffusion zones, for instance a 2 µm thick oxide layer and a 20 µm deep diffusion zone were produced after a 65-h treatment at 600˚C. It has been reported that elevated temperatures and prolonged durations result in poor interfacial bonding, cracks within the oxide layers and the formation of thick and brittle α-stabilized grains, i.e., α-case, underneath the oxides. Insufficient temperatures and durations on the other hand,
form discontinuous oxides and thin oxides that are unable to provide protection against sliding. It has been reported that thin, consistent oxide layers formed on top of deep diffusion zones provide better durability and resistance against adhesion and sliding. Several methods such as oxygen boost diffusion, Au pre-deposition and Pd-modification have been proposed for further optimization of the process [35, 40, 107-110].

2.5.3.2 Nitriding

Nitriding of titanium alloys for wear improvement has been practiced for many years. In conventional nitriding techniques liquid, solid or gas media are used to introduce nitrogen atoms to titanium substrates, e.g., salt bath treatments (Tiduran process), gas nitriding (nitrogen/ammonia atmosphere), and hot isostatic pressing (HIP), etc. however, presence of oxygen and air should be avoided in the treatments since titanium has a higher tendency to form TiO$_2$ than titanium nitrides [111, 112].

Plasma (ion) nitriding, originally developed to improve the wear and fatigue properties of ferrous alloys, has been extensively applied to titanium alloys during the past decades [113, 114]. The plasma nitriding treatment utilizes glow discharge which can be formed and sustained in several ways such as d.c. diode, radio frequency (r. f.), microwave, electron emission configurations, and magnetically-enhanced discharges for surface modification [65, 115]. Some of the recent developments in conventional plasma nitriding include intensifying the glow discharge through thermionically-assisted triode glow discharge system, plasma immersion ion implantation, electron cyclotron resonance, and so on. The intensified plasma-assisted processes (IPAP) provide extra electrons colliding with ionized gas molecules and increase the degree of ionization. The
higher density of energetic ions increases the kinetics and efficiency of nitriding at lower treatment temperatures (less than 500°C), pressures and durations. Significant improvements in surface hardness, depth of nitrided layers and tribological and fatigue properties will be achieved [116-121].

2.5.4 Duplex treatments

One of the main reasons for premature failure of thin coatings on titanium alloys and their lack of adhesion especially at high loading conditions is extensive plastic deformation of titanium substrates. It has been well-established that coatings with gradient diffusion boundaries not only can withstand higher contact stresses but also exhibit a higher load bearing capacity under sliding motion compared with those with discrete boundaries to their substrates [122].

With that in mind, more recently duplex treatments have been introduced and developed in surface engineering of titanium alloys [92, 123-127]. In an investigation by Dong et al. [128, 129], the low friction and high wear resistance of DLC coatings was combined with deep case hardening of oxygen diffusion hardening (ODH). In their investigation an amorphous/hydrogenated carbon a-C:H or DLC with a small Ti content was deposited on an oxygen diffused Ti-6Al-4V substrate with a graded Ti/TiN/TiCN/TiC interlayer to provide a better coating adhesion. A series of indentation, ball on disc and scratch tests confirmed that the load bearing capacity was considerably enhanced by the duplex treatment. In a similar investigation by the same authors, Ti-8.5Si alloy was duplex-treated by electron beam surface melting and plasma nitriding and a hardened depth of approximately 450 µm was achieved. They found that the load bearing
capacity of the duplex treated material was four orders of magnitude higher than that of the plasma nitriding alone owing to the high hardness of the electron beam-affected subsurface that provided a strong support for the nitride layer. Moreover, the integrity of surface nitride layer was maintained through the wear tests, leading to three orders of magnitude reduction in wear rate compared to the untreated Ti alloy [130].

2.6 Plasma Nitriding of Titanium Alloys

2.6.1 Fundamentals of Plasma Nitriding

In a conventional plasma nitriding treatment an electrical glow discharge is utilized to provide heat and active nitrogen flux for surface modification [65, 131]. The growing interest in this treatment by industry is due to its minimized environmental hazards and potential flexibility in modifying surface/subsurface properties by changing treatment parameters [81, 132, 133]. Also, the uniformity of coatings produced by this process allows the engineers to exercise greater control over the process, all the while being cost effective for mass production [134].

In this process, an external voltage is applied to the anode (nitriding chamber) and the cathode (workpiece) which ionizes the gas mixture that fills up the space between them. The gas mixtures are normally composed of a buffer gas (e.g., Ar or H₂) and a reactant gas (e.g., N₂). An electrical current is sustained by the negative flow of electrons towards the anode and the positive flow of ions towards the cathode. Figure 2.11 is a schematic illustration of the current density-voltage characteristic of a glow discharge. Plasma nitriding is performed in the abnormal glow region where a uniform, stable glow
covers the workpiece and current density is easily-controllable as it is directly proportional to voltage drop [113, 135].

The applied voltage can be provided by both d.c. and pulsed power supplies. A d.c. power supply applies a continuous voltage which determines the amount of heat input to the system and may result in localized heating, overheating of thin sections, the hollow cathode effect\(^3\), arcing, and damages to the surface finish. Utilizing a voltage-current pulsed power supply controls the heat input to the system with duty cycles usually in the order of 10-50\% of the total cycles and thus does not cause any adverse effects on nitrogen activity or nitriding time [136].

The applied voltage accelerates electrons originating from the cathode towards the vacuum where they collide with gas molecules within a few millimetres of the cathode and generate a large fraction of positive ions. The positive ions subsequently accelerate towards the cathode over a comparatively short distance and transfer their energy in the form of heat and kinetic energy. As a result, chemical reaction initiates and secondary electrons are produced that help maintain the abnormal glow. This mechanism eliminates the costly pre-cleaning operations, makes nitriding feasible at temperatures lower than those in the conventional nitriding techniques, and enhances deposition rates at lower surface temperatures [137].

Typical plasma nitriding treatments for titanium alloys are carried out under a nitriding atmosphere composed of nitrogen, nitrogen-argon, nitrogen-hydrogen and nitrogen-cracked ammonia gas mixtures and pressures that vary in the range of 0.5-1.3

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\(^3\) Hollow cathode effect is localized heating of workpiece surface at narrow openings, deep holes, slots, etc. where generation of charge carriers is faster than their annihilation and thus the glow discharge resistance decreases leading to a rise in electrical current and temperature.
KPa. The nitriding duration and temperature are usually in the range of 24-80 hours and 700-1000˚C [138-142].

2.6.2 The Effect of Plasma Nitriding on Microstructure of Titanium Alloys

Plasma nitrided titanium alloys have a golden appearance, but are generally less bright and uniform in coloration compared to PVD coatings due to higher surface roughness and a mixture of TiN and Ti$_2$N nitrides. They may exhibit edge effect due to the non-uniformity of sputtering and plasma field close to the edges [143].

Different layers develop on the surface of plasma nitrided titanium alloy and their occurrence, thickness and properties are dependent on the processing parameters. The mechanisms proposed to explain the mechanism of plasma nitriding include the adsorption of atomic nitrogen model, the Kölbl’s model and the NH$^+$ radical model.

According to the Kölbl’s model, plasma nitriding initiates with sputter-cleaning of the surfaces followed up reaction of the sputtered atoms with nitrogen and subsequent deposition of nitride compounds on the surface. The NH$^+$ radical model, in the presence of hydrogen in the nitriding gas mixture, is based on the formation of NH$^+$ and NH$_2^+$ molecular ions and radicals and their adsorption on the surface of work piece which is followed by dissociation of radicals and diffusion of nitrogen atoms [65, 113, 138, 144].

The formation of surface layers during plasma nitriding is according to the Ti-N binary phase diagram (Figure 2.12). The resulting microstructure consists of a thin compound layer mainly composed of TiN and Ti$_2$N on the surface followed by a nitrogen diffusion zone (Figure 2.13). The structure and properties of these features will be discussed in detail here. The compound layer consists of cubic TiN with FCC crystal
structure (Fm-3m) and Ti$_2$N with a tetragonal crystal structure (P4$_2$-mnm). The TiN phase, also called the $\delta$-phase, is stable over a wide range of nitrogen contents; TiN$_x$ (0.43 < x < 1.08) and has a typical hardness of 2500 HV. The Ti$_2$N phase, also called the $\varepsilon$-phase, has maximum hardness of 1500 HV [145-148].

Raveh et al. [149] reported that the orientation of TiN and Ti$_2$N phases is strongly related to the nitriding gas composition. When plasma nitriding was performed in a N$_2$-H$_2$ atmosphere, they found that fine TiN crystallites were randomly oriented while larger Ti$_2$N crystallites were highly oriented in the (002) direction. Lakshmi et al. [150] reported the formation of TiN$_{0.26}$ in addition to TiN and Ti$_2$N phases in the compound layer of plasma nitried Ti-6Al-4V. Their nitriding treatments were conducted at 800˚C and 900˚C for various durations (4-32 hours).

The diffusion zone is formed by dissolution of nitrogen interstitial atoms in the titanium structure with a diffusion profile beneath the compound layer. The diffusion zone is effectively strengthened by incorporation of nitrogen atoms and therefore a deep diffusion zone is favorable to provide a mechanical support for the compound layer on the surface [85, 151]. It has been established that the interaction of nitrogen with titanium alloys and the depth of nitrogen diffusion is influenced by the phase composition of titanium alloys since nitrogen has different solubility limit and diffusivity in $\alpha$ and $\beta$ structures [114, 152, 153]. The solubility limit of nitrogen in the $\beta$ phase is significantly lower than that of the $\alpha$ phase but it diffuses three times faster in the $\beta$ phase [154, 155]. A study conducted by Il’in et al. [152] revealed that the diffusion of nitrogen was hindered in $\alpha$-titanium alloys by the addition of $\alpha$-stabilizing elements, e.g., aluminum (Figure 2.14-a). In $\beta$ titanium alloys, despite the higher diffusivity of nitrogen, the depth
of nitrogen diffusion was minimal due to limited solubility. The diffusion zone formed in these alloys contained transformed α grains since nitrogen is an α stabilizer. Deep diffusion zones were achieved in α+β structures due to a combination of both high nitrogen solubility and diffusivity (Figure 2.14-b).

Plasma nitriding of α+β and β titanium alloys is performed at high temperatures (>800˚C) and long durations, a continuous layer of nitrogen stabilized α-titanium, i.e., α-case, forms underneath the compound layer (Figures 2.15). The α-case is a brittle layer with a hardness of 800-1000 HV and its formation is considered detrimental for ductility and the fatigue strength. When the plasma nitriding treatment of Ti-6Al-4V was carried out below 800˚C, the α-case was in the form of columnar α grains in a matrix of α+β phases underneath the compound layer [81, 145-148, 156]. The formation of α-case similarly occurs in α-titanium alloys; however, it is more difficult to distinguish it from the matrix. According to Bell et al. [81] it is easier to observe the α-case in α-Ti alloys when hydrogen pick up takes place during the plasma nitriding treatment, as hydride precipitation within the substrate creates contrast against the α-case (Figure 2.16). This is due to the higher solubility of hydrogen in the β phase that transforms to α+hydrides upon cooling.

The microstructure of the above-mentioned features depends on the nitriding conditions. da Silva et al. [157] used x-ray diffraction measurements to study the effect of nitriding time, gas mixture composition, temperature, and total pressure on the near surface composition of Ti-6Al-4V alloy. They reported that the near surface composition was a very complex function of the above parameters among which temperature had the most significant influence. Certain treatment durations were needed before TiN and Ti₂N
showed up in the x-ray diffraction patterns and the durations remarkably decreased upon increasing the temperature. In addition, the effect of total pressure was reported to be minor within the ranges used, but increasing partial pressure of nitrogen resulted in more defined Ti$_2$N reflections and the appearance of TiN peaks in the diffraction pattern. Apart from titanium nitrides, reflections of V$_2$O, orthorhombic TiO$_2$, and nitrogen deficient $\zeta$-Ti$_4$N$_{3-x}$ nitride were also observed for some nitriding conditions. The shift in $\beta$ phase reflections indicated lattice distortions (and probably residual strains) induced by nitriding in this phase.

Yildiz et al. [158] reported that increasing the temperature and time of nitriding, increased the intensity of TiN phase and surface roughness as well as hardness and depth of the diffusion zone. They also found segregation of aluminum and the formation of an aluminum-rich layer just below the compound layer which had an adverse effect on the diffusion rate of nitrogen into the substrate. The presence of the aluminum-rich layer (Figure 2.17) has been also confirmed by other researchers [159, 160]. Raveh et al. [149] carried out a comprehensive analysis on the nature of the boundary layer between the compound layer and the bulk by transmission electron microscopy [161], Auger electron spectroscopy coupled with scanning Auger microscopy (AES/SAM) and observed clusters of small, closely spaced precipitates (50-100 Å in size) which contained aluminum, vanadium and chromium in addition to iron (\(\alpha\) and \(\gamma\)-Fe).

The pressure and composition of the nitriding gas also has a significant effect on the microstructure of plasma nitrided titanium alloys [150, 162]. For instance, in the presence of hydrogen in the nitriding plasma, the penetration of nitrogen is increased in the titanium structure. The following mechanisms have been proposed:
Hydrogen reacts with and removes the inherent oxide scale on the surface of titanium. The formation of NH\(^+\) and NH\(^{2+}\) molecular ions and radicals in the hydrogen-containing plasmas facilitates the adsorption process.

The addition of Ar on the other hand, reduces the depth of nitrogen diffusion and causes random formation of Ti\(_2\)N and TiN phases through sputtering/redeposition reactions of the TiN phase formed on the surface or by the homogeneous reactions in the plasma [65, 138, 146, 147].

2.6.3 The Effect of Plasma Nitriding on Tribological Behaviour of Titanium Alloys

Although the positive effect of plasma nitriding on improving the wear resistance of titanium alloys is well-established, there are still discrepancies in the literature as the efficiency of nitriding in that matter has been found to be a function of treatment parameters as well as sliding condition. Several factors are known to play influential roles on the tribological properties of plasma nitrided surfaces including the hardness of surface layers, the surface roughness, the formation of brittle microstructural features by nitriding, and the depth of solid solution strengthening by the nitrogen interstitial atoms.

One of the earliest studies on the correlation of plasma nitriding and wear properties belongs to Bell et al. [81]. The results of their wear tests on plasma nitrided (800°C, 12 hours, N\(_2\) atmosphere) and untreated Ti-6Al-4V alloy under dry and lubricated conditions revealed that the extreme wear and rapid rise in coefficient of friction of the untreated alloy were effectively avoided by plasma nitriding. The nitried surfaces showed antiscuffing characteristics and low coefficient of friction and endured the applied loads without any signs of failure (Figure 2.18).
Taktak et al. [163] performed plasma nitriding at different temperatures ranging from 700˚C to 900˚C and reported that the treatment at 900˚C for 12 hours (longest duration and highest temperature) produced the best wear resistance. In their investigation the reduction in wear rate and coefficient of friction values after plasma nitriding were related to the formation of a thick and hard compound layer on the surface as the failure of the compound layer at high applied loads resulted in a wear transition that moved the wear rate values close to those of the untreated substrate.

Higher nitriding temperatures of 900˚C, 1000˚C, and 1100˚C were investigated in the work of Shashkov et al. [99]. They reported that the hardening of titanium alloys at temperatures exceeding 900˚C is accompanied by their embrittlement and this was correlated to the formation of nitride layers and microstructural changes in the bulk structure (e.g., grain coarsening). According to their wear test results some wear resistance was achieved at 900˚C, however, at higher temperatures wear resistance was reduced due to the embrittling effect of the nitriding process.

Yilbas et al. [164] conducted pin-on-disk (to study wear rate) and ball-on-disk (to study friction behaviour) tests against ruby counterpart in lubricated conditions. In their experiments, severe wear and scuffing of the untreated alloy began after a few cycles and caused an abrupt rise in the friction coefficient but the plasma nitrided surfaces displayed lower coefficients of friction before the breakthrough of nitrided layers. The breakthrough was postponed for the treatment at a higher temperature of 520˚C which was attributed to its higher hardness of the nitrogen diffusion zone. Relatively high wear rates were observed for the untreated alloy but the nitrided surfaces experienced no significant wear scar before the compound layer failure. The nitrided surfaces at 520˚C
exhibited higher wear resistance compared to those treated at 450°C which was attributed to a thicker and harder diffusion zone.

One of the most comprehensive studies on the tribological behaviour of plasma nitrided titanium alloys was conducted by Molinari et al. [148]. They reported that the wear resistance was a function of testing conditions, the microstructure and the surface roughness of the nitrided surfaces. At low sliding speeds and normal loads nitriding increased the wear resistance. However, at high applied loads compound layer failed and the fragments contributed to third body abrasion leading to higher wear rates than the untreated alloy. At high sliding speeds the plasma nitrided surfaces showed reduced wear rates. This trend was more significant for the plasma nitrided surface with a thicker compound layer and a deeper of diffusion zone.

Straffelini et al. [24] found that under lubricated rolling-sliding conditions the untreated titanium alloys had a better wettability and thus lower coefficient of friction compared to the plasma nitrided surfaces due to its ionic character. The wear resistance, however, improved by nitriding to a limited degree by an 8-hour treatment and to a further extent by a 24-h treatment (Figure 2.19).

The positive role of a deep diffusion zone in tribological behaviour of plasma nitrided Ti alloys was clarified by several researchers [143, 165]. Nolan et al. [143] reported lower wear rates for plasma nitrided Ti alloy compared to PVD coated surfaces with the same thickness of titanium nitride layer. They suggested that the diffusion of nitrogen atoms in the plasma nitrided microstructure strengthened the \( \alpha \)-Ti phase by solid solution and dispersion hardening and the diffusion zone provided support for the compound layer and decreased the chances of interfacial debonding.
The effect of different microstructural features on the wear performance of plasma nitrided titanium alloys was studied by Cassar et al. [165]. They evaluated the reciprocating-sliding wear behaviour of plasma nitrided Ti surfaces against WC-Co and sapphire counterface materials. They found that a thin compound layer with lower hardness provided better wear resistance especially at high loads because it was better supported by a deep diffusion zone. A thin compound layer could effectively absorb the deflections of the substrate, while spallations were inhibited since the maximum shear zone was constrained within the diffusion zone.

Bloyce et al. [123] explained that under compressive forces of the counterface, the substrate at the front of contact areas experiences severe plastic deformation when the maximum applied stress exceeds that of the yield strength of the material. However, the TiN/Ti$_2$N ceramic coating cannot conform to the plastic deformation and fractures due to its low toughness. At the center of contact areas severe plastic deformation is evidenced by elongate grains of the subsurface in the sliding direction as a result of tangential forces. At the end of contact areas plastic pile-up of substrate material leads to the spallation and delamination of surface nitride layers.

The surface roughness and topography developed during plasma nitriding is another influential factor on the sliding behaviour. Salehi et al. [80] investigated the effect of surface topography on the wear behaviour of PVD TiN coatings and plasma nitrided Ti-6Al-4V alloys under self-mated conditions and against alumina counterparts. They found that the thickness of compound layer and surface roughness both increased with treatment temperature and proposed that sputtering is responsible for the changes in
surface roughness. The nitrided surfaces produced at higher temperatures suffered from significant mass loss which was attributed to the higher roughness of the surfaces.

The results of pin-on-disk wear tests on plasma nitrided Ti-6Al-4V surfaces against WC-Co counterface by Yildiz et al. [158] showed that the steady state coefficient of friction was similar to that of the untreated alloy (0.45) but it was higher at the beginning of the tests. This effect was more pronounced for treatments at higher temperatures and durations and was attributed to the higher surface roughness values. The wear rate, however, was reduced by nitriding due to the rise in surface hardness and the highest temperature and duration treatment resulted in the lowest wear rate value (Table 2.2).

Table 2.2 The plasma nitriding conditions in the study by Yildiz et al. and the corresponding properties and wear rates [158]

<table>
<thead>
<tr>
<th>Nitriding parameters</th>
<th>Compound layer (µm)</th>
<th>Surface roughness (Ra)</th>
<th>Surface hardness (HV_{0.1})</th>
<th>Wear rate × 10^{-6} (mm³/Nm)</th>
<th>Average coefficient of friction</th>
</tr>
</thead>
<tbody>
<tr>
<td>650°C – 1 h</td>
<td>0 - 1</td>
<td>0.27 - 0.32</td>
<td>580 - 620</td>
<td>3.34</td>
<td>0.42 - 0.46</td>
</tr>
<tr>
<td>650°C – 2 h</td>
<td>0 - 1</td>
<td>0.17 - 0.30</td>
<td>780 - 830</td>
<td>1.78</td>
<td>0.42 - 0.45</td>
</tr>
<tr>
<td>650°C – 4 h</td>
<td>0 - 2</td>
<td>0.28 - 0.33</td>
<td>980 - 1010</td>
<td>1.82</td>
<td>0.48 - 0.52</td>
</tr>
<tr>
<td>700°C – 1 h</td>
<td>1 - 3</td>
<td>0.29 - 0.34</td>
<td>620 - 680</td>
<td>2.13</td>
<td>0.44 - 0.47</td>
</tr>
<tr>
<td>700°C – 2 h</td>
<td>2 - 3</td>
<td>0.30 - 0.36</td>
<td>820 - 880</td>
<td>1.28</td>
<td>0.44 - 0.48</td>
</tr>
<tr>
<td>700°C – 4 h</td>
<td>2 - 3</td>
<td>0.16 - 0.26</td>
<td>1180 - 1230</td>
<td>0.67</td>
<td>0.46 - 0.50</td>
</tr>
<tr>
<td>750°C – 1 h</td>
<td>2 - 3</td>
<td>0.31 - 0.33</td>
<td>880 - 930</td>
<td>0.14</td>
<td>0.50 - 0.55</td>
</tr>
<tr>
<td>750°C – 2 h</td>
<td>3 - 5</td>
<td>0.30 - 0.35</td>
<td>1225 - 1275</td>
<td>0.89</td>
<td>0.48 - 0.53</td>
</tr>
<tr>
<td>750°C – 4 h</td>
<td>3 - 5</td>
<td>0.25 - 0.35</td>
<td>1375 - 1425</td>
<td>0.62</td>
<td>0.49 - 0.55</td>
</tr>
<tr>
<td>Ti-6Al-4V</td>
<td>-</td>
<td>0.06 - 0.10</td>
<td>360 - 380</td>
<td>3</td>
<td>0.42 - 0.46</td>
</tr>
</tbody>
</table>
2.6.4 The Effect of Plasma Nitriding on Fatigue Behaviour of Titanium Alloys

The positive effect of plasma nitriding in increasing the fatigue endurance limit and fatigue strength of most steels is well-established. The nitride forming elements in steels, e.g., chromium, aluminum, vanadium, and titanium are capable of forming sub-microscopic precipitates during nitriding that are only a few hundred atomic planes in magnitude and are coherently bonded to the matrix. These precipitates strengthen the substrate and induce residual compressive strains that retard the crack propagation in the diffusion zone. Nonetheless, unlike steels, nitriding of titanium alloys does not promote any precipitation hardening mechanisms and strengthening of titanium only occurs by the interstitial solid solution hardening [166].

Unfortunately, similar to other surface engineering techniques that improve the wear resistance of titanium alloys, nitriding is accompanied by an inevitable side effect on the fatigue properties [81, 85, 167-169]. The elevated temperatures involved in the nitriding procedures is an influential factor in the reduction of fatigue strength [142, 170]. High nitriding temperatures (>700°C) are needed to produce a moderate nitrieded depth in titanium alloys, due to the slow kinetics of nitrogen diffusion. The gas nitriding treatments are normally performed at temperature ranges of 750-1000°C for several hours leading to significant grain growth and overaging of the microstructure [81]. Since plasma nitriding and gas nitriding generate similar microstructural features in titanium alloys and affect the fatigue properties in the same manner, gas nitriding investigations have been considered as equally important in this section.
Morita et al. [171] investigated the effect of gas nitriding on fatigue properties of pure titanium and reported that the low fracture toughness of the compound layer and grain growth simultaneously influence the fatigue strength. Their fractographic observations revealed that fatigue cracks initiated by brittle fracture of the compound layer. They proposed that the stiffness gradient between the compound layer (E=426 GPa) and the substrate (E=100 GPa) leads to stress concentration in this layer that overshadows the effect of residual compressive stresses and results in brittle fracture at the surface and reduced fatigue strength. They also found that the fatigue strength of nitrided titanium shows a Hall-Petch relationship with the grain size. Consequently, they reported promising results by inhibiting grain growth through a low temperature nitriding process.

Similarly, Tokaji et al. [172] found deterioration of the fatigue strength and endurance limit for Ti–6Al–4V (an α+β Ti alloy) and Ti-15Mo-5Zr-3Al (a β-Ti alloy) after gas nitriding at different temperature (750-850˚C) and durations (4-60 h). In order to exclude the effect of nitriding on the substrate microstructure, a series of titanium alloys were also subjected to the same heat treatment cycles for comparison. They found that the fatigue strength of plasma nitrided Ti-6Al-4V alloy slightly increased after a 4-hour treatment compared to the annealed alloy. After 15 hours of nitriding, however, the fatigue strength was significantly reduced. The adverse effect of nitriding duration on fatigue properties was also observed in Ti-15Mo-5Zr-3Al alloy. The authors suggested that the formation of the compound layer and diffusion zone were both responsible for impaired fatigue properties. In order to confirm their findings they removed the nitrided
surface layers by electropolishing and found improvements in fatigue life by complete removal of the compound layer and partial removal of the diffusion zone (Figure 2.20).

Nishida et al. [167] reported that the fatigue strength of the plasma nitrided Ti-6Al-4V was lower than the untreated alloy but higher than the vacuum annealed alloy with the same heat treatment history. Their findings indicated that the fatigue endurance limit was inversely related to the plasma nitriding temperature and increased by about 30 MPa when the brittle compound layer was removed after plasma nitriding.

The findings of Bell et al. [81, 173] indicated a reduction in fatigue limit of Ti-6Al-4V alloy by plasma nitriding at different temperatures ranging between 700°C and 1000°C. They correlated the deterioration of fatigue properties to the thickness of the α-stabilized layer (the α-case). In the investigation performed by Raveh et al. [147] the fatigue crack initiation was correlated with the surface hardness, residual microstrains in the nitrided layers, crystallographic orientation of different phases, and segregation of alloying elements near the surface region. An inverse relationship was reported between the surface hardness value and number of cycles for fatigue crack initiation. The resistance to fatigue crack initiation decreased with the TiN content in the compound layer due to the surface embrittlement. Moreover, incorporation of Ar in the nitriding plasma decreased the crack initiation resistance possibly as a result of inducing microstrains in the nitrided layers.

Kralya et al. [174] studied the fatigue performance of different wear-resistant coatings and indicated that the coatings with higher hardness and stiffness possessed lower fatigue limits. The maximum reduction of the fatigue strength was observed for TiN coatings regardless of their deposition method. However, the presence of a diffusion
zone and plasma-spraying of different intermediate Ti-Ti$_2$N layers alleviated the negative effect of the nitride layers on fatigue probably by decreasing the internal stress levels.

Steinert et al. [175] observed that the nitrided Ti-6Al-4V (870°C for 8 hours in a nitrogen-ammonia atmosphere (95:5)) showed a 20% higher fatigue strength compared to a TiN-coated alloy by the PVD method and slightly higher strength compared to the electropolished untreated alloy. Fractographic observations revealed that while the cracks initiated from multiple locations on the surface of gas nitrided alloy, there was only one single crack initiation site on the surface of PVD coated alloy. It was proposed that the steep stiffness gradient between the TiN coating deposited by the PVD treatment and the Ti substrate resulted in early crack nucleation. However, for the gas nitrided alloy, the compressive residual stress in the compound layer and diffusion zone suppressed dislocation slip and early crack initiation and resulted in a higher fatigue strength.

Conversely, according to Sobiecki et al. [176] plasma nitriding of Ti-1Al-1Mn alloy at 800°C for 3 and 12 hours increased the fatigue strength of the alloy from 350 to 390 MPa. However, when air was introduced into the plasma, the hardness and fatigue strength decreased likely due to the formation of TiO$_2$, a hard and brittle phase, in the near-surface region. Rajasekaran et al. [177] also reported improvements in both uniaxial plain fatigue and fretting fatigue behaviour of plasma nitrided Ti-6Al-4V alloy (500°C for 6 h in N$_2$-H$_2$ (3:1) atmosphere). Lower surface roughness, generation of compressive residual stresses on the surface, and higher surface hardness were considered the main responsible factors for the fatigue improvements. The surface hardness after plasma nitriding (390 HV$_{0.2}$) was slightly higher than the untreated material (330 HV$_{0.2}$) and the surface roughness was reduced (R$_a$ decreased from 0.80 µm to 0.55 µm) by plasma
nitriding due to the smoothing of the pretreatment grinding marks by sputtering. Furthermore, compressive residual stresses developed on the surface (in the order of 40 MPa) due to nitrogen diffusion in the titanium lattice. Fretting test results also indicated lower friction forces and shallower fretting scars for nitrided samples at all stress levels.

Contradictory results were reported by Mubarak Ali et al. [169] who carried out plasma nitriding on Ti-6Al-4V alloy at 520°C for 4 and 18 hours and found that both plain and fretting fatigue lives were reduced by plasma nitriding. The samples that were nitrided in a nitrogen-hydrogen (3:1) atmosphere showed inferior results compared with those nitrided in a pure nitrogen atmosphere likely due to the higher hardness of surface layers in the former nitriding conditions.

Rodriguez et al. [178] reported that the low cycle fatigue resistance of Ti-6Al-4V alloy deteriorated after nitriding. They carried out several nitriding treatments at 850°C and 900°C for 1 and 4 hours and noted that the fatigue results of the nitrided samples were similar to — or even slightly better than — those that went through the same treatment under vacuum. Therefore, the reduction of low cycle fatigue resistance was attributed to the microstructural changes from mill-annealed to Widmanstätten structure. They proposed that when the imposed strains during cyclic loading were not sufficiently high for compound layer failure, the residual compressive strains on the surface of nitrided samples could slow down the crack nucleation process. However, at high cyclic strains due to the stiffness difference between Ti-6Al-4V (100 GPa) and titanium nitrides (300-400 GPa), cracks nucleated and propagated in the brittle compound layer (Figure 2.21). Surface roughness was also found to be an influential factor since an increase in
the average surface roughness during the nitriding process led to stress concentration at
the surface and promoted early fatigue crack nucleation [178].

2.7 The Combined Effect of Cold Working and Diffusion Treatments

Many surface modification techniques such as shot peening, laser peening, and
burnishing have been developed to increase the fatigue life of metals by introducing
compressive residual stress in the surface layers. Shot peening is one of the most
common and effective treatments in this category in which impingement of high-velocity
shots, under controlled conditions, introduces compressive stresses in the surface layers.

In addition to the development of a surface residual stress profile, shot peening
results in surface roughening, strain hardening and the formation of a subsurface plastic
deformation zone. The extent of these changes is largely dependent on the mechanical
properties of the target material, peening intensity, hardness and size of the shots, nozzle
characteristics, air pressure, impact angle, exposure time, and relative linear or rotational
speed of peening. Various types of shots such as cast steel shots, cut wire shots, glass
beads, and zirconium shots are available and the air blast can be delivered by either
suction blast or pressure blast depending on the budget, target substrates and the required
precision.

In terms of improvement of fatigue life and retarding fatigue crack initiation and
propagation by shot peening, surface roughening favours early nucleation of cracks,
while strain hardening and the residual compressive stresses on the surface reduce the
driving force for crack propagation, by increasing the resistance to plastic deformation
and providing a crack closure mechanism. Moreover, recently improvements in the
sliding wear behaviour and tensile properties have been reported by shot peening due to its surface hardening effect [179].

Experimental studies have shown that a severely deformed surface layer can also be introduced by shot peening, which leads to significant grain refinement close in the outmost layer and generation of non-equilibrium defects in the subsurface region [180-183]. The thickness of this severely deformed layer can vary in the range of 10 - 80 µm depending on the microstructure and properties of the substrate material; metals of a lower yield strength experience a more intense plastic deformation that extends deeper into the substrate [184].

A high energy shot peening treatment by Han et al. [185] resulted in the formation of a nanostructured layer on the surface of Ti-4Al-2V alloy. Moreover, this treatment also introduced microstructural changes, e.g., twinning and grain refinement that extended to approximately 230 µm below the surface. They proposed that the grain refinement occurs through various mechanisms such as the “formation of dislocation walls and tangles”, “dislocation movement and twinning” and “mechanical twinning” depending on the crystal structure and stacking fault energy (SFE) of metals. For the case of Ti-4Al-2V alloy, mechanical twinning was recommended to have major contributions in grain refinement due to the HCP structure and high stacking fault energy (SFE>300 mJ/m²). The high level of plastic deformation induced by shot peening resulted in activation of many slip systems and a high density of dislocations within the twin bands. Subsequently dislocation walls were formed which in turn generated submicron-sized grains, small misoriented subgrains and finally equiaxed fine nanograins (35 ± 5 nm). Further studies
were performed by Thomas et al. [186] to understand the effect of temperature and alloy composition on the subsurface microstructure of shot peened titanium alloys.

It has been shown that alteration of surface microstructure by introducing high-diffusivity paths such as grains boundaries, dislocations and atomic level microstructural defects by shot peening can be employed to accelerate the diffusion of interstitial atoms [182]. Thomas et al. [187, 188] reported that generation of a high density of twin boundaries and dislocations in the near surface region of a near-α titanium alloy after shot peening, increased the oxygen uptake during the following thermal exposure in air (Figure 2.22). Moreover, the high stored energy associated with the higher density of these non-equilibrium defects increases chemical reactivity of surfaces and enhances the kinetics of surface reactions [183]. Several researchers have confirmed that microstructural changes brought by severe plastic deformation in ferrous alloys enhanced the nitrogen diffusion rate during the posterior nitriding treatments, and increased the efficiency of nitriding at lower temperatures [180-183].

The effect of shot peening after diffusion treatments has also been studied in the literature. In a recent study Bansal et al. [189] designed a series of duplex treatments for Ti-6Al-4V alloy composed of diffusion treatments (nitriding and oxygen diffusion) followed by mechanical working (shot peening and planishing). The results of dry reciprocating ball-on-disk wear tests against stainless steel 440C and silicon nitride sliders indicated improvements in wear resistance by introducing a short period of low friction and lower volumetric wear.

In summary, the literature review presented here revealed that plasma nitriding is a promising surface engineering technique for increasing the wear resistance of titanium
alloys, a common problem that restricts their extensive application in various sectors of industry. However, similar to conventional gas nitriding treatments on titanium alloys, plasma nitriding has a detrimental side effect on the fatigue strength which is a serious concern for applications where components are subjected to cyclic loads. The correlation between the plasma nitrided microstructure and wear and fatigue performance of nitrided titanium alloys is not well established. Moreover, the mechanisms by which the nitrided microstructure affects the formation and propagation of cracks under cyclic loads and sliding contact are not clear. Thus, there is a need for a systematic investigation on the effect of nitriding conditions on the plasma nitrided microstructure in titanium alloys. The microstructure relationship with wear resistance and the fatigue strength should also be clarified in order to discover new approaches to improve the former without scarifying the latter by tailoring the microstructure.
Figure 2. 1 A schematic representation of slip planes and slip directions in HCP α titanium [1].

Figure 2. 2 The effect of annealing temperature and rate of cooling on microstructure of Ti-6Al-4V alloy. (a) α’ martensite, (b) primary α+α’ martensite+retained β, (c) primary α+α’ martensite+retained β, (d) primary α+metastable β, (e) acicular α + β, (f) primary α and acicular α+β, (g) primary α and acicular α + β, (h) primary α and β, (i) plate-like α and β, (j) equixed α and intergranular β, (k equixed α and intergranular β, (l) equixed α and intergranular β [9].
Figure 2. 3 Optical micrographs showing the effect of cooling rate from the β phase field on the microstructure of Ti-6Al-4V alloy. (a) Furnace cooling (1°C/min) results in the formation of plate-like α within the β grains and at the β grain boundaries. (b) Typical commercial cooling (100°C/min) results in the formation of a Widmanstätten type of microstructure consisting of colonies of acicular α in a matrix of β and α layers at prior β grain boundaries (basket-weave structure). (c) Water quenching of relatively thin sections (800°C/min) resulting in the formation of needle-like α’ martensite [190].

Figure 2. 4 Variation of yield strength and tensile elongation with the cooling rate from the β phase field for the lamellar microstructures in Ti-6Al-4V and other α+β titanium alloys [190].
Figure 2. 5 An optical micrograph from bimodal (duplex) microstructure in Ti-6Al-4V alloy. The microstructure consists of equiaxed primary α grains in a matrix of transformed β [191].

Figure 2. 6 Typical crack front profiles observed in Ti-6Al-4V alloy in (a) bimodal and (b) fully lamellar microstructures (R = 0.1, da/dN ~ 10^{-10} m/cycle). The significantly rougher crack front profile in the fully lamellar microstructure is responsible for its superior fatigue crack growth properties. The arrows show the direction of crack propagation [19].
Figure 2.7 The effect of d-valence character of metallic bonding of several metals on their coefficient of friction when sliding against (a) themselves and (b) SiC single crystal under vacuum at low load and sliding velocity [37].

Figure 2.8 The relationship between coefficient of friction (COF) and the ideal tensile strength for metals in contact with themselves. The tests were conducted at room temperature at a sliding velocity is 0.7 mm/min and an applied load of 0.01 N under vacuum. Due to its lower theoretical cohesive strength, the stress required to separate Ti planes apart (cohesive force) during sliding contact is lower and thus extensive material transfer and adhesion takes place during sliding action of Ti surfaces [38].
Figure 2. 9 Cross-sectional images of Ti-6Al-4V after wear tests against AISI M2 counterface. (a) The formation of surface oxide scales and oxidative wear mechanism at low sliding speeds (0.3 m/s), (b) The formation and delamination of mechanically mixed layer (MML) accompanied by subsurface plastic deformation characteristics of delamination wear mechanism at high sliding speeds (0.8 m/s) [25].

Figure 2. 10 A schematic wear map showing different wear mechanisms for the Ti-6Al-6V-2Sn alloy sliding against AISI steel counterface [60].
Figure 2. 11 Electrical characteristics of a glow discharge plasma [135].

Figure 2. 12 Ti-N binary phase diagram [192].
Figure 2. 13 Schematic illustration of the plasma nitrided microstructure in titanium alloys [192].

Figure 2. 14 (a) Microhardness-depth profiles of the surface of plasma nitried titanium alloys, (1) commercially pure titanium and (2) VT5 alloy (containing 5.4% Al). The addition of aluminum (α stabilizing element) decreased the diffusion rate of nitrogen atoms. (b) The effect of β phase on the depth of nitrogen diffusion during plasma nitriding of titanium alloys at (1) 550˚C and (2) 600˚C [152].
Figure 2. 15 Optical micrographs of Ti-6Al-4V alloy after plasma nitriding in nitrogen for 3 hours at 1000°C showing the formation of an α-case underneath the compound layer at (a) low magnification and (b) high magnification [81].

Figure 2. 16 An optical micrograph showing the formation of an α-case in commercially pure (CP) titanium plasma nitrided in a 95% N₂ - 5% H₂ atmosphere at 1000°C for 16 hours. The α-case is distinguished due to absence of hydride precipitation in this phase while extensive precipitation occurred in the substrate [81].

Figure 2. 17 (a) A cross-sectional backscattered electron (BSE) image of the plasma nitrided Ti-6Al-4V and (b) the corresponding auger electron spectroscopy (AES) map of the aluminum distribution confirming the presence of an aluminum-rich layer underneath the compound layer [158].
Figure 2. 18 Wear test results on plasma nitrided Ti-6Al-4V after a 12-hour treatment at 850°C in a nitrogen atmosphere. The wear tests were performed against AISI 1137 steel counterface using SAE 30 oil as a lubricant [81].

Figure 2. 19 Wear test results for untreated and plasma nitrided Ti-6Al-4V alloys. The limited improvement of wear resistance with an 8-h treatment was attributed to insufficient depth of hardening and thus lack of support for the compound layer resulted in delamination of this layer. A longer nitriding treatment (24 h), on the other hand, promoted a deeper diffusion zone and resulted in better sustainment of the compound layer on the surface [24].
Figure 2.20 The S-N curve obtained by rotating bending test \( R = -1 \) for Ti-6Al-4V alloy. STA: solution treated at 950°C for 1 hour and aged at 540°C for 4 hours, A4 and N4 were annealed and nitrided at 850°C for 4 hours and A15, N15 were annealed and nitrided at 850°C for 15 hours, respectively [172].
Figure 2.21 (a) Fracture surface of nitrided Ti-6Al-4V alloy (900°C for 1 hour) after low cycle fatigue test under $\pm 5 \times 10^3$ cyclic strains. (b) The fatigue crack initiated by transgranular brittle fracture at the nitrided surface layer [178].

Figure 2.22 A cross-sectional polarized micrograph of mechanical twins in the subsurface of an $\alpha$-titanium alloy after shot peening [187].
CHAPTER 3:
MATERIALS AND EXPERIMENTAL DETAILS

In this chapter, the plasma nitriding treatment set-up used for surface modification of Ti-6Al-4V alloy will be explained and the procedure taken to optimize the process parameters will be discussed in detail. Shot peening will be introduced as a pretreatment step to plasma nitriding of Ti-6Al-4V alloy to enhance the nitriding kinetics by alteration of the near-surface microstructure. Subsequently, the experimental methods that were used to characterized the microstructure and study the mechanical properties and tribological performance of Ti-6Al-4V alloy before and after the nitriding treatment will be presented.

The microstructural characterization consisted of analysis of surface topography and chemical composition, cross-sectional metallography of nitrided alloys and microhardness measurements. Analytical microscopy techniques were utilized to study and identify the microstructural features of nitrided alloys. Uniaxial tensile tests, cryogenic fractures and rotation bending fatigue tests were utilized to assess the mechanical properties of treated and untreated alloys. For evaluation of tribological properties, microscratch and ball-on-disk wear tests were carried out and microscratch testing was found to be a useful technique in studying the adhesion properties of nitrided surfaces under sliding conditions.
3.1 Plasma Nitriding of Ti-6Al-4V Alloy

Plasma nitriding treatments were carried out on extra low interstitial (ELI) grade of Ti-6Al-4V alloy purchased from Titanium Metals Corporation (TIMET) in the form of 3 mm thick plates and 9.5 mm diameter bars. The chemical analysis of the as-received alloy is summarized in Table 3.1. The chemical content of metallic elements was determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES). The hydrogen, oxygen and nitrogen contents were determined by inert gas fusion and the carbon value by combustion.

<table>
<thead>
<tr>
<th>Element</th>
<th>Fe</th>
<th>V</th>
<th>Al</th>
<th>C</th>
<th>O</th>
<th>N</th>
<th>H</th>
<th>Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt.%</td>
<td>0.17</td>
<td>4.10</td>
<td>5.98</td>
<td>0.007</td>
<td>0.13</td>
<td>0.012</td>
<td>0.009</td>
<td>balance</td>
</tr>
</tbody>
</table>

The as-received material was mill annealed at 760°C for 30 minutes and subsequently air cooled. Figure 3.1-a shows a typical secondary electron scanning electron microscopy image of the mill-annealed microstructure etched in glycerol+HF (1:1) solution\(^4\). The microstructure consisted of equiaxed α grains, retained β particles at α grain boundaries and fine recrystallized β particles inside the α grains. The α grains were delineated by the different orientation of fine recrystallized β particles inside the α grains (Figure 3.1-b).

The average α grain size and β phase content of the as-received alloy were 3.8 µm and 24%, respectively, measured using the Buehler OmniMet image analysis software.

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\(^4\) Hydrofluoric acid causes irreversible bone damage and a series of other serious health hazards. The HF-containing solution should be handled with extreme care.
The $\beta$ phase content of the alloy was determined following a procedure adopted from Tiley et al. [193] by overlaying a regular grid of points on the back-scattered electron SEM images and dividing the number of points within the $\beta$ phase by the total number of points.

The treatments were performed in an industrial unit located at Exactatherm Ltd. A cathodic cage was used to intensify the glow discharge and the test coupons were placed at the geometric center of the cage in order to avoid common problems associated with DC plasma nitriding such as arcing damage, hollow-cathode and edging effect. No auxiliary heating was used and the heat input was provided by the glow discharge. Schematic illustrations of the nitriding chamber are presented in Figure 3.2 and the plasma nitriding set up is shown in Figure 3.3.

A total number of 46 runs were tried under different conditions of time, temperature, nitriding atmosphere, etc. in order to find out the optimal treatment parameters that resulted in improved wear and fatigue properties. The samples were treated at different temperatures (ranging from 500°C to 900°C), durations (ranging from 4 to 87 h), and pressures (ranging from 67 to 533 Pa). The nitrogen content of the nitriding gas varied between 1.5 to 75% and both Ar and H$_2$ were used as the process gas. The effect of cooling media was also studied by cooling down the samples inside the chamber under vacuum and H$_2$ atmosphere. The details of treatment conditions for the nitriding trials are tabulated in Table 3.2.

Prior to each treatment the chamber was cleaned through a couple of filling/evacuation steps using Ar-H$_2$ (1:1) mixture. The plasma nitriding experiments

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5 Exactatherm Ltd., 2381 Anson Dr., Mississauga, ON L5S 1G1
began with sputter cleaning and heating the samples to the treatment temperature in the Ar-H$_2$ (1:1) atmosphere. A bias voltage of approximately 600 V was utilized to maintain a stable glow discharge and the sputter cleaning and heating step took approximately 2-3 hours (depending on the nitriding temperature). The chamber atmosphere was switched upon reaching the desired temperature and the nitriding mixture was purged into the chamber. Consequently, when the nitriding treatment was completed the samples were cooled down to 150°C inside the furnace in vacuum.

3.1.1 Process Optimization

During the first 10 trials it was found that iron and carbon contaminants from the interior walls and floor of the nitriding chamber deposited on the surface of titanium coupons. The resulting contaminant compounds interfered with the nitriding process and the nitrogen diffusion. Therefore, the samples were placed on titanium stands inside a cathodic cage made of Ti-6Al-4V alloy, the chamber floor was covered with a titanium plate and the thermocouple stand was also made of a titanium alloy.

For most of the trials (after trial #15), the polished surfaces of test coupons and fatigue and tensile samples were chemically activated before being placed inside the nitriding chamber. The chemical activation pretreatment was carried out by immersing the samples in an aqueous solution containing 1% HF and 15% HNO$_3$ for 5 minutes prior to each test. In the nitriding process of fatigue and tensile samples, a uniform glow discharge was achieved surrounding the samples by hanging them inside the nitriding cage using titanium wires, as schematically shown in Figure 3.2-c. For this purpose, a small hole was drilled on the grip section of each sample.
Table 3.2 The plasma nitriding conditions tried in this research

<table>
<thead>
<tr>
<th>Trial No.</th>
<th>Time (h)</th>
<th>Temperature (°C)</th>
<th>Pressure (Pa)</th>
<th>Atmosphere</th>
<th>Other conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Test coupons were located inside a TiN coated steel cathodic cage</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>1</td>
<td>4</td>
<td>700 ± 5</td>
<td>47</td>
<td>75% N₂-balance Ar</td>
<td>Test coupon surface ground up to 600 grit silicon carbide paper</td>
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<tr>
<td>2</td>
<td>4</td>
<td>700 ± 5</td>
<td>80</td>
<td>75% N₂-balance Ar</td>
<td>Test coupon surface polished to 1µm diamond suspension</td>
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<tr>
<td>3</td>
<td>8</td>
<td>700 ± 5</td>
<td>64</td>
<td>3% N₂-balance Ar</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>8</td>
<td>700 ± 5</td>
<td>64</td>
<td>3% N₂-balance Ar</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>24</td>
<td>700 ± 5</td>
<td>58</td>
<td>3% N₂-balance Ar</td>
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</tr>
<tr>
<td>6</td>
<td>24</td>
<td>700 ± 5</td>
<td>58</td>
<td>3% N₂-balance Ar</td>
<td>A leaking problem was addressed</td>
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<td>7</td>
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<td>58</td>
<td>50%H₂-1.5%N₂-balance Ar</td>
<td>Test coupons were located in a modified TiN coated steel cathodic cage</td>
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<td>9</td>
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<td>Cathodic cage was removed</td>
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<td>10</td>
<td>24</td>
<td>600 ± 5</td>
<td>67</td>
<td>3% N₂-balance Ar</td>
<td>The nitriding chamber was cleaned, the interior walls were covered with stainless steel foil</td>
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<td><strong>Test coupons were located inside a Ti-6Al-4V cathodic cage</strong></td>
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<td>12</td>
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<td>Boost-diffusion cycles</td>
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<tr>
<td>13</td>
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<td>3% N₂-balance Ar</td>
<td>Boost-diffusion cycles</td>
</tr>
<tr>
<td>14</td>
<td>24</td>
<td>600 ± 5</td>
<td>67</td>
<td>3% N₂-balance Ar</td>
<td>Boost-diffusion cycles</td>
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<td><strong>Surface activation pretreatment in an aqueous solution containing 1% HF + 15% HNO₃ for 5 min</strong></td>
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<td>3% N₂-balance H₂</td>
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</tr>
<tr>
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<td>3% N₂-balance H₂</td>
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Table 3.2 The plasma nitriding conditions tried in this research (Continued)

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<td>19</td>
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<td>20-28</td>
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<td>67</td>
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<td>600 ± 5</td>
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<td>600 ± 10</td>
<td>69</td>
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<tr>
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<td>3% N\textsubscript{2}-balance H\textsubscript{2}</td>
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<td>3% N\textsubscript{2}-balance H\textsubscript{2}</td>
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<tr>
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<td>700 ± 15</td>
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<td>3% N\textsubscript{2}-balance H\textsubscript{2}</td>
</tr>
<tr>
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<td>600 ± 5</td>
<td>507</td>
<td>3% N\textsubscript{2}-balance H\textsubscript{2}</td>
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<td>67</td>
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<td>600 ± 5</td>
<td>67</td>
<td>3% N\textsubscript{2}-balance H\textsubscript{2}</td>
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<td>79</td>
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<tr>
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<td>24</td>
<td>900 ± 5</td>
<td>427</td>
<td>3% N\textsubscript{2}-25% Ar-balance H\textsubscript{2}</td>
</tr>
<tr>
<td>45</td>
<td>24</td>
<td>600 ± 5</td>
<td>475</td>
<td>3% N\textsubscript{2}-25% Ar-balance H\textsubscript{2}</td>
</tr>
<tr>
<td>46</td>
<td>24</td>
<td>900 ± 5</td>
<td>68</td>
<td>3% N\textsubscript{2}-balance H\textsubscript{2}</td>
</tr>
</tbody>
</table>
3.1.2 Shot Peening Pretreatment and Fabrication of SPD Surface Layer

The shot peening pretreatment was carried out on 2 cm × 2 cm test coupons cut from a mill-annealed ELI-grade Ti–6Al–4V plate in an industrial shot peening facility. The surfaces were blasted in an air powered system at 90 psi (~ 621 Pa) for 30 s with S–460 grade steel shots with an average diameter of 1.2 mm. The top surface of the coupons was completely covered with shot peening collision dents — 100% coverage. The severe plastic deformation (SPD) imposed on the surfaces by shot peening increased the surface roughness. The average surface roughness (R_a) and peak-to-valley ratio (R_t) of shot peened surfaces as measured by optical surface profilometry were 6.27 ± 0.02 μm and 108.07 ± 10.5 μm, respectively. Subsequently, an approximately 2 μm thick layer was removed from the surface of the shot peened samples by mechanical grinding to eliminate surface oxide scales and other contaminants. The surfaces were then polished with 3 μm diamond suspension and chemically activated (as explained in 3.1.1) prior to the plasma nitriding treatment to remove the inherent oxide scales from the surface. The samples were placed inside a Ti cathodic cage in the nitriding chamber and plasma nitriding was performed at 600°C for 24 h in an atmosphere containing 6% N_2. The working pressure was approximately 67 Pa and the glow discharge was maintained at a voltage of 600 V. Subsequently, the nitrided samples were cooled down to room temperature under vacuum conditions. A set of untreated Ti–6Al–4V samples were also prepared and nitrided under the same conditions for comparative reasons.
3.2 Mechanical Testing Methods

3.2.1 Uniaxial Tensile Tests

The tensile samples were small-sized specimens that measured 6 mm in diameter and 24 mm in length at the gauge section (Figure 3.4-a) conforming to the specifications outlined in the ASTM E8 standard [194]. The samples were machined from the as-received rods. After machining, the gauge section of samples were mechanically polished using silicon carbide emery paper (240, 320, 400, 600, and 1500 grit) and subsequently polished using 3 µm and 1 µm diamond suspensions on medium-napped polishing cloth (MicroCloth, Buehler). The polished samples were ultrasonically washed in an ethanol bath and dried in cool air. The polished gauge section of tensile samples had an average surface roughness (Ra) and root mean squared roughness (RMS) of 0.14 µm and 0.18 µm, respectively.

The uniaxial tensile tests were conducted with MTS Criterion-43 electromechanical universal testing equipment (Figure 3.5). All the tests were carried out at a loading rate of 0.5 mm/min and the strain values were measured using an axial extensometer clipped to the gauge lengths. The load cell and the extensometer had an accuracy better than ± 0.5% of the applied load/strain. After the experiments, the engineering stress-strain curves were constructed based on the force-displacement data and the yield strength, ultimate tensile strength [72], modulus of elasticity and ductility (tensile elongation) were determined from the obtained results. The elastic modulus was the average slope of the linear section of the curve and the offset method, recommended by the ASTM E8 standard, was followed for determination of the yield strength.
3.2.2 Rotation Bending Fatigue Tests

The fatigue samples had an hour-glass configuration with a tapered length of 50 mm and a diameter of 5.6 mm in the thinnest section (Figure 3.4-b). These samples were also machined from the as-received bars and their gauge section were polished and prepared with the same procedure explained in 3.2.1 for tensile samples. Rotating bending fatigue tests were performed using a custom-made R.R. Moore machine manufactured at the University of Windsor. The tests were carried out under pure bending condition (R = –1) at a frequency of 3000 rpm. The first samples were tested at approximately 20 % of the tensile strength where failures were expected to occur at a relatively short number of cycles. The testing stress was decreased for the rest of the samples until at least three samples did not fail at $10^7$ cycles (run-out). The highest stress at the run-out was taken as the fatigue endurance limit. Subsequently, the stress-life (S–N) curves were constructed and used to evaluate the resistance to fatigue crack initiation.

3.3 Evaluation of Tribological Properties

3.3.1 Ball-on-disk Tests

Test coupons (2 cm × 2 cm) were cut from the as-received plates using a wire cut electrical discharge machine (EDM) for wear tests. The top surface of coupons was mechanically prepared by wet grinding on 240, 320, 400, 600, and 1500 grit silicon carbide emery paper, followed by polishing using 3 μm and 1 μm diamond suspensions on medium-napped polishing cloth (MicroCloth, Buehler). After polishing, the coupons were ultrasonically washed in an ethanol bath and dried in cool air.
The average surface roughness ($R_a$) and root mean square roughness (RMS) values for polished coupons were 0.04 µm and 0.05 µm, respectively as measured by optical surface profilometry. Two types of materials were used as counterface for the wear tests, AISI E52100 chrome steel and sapphire. The AISI E52100 chrome steel balls (6 mm diameter) were purchased from McMaster Carr and had a chemical composition of 0.95-1.10 wt.% C, 0.2-0.45 wt.% Mn, 0.25-0.35 wt.% Si, 1.3-1.6 wt.% Cr, balance Fe. The Sapphire balls (3 mm diameter) were purchased from Alfa Aesar and consisted of 99.9 wt.% Al$_2$O$_3$. The average surface roughness and some of the mechanical properties of counterface materials are listed in Table 3.3.

<table>
<thead>
<tr>
<th>Counterface material</th>
<th>Elastic modulus (GPa)</th>
<th>Hardness [195]</th>
<th>Poisson’s ratio</th>
<th>Average surface roughness (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AISI E52100 steel</td>
<td>203</td>
<td>800</td>
<td>0.3</td>
<td>0.05</td>
</tr>
<tr>
<td>Sapphire</td>
<td>430</td>
<td>~2300</td>
<td>0.27-0.3</td>
<td>0.04</td>
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</tbody>
</table>

### 3.3.1.1 Description of the Ball-on-disk Test Set-up

The ball-on-disk wear tests were performed using a Bruker’s Universal Mechanical Tester (UMT) tribometer. The instrument was positioned on a stable base and isolated from external interferences. The general view and different components of this tribometer are illustrated in Figure 3.6. A two-dimensional force sensor on the upper drive was capable of measuring friction and normal load in the range of 0.2 to 20 N with a resolution of 1 mN. The suspension springs that were mounted to the force sensor
helped maintain a constant load during the tests by compensating for variations in the distance between the surface of the test coupon and the force sensor in motion. The motorized rotational lower drive allowed rotation of the sample about a vertical axis with speeds varying from 0.001 to 3000 rpm with an acceleration/deceleration time of 5 sec.

The test coupons were positioned inside a sample holder designed to ensure a uniform and levelled gripping around the full circumference of the test coupon. Dry sliding wear tests were carried out at room temperature (25±3˚C) and the relative humidity of 25±5 RH% under different sliding conditions. The tests were performed at applied normal loads between 0.5-10 N and sliding speeds between 0.005-0.1 m/s. The total number of cycles varied between 200 to 5000 cycles (10-200 m).

3.3.1.2 Measurement of Coefficient of Friction and Wear Rate

Real-time dynamic load and tangential force values were recorded during the tests. After the tests, the obtained data were exported from the UMT Test Viewer software and the coefficient of friction values were calculated. The wear rates were determined by means of mass loss and volume loss measurements. The mass loss per unit distance was calculated by weighing the test coupons before and after each test using a Sartorius LE225D electronic balance to the precision of 0.01 mg. In order to find the volumetric wear values a methodology based on optical profilometry of wear tracks was adopted. This method is described in detail in section 3.4.2.2.
3.3.2 Microscratch Tests

3.3.2.1 Description of Microscratch Testing Set-up

Microscratch tests were utilized to study the friction behaviour and damage evolution of the plasma nitrided surfaces under sliding contact. The tests were carried out according to the ASTM C1624 standard [196] using a CSM Instruments Micro-Combi tester with a Rockwell C diamond stylus (Figure 3.7). The diamond indenter had a 120° apex angle and a hemispherical tip with a 200 µm radius and was checked under an optical microscope to be free of any damage and contamination prior to the tests.

The microscratch tester was capable of applying normal loads in the range of 0.03 – 30 N with a resolution of 0.3 mN and was equipped with an acoustic emission sensor attached to the loading arm and a built-in automated optical microscope. The optical microscope was used for initial assessment of coating damage after the scratch tests. In addition to the normal force, variations in tangential force (resolution of 0.3 mN), penetration depth (resolution of 0.3 nm), and acoustic emission signals were also measured and recorded during each test. Two types of tests were carried out, (i) progressively increasing load tests and (ii) constant load tests (loads selected according to the critical loads determined in (i). Lateral displacement speeds of 1 mm/min, 10 mm/min and loading rates of 10 N/min and 100 N/min were used in the experiments.

3.3.2.2 Microscratch Test at Progressively Increasing Loads

During the progressive tests the applied load linearly increased from 0.03 to 20 N as the stylus moved at a constant displacement speed on the sample’s surface. The critical
loads corresponding to the onset of coating failures were identified using acoustic emission signals and subsequent scanning electron microscopy (SEM) observations. Acoustic emission data was found useful in damage assessment as each brittle failure (cracking, chipping, spallation, delamination, etc.) produced an elastic wave signal detected by the acoustic emission detector of the testing apparatus.

3.3.2.3 Single and Multiple-pass Microscratch Test at Constant Loads

Single and multiple-pass microscratch tests were conducted at specific constant loads ranging from 0.5 N to 20 N to analyse the friction behaviour and adhesion of the plasma nitrided surfaces. The constant loads were selected based on critical failure loads obtained by progressive tests.

3.4 Characterization Methods

3.4.1 Surface Topography and Fractographic Studies

The morphology of surface features were studied under a FEI Quanta 200 scanning electron microscope located at Great Lakes Institute for Environmental Research, University of Windsor. The microscope featured a field emission gun (FEG) capable of accelerating voltages between 200 V and 30 kV. An Everhardt-Thornley secondary electron detector and a solid-state backscattered electron detector enabled imaging in both secondary electron (SE) and backscattered electron (BSE) imaging modes. The instrument was capable of imaging with 3.0 nm spatial resolution at 1 kV and 1.2 nm resolution at 30 kV (in the SE mode). The microscope was also equipped with an
energy dispersive x-ray spectroscopy (EDS) detector utilized for collecting spectra, line-scans and elemental mapping for chemical characterization of the areas under study. The morphology of surface features and their elemental analysis were studied at a low accelerating voltage of 5-10 kV which yielded a satisfactory combination between resolving surface details and low electron beam penetration. The fracture surfaces of tensile and fatigue samples were analyzed under the SEM at an accelerating voltage of 10 kV to investigate the failure micromechanisms.

3.4.2 Cross-sectional Investigation of Microstructures

For cross-sectional investigation of microstructures, the test coupons were sectioned using a low-speed diamond wheel saw to minimize subsurface damage. The sectioned pieces were cleaned in an ultrasonic ethanol bath and dried in cool air. For edge retention and protection of the near surface microstructure against mechanical damage, the desired surfaces were plated with electroless nickel prior to metallographic preparation (Buehler EdgeMet Electroless Nickel Kit).

A general purpose epoxy system with a peak temperature of 40°C and comparatively high hardness (80 Shore D hardness, equivalent to ~ 647 HV) was used to mount the cross sections (Buehler EpoxiCure). The metallographic procedure began with serial grinding of the surfaces of wet silicon carbide abrasive papers of 180, 240, 320, 400, 600, 800 grit in successive steps. Subsequently, two diamond polishing steps were performed with 3 μm and 1 μm polycrystalline diamond suspensions charged on medium-napped polishing cloths (Buehler MicroCloth). The polished samples were
cleaned in an ultrasonic ethanol bath prior to remove any particles of polishing procedure from the surfaces.

In order to reveal the microstructural features in our investigations the following etching solutions were selected from a list of etchants for titanium alloys [197]; Kroll’s reagent (2 mL HF + 5 mL HNO₃ + 100 mL H₂O) for general microstructural characterizations and Remington B etchant (10 mL HF+ 10 mL glycerin) for outlining the α grains. The mounted samples were coated with a thin carbon layer to increase the electrical conductivity and inhibit excessive charging during the SEM investigations and an accelerating voltage in the range of 10-15 kV was used in the electron microscopy observations.

3.4.3 Cryogenic Fracture analysis

Cryogenic fracturing is one of the useful techniques used for examining the cross-sectional structure of surface layers and coatings on metals by scanning electron microscopy. The method is rapid, simple and complimentary to the classical metallography methods consisting of mounting and polishing because it can reveal features that may be masked or exaggerated by artifacts made by mechanical metallographic preparation. The cryogenic fracturing technique has been found to be applicable to steels and alloys of aluminum, magnesium, and titanium [146, 198, 199].

In this investigation, this method was used as part of microstructural characterization of plasma nitrided Ti-6Al-4V alloy. A 5 mm × 25 mm section was cut from plasma nitrided test coupon using a diamond saw. In the middle of the thin sample, a 4 mm long notch was cut on the free surface using the wire EDM. The end of the notch
was 1 mm apart from the nitrided surface. The notched sample was subsequently submerged in liquid nitrogen until “frozen”, removed from the liquid nitrogen, and quickly fractured keeping the coating side in tension. The fractured surfaces were then examined under the SEM.

3.4.4 Examination of Wear Tracks, Scratch Tracks, and Wear Debris Particles

After the wear tests the morphology and composition of wear tracks, wear scars on counterface balls and wear debris particles were analyzed using the SEM/EDS. The images were captured at a moderately low accelerating voltage of 5-10 kV to minimize charging problems and prevent surface damage especially during examination of wear debris particles and sapphire counterface balls. The morphology of wear scars on counterparts was also observed under an optical microscope. A Keyence digital microscope (VHX-700 series) was utilized for this purpose with a large depth of field and high resolution (2.11 million Pixels) camera. The scratch paths were also studied using the SEM/EDS to complement the acoustic emission data and elucidate the coating failure events.

3.4.5 Surface Profile Measurements by Optical Interferometry

3.4.5.1 Surface Roughness Measurements

The surface roughness measurements were obtained using a Wyko – Veeco NT1100 optical profilometer (Figure 3.8). The light source in this white-light interferometer was a halogen lamp and the equipment was capable of providing three-
dimensional surface profile measurements under both VSI (Vertical Shift Interference) and PSI (Phase Shift Interference) modes. Most of the scans in this investigation were made under the VSI mode, which is more suitable for surfaces of rougher nature, with a vertical resolution better than 1 nm. Various surface height statistics such as maximum profile peak height ($R_p$), maximum profile valley depth ($R_v$), peak-to-valley difference ($R_t$), root mean squared roughness (RMS), average roughness ($R_a$) and so forth, were provided by the Wyko Vision analysis software. In this research, however, only RMS and $R_a$ parameters are used for representing the surface roughness.

### 3.4.5.2 Wear Rate Measurement

The optical profiles of wear tracks were used to calculate wear rates based on the volume of worn material. Depth profiles were taken at different locations perpendicular to the wear tracks. The obtained data was then exported to the SigmaPlot software where the worn areas were calculated. The wear rate was obtained by the following equation;

\[
\tilde{W} = A \times \frac{2\pi R}{s}
\]

(3.1)

where, $A$ is the average worn area over at least 30 measurements, $R$ is the radius of wear track and $s$ is the total sliding distance (Figure 3.9). In the wear tests where wear of the counterpart was the prevalent mechanism and significant material transfer was observed to the surface of test coupons, the wear rate of the counterface was calculated by the following equation;

\[
\tilde{W} = V_{\text{transferred}} / s = (H_{\text{ave}} \times A_{\text{ave}}) / s
\]

(3.2)
where, $H_{\text{ave}}$ and $A_{\text{ave}}$ are the average height and average surface area of transferred material to the surface of test coupons, respectively. The average height of transferred material ($H_{\text{ave}}$) was determined by the height histograms provided in the Vision analysis software and the area of transferred material ($A_{\text{ave}}$) was calculated using Buehler Omnimet image analysis software (Figure 3.10).

### 3.4.5.3 Scratch Hardness Measurement

For spherical and conical indenters scratch hardness value is defined as the vertical normal load per one half of the vertically projected area by the following equation:

$$H_s = \frac{8F}{\pi w^2}$$

(3.3)

where, $F$ and $w$ are the applied load and scratch width accordingly [200]. The optical profiles acquired on the scratch paths were utilized to calculate the scratch hardness values, using the above-mentioned equation, based on the scratch width measurements.

### 3.4.6 Surface Topography Imaging by Atomic Force Microscopy

The surface topography and roughness of the samples were studied using an atomic (scanning) force microscope (Bruker Inc. Nanoanalyzer). The measuring head was a piezoresonance probe (Berkovich tip) on a cantilever beam with high bending stiffness. The contact between the probe tip and the surface features were checked by variations in amplitude and frequency of probe oscillations.
3.4.7 Compositional Analysis by X-ray Diffraction Method

Phase constituents of the nitrided surface were identified using x-ray diffraction (XRD) analysis. The XRD tests were carried out using a Rigaku DMAX-1200 x-ray diffractometer equipped with a Cu $K_\alpha$ tube located at PROTO Manufacturing Ltd.\(^6\), and a Rigaku MiniFlex x-ray diffractometer with Cu $K_\alpha$ radiation located at the department of Chemical and Biochemical Engineering of the University of Western Ontario\(^7\). The obtained data were exported into a scientific data analysis and graphing software and the diffraction patterns were reconstructed and the diffraction peak positions (diffraction angle and d-spacing values) were identified. The XRD peaks were analyzed and indexed by assigning Miller indices to each peak according to the data available in the International Centre for Diffraction Data (ICDD) cards.

3.4.8 Elemental Analysis by Optical Emission and X-Ray Spectroscopic Methods

Glow discharge optical emission spectroscopy (GDOES) was utilized to determine variation of the atomic concentration of elements in the near surface region. The optical emission measurements were carried out using a Jobin Yvon GD-profiler HR located at the McMaster Steel Research Centre\(^8\). The chemical composition of the outermost surface layer of nitrided samples was studied by a Kratos AXIS Nova Spectrometer equipped with a monochromatic Al $K_\alpha$ x-ray tube located at Surface Science Centre of

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\(^6\) PROTO Manufacturing Ltd., 2175 Solar Crescent, Oldcastle, ON N0R 1L0  
\(^7\) Department of Chemical and Biochemical Engineering, University of Western Ontario, London, ON N6A 5B9  
\(^8\) Steel Research Centre, McMaster University, 1280 Main Street West, Hamilton, ON L8S 4L7
the University of Western Ontario. The XPS analysis on an area 300 µm × 700 µm with a pass energy of 160 eV.

3.4.9 Residual Stress Measurements by X-ray Diffraction

The developed residual stress level on the surface after plasma nitriding was measured with the \(\sin^2 \psi\) x-ray diffraction method using a laboratory non-destructive residual stress measurement LXRD system. The LXRD-Ypsi system is equipped with an automated focus pointer for convenient focusing and two x-ray detectors to collect diffracted beams from two directions thus providing twice as much data in the same amount of time simply by virtue of the design. The detectors were multi-channel solid state detectors with position sensitive scintillation providing sufficient speed, stability, with no dead time and a wide 2θ range which offers increased accuracy on materials with broad diffraction peaks. A titanium target was used for production of x-ray radiations. A rectangular aperture (1 mm × 5 mm) was selected and in order to clarify the diffraction pattern and increase the collected intensities the stage rotated by 360˚ and [201] crystallographic plane at the Bragg angle (2θ) of 144˚ were selected and the diffracted x-ray radiations were collected at 11 different tilt angles, (± 25°, ± 20°, ± 15.50°, ± 8.75°, ± 1.38°, 0). A five-step procedure was followed to calibrate the instrument prior to conducting the XRD residual stress measurements.

(i) Alignment of the x-ray beam and determining the background radiation (gain); Alignment of the beam was performed according to the ASTM E915 standard on stress-

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9 Surface Science Western, University of Western Ontario, 999 Collip Circle, London, ON N6G 0J3
10 PROTO Manufacturing Ltd., 2175 Solar Crescent, Oldcastle, ON N0R 1L0
free powder of the same material on which the residual stress was to be measured. In order to obtain the level of background radiation in a glass sample was used with a gain power of 26 kV at 10 mA.

(ii) Determination of the x-ray elastic constant; The x-ray elastic constant (XEC) is a function of mechanical properties of the material and the crystallographic plane selected to perform the measurements.

(iii) Evaluation of surface condition; Surface roughness, surface oxide layers, etc. were assessed since they influence the XRD residual stress measurement results.

(iv) Selection of the collection parameters; Collection parameters, e.g., collection time, number of $\psi$ tilts used for $d$-spacing-$\sin^2\psi$ plots, x-ray diffraction peak position, surface curvature, and beam size, were carefully selected in order to minimize the random and/or systematic errors in the results.

3.4.10 Focused Ion Beam Technique

In depth site-specific cross-sectional analysis of wear tracks and scratch paths were carried out using a LEO (Zeiss) 1540 XB focused ion beam (FIB)/SEM fitted with an energy dispersive spectrometer (EDS) located at the University of Western Ontario Nanofabrication facility\(^1\). Prior to the milling process, a thin layer of osmium (~ 3 nm) was deposited on the surfaces to increase their conductivity using an osmium plasma coater. This thin layer of amorphous osmium prevented samples from charging and enhanced the secondary electron yield.

\(^1\) Western Nanofabrication facility, Physics & Astronomy Building, University of Western Ontario, London, ON, N6A 3K7
After locating the region of interest, a 2 µm thick layer of platinum was deposited on the selected area using a gas injection system prior to milling to prevent surface features from damage during the milling process (Figure 3.11-a). The ion milling began by cutting a trench normal to the deposited platinum layer, using Ga ions from a Ga-based liquid metal ion-source (LMIS), at an accelerating voltage of 30 kV (Figure 3.11-b). The beam currents varied from 10 nA (rough milling) to 200 pA (polishing). The final polishing step was conducted at a low ion-beam current of 80 pA to minimize the beam damage (Figure 3.11-c). All the FIB trenches were made parallel to the scratch direction of the scratch paths and sliding direction of the wear tracks. The ion-milled trenches were imaged using a 1 kV electron beam located at a 54° angle (Figure 3.12).

3.4.11 Analytical Transmission Electron Microscopy

3.4.11.1 TEM Sample Preparation by the FIB Milling Lift-out Technique

In this research the FIB milling lift-out technique [202] was utilized for TEM thin-foil sample preparation which enables fabrication of TEM samples with around 50 nm thicknesses for high-resolution TEM imaging and electron energy loss spectroscopy (EELS). The TEM samples were prepared using a dual beam Zeiss NVision 40 equipped with a FIB milling instrument and a Schottky field emission gun (FEG) filament scanning electron microscope (SEM) located at the Canadian Centre for Electron Microscopy (CCEM)12. The FEG electron gun delivered high beam currents in small probe diameters for acquisition of high resolution images. The system also featured a secondary ion and

12 Brockhouse Institute for Materials Research
B161 A. N. Bourns Building, 1280 Main Street West, Hamilton, ON, L8S 4M1
electron (SI/SE) detector and an Oxford energy dispersive spectrometer (EDS) equipped with a silicon drift detector (SDD) that allowed simultaneous imaging, elemental analysis and mapping the spatial distribution of elements.

The initial and essential stage was the deposition of a thin (1-2 µm) layer of tungsten on the region of interest (milling site) to protect the surface features from the milling damage. The subsequent stages were then followed. A large probe size (2.5 µm) was used for fast ion milling to cut two trenches on either side of the tungsten layer deposited on the area of interest (Figure 3.13-a). The trenches themselves were approximately twenty microns wide, fourteen microns long and ten to fifteen microns deep. Smaller probe sizes of 27 nA, 13 nA, and 6.2 nA were used to polish both sides of the sample to a thickness of approximately 1 µm. The sample was then tilted (45 to 60°) and frame cuts on the bottom, left side, and a portion of the right side, mill the TEM sample free from the bulk sample (Figure 3.13-b). The TEM sample was bonded to a micromanipulator with depositing a layer of tungsten (Figure 3.13-c). The attachment bond on the top right corner of the TEM sample was milled away and the TEM sample was lifted out and moved over to a copper grid using the micromanipulator (Figure 3.13-d). The sample was attached to the copper grid with deposition of tungsten layer and milled free from the micromanipulator (Figure 3.13-e). Ion milling continued on both sides of the sample with a smaller beam current to obtain electron transparency (a thickness of between 50 and 120 nm). This stage also cleaned any possible damages due to imaging using the ion beam in the previous steps (Figures 3.13-f, 3.13-g). The images from TEM samples were taken with an electron beam.
3.4.11.2 Imaging in the TEM, STEM and HRTEM Modes

Detailed cross-sectional investigation of the nitrided microstructures was carried out using the Titan 80-3000 scanning/transmission electron microscope (S/TEM) manufactured by FEI Company located at the Canadian Centre for Electron Microscopy. The instrument was fitted with a field emission gun X-FEG Schottky emitter and a monochromator that lowered the energy spread of the electrons below 0.25 eV. Below the electron source and the monochromator an accelerator enabled a wide acceleration voltage range of 80 to 3000 kV. The microscope resolved the TEM images to 0.09 nm (at 80 kV) with image aberration correction. On-axis bright field and high angle annular dark field (HAADF) detectors collected elastically and inelastically scattered electrons for bright field and dark field images in the STEM mode. As low as 0.06 nm (at 300 kV) could be resolved in the STEM imaging mode. Depending on the orientation of the sample with respect to the incident electron beam, the Bragg-diffraction scattered electrons could also be collected by the HAADF detector and thus the HAADF signal contained information about both the chemical composition (Z-contrast) and the diffraction contrast. This is a useful tool for studying grain size and crystal defects, e.g., dislocations and strain fields. A large tilt range (up to ± 35°) for the TEM samples in this instrument enabled adjustment of the polycrystalline materials in the desired orientation.

High-resolution TEM imaging (HRTEM) generated images with atomic-scale resolution. The DigitalMicrograph [203] software by Gatan Inc. was used to obtain fast Fourier transform (FFT) patterns from high-resolution images which contain the same structural information as the electron diffraction patterns.
3.4.11.3 Chemical Analysis using EDS, SAED and EELS

The S/TEM was equipped with an energy dispersive x-ray spectrometer for low concentration chemical analysis, collecting and analyzing spectra, line scans and chemical maps. The x-ray microanalysis was coupled with electron diffraction patterns and electron loss energy loss spectroscopy (EELS) to obtain structural information and identify the chemical composition of different microstructural features. The EELS spectroscopic study was conducted with a resolution of 30 pm using a high resolution electron energy loss spectrometer (Gatan 865).

3.4.12 Microhardness Measurements

3.4.12.1 Description of Microindentation Testing

Microindentations were made by a diamond Vickers indenter using a CSM Instruments Micro-Combi Tester. The indentation tester is a high-precision instrument used for determination of mechanical properties (e.g., hardness, elastic modulus, etc.) of thin films, coatings and substrates. The microhardness values are determined from indentations made by a Vickers diamond tip based on loading-unloading curves using the Oliver and Pharr method [204]. The instrument benefits from a unique surface referencing technique, automated optical microscopic inspection and ability to perform continuous multi-cycle indentations. The range of applied load is from 0.03-30N with a resolution of 0.3mN, depth resolution is 0.3 nm and the loading rate can be increased up to 300 N/min.
3.4.12.2 Determination of Near-Surface Microhardness Profile

Microhardness-depth profiles were obtained by microhardness measurements on cross sections tapered at an angle of 5.6°, providing 10 times magnification of the subsurface region. For each indentation a maximum load of 245 mN was applied at 490 mN/min loading rate and removed at the same rate after 10 seconds. The microhardness distribution against depth was used to assess the thickness of nitrogen diffusion zone due to the hardening effect of nitrogen interstitials.
Figure 3.1 (a) A secondary electron SEM image showing the microstructure of as-received Ti-6Al-4V (ELI grade) used in this research, the microstructure consisted of equiaxed α grains, retained β particles at α grain boundaries, and fine recrystallized β particles inside the α grains. (b) A higher magnification SEI showing that the α grains were delineated by different orientation of fine recrystallized β particles (etched in glycerol + HF (1:1) solution).
Figure 3. 2 (a) A schematic presentation of the plasma nitriding facility; no external heating source was used, (b) the titanium coupons were placed on titanium stands inside a cathodic cage that was also made from a titanium alloy to minimize contamination. (c) Schematic illustration of plasma nitriding set up for tensile and fatigue samples. The samples were hung inside the cathodic cage using titanium wire in order to ensure the uniform formation of plasma surrounding the samples.
Figure 3. 3 (a) The plasma nitriding unit located at Exactatherm Ltd. used in this research. (b) A titanium cage was used to intensify the glow discharge. (c) The test coupons were placed in the geometric center of the titanium cage.
Figure 3.4 Schematic representations showing the dimensions of (a) tensile and (b) fatigue samples.

![Diagram showing tensile and fatigue sample dimensions](image)

Gauge length = 24mm
D = 6mm
A = 30mm

Figure 3.5 MTS Criterion-43 electromechanical universal testing equipment used to perform tensile test in this research, (b) a clip-on axial extensometer was used to measure the strain values.

![MTS Criterion-43 equipment](image)

Strain gauge
Tensile sample
Figure 3.6 (a) Bruker’s Universal Mechanical Tester (UMT) tribometer used for wear tests. In this research, the enclosed area is where the image shown in “b” was taken. (b) The lower rotational drive used for ball-on-disk tests and the friction/force sensor on the upper drive. The enclosed area is the location where the image shown in “c” was taken. (c) The ball-on-disk test set-up showing the suspension springs, upper sample holder (ball holder) and lower sample holder (test coupon holder).
Figure 3. 7 CSM Instruments Micro-Combi Tester with the microscratch test set-up showing the automated stage, optical microscope and the diamond Rockwell indenter.
Figure 3. 8 An optical surface profilometer (Veeco, Wyko) was used in this research to measure the surface roughness after nitriding treatments.

Figure 3. 9 (a) Three-dimensional (3D) and (b) two-dimensional (2D) optical profilometry images of the wear tracks used for measuring the worn area and wear rates after the wear tests in this investigation.
Figure 3.10 (a) A typical three-dimensional optical surface profile of the wear track on plasma nitrided Ti-6Al-4V tested against AISI 52100 steel counterface, (b) height histogram obtained from the profile shown in “a” based on which the average height of transferred material was estimated, (c) two-dimensional optical surface profile from “a”, (d) calculation of accumulated area using an image analyzer software.
Figure 3. 11 Scanning electron micrographs illustrating the procedure of focused ion beam (FIB) milling to study the cross section of scratch paths and wear tracks in this investigation. (a) Deposition of a platinum layer on the selected area using a gas injection system prior to milling to prevent surface features from damage during the milling process. (b) Cutting a trench normal to the deposited platinum layer, using gallium (Ga) ions at an accelerating voltage of 30 kV and beam current of 10 nA (rough milling). (c) Polishing the milled cross section with progressively decreasing ion beam currents from 200 to 80 pA.
Figure 3. The focused ion beam (FIB)/SEM were used for in-depth site-specific cross-sectional analysis of wear tracks and scratch paths in this research. Imaging from the ion-milled trenches was performed using the electron beam at an angle of 54°.
Figure 3. 13 SEM images illustrating the procedure of TEM sample preparation using the focused ion beam (FIB) milling lift-out technique. An approximately 1 µm thick layer of tungsten (W) was deposited on the region of interest to protect surface features from the milling damage. (a) Two trenches were cut on either side of the tungsten layer using a Ga ion beam, (b) a frame cut was made on the bottom of the TEM sample, (c) frame cuts were also made on the left side and a portion of the right side of the TEM sample and the TEM sample was attached to a micromanipulator by deposition of a tungsten layer, (d) the TEM sample was cut free from the bulk, (e) TEM sample was lifted out by the micromanipulator and carried to a copper grid, (f) TEM sample was joined to the copper grid using a layer of tungsten and the micromanipulator was detached, (g) further milling continued on both sides of the TEM sample, (h) electron transparency was achieved.

96
CHAPTER 4: RESULTS

In this chapter, first a summary of the results obtained from evaluation of mechanical and tribological properties of the as-received Ti-6Al-4V alloy will be presented. Subsequently the results of plasma nitriding treatments conducted under different conditions which led to the optimization of the process will be presented. This section includes characterization of nitrided microstructures to study the effect of plasma nitriding duration, temperature, pressure and composition of the nitriding environment. For selected nitriding treatments, the microstructural analyses are coupled with evaluation of mechanical properties, e.g., tensile and fatigue testing and assessment of sliding behaviour by microscratch tests. For the optimized nitriding conditions, analytical microscopy techniques, e.g., scanning/transmission electron microscopy (S/TEM) were utilized for microstructural characterization and the microstructural features were identified with elemental and phase identification techniques such as the x-ray energy dispersive spectroscopy (EDS), glow discharge optical emission spectroscopy (GDOES), electron energy loss spectroscopy (EELS), and selected area electron diffraction patterns (SAD). The mechanical properties and tribological behaviour of the plasma nitrided alloy will be presented and compared with those of the untreated alloy and a high temperature treatment. The mechanical properties were studied using uniaxial tensile tests, rotation bending fatigue tests and cryogenic fracture analysis and the tribological behaviour were evaluated using microscratch and ball-on-disk tests.

In the final section, shot peening was introduced as a pretreatment process to plasma nitriding. The microstructure of shot peened surface before and after plasma
nitriding were analyzed using SEM and TEM techniques. The sliding resistance and fatigue behaviour of the plasma nitrided alloy with the pretreatment were also investigated using microscratch and ball-on-disk tests and rotation bending fatigue tests.

4.1 Mechanical Properties of Ti-6Al-4V Alloy

4.1.1 Tensile Tests

The engineering stress-strain curves constructed from force-displacement curves after the uniaxial tensile tests on the mill-annealed Ti-6Al-4V alloy (base alloy) are given in Figure 4.1. The alloy displayed an initial elastic deformation behaviour with a maximum elastic strain of approximately 1% followed by yielding at about 940 MPa. The plastic deformation then continued with some strain hardening until the tensile strength (TS) of about 1045 MPa and the onset of the necking phenomenon. The plastic deformation continued locally in the necking region up to the final fracture at around 812 MPa. The average offset yield strength of the alloy (0.2% offset) was 939.5 MPa. The experiment was repeated twice with similar results. The obtained results (Tabulated in Table 4.1) were in agreement with those reported in the literature for Ti-6Al-4V alloy with a mill-annealed microstructure [2].

Table 4.1 Tensile properties of the mill-annealed Ti-6Al-4V alloy used in this research

<table>
<thead>
<tr>
<th>Tensile strength (MPa)</th>
<th>Yield Strength (Offset = 0.2%) (MPa)</th>
<th>Elastic Modulus (GPa)</th>
<th>Tensile Elongation (%)</th>
<th>Fracture Stress (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1044.8 ± 10.3</td>
<td>939.5 ± 3.5</td>
<td>102.6 ± 3.9</td>
<td>13.9 ± 0.21</td>
<td>812.4 ± 10.3</td>
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Fracture surface observations by stereo microscopy (Figure 4.2) showed that the Ti-6Al-4V alloy had a ductile “cup and cone” type of failure. The fracture surface consisted of a flat, dull region in the middle surrounded by the shear lips at a 45˚ angle. Further investigations of the morphology on the tensile fracture surfaces by scanning electron microscopy (SEM) (Figure 4.3-a) revealed that the shear area was characterized by elongated dimples while in the middle of samples the dimples had equiaxed morphology (Figure 4.3-b). Figure 4.4 is a secondary electron SEM image from the shear lip region after being immersed in Kroll’s reagent showing homogenous deformation of the α phase and β particles under tensile loads.

4.1.2 Fatigue Tests

Figure 4.5 is the S-N curve (alternating stress vs. number of life cycles) obtained from the rotation bending (pure bending, R = -1) fatigue tests on Ti-6Al-4V alloy. The highest stress value obtained at $10^7$ cycles (run-out) was 721 MPa and represented the fatigue endurance limit of the alloy.

Fractographic investigations were carried out for failures in both the low cycle (less than $10^5$ cycles) and high cycle (more than $10^5$ cycles) regions. A secondary electron SEM micrograph from fatigue fracture at 761 MPa ($N_f = 1.1 \times 10^5$ cycles, high cycle fatigue region) is shown in Figure 4.6-a. There was one source of fatigue crack initiation located close to the surface of the sample. Fatigue crack propagation had two different morphologies in Regions I and II before leading to the final rupture.

A higher magnification view of the fatigue crack initiation site (Figure 4.6-b) showed signs of distortion and plastic deformation. Crack propagation in Region I
(Figure 4.6-c), relatively smooth surfaces with microcracks and striations perpendicular to the crack growth direction. The average striation spacing in this region was measured at 0.6 µm/cycle from SEM images (similar to Figure 4.6-e) and using the empirical relationship of $\text{Striation spacing} \approx 6 \left(\Delta K/E\right)^2$ [205] leads to an estimation of cyclic stress intensity factor at about 35 MPa√m. Crack propagation in Region II consisted of ripple marks and microcracks perpendicular to the propagation direction as shown in Figure 4.6-d. The final rupture region consisted of dimples indicating a ductile type of failure.

Figure 4.7-a is a secondary electron SEM micrograph from fatigue fracture at 816 MPa ($N_f = 4.3 \times 10^4$ cycles, low cycle fatigue region). Similar to the high cycle region, the fatigue crack originated close to the surface and propagated with two different morphologies in Regions I and II prior to the final rupture. Figure 4.7-b shows a higher magnification view of the fatigue crack origin and Figure 4.7-c, d illustrate the relatively smooth morphology of crack propagation in Region I and the striations in this region. The average striation spacing in this region was measured at 1.1 µm/cycle from SEM images (similar to Figure 4.7-d) and using the empirical relationship of $\text{Striation spacing} \approx 6 \left(\Delta K/E\right)^2$ [205] leads to an estimation of stress intensity factor at about 48 MPa√m. Higher magnification view of crack propagation in Region II (Figure 4.7-e) revealed ripple marks and microcracks perpendicular to the propagation direction. The final rupture was in a ductile manner evidenced by abundant dimples in this region (Figure 4.7-f).
4.2 Tribological Properties of Ti-6Al-4V Alloy

4.2.1 Wear Rate

The variation of wear rates with applied normal load obtained by ball-on-disk wear tests on Ti-6Al-4V alloy against AISI 52100 steel counterface is presented in Figure 4.8. The wear tests were carried out at 0.1 m/s sliding speed for a total sliding distance of 200 m (5000 cycles) as explained in Section 3.3. The wear rates were calculated based on both mass loss measurements (Figure 4.8-a) and volumetric wear measurements by optical profilometry (Figure 4.8-b). Furthermore, the volumetric wear values were also estimated based on mass loss measurements with dividing the mass loss values by the density of the Ti-6Al-4V alloy (4.43 g/cm\(^3\)). A comparison is made between the measured and calculated volumetric wear values in Figure 4.8-b.

The wear rates tend to increase with the applied normal load. Figure 4.8-a shows that the increasing trend follows a linear trend when wear rates were measured using weight loss before and after each test. However, there seems to be a change in the slope of the curve towards a higher value after 2 N applied load according to volumetric measurements (Figure 4.8-b).

4.2.2 Friction Behaviour

Figure 4.9-a illustrates variation of coefficient of friction (COF) recorded during ball-on-disk wear tests with the sliding distance at different applied loads of 0.8 N, 1.2 N, 2 N, 3.5 N, and 5 N. It was observed that at all loading conditions a steady-state condition is reached after an initial running-in period varying between 50 - 60 m. During the steady
state stage, Ti-6Al-4V surfaces showed an unstable friction behaviour with large fluctuations in COF values. In Figure 4.9-b the average COF value in the steady state region is plotted against the applied normal load during each test. In general it was observed that the average COF value decreased with the applied normal load.

4.2.3 SEM Observations of Worn Surfaces and Wear Debris Particles

Wear Test at Low Loads (F = 0.8 N)

Figure 4.10-a is a three dimensional optical profile of the wear track on the surface of Ti-6Al-4V alloy tested at 0.8 N applied normal load against AISI 52100 steel counterface. The worn surface consisted of ploughing grooves parallel to the sliding direction and occasional accumulation of material on the wear track. A two dimensional cross sectional surface profile of the wear track is given in Figure 4.10-b showing the extent of material loss from the surface.

Figure 4.11 is a back-scattered SEM image from the worn surface of Ti-6Al-4V alloy at an applied load of 0.8 N and sliding speed of 0.1 m/s after 200 m. The wear track consisted of dark grey patches of accumulated material on the surface as well as ploughing grooves. The enclosed area is the location where higher magnification images illustrated in Figure 4.12 were taken. Closer inspection of worn surface revealed that the dark grey patches consisted of flat plateaus of accumulated material (Figure 4.12-a). The plateaus were surrounded by scattered wear debris particles (Figure 4.12-b) and microcracks were frequently observed within the plateaus (Figure 4.12-c). The worn surface was severely abraded as evidenced by ploughing grooves (Figure 4.12-d is an illustration) and fine debris particles were also observed inside the grooves. A typical
EDS analysis of the dark grey regions (plateaus) is shown in Figure 4.13. The presence of oxygen and iron as well as constituent elements of the Ti-6Al-4V alloy (Ti, Al, V) were detected in the spectrum. Figure 4.14-a is a back-scattered SEM image of the wear scar on the steel counterface after sliding against Ti-6Al-4V surface at an applied load of 0.8 N. The wear scar contained signs of abrasion and ploughing grooves parallel to the sliding direction and material accumulation was observed on one side of the wear scar. A higher magnification view of the accumulated material is shown in Figure 4.14-b. According to the EDS analysis the accumulated material found on the worn surface of the counterface had a similar elemental composition to that of the plateaus on the Ti-6Al-4V wear track (Figure 4.13).

The generated wear debris particles during wear tests at 0.8 N applied load were collected and analyzed under the SEM. They were of two different morphologies; platelets which were approximately 20 µm long and 10 µm wide (Figure 4.15-a) and fine equiaxed particles ranging from 0.3 µm to 3 µm in diameter (Figure 4.15-b). A typical EDS spectrum of the wear debris particles is given in Figure 4.15-c showing that the elemental analysis of wear debris was composed of iron, oxygen, titanium, aluminum and vanadium, similar to that of the dark grey plateaus on the wear tracks (Figure 4.13).

**Wear Test at High Loads (F = 5 N)**

Post-test observations of the worn surfaces after sliding under 5 N applied normal load by optical profilometry showed severe damage to the Ti-6Al-4V surface characterised by deep and wide wear tracks (Figure 4.16). Figure 4.17 is a back-scattered electron image showing the typical wear track morphology after sliding against AISI
52100 steel counterface at an applied normal load of 5 N. Severe wear of Ti-6Al-4V alloy was evidenced by deep and wide abrasion grooves, large plateaus of accumulated material (appeared as dark grey patches), and substantial wear debris generation. Figure 4.18-a illustrates the morphology of features on the wear track more clearly, the enclosed areas marked as “b” and “c” are the locations were higher magnification images were taken. The abrasion grooves parallel to the sliding direction and scattered fine debris particles on the wear track are shown in Figure 4.18-b. Figure 4.18-c is a high magnification image of the dark grey patches indicating that they were fragmented. The EDS analysis (Figure 4.19) indicated that in these regions in addition to titanium, aluminum and vanadium from the alloy, iron and oxygen were also present. The iron content of the plateaus at high loads (e.g., 5 N) was higher compared to that of the lower loads (e.g., 0.8 N).

Secondary electron SEM images from three different wear morphologies generated at this loading condition and their corresponding elemental analysis are shown in Figure 4.20. The cutting chip-like debris with the same chemical composition of the titanium alloy (Figure 4.20-a, Figure 4.20-d), platelet particles with sliding marks (Figure 4.20-b) and loose fine particulates (Figure 4.20-c). According to the EDS results the platelet particles and fine particulates had the same chemical composition composed of oxygen and iron in addition to titanium, aluminum and vanadium (Figure 4.20-d). Examination of the wear scar on the steel counterface also indicated that it experienced severe ploughing and abrasion characterized by scratches parallel to the sliding direction (Figure 4.21).
4.2.1.4 Cross-sectional Examination of the Wear Tracks by the FIB Milling Technique

Wear Test at Low Loads (F = 0.8 N)

Figure 4.22-a is a back-scattered SEM micrograph of the wear track on the surface of Ti-6Al-4V alloy after ball-on-disk wear test at 0.8 N applied load (the sliding speed and distance were 0.1 m/s and 200 m, respectively). The location were focused ion beam (FIB) milling was performed is marked on the image and the enclosed area is the region were EDS analysis was performed. Figure 4.22-b shows the location of FIB trench more clearly. According to the elemental analysis the worn surface in the vicinity of FIB trench contained oxygen and traces of iron in addition to titanium, vanadium and aluminum (Figure 4.23).

A general view of the ion milled cross section of the 0.8 N wear track is shown in Figure 4.24-a. It consisted of a dark grey layer with a clear interface with the subsurface region (light grey region). This layer which consists of voids and signs of deformation and agglomeration is called the mechanically mixed layer (MML) and is likely formed by compacting and agglomeration of particles (Figure 4.24-b). A delamination was also observed within this layer (Figure 4.24-c). Figure 4.24-a is a cross-sectional SEM micrograph showing the location where EDS mapping was carried out. Figure 4.25-b through 4.25-f confirm that the MML was composed of oxygen in addition to Ti, V, and Al and the delamination occurred within this layer. The amount of Fe within this layer was negligible.
Wear Test at High Loads (F = 5 N)

Figures 4.26-a, 4.26-b are back-scattered electron SEM images of the wear track of Ti-6Al-4V alloy at 5 N load wear test before and after ion milling. The FIB trench was located at a plateau of accumulate material on the wear track, Figures 4.26-c, 4.26-d show this location more clearly before and after ion milling.

A general view of the ion milled cross section of Ti-6Al-4V worn surfaces at 5 N applied load is shown in Figure 4.27-a. Occasional white streaks were observed inside the mechanically mixed layer (MML) as marked by the arrows. The white streaks were observed at a higher magnification in Figure 4.27-b. The elongation of grains in the subsurface region parallel to the sliding direction suggested severe plastic deformation in this region (as indicated by the arrows in Figure 4.27-c).

EDS mapping was performed on the ion milled cross section at the location enclosed in Figure 4.28-a. The distribution of oxygen, aluminum, titanium, vanadium, and iron are given in Figure 4.28-b through f. It was observed that the white streaks in the MML were rich in iron (Figure 4.28-f).

4.3 Optimization of the Plasma Nitriding Treatment

The results obtained from performing the plasma nitriding treatment under different conditions of temperature, duration, pressure and composition of the nitriding atmosphere, etc. are presented in this section.
4.3.1 Nitriding Duration

Plasma nitriding was performed at 600°C, under a nitriding atmosphere of 3% N₂-balance H₂ at 67 Pa, for different durations of 24 h, 45 h, 48 h, and 87 h to investigate the effect of nitriding duration on microstructure and properties. The surfaces Ti-6Al-4V samples were activated in an aqueous solution containing 1% HF and 15% HNO₃ for 5 minutes prior to the nitriding treatments. The results from 24 h and 45 h treatments will be compared in this section.

4.3.1.1 Surface Topography and Composition

The results of surface roughness measurements, represented by average roughness average (Rₐ) and root mean squared roughness (RMS) are presented in Table 4.2; each reported value is the average of at least three measurements. The average surface roughness increased by ~30% after plasma nitriding treatment for 24 hours at 600°C and by a further ~23% when plasma nitriding was extended to 45 hours.

<table>
<thead>
<tr>
<th>Surface condition</th>
<th>Rₐ (µm)</th>
<th>RMS (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polished</td>
<td>0.03 ± 0.01</td>
<td>0.04 ± 0.01</td>
</tr>
<tr>
<td>Polished + surface activation</td>
<td>0.23 ± 0.01</td>
<td>0.29 ± 0.01</td>
</tr>
<tr>
<td>Plasma nitrided for 24 h</td>
<td>0.30 ± 0.05</td>
<td>0.38 ± 0.06</td>
</tr>
<tr>
<td>Plasma nitrided for 45 h</td>
<td>0.37 ± 0.05</td>
<td>0.48 ± 0.06</td>
</tr>
</tbody>
</table>
The XRD spectra of the plasma nitrided surfaces after 24- and 45-h treatments at 600°C are presented in Figure 4.29. The XRD peaks were analyzed and indexed using JCPDS cards for TiN (PDF#38-1420), Ti₂N (PDF#17-0386, 76-0198, 73-0959), α-Ti (PDF# 44-1294) and TiN₀.₃ (PDF #41-1352). For both nitriding treatments Ti₂N, TiN₀.₃, α-Ti and traces of TiN were detected in the diffraction patterns. The significant contribution of α-Ti peaks from the substrate in the diffraction pattern was due to the x-ray depth of penetration as a result of the thin morphology of this layer.

4.3.1.2 Microstructural Characterization

Cross-sectional SEM micrographs of microstructures of plasma nitrided Ti-6Al-4V alloy at 600°C after 24- and 45-h treatments are illustrated in Figure 4.30. The plasma nitrided microstructure consisted of thin compound layers and deep diffusion zones (identified by dissolution of fine recrystallized β particles inside the α grains).

The thickness of compound layer and depth of diffusion zone were measured using an image analysis software and the results are tabulated in Table 4.3. It was found that increasing the duration of nitriding from 24 to 45 hours (more than twice) resulted in a ~ 14% increase in the depth of nitrogen diffusion. The thickness of the compound layer was slightly decreased after the 45-h treatment compared to the 24-h treatment.

The effect of plasma nitriding duration on bulk microstructure of the Ti-6Al-4V alloy was also investigated. It was found that regardless of the nitriding duration, after plasma nitriding treatments at this temperature (600°C), the substrate maintained its mill-annealed microstructure. However, the average α grain size increased by 40% and 60% after a 24 h and 45 h treatments, respectively (Table 4.4).
Table 4.3 Results obtained from measurement of microstructural features for 600°C plasma nitriding treatments for different durations measured using an image analysis software based on cross-sectional SEM micrographs

<table>
<thead>
<tr>
<th>Nitriding duration (h)</th>
<th>Thickness of compound layer (µm)</th>
<th>Depth of diffusion zone (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>24</td>
<td>1.9 ± 0.5</td>
<td>44.4 ± 5.6</td>
</tr>
<tr>
<td>45</td>
<td>1.0 ± 0.5</td>
<td>49.9 ± 6.4</td>
</tr>
</tbody>
</table>

Table 4.4 Average α grain size measurement results in the substrate; measured using an image analyzing software based on cross-sectional SEM micrographs (at least 300 grains)

<table>
<thead>
<tr>
<th>Sample Condition</th>
<th>Average α grain size (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated Ti-6Al-4V alloy</td>
<td>3.0 ± 1.3</td>
</tr>
<tr>
<td>Plasma nitriding for 24 h</td>
<td>4.2 ± 1.6</td>
</tr>
<tr>
<td>Plasma nitriding for 45 h</td>
<td>4.9 ± 1.9</td>
</tr>
</tbody>
</table>

4.3.1.3 Microhardness Profiles

Due to the solid solution hardening effect of nitrogen interstitial atoms in titanium alloys (especially α-Ti), the microhardness-depth profiles were utilized to confirm the depth of the nitrogen diffusion zone. All of the microindentations were made at a maximum applied normal load of 245 mN and averaged over at least three measurements. The depth of diffusion zone was defined as the distance from the compound layer interface where the hardness value reached that of the substrate. The depth of the hardening by plasma nitriding was estimated at about 45 µm and 60 µm after 24-h and
45-h treatments, respectively (Figure 4.31) indicating that increasing the nitriding duration by more than twice resulted in 33% increase in the depth of nitrogen diffusion.

4.3.1.4 Evaluation of the Nitrided Surfaces

In order to study the performance of plasma nitrided surfaces under sliding conditions microscratch tests were performed at constant loading conditions (5 N, 10 N, 20 N). The results indicated that plasma nitriding resulted in a reduction of coefficient of friction (COF) at all the tested loading conditions. However, different trends were observed for plasma nitrided surfaces for 24 and 45 hours at low (5 N, 10 N) and high (20 N) loads (Figure 4.32). At low loading conditions (5 N) the 24-h plasma nitrided surface had an average steady state COF value of 0.03 ± 0.001, while the average COF for the 45-h treatment was 0.10 ± 0.01. These values are considerably lower than that of the untreated Ti-6Al-4V alloy (0.24 ± 0.01), which shows improvements in the sliding behaviour by plasma nitriding treatment. The same trend was also observed at 10 N.

At high loading conditions (20 N), the average steady state COF value for the untreated alloy was 0.42 ± 0.04 while the plasma nitrided surfaces after 24-h and 45-h treatments both showed similar COF values of 0.17 ± 0.005. The higher COF value for the 45-h plasma nitriding condition at low loads can be attributed to the higher surface roughness obtained for this run. Therefore, 24 hours was selected as the optimum nitriding duration in plasma nitriding of Ti-6Al-4V alloy in this work.
4.3.2 Nitriding Atmosphere (Pressure and Composition)

In order to investigate how the nitriding gas composition and pressure affect the plasma nitriding microstructure and properties, the nitriding treatment was carried out at different chamber pressures of 67 Pa, 400 Pa, and 520 Pa and atmospheres with nitrogen contents (1.5%, 3%, and 6%) and carrier gas (H\(_2\) and Ar). The nitriding temperature, pressure and pretreatment conditions were kept constant (600˚C, 24 hours, surface activation for 5 min) for all the tests (Table 4.5).

<table>
<thead>
<tr>
<th>Temperature (˚C)</th>
<th>Duration (h)</th>
<th>Pressure (Pa)</th>
<th>Gas composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>600</td>
<td>24</td>
<td>67, 400, 520</td>
<td>3% N(_2)– balance H(_2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>67</td>
<td>1.5%, 3%, 6% N(_2)– balance H(_2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>67</td>
<td>3% N(_2)– balance Ar</td>
</tr>
</tbody>
</table>

4.3.2.1 Surface Topography and Composition

Table 4.6 presents the results of surface roughness measurements for selected nitriding treatments. According to the measurement results, the nitrogen content and nitriding pressure did not have a significant influence on the surface roughness as similar values were obtained for 3% and 6% N\(_2\) as well as 67 Pa and 400 Pa atmospheres. However, switching the carrier gas from H\(_2\) to Ar resulted in a noticeably low roughness value of 60 nm.

Figure 4.33 shows the XRD spectra obtained from the plasma nitrided surfaces under 3% and 6% N\(_2\) atmospheres. The TiN, Ti\(_2\)N, α-Ti phases and traces of TiN\(_{0.3}\) were
detected in both spectra. This indicated that increasing the nitrogen content in the nitriding atmosphere from 3% and 6% N₂ did not have a significant effect on the surface composition. Figure 4.34 is the XRD spectrum of the plasma nitrided Ti-6Al-4V treated in an atmosphere containing 3% N₂-balance Ar. Abundant α-Ti peaks and a few TiN and Ti₂N reflections were detected in the spectrum when Ar was utilized as the carrier gas. The abundance of α-Ti peaks (from the substrate) found in the diffraction pattern along with a few reflections from TiN and Ti₂N nitrides indicates the thin morphology of the compound layer and is likely due to the sputtering effect of heavy Ar atoms.

<table>
<thead>
<tr>
<th>Surface condition</th>
<th>N₂ content (%)</th>
<th>Carrier gas</th>
<th>Rₐ (µm)</th>
<th>RMS (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polished</td>
<td>-</td>
<td>-</td>
<td>0.03 ± 0.01</td>
<td>0.04 ± 0.01</td>
</tr>
<tr>
<td>Polished + surface</td>
<td>3</td>
<td>H₂</td>
<td>0.23 ± 0.01</td>
<td>0.29 ± 0.01</td>
</tr>
<tr>
<td>activation</td>
<td>6</td>
<td>H₂</td>
<td>0.30 ± 0.05</td>
<td>0.38 ± 0.06</td>
</tr>
<tr>
<td>Plasma nitrided at 67 Pa</td>
<td>3</td>
<td>Ar*</td>
<td>0.06 ± 0.01</td>
<td>0.08 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>H₂</td>
<td>0.30 ± 0.03</td>
<td>0.37 ± 0.05</td>
</tr>
<tr>
<td>Plasma nitrided at 400 Pa</td>
<td>3</td>
<td>H₂</td>
<td>0.28 ± 0.03</td>
<td>0.36 ± 0.04</td>
</tr>
</tbody>
</table>

* Without surface activation pretreatment

4.3.2.2 Microstructural Characterization

Scanning electron SEM images of the cross section of plasma nitrided alloy at a total pressure of 400 Pa are shown in Figure 4.35. The microstructure consisted of a 1.1 µm thick compound layer and a 2.4 µm thick α-case on top of a 17.2 µm deep diffusion zone. Therefore, it can be concluded that increasing the nitriding pressure from 67 Pa to
400 Pa retarded the diffusion of nitrogen atoms and resulted in a shallower depth of
diffusion. The formation of an α-case underneath the compound layer is likely due to the
higher activity of nitrogen atoms/ions in the plasma.

Figure 4.36 is a cross-sectional SEM images showing the plasma nitrided
microstructure treated in an atmosphere of 3% N$_2$-balance Ar showing the formation of a
3.1 µm thick compound layer on an 11.0 µm deep diffusion zone. Comparing the
obtained results with those of the treatment in which H$_2$ was used as a carrier gas showed
a thicker compound layer and shallower diffusion zone when Ar was used in the gas
mixture. Moreover, the presence of microvoids underneath the compound layer (as
marked in Figure 4.36) is likely due to the sputtering effect of heavy Ar atoms in the
plasma. Increasing the nitrogen content in the nitriding gas from 3% to 6% on the plasma
nitrided microstructure resulted in the formation of a 1.2 µm thick compound layer and
20.4 µm diffusion zone as shown in Figure 4.37. The thickness of compound layer,
thickness of the α-case, and the depth of the diffusion zone were measured using an
image analyzing software for each plasma nitriding condition based on the SEM
observations. The microstructural analyses results are summarized in Table 4.7.

Table 4. 7 Results obtained from measurement of microstructural features for 600˚C plasma nitriding
treatments for different durations measured using an image analysis software based on cross-sectional SEM
micrographs

<table>
<thead>
<tr>
<th>Surface condition</th>
<th>N$_2$ content (%)</th>
<th>Carrier gas</th>
<th>Compound layer thickness (µm)</th>
<th>α-case thickness (µm)</th>
<th>Depth of diffusion zone (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plasma nitrided at 67 Pa</td>
<td>3</td>
<td>H$_2$</td>
<td>1.9 ± 0.5</td>
<td>-</td>
<td>44.4 ± 5.6</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>Ar*</td>
<td>3.1 ± 0.11</td>
<td>-</td>
<td>11.0 ± 1.6</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>H$_2$</td>
<td>1.2 ± 0.2</td>
<td>-</td>
<td>20.4 ± 3.3</td>
</tr>
<tr>
<td>Plasma nitrided at 400 Pa</td>
<td>3</td>
<td>H$_2$</td>
<td>1.1 ± 0.2</td>
<td>2.4 ± 0.4</td>
<td>17.2 ± 3.1</td>
</tr>
</tbody>
</table>
The effect of plasma nitriding duration on the grain size of the Ti-6Al-4V substrate was also investigated. As expected, the nitriding composition and pressure did not influence the grain size of the substrate (Table 4.8). A 24-h treatment at 600°C resulted in approximately 40% increase in the average α grain size, irrespective of the nitriding gas composition.

Table 4.8 Average α grain size measurement results in the substrate; measured using an image analyzing software based on cross-sectional SEM micrographs

<table>
<thead>
<tr>
<th>Surface condition</th>
<th>N₂ content (%)</th>
<th>Carrier gas</th>
<th>Average α grain size (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated Ti-6Al-4V alloy</td>
<td>-</td>
<td>-</td>
<td>3.0 ± 1.3</td>
</tr>
<tr>
<td></td>
<td>3 H₂</td>
<td>4.2 ± 1.6</td>
<td></td>
</tr>
<tr>
<td>Plasma nitrided at 67 Pa</td>
<td>3 Ar</td>
<td>6.3 ± 2.6*</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6 H₂</td>
<td>4.1 ± 1.6</td>
<td></td>
</tr>
<tr>
<td>Plasma nitrided at 400 Pa</td>
<td>3 H₂</td>
<td>4.4 ± 2.6</td>
<td></td>
</tr>
</tbody>
</table>

* The average grain size in the substrate was 5.1 ± 2.9 µm.

4.3.2.3 Microhardness Profiles

Microhardness measurements on the cross section of plasma nitrided samples revealed that an increase in the nitrogen content of the nitriding medium from 3% to 6% decreased the hardness and depth of nitrogen diffusion (Figure 4.38). As mentioned in the microstructural characterization results switching the nitriding buffer gas from Ar to H₂ resulted in reduction of nitrogen diffusion depth. This was also confirmed by microhardness results as shown in Figure 4.39. Both the hardness and depth of diffusion are lower for the nitriding atmosphere with 3% N₂-balance Ar.
Microhardness-depth profiles for plasma nitriding in atmospheres with different pressures of 67 Pa and 400 Pa are presented in Figure 4.40. It can be observed that nitriding at a lower pressure resulted in a deeper diffusion zone, however, by increasing the pressure higher hardness values were obtained in the surface vicinity. According to the microstructural characterization results, a low nitriding pressure (67 Pa) and nitrogen content (3%) and incorporation of H₂ as the buffer gas in the nitriding atmosphere resulted in a significant depth of nitriding and therefore the above-mentioned conditions have been adopted as optimized atmosphere conditions in this work.

4.3.3 Nitriding Temperature

Plasma nitriding was performed at 500°C, 600°C, 700°C, and 900°C while keeping the other nitriding conditions constant to investigate the effect of nitriding temperature on microstructure, composition and properties. The nitriding conditions are specified in Table 4.9. The surfaces Ti-6Al-4V samples were activated using an aqueous solution containing 1% HF and 15% HNO₃ for 5 minutes prior to the nitriding treatment.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Duration (h)</th>
<th>Pressure (Pa)</th>
<th>Gas composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>500, 600, 700, 900</td>
<td>24</td>
<td>67</td>
<td>3% N₂-balance H₂</td>
</tr>
</tbody>
</table>

Table 4.9 Plasma nitriding conditions selected for investigating the effect of nitriding temperature
4.3.3.1 Surface Topography and Composition

Surface roughness, represented by average roughness average ($R_a$) and root mean squared roughness (RMS), was measured over an area of $450 \mu m \times 600 \mu m$ using optical profilometry. The results are presented in Table 4.10; each reported value is the average of at least three measurements. The average surface roughness increased by ~30% after plasma nitriding treatment at 600°C and by ~87% after plasma nitriding treatment at 900°C.

Table 4.10 Surface roughness measurement results obtained by optical profilometry

<table>
<thead>
<tr>
<th>Surface condition</th>
<th>$R_a$ (µm)</th>
<th>RMS (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polished</td>
<td>0.03 ± 0.01</td>
<td>0.04 ± 0.01</td>
</tr>
<tr>
<td>Polished + surface activation</td>
<td>0.23 ± 0.01</td>
<td>0.29 ± 0.01</td>
</tr>
<tr>
<td>Plasma nitrided at 500°C</td>
<td>0.35 ± 0.03</td>
<td>0.45 ± 0.03</td>
</tr>
<tr>
<td>Plasma nitrided at 600°C</td>
<td>0.30 ± 0.05</td>
<td>0.38 ± 0.06</td>
</tr>
<tr>
<td>Plasma nitrided at 700°C</td>
<td>0.48 ± 0.02</td>
<td>0.60 ± 0.03</td>
</tr>
<tr>
<td>Plasma nitrided at 900°C</td>
<td>0.43 ± 0.02</td>
<td>0.55 ± 0.02</td>
</tr>
</tbody>
</table>

The surface topography of plasma nitrided Ti-6Al-4V coupons after 24-hour treatments at different temperatures was studied under the SEM. Figure 4.41 presents secondary electron SEM images from the surface topography of plasma nitrided Ti-6Al-4V at 500°C consisting of fine spherical and conical features with a maximum height of ~1.8 µm.

After plasma nitriding at 600°C the conical features had a maximum height of ~2.0 µm and covered the surface more uniformly as shown in Figure 4.42. A two-
dimensional view of the conical features is shown in Figure 4.43 which is a typical atomic force microscopy (AFM) image of the surface topography of plasma nitrided sample at 600°C after a 24-hour treatment. Plasma nitriding features covered the entire surface after plasma nitriding at 900°C and reached a maximum height of ~2.9 µm (Figure 4.44).

XRD spectra of the plasma nitrided surfaces after 24-hour treatments at 500°C, 600°C, and 900°C are given in Figure 4.45. It was observed that the compound layer formed at 500°C mainly consisted of Ti2N and TiN0.3 (Figure 4.45-a). The significant contribution of α-Ti peaks from the substrate in the diffraction pattern was due to the x-ray depth of penetration as a result of the thin morphology of this layer. Both the number and intensity of TiN and Ti2N peaks increased in the XRD pattern of the plasma nitrided surface at 600°C as shown in Figure 4.45-b. The α-Ti peaks were shifted towards slightly higher diffraction angles probably due to the dissolution of nitrogen interstitial atoms. High-intensity peaks of TiN and Ti2N nitrides appeared in the XRD spectrum of the 900°C plasma nitriding treatment (Figure 4.45-c). The presence α-Ti was limited in this pattern likely due to the formation of a thick (5.8 µm) compound layer.

4.3.3.2 Microstructural Characterization

The microstructure of plasma nitrided Ti-6Al-4V alloy after 24-hour treatments at different temperatures was studied under the SEM. At the lowest nitriding temperature in this investigation (500°C) the plasma nitrided microstructure consisted of a thin (0.2 µm) compound layer and a shallow (10.6 µm) diffusion zone. Figure 4.46 is a typical secondary electron SEM micrograph of this microstructure. The diffusion zone was
differentiated by the dissolution of fine recrystallized β particles inside the α grains as a result of nitrogen diffusion since nitrogen is an α-stabilizing element. Increasing the nitriding temperature resulted in an increase in the thickness of the compound layer and depth of the diffusion zone (Table 4.11).

Table 4.11 Results obtained from measurement of microstructural features for 24-hour plasma nitriding treatments at different temperatures measured using an image analysis software based on cross-sectional SEM micrographs

<table>
<thead>
<tr>
<th>Nitriding temperature (°C)</th>
<th>Thickness of compound layer (µm)</th>
<th>Thickness of α-case (µm)</th>
<th>Depth of diffusion zone (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>0.2 ± 0.06</td>
<td>-</td>
<td>10.6 ± 2.6</td>
</tr>
<tr>
<td>600</td>
<td>1.9 ± 0.5</td>
<td>-</td>
<td>44.4 ± 5.6</td>
</tr>
<tr>
<td>700</td>
<td>4.3 ± 0.7</td>
<td>4.2 ± 1.0</td>
<td>54.9 ± 15.1</td>
</tr>
<tr>
<td>900</td>
<td>5.8 ± 0.7</td>
<td>19.3 ± 2.8</td>
<td>101.6 ± 19.3</td>
</tr>
</tbody>
</table>

Typical cross-sectional SEM images of the microstructure of plasma nitrided Ti-6Al-4V at 600°C (after 24 hours) is shown in Figure 4.47. A 1.9 µm thick compound layer covered the surface uniformly followed by a 44.4 µm diffusion zone. Closer inspection of the near-surface microstructure was carried out by imaging FIB-milled cross sections as shown in Figure 4.48. Figure 4.48-a shows the location on the plasma nitrided surface where FIB milling was performed and Figure 4.48-b is a back-scattered electron SEM image showing the microstructure at the surface vicinity. The compound layer/diffusion zone interface could not be clearly identified from this image. A well-bonded interface was evidenced by the absence of microvoids or gaps in the microstructure.
Similar microstructural features developed in plasma nitrided Ti-6Al-4V alloy after 700°C and 900°C treatments (for 24 hours). Figure 4.49-a presents the microstructure of plasma nitrided alloy at 900°C; at this temperature, the thickness of the compound layer and the depth of the diffusion zone were 5.8 µm and 101.6 µm, respectively. Furthermore, the presence of a region that was completely depleted of β particles was detected during the SEM observations. This region was 19.3 µm thick and was located beneath the compound layer (Figure 4.49-b) and will be referred to as the “α-case” or the “β-free zone” in this work. Closer inspection of the compound layer/α-case interface revealed the presence of a distinct layer with an approximate thickness of 2.4 µm (Figure 4.49-c). Energy dispersive x-ray spectrometry (EDS) line-scan analysis revealed the distribution of Ti, Al, V, and N elements underneath the compound layer (Figure 4.50). A higher concentration of Al was found in this region (Al-rich layer) indicating the segregation of Al underneath the compound layer.

Cross-sectional analysis of the plasma nitrided surfaces at 900°C was complemented by FIB milling technique. Figure 4.51 presents a typical back-scattered electron SEM image of the ion milled cross section. The grains in the compound layer were approximately 1-3 µm in size and were differentiated on account of their different contrasts.

The effect of plasma nitriding treatments on bulk microstructure of the Ti-6Al-4V alloy was also investigated. It was found that after plasma nitriding at 500°C and 600°C the substrate maintained its mill-annealed microstructure similar to that of the untreated alloy. However, the grain size measurements revealed an increase in the average α grain
size (Table 4.12). The average α grain size increased by 13% and 40% after 24-h treatments at 500˚C and 600˚C, respectively.

Conversely, the substrate experienced substantial grain growth and microstructural transformations after plasma nitriding treatments at 700˚C and 900˚C. Figure 4.52 is a typical microstructure of Ti-6Al-4V substrate after a 24-hour plasma nitriding treatment at 900˚C. The microstructure of the substrate transformed from a mill-annealed microstructure (inter-connected equiaxed α grains + intergranular β particles) to a bimodal microstructure (equiaxed α grains + grains with α/β lamellae). Furthermore, the average bulk grain size was measured at 14.1 µm after the nitriding treatment at 900˚C which indicates approximately 370% increase in the average grain size compared with the untreated alloy.

Table 4.12 Average α grain size measurement results in the substrate; measured using an image analyzing software based on cross-sectional SEM micrographs

<table>
<thead>
<tr>
<th>Sample Condition</th>
<th>Average α grain size (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated Ti-6Al-4V alloy</td>
<td>3.0 ± 1.3</td>
</tr>
<tr>
<td>Plasma nitriding at 500˚C</td>
<td>3.4 ± 1.8</td>
</tr>
<tr>
<td>Plasma nitriding at 600˚C</td>
<td>4.2 ± 1.6</td>
</tr>
<tr>
<td>Plasma nitriding at 700˚C</td>
<td>9.4 ± 3.7</td>
</tr>
<tr>
<td>Plasma nitriding at 900˚C</td>
<td>14.1 ± 4.2</td>
</tr>
</tbody>
</table>

4.3.3.3 Microhardness Profiles

Since nitrogen interstitial atoms have a solid solution hardening effect in titanium alloys, the microhardness-depth profiles were utilized to confirm the depth of nitrogen diffusion zone. The microindentations were made using a diamond Vickers indenter at a
maximum applied normal load of 245 mN and the obtained hardness values were averaged over at least three measurements. The measured microhardness profiles for different plasma nitriding temperatures are compared in Figure 4.53. The depth of diffusion zone was estimated at the distance from the compound layer interface where the hardness value reached that of the substrate. A shallow diffusion zone of approximately 15 µm was obtained for the 500˚C treatment while the depth of the diffusion zone was estimated at 45 µm and 110 µm for the 600˚C and 900˚C treatments, respectively. The results were in agreement with cross-sectional SEM observations.

In summary, a dilute nitriding atmosphere containing 3% N₂ resulted in a higher depth of diffusion zone compared with lower (1.5%) and higher (6%) nitrogen contents. Utilization of H₂ as buffer gas also resulted in a deeper diffusion zone and thicker compound layer compared to Ar. plasma nitriding treatment at a low temperature of 500˚C inhibited significant microstructural changes to the substrate; however, insufficient depth of nitriding was detected after this run (~ 15 µm). Conversely, while significant depth of nitrogen diffusion (55-100 µm) was achieved by nitriding at elevated temperatures (e.g., 900˚C), however, it was accompanied by the formation of a thick α-case as well as microstructural transformations in the substrate that are deleterious for the mechanical properties especially the fatigue strength. It was also found that increasing the nitriding duration from 24 hours to 45 hours (more than twice) in a nitriding treatment at 600˚C resulted in only a 33% rise in the depth of nitriding. Therefore plasma nitriding at 600˚C for 24 hours in a dilute nitriding atmosphere (3% N₂-balance H₂) was selected as the optimum nitriding treatment in this work. Plasma nitriding at 900˚C has been used throughout this thesis for the purpose of comparison.
4.4. Analytical Microscopy Studies and Characterization of Plasma Nitrided Ti-6Al-4V Alloy

4.4.1 TEM/EELS Analysis

Analytical microscopy investigations of the plasma nitrided surfaces (600°C, 24 h) were performed by transmission electron microscopy [161]. Figure 4.54-a is a typical scanning TEM (STEM) image of the cross section of plasma nitrided alloy. The interface between the compound layer and the diffusion zone interface could not be clearly delineated. Electron energy loss spectroscopy (EELS) analysis line scan was performed to estimate the thickness of the compound layer. The white line marked on the image indicates the region where the EELS line scan was acquired. Figure 4.54-b is a typical EELS spectrum collected from the compound layer (location marked as “1” in Figure 4.54-a). Two titanium peaks were detected at 456 eV and 461 eV and a nitrogen peak was detected at 401 eV. Figure 4.54-c is a typical EELS spectrum collected from the diffusion zone (location marked as “2” in Figure 4.54-a). Only titanium peaks were detected in this spectrum. Figure 4.54-d is the EELS line scan showing the distribution of Ti and N elements within about 5 µm from the surface. The thickness of the compound layer was around 2 µm according to the N profile. It should be noted that the interstitial nitrogen content of the diffusion zone was not picked up in this line scan. For spectroscopic identification of interstitial elements atomic resolution EELS should be performed by scanning the probe across columns of atoms [206].

Figure 4.55 exhibits a bright-field TEM image of the general morphology of the plasma nitrided (600°C for 24 hours) microstructure in the surface vicinity. Similar to the STEM mode, no distinct interface was detected between the compound layer and the
diffusion zone showing that the compound layer was well-bonded to the underlying substrate. The enclosed areas are the locations where closer observations at higher magnifications were performed. Figures 4.56-a and 4.56-b are higher magnification bright field TEM images of the regions marked as “a” and “b” in Figure 4.55. A distinct grain structure was observed in the compound layer that was easy to distinguish from that of the underlying diffusion zone. The grains in the compound layer were in the size range of 480 ± 20 nm while the grain size in the diffusion zone was around 4 µm. Furthermore, the presence of a 5-6 nm layer was also revealed on the surface which was characterized using the x-ray photoelectron spectroscopy (XPS) analysis as will be explained in the next section.

A Bright-field TEM image of location “c” in Figure 4.55 and the corresponding selected area electron diffraction pattern (SAD) are illustrated in Figure 4.57. The micrograph shows a couple of grains in the compound layer. The corresponding diffraction pattern indicated reflections of cubic TiN (Fm-3m) with a rock-salt (NaCl) structure in the marked region. Similarly Figure 4.58 is a bright-field TEM image of the compound layer acquired from a different location in the surface vicinity and the corresponding selected SAD pattern. Reflections of tetragonal Ti$_2$N (P4$_2$/mm) structure were detected in this region. A typical high resolution TEM (HRTEM) image of the compound layer is illustrated in Figure 4.59 combined with fast Fourier transform (FFT) and inverse FFT of different within the image revealed presence of Ti$_2$N planes in two different orientations (Figures 4.59-b, 4.59-c). These finding indicate that the compound layer was composed of TiN and Ti$_2$N titanium nitrides with a fine grain size (~ 480 nm). Figure 4.60 is a bright-filed TEM image taken from location “d” in Figure 4.55
(approximately 2 µm beneath the surface). This figure elucidated that a clear interface could not be identified between the compound layer and the diffusion zone. No microcracks or voids were observed in the interfacial region and the grains in the compound layer and diffusion zone were attached together over a well-bonded interface.

A typical Bright-field TEM image of the diffusion zone (location “e” in Figure 4.55) is shown in Figure 4.61. The selected area electron diffraction pattern obtained from one of the grains in this region corresponded to α-Ti crystal structure (P63/mmm).

4.4.2 XPS Analysis

The chemical composition of the plasma nitrided surface (to an effective depth of ~ 10 nm) was studied using x-ray photoelectron spectroscopy (XPS) measurements. A survey scan with a wide energy range of 0-1100 eV was carried out over an analysis area of 300 µm × 700 µm with a pass energy of 160 eV. The resulting spectrum (Figure 4.62) indicated presence Ti(2p) at 457.3 eV, N(1s) at 396.4 eV, and O(1s) at 531.5 eV. Subsequently, high resolution analyses were acquired for each of the constituent species (Ti, N, O) over an analysis area of 300 µm × 700 µm with a pass energy of 20 eV (0.1 eV steps) to elucidate the type of chemical bonds present on the surface. The obtained binding energies (Table 4.13) were compared with those reported in the literature [207-211] to identify the different phase compositions.

The rather complicated Ti(2p) spectrum was deconvoluted into six Ti(2p) components of 464.1 eV, 462.7 eV, 461.1 eV, 458.4 eV, 457.0 eV, and 455.0 eV. The XPS data corresponding to N(1s) was also fitted into three peaks of 398.6 eV, 397.1 eV, and 396.0 eV. The binding energies of Ti(2p) and N(1s) peaks at 455.0 eV and 397.1 eV,
respectively, showed the presence of Ti-N bonds. The Ti(2p) peaks identified at 457.0 eV, 461.1 eV and N(1s) at a binding energy of 396.0 eV also corresponded to the formation of Ti-N bonds [209, 212]. The Ti-N bonds also had shake-up peaks with an energy difference of about 2 eV with the main peaks at 462.7 eV, 457.0 eV for Ti(2p) and 396 eV for N(1s). Besides the formation of titanium nitrides, there was a possibility of contribution of oxynitrides to the spectrum. The detected oxygen O(1s) peaks at 533.5 eV, 529.9 eV, 531.9 eV and Ti(2p) peaks at 458.4 eV, 464.1 eV and N(1s) at 398.6 eV, 400.4 eV may be due to the formation Ti-O and Ti-O-N bonds.

The presence of oxygen as revealed by the XPS spectra in the form of sub-stoichiometric surface oxynitrides was not detected in the TEM/EELS analysis showing that it was restricted to a less than 10 nm thickness on the surface. The formation of superficial oxynitrides on the plasma nitrided surface likely occurred due to the partial oxidation of titanium nitride exposed to air at room temperature (since titanium oxide is thermodynamically more favourable [213]) and not during the plasma nitriding procedure.

4.4.3 Glow Discharge Spectroscopy

The distribution profile of elements near the plasma nitrided surface obtained by glow discharge optical emission spectroscopy (GDOES) is shown in Figure 4.63. A nitrogen-rich layer, corresponding to the formation of the compound layer, extended to about 2 µm below the surface. There is a small increase in the aluminum content beneath the compound layer which may account for an Al-enriched region beneath the compound
layer. It should be noted that the nitrogen concentration in the diffusion zone could not be measured accurately possibly since it is below the sensitivity of GDOES [214].

Table 4. 13 The binding energies of the Ti (2p₁, 2p₃), N (1s), and O (1s) bonds

<table>
<thead>
<tr>
<th>Bond</th>
<th>Binding Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti₂O</td>
<td>464.1</td>
</tr>
<tr>
<td>Ti₂N (Ti₂N)</td>
<td>462.7</td>
</tr>
<tr>
<td>TiN (TiN)</td>
<td>461.1</td>
</tr>
<tr>
<td>Ti₂O</td>
<td>458.4</td>
</tr>
<tr>
<td>Ti₂N (Ti₂N)</td>
<td>457.0</td>
</tr>
<tr>
<td>TiN (TiN)</td>
<td>455.0</td>
</tr>
<tr>
<td>O-Ti</td>
<td>533.5</td>
</tr>
<tr>
<td>O-Ti</td>
<td>531.9</td>
</tr>
<tr>
<td>O-Ti</td>
<td>529.9</td>
</tr>
<tr>
<td>N-O</td>
<td>400.4</td>
</tr>
<tr>
<td>N-O</td>
<td>398.6</td>
</tr>
<tr>
<td>N-Ti (TiN)</td>
<td>397.1</td>
</tr>
<tr>
<td>N-Ti (Ti₂N)</td>
<td>396.0</td>
</tr>
</tbody>
</table>

The oxygen profile has a peak on the nitrided surface which abruptly reaches zero below the surface. This is in agreement with the detection of stoichiometric surface oxynitrides on the surface of the nitrided alloy according to the XPS results (Section 4.4.2). The presence of oxygen on the plasma nitrided surface is likely due to the partial oxidation of the titanium nitride in ambient environment after plasma nitriding (since titanium oxide is thermodynamically more favourable [213]).
4.5 Residual Stress Measurement

The obtained XRD pattern was in the form of a doublet consisting of two overlapping peaks. The x-ray data collected from an untreated Ti-6Al-4V coupon revealed that one of the peaks belonged to the titanium substrate. The contribution of titanium substrate in the pattern was due to the depth of x-ray penetration. In order to separate the two peaks, the $K_{\alpha}$ radiation (2.7497 Å) and the Bragg angle of 141.2° were used for the TiN coating and the $K_{\beta}$ radiation (2.51391 Å) and the Bragg angle of 144° were used for the substrate and the corresponding x-ray elastic constants were employed for calculation of residual stresses in each phase. The obtained results for two treatments performed at 600°C are tabulated in Table 4.14. The repeatability of test results was confirmed by performing a second measurement.

Table 4.14 The obtained results from residual stress measurements on the surface of plasma nitrided Ti-6Al-4V alloy

<table>
<thead>
<tr>
<th>Plasma nitriding condition</th>
<th>Thickness of compound layer (µm)</th>
<th>Depth of diffusion zone (µm)</th>
<th>Residual stress in the coating (MPa)</th>
<th>Residual stress in the substrate (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature: 600°C</td>
<td>1.9 ± 0.5</td>
<td>44.4 ± 5.6</td>
<td>-530.9 ± 55.2 (compressive)</td>
<td>+213.7 ± 34.5 (tensile)</td>
</tr>
<tr>
<td>Pressure: 67 Pa</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Atmosphere: 3% N$_2$-balance H$_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Duration: 24 h</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
4.6 Mechanical Properties of Plasma Nitrided Ti-6Al-4V Alloy

4.6.1 Tensile Tests

The stress-strain curves of the plasma nitrided alloy at two different nitriding temperatures of 600°C, 900°C for 24 h are presented in Figure 4.64; for comparison purposes the stress-strain curve of the untreated Ti-6Al-4V alloy is also plotted in the same graph. It was found that the tensile strength and yield strength of the alloy were not affected by the treatment and the shapes of the stress-strain curves were similar. However, the ductility (tensile elongation) decreased from 13.9 to 7.8 after this treatment. In comparison, plasma nitriding at a high temperature of 900°C resulted in significant reduction of tensile strength, yield strength, and ductility of the alloy (Table 4.15).

The plasma nitrided samples exhibited a cup-and-cone fracture morphology after tensile tests, characteristic of a ductile type of failure. The SEM observations of the fracture surfaces revealed that the fracture surfaces consisted of a dimpled rupture region at the center surrounded by shear lips (Figure 4.65-a). A narrow rim of flat fracture with cleavage facets encircled the above-mentioned regions (Figure 4.65-b). These cleavage facets surrounding the fractured area were not observed in the fracture surfaces of untreated Ti-6Al-4V alloy tested under the same conditions (Figure 4.3). Closer inspection of the near surface region revealed the presence of microcracks initiating from the surface (Figure 4.65-c). This indicated that the compound layer could not comply with the plastic deformation of the substrate and failed in a brittle manner. The bulk Ti-6Al-4V alloy, however, failed in a ductile manner as evidenced by presence of dimples as shown in Figure 4.65-d.
Table 4. Tensile data obtained from uniaxial tensile tests on untreated Ti-6Al-4V alloy and plasma nitrided alloy at 600°C and 900°C

<table>
<thead>
<tr>
<th></th>
<th>Tensile strength (MPa)</th>
<th>Yield strength (MPa)</th>
<th>Elongation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated Ti-6Al-4V alloy</td>
<td>1045.0 ± 9.9</td>
<td>940.0 ± 3.5</td>
<td>13.9 ± 0.2</td>
</tr>
<tr>
<td>Plasma nitrided Ti-6Al-4V at 600°C</td>
<td>1050.0 ± 4.6</td>
<td>908.0 ± 3.0</td>
<td>7.8 ± 0.2</td>
</tr>
<tr>
<td>Plasma nitrided Ti-6Al-4V at 900°C</td>
<td>913.3 ± 18.9</td>
<td>874 ± 2.0</td>
<td>1.9 ± 0.2</td>
</tr>
</tbody>
</table>

Under tensile loading, circumferential (secondary) microcracks were found on the surface of the nitrided alloy. These cracks were perpendicular to the tensile loading direction and were connected at a 45° angle relative to the loading direction (Figure 4.66).

4.6.2 Cryogenic Fracture Tests

Figure 4.67-a is the near-surface cryogenic fracture (cryo-fracture) microstructure of the plasma nitrided Ti-6Al-4V. The diffusion zone, extending to approximately 40 µm below the surface, showed characteristic features of a brittle type of failure (cleavage facets). This indicated that the diffusion zone was effectively hardened by interstitial nitrogen dissolution. The cleavage facets revealed features related to the direction of local crack propagation; such as the parallel step-like flat features. There was a transition from the brittle fracture (cleavage facets) in the surface vicinity to ductile fracture in the core (dimples and tear ridges) indicating that the brittle fracture observed in the diffusion zone gradually faded into a ductile type of failure in the Ti-6Al-4V substrate.

Closer examination of the fracture surfaces revealed the presence of lateral microcracks below the compound layer. These microcracks propagated parallel to the surface into the diffusion zone (Figures 4.67-b, 4.67-c). It was observed that the
microcracks were deflected (Figure 4.67-d) or stopped (Figure 4.67-e) when they reached
the β particles inside the diffusion zone. It appears that the β particles acted as crack
arrester sites in the diffusion zone.

4.6.3 Fatigue Tests

Figure 4.68 represents the stress amplitude against the number of cycles to failure
(S–N) curves for the plasma nitrided (600°C, 24 h) and untreated Ti-6Al-4V alloys. It
was observed that at relatively high stress amplitudes (N ≤ 10⁵; low cycle fatigue region)
the nitried samples failed after a definite number of cycles. However, at lower stress
amplitudes (N > 10⁵; high cycle fatigue region) they did not experience any failure until
the tests were stopped at 10⁷ cycles (run-out). The fatigue endurance limit was reduced
by 23% after the nitriding treatment.

Fractography observations were carried out on the fatigue fracture surfaces to
elucidate the failure mechanisms. Figure 4.69-a is a typical fatigue fracture surface of the
plasma nitrided Ti-6Al-4V tested in the low cycle fatigue (LCF) region (569 MPa). The
fracture surface revealed a single fatigue crack initiation source on the surface, a smooth
area of crack propagation (Region I), followed by a rough propagation area (Region II)
and the final rupture region. Signs of brittle fracture and fragmentation of the compound
layer were observed frequently at the crack initiation site (Figure 4.69-b). However,
closer inspection of this area revealed the presence of striation-like patterns and signs of
plastic deformation in the compound layer (Figure 4.69-c). The first stage of crack
propagation (Region I) was a smooth area with radial marks in the macroscopic scale and
striations and microcracks perpendicular to the propagation direction at higher
magnifications (Figures 4.69-d, 4.69-e). The second stage of crack propagation (Region II) had a rippled appearance composed of dimples (Figure 4.69-f) which gradually changed to a rougher appearance close to the final rupture region.

4.7 Tribological Properties of Plasma Nitrided Ti-6Al-4V Alloy

4.7.1 Microscratch Tests

A. Microscratch Tests at Progressively Increasing Applied Load

The diamond stylus was drawn across nitrided surfaces as the applied load increased linearly from 0.3 N to 20 N while acoustic emission signals and frictional forces were recorded. Acoustic emission signals were found to be an effective means of determining critical failure loads during sliding contact as each microcrack observed under the microscope, had an acoustic emission peak associated with it at the same position along the scratch track with its magnitude being proportional to the area of corresponding failure (Figure 4.70). Angular cracks initiated close to the edges of scratch path at a critical normal load ($L_{c1}$) of 0.75 N. The tensile cracks were formed when the applied normal load exceeded the second critical value ($L_{c2} \approx 8$ N); these cracks were observed inside the scratch path, perpendicular to the scratch direction. As the applied load increased further, angular and tensile cracks continued to grow until they joined together at $L_{c3} \approx 15.7$ N and formed semi-circular cracks. These cracks extended through the scratch width and generated large, sharp acoustic emission levels.
B. Microscratch Tests Constant Applied Loads

Following the investigation of failure events at progressive loading conditions, a series of microscratch tests was performed to investigate the crack initiation and propagation mechanisms under constant loading conditions. Figure 4.71-a shows the variation of the coefficient of friction with sliding distance during microscratch tests for the plasma nitrided (600°C, 24 h) and untreated alloy tested at an applied normal load of 5 N. The figure shows that the nitriding treatment had a significant effect in lowering the coefficient of friction. The average coefficient of friction values for plasma nitrided and untreated Ti-6Al-4V alloy tested at different loads are shown in Figure 4.71-b. The figure indicates that there was a substantial reduction in the average coefficient of friction values by the nitriding treatment. This effect was more significant at higher loads, e.g., 10 N – 20 N. The main observations arising from characterization of surface and subsurface failure phenomena can be summarized as follows.

\[ \text{Load} < L_{1c} (=0.75N) \]

Figure 4.72-a shows that at low loads (e.g., 0.5 N, mean Hertzian pressure (\(p_m\)) of 3.8 GPa) some of the asperities were flattened. Microcracks were observed on the surface of flattened asperities (Figure 4.72-b). Figure 4.73-a is a FIB-milled (focused ion beam) section corresponding to the location marked in Figure 4.73-b. Closer cross-sectional observations revealed that nucleation of subsurface microvoids that appear to be at grain boundaries in the compound layer as marked on the image.

\[ L_{1c} \leq \text{Load} < L_{2c} (=8N) \]

As the applied load increased to 1 N (\(p_m = 4.8 \text{ GPa}\)) the fraction of flattened asperities within the scratch tracks increased as illustrated in and angular cracks were
observed on the surface as illustrated in Figure 4.70. At this stage some asperity tips also detached from the surface and formed debris particles. Figure 4.74-a shows the scratch track at an applied load of 1 N. Figure 4.75 is a cross-sectional view of the location indicated in Figure 4.74-b prepared by FIB milling. It can be observed that the microcracks which initiated from the surface or subsurface microvoids appear to have grown intergranularly in the compound layer.

\[ L_{\varepsilon_1} \leq \text{Load} < L_{\varepsilon_2} (=15.7 N) \]

Figure 4.76-a is a back-scattered electron SEM image of the scratch track made at 10 N \((p_m = 10.4 \text{ GPa})\). The tensile cracks formed within the scratch paths have been marked in Figure 4.76-b. Cross-sectional observation of scratch paths using the FIB milling technique (Figure 4.77) revealed that in this loading region, through-thickness microcracks continued their propagation likely along grain boundaries across the compound layer and into the diffusion zone.

\[ \text{Load} > L_{\varepsilon_3} \]

At the normal load of 20 N \((p_m = 13.1 \text{ GPa})\), semi-circular cracks were observed within the scratch paths (Figure 4.78). SEM observations of the FIB-milled cross section of a couple of these cracks (as marked in Figure 4.78-b) to investigate their depth of penetration are illustrated in Figure 4.79. The propagation of the cracks surpassed the compound layer. There were neither any signs of failure at the interface nor any signs of compound layer chipping/delamination. The microcracks were finally stopped at \(\beta\) particles located at \(\alpha\) grain boundaries within the diffusion zone. This is shown more clearly in Figure 4.79-b. For comparison purposes, the microscratch tests were conducted.
under the same conditions on plasma nitrided surfaces at high temperature (900°C). The results obtained are also presented here:

A. Microscratch Tests at Progressively Increasing Applied Load

The combined results of acoustic emission output and SEM observations of scratch tracks after progressive loading microscratch test (0.3 N to 20 N) are presented in Figure 4.80. Different failure events were observed for high-temperature plasma nitrided surfaces at 900°C compared with those of the low-temperature treatment (600°C) under sliding conditions. The failure events for 900°C-nitriding began with fracture of asperity tips at 0.5 N ($L_{c1}$) and the tensile cracks were formed at the second critical applied normal load of 1.5 N ($L_{c2}$). As the applied normal load exceeded the third critical value ($L_{c2} \approx 5.5$ N); buckling and partial delamination of the compound layer was observed at different locations across the scratch path.

B. Microscratch Tests Constant Applied Loads

Figure 4.81 is a comparison between the coefficient of friction vs. sliding distance curves during microscratch tests performed at a constant applied load of 5 N on surfaces that were plasma nitrided at 600°C and 900°C for 24 hours. It can be observed that a higher nitriding temperature resulted in higher coefficient of friction with larger fluctuations. The average coefficient of friction values were 0.05 ± 0.005 and 0.06 ± 0.02 and for 600°C and 900°C treatments, respectively. The characterization results of surface and subsurface failure events are summarized as follows.

$Load < L_{c3} (= 1.5N)$
A back-scattered electron image of the scratch path after microscratch testing at an applied load of 1 N ($p_m = 4.8$ GPa) is presented in Figure 4.82-a. The flattened asperities were fractured and debris particles were generated at this load (Figure 4.82-b). The cross-sectional SEM observations revealed the presence of subsurface microcracks growing parallel to the scratch direction in the compound layer as marked in Figure 4.83.

$$Load > L_{c1}(=5.5N)$$

At applied loads higher than 5.5 N buckling and partial delamination of plasma nitrided surface were observed. In Figure 4.84 several occurrences of buckling after microscratch testing at load of 20 N ($p_m = 13.1$ GPa) are shown. SEM observations of the FIB-milled cross sections revealed that a thin ($< 1$ µm) section from the top of the compound layer was detached (Figure 4.85-a). Another interesting observation was the formation and propagation of subsurface microcracks towards the substrate normal to the scratch direction. These microcracks have been marked on Figure 4.85-b and their propagation is likely along grain boundaries of the compound layer.

These results indicated that the surfaces that were treated with low-temperature plasma nitriding (600°C) had a better sliding performance, in terms of coefficient of friction and resistance to compound layer spallation and surface crack propagation, compared with the nitrided surfaces at a higher temperature of 900°C. Therefore, the rest of tribological studies were carried out on the low-temperature nitriding samples.

### 4.7.2 Ball-on-disk Wear Tests

The tribological behaviour of plasma nitrided surface were studied using a ball-on-disk test configuration against AISI 52100 steel and alumina counterface balls under
dry sliding conditions. The wear tests were performed under a range of applied normal loads (0.5 N – 10 N) at 0.01 m/s sliding speed for 200m (5000 cycles). At several parts throughout this section the results have been compared with those of untreated Ti-6Al-4V alloy tested under the same conditions for comparison purpose.

4.7.2.1 Wear Tests against AISI 52100 Steel Counterface

4.7.2.1.1 SEM Observations of the Wear Tracks and Debris Particles

Visual observations revealed the formation of black wear tracks and black wear debris after the wear tests at all loading conditions. The morphology of wear tracks on the surface of plasma nitrided coupons sliding against AISI 52100 steel balls at different applied loads of 0.5 N, 1 N, 2 N, and 3 N are shown in Figure 4.86. At low loads (0.5 N, 1 N) patches of transferred material were observed on the wear tracks. As the applied load increased, the volume fraction of the wear tracks covered with the transferred material gradually increased until the wear tracks were completely covered with transferred material at 3 N.

The process of generation of the transferred layers were studied by stopping the wear tests at different sliding distances. Figure 4.87-a shows the wear track on the surface of plasma nitrided coupon after 10 m at 0.5 N. The transferred material was smeared on the surface and at several locations the fracture of transfer layer and the formation debris particles were observed (Figure 4.87-b). Figure 4.88 is a three-dimensional optical profilometry image of the plastic deformation of the transfer layer in relation to the sliding direction. In addition to the wear debris generated due to the fracture of transfer layer, cutting chip-like debris were also occasionally observed scattered around the wear
track. A back-scattered electron SEM image of a couple of these wear debris particles is shown in Figure 4.89. The EDS analysis indicated that these particles were rich in Fe and Cr and. Thus it is likely that abrasion was the dominant mechanism at the onset of wear.

As the sliding continued the thickness and size of the transfer layers increased. Closer SEM observations revealed severe deformation of the transfer layers evidenced by abrasion grooves (Figure 4.90-a). Moreover, spallation and fracture of the layers were also detected at several locations (Figure 4.90-b). Similar observations were made at higher loading conditions. Figure 4.91 is a secondary electron SEM image of the transferred material on the surface of a plasma nitrided coupon tested at 2 N (sliding distance: 200 m, sliding speed: 0.1 m/s) and a typical EDS spectrum collected from this layer. It was observed that the Fe and O were the main constituents of the transferred material. It appears that the transfer layers consist of some kind of iron oxide formed by Fe transfer from the counterface and its oxidation during sliding. The small Ti peaks observed in the EDS pattern are reflections from the titanium nitrides in the plasma nitrided surface possibly due to the x-ray depth of penetration.

Similar morphologies were observed in the wear debris particles generated at all loading conditions: (i) cutting chip-like particles, (ii) fine equiaxed particles and (iii) platelets (Figure 4.92). The debris formation mechanisms can be elucidated based on SEM micrographs of the wear track at 3 N shown in Figure 4.93. The oxide layers that accumulated on the plasma nitrided surface were surrounded by fine wear debris particles. Severe abrasion and fragmentation of the oxide plateaus can be clearly seen in Figure 4.93-c.
In order to elucidate the effect of sliding on the surface of plasma nitrided alloys, the iron oxide transfer layers were dissolved in an aqueous solution containing hydrochloric acid. Figures 4.94-a and 4.94-c show a three-dimensional optical profilometry image and a secondary electron SEM image of a patch of oxide layer on the wear track of the plasma nitrided alloy tested at 2 N and 0.1 m/s for 200 m. Figures 4.94-b, 4.94-d exhibit the same location after being immersed in an aqueous solution containing hydrochloric acid. It can be observed that most part of the oxide layer has been dissolved. Figures 4.94-e, 4.94-d are high magnification SEM images of the same location showing that after dissolution of the oxide layer, the plasma nitride surface underneath was completely intact and unaffected by the sliding contact expect for minor polishing of the asperity tips.

4.7.2.1.2 Wear of the Steel Counterface

Optical microscopy images of the wear scars on SAE 52100 steel balls sliding against plasma nitrided surfaces at different loading conditions of 0.5 N, 1 N, 2 N, and 3 N are illustrated in Figure 4.95. Signs of abrasion in the form of ploughing grooves in sliding direction were clearly seen in all of the wear scars. The worn surface were measured using Buehler image analyzing software and the results obtained were plotted as a function of applied normal load during the wear tests as shown in Figure 4.96. There appears to be a linear relationship between the surface area of wear scars on steel counterface balls and the applied load.

Generation of iron-rich oxide layers to the plasma nitrided surfaces contributed to mass gain and negative wear rates. The amount of mass gain was calculated by
measuring the volume of transfer layers using optical profilometry and the volumetric wear was subsequently calculated as showed an increasing trend with the applied load exerted during wear tests as illustrated in Figure 4.97.

4.7.2.1.3 Friction Behaviour

Figure 4.98 is variation of the coefficient of friction with the sliding distance at different applied loads. As the applied load increased from 0.75 to 3 N, the break-in period duration decreased indicating that the initiation time for the oxide layer formation decreased with increasing the contact load. Within the steady-state region similar friction behaviour was observed at all tested applied loads.

Comparing the friction behaviour of plasma nitrided surfaces and untreated Ti-6Al-4V tested under the same conditions (Figure 4.99), it was found that the plasma nitrided surfaces had a shorter break-in period. On the other hand, the untreated Ti-6Al-4V suffered larger fluctuations and a slightly higher coefficient of friction in the steady state region. The shape of the COF curves during the break-in period also implied that different wear mechanisms have been involved.

The average coefficient of friction (COF) values in the steady state region were calculated and plotted against the applied load during wear tests in Figure 4.100. A decreasing trend was observed in both cases with increasing the applied load. The plasma nitrided surfaces exhibited a slightly lower COF value compared with the untreated alloy.
4.7.2.2 Wear Tests against Alumina Counterface

4.7.2.2.1 Observation of the Wear Tracks and Wear Debris

Similar features were observed on the worn surfaces of plasma nitrided Ti-6Al-4V alloy against alumina counterface when the applied normal load was less than 5 N. A typical back-scattered electron SEM micrograph of the wear track tested at 2 N is shown in Figure 4.101-a. The worn surfaces were smoothened and consisted of dark grey patches in a light grey background and occasionally microcracks were observed on the wear tracks perpendicular to the sliding direction. Figure 4.101-b illustrates a more clear view of these microcracks. The EDS analysis revealed that the presence of Al, Ti, O and N elements on the worn surfaces, however, the dark patches were richer in Al and O. No detectable wear debris particles were generated under these loading conditions.

Increasing the applied normal load resulted in removal of the compound layer and exposure of the Ti-6Al-4V substrate as shown in Figure 4.102. Closer inspection of the wear tracks revealed severe plastic deformation and abrasion grooves and the formation of plateaus with a layered structure on the worn surfaces. The plateaus consisted of microcracks perpendicular to the sliding direction and were fractured at several locations (Figure 4.103).

The wear debris particles detected under these conditions are illustrated in Figure 4.104. They were in the form of platelet debris, cutting-chip like and fine debris particles. These observations were compared with those of the untreated Ti-6Al-4V surfaces tested under the same conditions. Figure 4.105 exhibits typical secondary and back-scattered electron SEM images of the worn surface of untreated Ti-6Al-4V tested against alumina
counterface. Severe plastic deformation and abrasion were found on the wear tracks. In addition to deep and continuous abrasion grooves on the surface, microcracks were found perpendicular to the sliding direction and occasionally fracture and removal of material were also observed. Accumulation of material on the worn surfaces in the form of plateaus was another notable observation on the wear tracks. These features are illustrated in Figure 4.106. Wear debris particles were found to be of the same morphologies as the plasma nitrided surfaces (Figure 4.107).

4.7.2.2.2 Optical Profilometry of the Wear tracks and Wear rate Determination

Figure 4.108 and Figure 4.109 are typical three-dimensional and two-dimensional optical profilometry images of the worn surfaces on the plasma nitrided Ti-6Al-4V surface at 5 N and 10 N, respectively. At low loads, wear was restricted to polishing wear and flattening of the surface asperities which is in agreement with the SEM observations. No indication of the removal of the compound layer was detected under these loading conditions. At higher loading conditions however, wear tracks were typically 600 µm wide and 20 µm deep. Therefore, it appears that the compound layer and part of the diffusion zone were removed during the wear test.

The amount of volume loss after the wear rates calculated based on optical profilometry images showed an average value of 0.007 ± 0.003 mm³/m after wear tests at 5 N. This value increased to 3.0 ± 0.48 mm³/m for wear tests at applied load of 10 N. In Figure 4.110 typical two-dimensional profiles of the wear tracks for plasma nitrided and untreated Ti-6Al-4V surfaces are compared. Wider and deeper wear tracks were formed on the surface of the untreated alloy after wear testing under the same conditions.
The wear rates were determined for the untreated surfaces and compared with those of the plasma nitrided alloy (at the high contact load of 10 N). It was found that the untreated Ti-6Al-4V surfaces had a wear rate of $5.5 \pm 1.4 \text{ mm}^3/\text{m}$, which is 83% higher than the plasma nitrided alloy tested under the same conditions.

4.7.2.2.3 Friction Behaviour

Figure 4.111 shows the variation of coefficient of friction (COF) with the sliding distance of the plasma nitrided surfaces sliding against alumina at applied normal loads of 2 N, 5 N, and 10 N. Different friction behaviours were observed at low loads (2 N, 5 N) compared with 10 N. At 5 N, the sliding pair (plasma nitrided Ti-6Al-4V/alumina) reached a steady state condition after a relatively long break-in period of approximately 80 m. The average COF value in the steady-state region was $0.63 \pm 0.02$. It appeared that the sliding pair did not reach a steady state condition at 2 N and the break-in region continued until the end of the wear test at 200 m. As the applied load was increased to 10 N, however, a different friction behaviour prevailed. At this load, a steady state condition was reached after a relatively short break-in period of approximately 10 m and the average COF value in the steady state region was $0.34 \pm 0.006$.

Comparing the friction behaviour of plasma nitrided and untreated Ti-6Al-4V tested against alumina at a high normal load of 10 N (Figure 4.112), it was found that they showed different friction behaviours during the break-in period but reached similar steady state values afterwards. For the untreated alloy, the COF had a maximum value of 0.40 at the beginning of the test which gradually decreased to reach the steady state value
of 0.34. The COF of the plasma nitrided surface, on the other hand, initially had a minimum value of 0.17 which gradually increased to reach its steady state value.

4.7.2.2.4 Cross-sectional SEM Observation of Worn Surfaces

Figure 4.113-a is a secondary electron SEM micrograph of the cross section of wear track on the plasma nitrided Ti-6Al-4V alloy tested at 10 N. The formation of a mechanically mixed layer (MML) was occasionally observed on the surface. Severe plastic deformation was also observed underneath the MML as evidenced by the elongation of \( \beta \) particles. This is clearly seen in Figure 4.113-b. The evolution of the microcracks under the MML was found to be the result of coalescence of microvoids as illustrated in Figure 4.114. This is likely the evidence of the formation of shear bands in the subsurface region during wear test.

4.8 Shot Peening Pretreatment

4.8.1 Microstructural Characterization of Ti-6Al-4V Alloy Subjected to Shot Peening Pretreatment

Figures 4.115-a, 4.115-b are secondary electron SEM images of the surface morphology of Ti-6Al-4V coupons before and after the shot peening treatment. The as-received microstructure (Figure 4.115-a) contained equiaxed \( \alpha \) grains with fine recrystallized \( \beta \) particles and intergranular retained \( \beta \) particles at \( \alpha \) grain boundaries. The \( \alpha \) grains were differentiated by the different orientation of recrystallized \( \beta \) particles inside each grain. After the shot peening pretreatment, a thin layer (< 2 \( \mu \)m) was polished (using 3 \( \mu \)m diamond suspension) from the surface of coupons to remove oxide scales and
contaminations. No remnant oxide phases or contaminants were detected on the surface of the shot peened samples after polishing (Figure 4.115-b). The severe plastic deformation was evidenced by the abundance of twins inside the $\alpha$ grains. The extent of deformation appeared to be different in each grain and was possibly a function of their orientation.

The distribution of $\alpha$ grain size was obtained by measuring the surface area of each individual grain using an image analyzing software. The results indicated a reduction in the average $\alpha$ grain size on the surface after the pretreatment as the peak corresponding to the highest grain frequency shifted towards a smaller value in the shot peened coupon (Figure 4.116). The mean $\alpha$ grain size, calculated based on the weighted average areas, decreased from 4.5 $\mu$m to 3.8 $\mu$m after the shot peening treatment.

Figure 4.117-a shows the subsurface microstructure of the shot peened coupons. An approximately 5 $\mu$m thick severe plastic deformation (SPD) layer was observed on the surface. Extensive plastic deformation in this layer is evident by the elongation of intergranular $\beta$ particles parallel to the shot peened surface, which is quite distinguishable from the equiaxed microstructure of the bulk (Figure 4.117-b). According to the microhardness measurements on the cross-sectional samples, the SPD layer had an average hardness value of 517 ± 28 HV, which is almost 20% higher than the bulk hardness (430 ± 8 HV).

Below the SPD layer, plastic deformation was dominated by mechanical twinning and extended to a depth of approximately 40 $\mu$m. Multiple twinning systems with different orientations can be observed to a depth of ~ 20 $\mu$m as illustrated in Figure 4.117-c. Farther from the surface, however, only single-system twinning was observed.
(Figure 4.117-d). This figure also showed that the distribution of mechanical twins in the subsurface area was not uniform and they appeared to be randomly distributed underneath the surface.

4.8.2 Microstructural Characterization of Ti-6Al-4V Alloy with the Shot Peening Pretreatment Subjected to Plasma Nitriding

Plasma nitriding treatments were carried out at 600°C for 24 hours in an atmosphere containing 6% N₂-balance H₂ and the surface were activated in an aqueous solution containing 1% HF and 15% HNO₃ for 5 min. After plasma nitriding, similar surface topographies developed on the surfaces of both the shot peened (SP-PN) and untreated (PN) coupons. In both cases conical features of different sizes were observed on the surfaces. Figure 4.118 shows the typical surface morphology of a plasma nitrided sample. The average surface roughness (Rₐ) and the peak-to-valley ratio (Rₚ) measured over an area of 225 × 300 µm² were 0.32 ± 0.04 µm and 3.2 ± 0.70 µm, respectively.

Figure 4.119-a, b present the cross-sectional microstructures of plasma nitrided Ti-6Al-4V alloy with and without the shot peening pretreatment. In both cases, a compound layer was formed on the surface, followed by a nitrogen diffusion zone. The diffusion zone was distinguished by the dissolution of fine β particles in the equiaxed α grains. The mechanical twins can be observed in the shot peened samples after plasma nitriding. The depth of the diffusion zone was measured as 27.6 ± 5.2 µm and 19.4 ± 3.9 µm for the plasma nitrided alloy with the shot peening pretreatment (SP-PN) and without the pretreatment (PN), respectively.

The microhardness variation with distance from the nitrided surfaces is presented in Figure 4.120. The hardening effect of nitrogen interstitials in the titanium crystal
structure was used to estimate the depth of nitrogen diffusion and the depth of diffusion zone was defined as the distance from the compound layer interface, where the hardness value reaches that of the substrate. The effect of shot peening pretreatment and nitrogen interstitials in strengthening of the titanium structure is evident by comparing the hardness profiles of PN and SP-PN samples. While the diffusion zone extended to about 25 µm beneath the compound layer interface of the PN sample, it extended to 35 µm (approximately 50% greater depth) and possessed higher hardness values in the SP-PN sample.

Transmission electron microscopy [161] examinations clarified the microstructural features developed in the compound layer. Figure 4.121-a is a bright field TEM image of the cross section of SP-PN sample and Figure 4.121-b is the scanning transmission electron microscopy (STEM) image of the same area. The compound layer was distinguished by its distinctive texture and finer grains compared with the large grains observed in the diffusion zone. The results were also confirmed by electron energy loss spectroscopy (EELS) maps. It was found that the compound layer was well-bonded to its underlying diffusion zone across a coherent interface. The contrast observed between different grains in the diffusion zone is due to their different orientations relative to the incident beam. Microscopic signs of plastic deformation in the SPD layer were evident even after plasma nitriding. Crystal defects, pile-up of dislocations, and dislocation networks can be observed inside the α grains in the diffusion zone in Figure 4.121-a.

Figures 4.122-a, 4.122-c were taken from approximately 5 µm below the nitrided surface. The dark contours in different orientations in Figure 4.122-a represent
dislocation pile-ups and sub-grain boundaries. Figure 4.122-b is the selected area electron diffraction (SAD) pattern from the marked grain in Figure 4.122-a that conforms to the $\alpha$-Ti structure ($\text{P6}_3/\text{mmc}$ space group). Figure 4.122-c shows micro-twins in two different orientations inside an $\alpha$ grain in the diffusion zone.

The compound layer was composed of two different layers as illustrated in Figure 4.123-a. The compound layer inner layer was approximately 0.5 µm thick and contained fine grains (0.1-0.5 µm in diameter) with parallel fringes in different orientations (Figure 123-b). The corresponding electron diffraction pattern from the enclosed region in Figure 123-b indicated that this region was composed of tetragonal Ti$_2$N ($\text{P4}_2\text{-mnm}$) crystals (Figure 4.123-d). The compound layer outer layer had a nanocrystalline structure and was approximately 0.6 µm thick, as shown in Figure 4.123-c. The rings in the SAD pattern from this layer conformed well to d-spacing values of the FCC TiN structure (Figure 4.123-e).

Figure 4.124-a is a cross-sectional TEM micrograph of the plasma nitrided alloy without the shot peening pretreatment (PN sample). The bend contours inside the grains in the diffusion zone, indicate the presence of residual strains, likely due to the dissolution of nitrogen interstitials. Grain boundaries can be distinguished through the discontinuity of these fringes. The compound layer had an average thickness of 1.1 ± 0.4 µm, and the grains in this layer can be differentiated on account of their lamellar morphology with parallel streaks in different orientations. The compound layer grains had an average size of 1.5 µm measured using an image analysing software. Figure 4.124-b is the corresponding diffraction pattern from the enclosed region in Figure 4.124-
a. Reflections from cubic TiN (rock salt structure, Fm-3m) and tetragonal Ti$_2$N (P4$_2$/mnm) crystals were found in the pattern.

In Figure 4.125 the x-ray diffraction (XRD) pattern for the plasma nitrided surface subjected to the shot peening pretreatment (SP-PN sample) is plotted and compared with that of the plasma nitrided surface without the pretreatment (PN sample). Peak analyses showed three nitride phases of cubic TiN (Fm-3m), tetragonal Ti$_2$N (P4$_2$/mnm), and HCP TiN$_{0.3}$ (P6$_3$/mmc) in addition to HCP $\alpha$-Ti (P6$_3$/mmc) in the PN sample. This is in agreement with the results reported from the plasma nitriding of Ti-6Al-4V alloy by other researchers [145, 147]. On the surface of SP-PN coupons, however, Ti$_2$N appears to be the dominant nitride phase and major reflections from $\alpha$-Ti are also apparent. The low-intensity of TiN peaks in this spectrum may be due to their ultra-fine grain size (nanocrystalline).

4.8.3 Sliding Performance of Plasma Nitrided Ti-6Al-4V Surface Subjected to the Shot Peening Pretreatment

4.8.3.1 Microscratch Tests

The scratch tracks from single-pass microscratch tests at 5 N, 10 N, and 20 N applied normal loads were examined by optical profilometry. The results revealed that the plasma nitrided samples without the pretreatment (PN samples) developed deeper and wider scratches in all of the applied loading conditions. Figure 4.126 illustrates the two-dimensional optical profiles of scratch tracks made at 10 N.

Based on the two-dimensional profiles, the width of the scratch paths was carefully determined and the corresponding scratch hardness value was calculated at each
loading condition. For conical indenters scratch hardness value [73] is defined as the vertical normal load per one half of the vertically projected area and is calculated using the equation below,

\[ H_s = \frac{8F}{\pi w^2} \]  

(4.1)

where, \( F \) and \( w \) are the applied load and scratch width, respectively [200]. The obtained scratch hardness values are plotted against the applied load in Figure 4.127. The shot peening pretreatment resulted in higher scratch hardness values. However, this effect is more evident at lower loads (e.g., 5 N), where the depth of scratch path is comparable to the compound layer thickness and the effect of subsurface deformation is minimal.

Although the hardness of nanocrystalline TiN films is a function of various parameters such as texture, N/Ti ratio, size of nanograins, etc. the average scratch hardness value obtained at 5 N is in agreement with the values reported in the literature [215, 216].

Acoustic emission signals and SEM observations of scratch paths were used to study failure mechanisms during multiple-pass microscratch tests (five passes). The occurrence of compound layer spallation after two passes in the PN sample was accompanied by a significant rise in the intensity of acoustic emission signals, as marked by sharp peaks in Figure 4.128-a.

On the contrary, no delamination was observed in SP-PN samples tested under the same loading conditions (Figure 4.128-b). The SEM images from damage evolution in SP-PN and PN samples after multiple-pass microscratch tests (five sliding passes at 20 N) are shown in Figures 4.129 and 4.130, respectively. Figure 4.129 illustrates that failure events in the SP-PN samples were restricted to tensile cracks perpendicular to the scratch direction inside the scratch paths and angular cracks at the scratch rims. No
evidence of interfacial delamination was observed. The PN surfaces, on the other hand, experienced occasional chipping of the compound layer around the scratch rims (Figures 4.130-b, 4.130-c).

4.8.3.2 Ball-on-disk Tests

The ball-on-disk wear tests were performed on SP-PN (plasma nitrided with the shot peening pretreatment) and PN (plasma nitrided without the pretreatment) Ti-6Al-4V coupons against sapphire counterface balls (3 mm diameter) at different loads of 1 N, 2 N, 3 N, 4 N, and 5 N at two sliding speeds of 0.005 m/s and 0.01 m/s. All the tests ran for a sliding distance of 10 m (2000 cycles). The results were classified into three different subsections as presented below.

I) Low loads (< 5 N)

Both SP-PN and PN surfaces exhibited the same type of wear behaviour at low loads (< 5 N). Figure 4.131-a is a typical back-scattered SEM micrograph of the wear track on the surface of PN sample tested at 2 N, 0.005 m/s. The micrograph shows generation of patches of material which appear as dark grey areas on the worn surfaces. Figure 4.131-b is a higher magnification view of the above-mentioned features where the energy dispersive spectroscopy (EDS) analysis was performed. The corresponding EDS analysis (Figure 4.131-c) indicated the presence of Al, O, Ti, and N elements in the dark grey regions. Similar features were observed on the surface of SP-PN samples after wear tests at low loads (< 5 N) for both low and high sliding speeds (0.005, 0.01 m/s).
II) High load (5 N), Low sliding speed (0.005 m/s)

Different wear behaviours were observed for the SP-PN and PN surfaces during wear tests at high loads (5 N) and low sliding speed (0.005 m/s). SEM observations revealed that the wear track on the SP-PN surface appeared to be completely covered with a light grey layer composed of dark patches (Figure 4.132-a). Adhesion failures and interfacial delamination were not observed, however, occasionally microcracks were seen inside the wear tracks (Figure 4.132-b). The EDS spectra revealed that the light grey areas in the wear track were rich in Ti, N and Al elements (Figure 4.132-c) and the dark grey areas had abundance of O in addition to Ti, N and Al elements (Figure 4.132-d). Wear debris were infrequently observed in the wear tracks. A typical secondary electron SEM image of the morphology of debris particles is shown in Figure 4.133. According to the EDS analysis these particles consisted of Al, Ti, O and N elements.

In Figures 4.134-a and 4.134-b typical secondary and back-scattered electron SEM micrographs of the wear track on the PN surface (plasma nitried without the shot peening pretreatment) are exhibited. The worn surface, tested against alumina counterface at 5 N applied load and 0.005 m/s sliding speed, consisted of a mixture of dark and light grey areas. Due to the presence of Ti, Al, O and N elements, this layer will be called the mechanically mixed layer. Abrasion grooves and signs of delamination were also observed inside the mechanically mixed layer. Higher magnification images of the occurrence of delamination within the mechanically mixed layer and the presence of abrasive grooves inside the layer are more clearly seen in Figures 4.135-a, 4.135-b, respectively.
III) High load (5 N), High sliding speed (0.01 m/s)

Figure 4.136 is a typical secondary electron SEM micrograph of the worn surface on the plasma nitried surface without the shot peening pretreatment (PN sample) tested at 5 N applied load and 0.01 m/s sliding speed. The compound layer was completely removed and the Ti-6Al-4V substrate exposed under the above-mentioned wear testing conditions. The wear track was severely abraded and the wear debris were also scattered inside and around the wear tracks. The EDS analysis obtained from the wear debris indicated presence of N, Ti, Al, V, and O elements.

On the contrary, the SEM observations of the wear tracks on SP-PN surfaces revealed that the plasma nitride surface endured similar sliding conditions (5 N applied load, 0.01 m/s sliding speed) without spallation or removal of the compound layer (Figure 4.137-a). The worn surfaces were covered with a layer that appeared to consist of a combination of dark and light grey areas under the back-scattered electron imaging mode. The layer was rich in Ti, Al, O, and N according to the EDS analysis (mechanically mixed layer). However, the Al and O peaks showed higher intensities in the dark grey areas (Figures 4.137-b, 4.137-c).

Variation of coefficient of friction (COF) with the applied normal load obtained by ball-on-disk wear tests against alumina counterface balls (3 mm diameter) at 0.005 m/s are compared in Figure 4.138 for plasma nitried Ti-6Al-4V alloy with and without the shot peening pretreatment. The average COF values for PN surfaces tend to increase with the applied load at a higher rate compared with those of the SP-PN surfaces. A further notable feature is that for all the tested loads, the SP-PN surfaces indicated lower average COF values. This trend is more significant at the highest applied load of 5 N.
where the average COF value of PN surface is more than twice that of the SP-PN condition.
Figure 4.1 Engineering stress-strain curves for mill-annealed Ti-6Al-4V alloy used in this research (loading rate: 0.5 mm/min).

Figure 4.2 A typical stereo micrograph from the fracture surface of Ti-6Al-4V alloy after uniaxial tensile test showing a ductile "cup and cone" type of failure.
Figure 4.3 Typical secondary electron SEM images of the fracture morphology of Ti-6Al-4V alloy after tensile tests. (a) Ductile type of failure consisting of a dimpled region at the center surrounded by shear lip, the enclosed areas are the locations where higher magnification images were taken. (b) A higher magnification view of the equiaxed dimples in the middle region.
Figure 4.4 Secondary electron SEM image from the tensile fracture morphology of Ti-6Al-4V alloy (shear lip region) after being immersed in Kroll’s reagent showing homogenous deformation of the $\alpha$ phase and $\beta$ particles under tensile loads. The light grey particles marked on the image are $\beta$ particles in the dark grey background which is the $\alpha$ phase.

Figure 4.5 The S-N curve obtained from rotation bending fatigue tests on Ti-6Al-4V alloy.
Figure 4.6 (a) A secondary electron SEM micrograph from fatigue fracture at 769 MPa ($N_f = 1.1 \times 10^5$ cycles, high cycle fatigue region). Only one origin of fatigue crack initiation was observed which was located close to the surface of the sample. Fatigue crack propagated with two different morphologies in Regions I and II leading to the final rupture. (b) A higher magnification view of the fatigue crack initiation site which shows signs of distortion and plastic deformation. (c) A higher magnification view of crack propagation in Region I, relatively smooth surfaces with microcracks and striations perpendicular to the crack growth direction. (d) A higher magnification view of crack propagation in Region II consisting of ripple marks and microcracks perpendicular to the propagation direction. (e) Striations in the crack propagation Region I. (f) Dimples in the final rupture region indicating a ductile type of failure.
(a) Region I Region II

(b) Origin

1mm

20um
Figure 4.7 (a) A secondary electron SEM image of the fatigue fracture at 816 MPa ($N_f = 4.3 \times 10^4$ cycles, low cycle fatigue region). The fatigue crack initiated at one location close to the surface and propagated with two different morphologies in Regions I and II leading to the final rupture. The arrows show the crack propagation direction. (b) A higher magnification view of the fatigue crack initiation site. (c) A higher magnification view of the crack propagation in Region I showing relatively smooth surfaces. (d) Striations in the enclosed area marked in (c) within the crack propagation Region I. (e) A higher magnification view of crack propagation in Region II consisting of ripple marks and microcracks perpendicular to the propagation direction. (f) Dimples in the final rupture region indicating a ductile type of failure.
Figure 4.8 The variation of wear rate as a function of applied load during ball-on-disk wear tests on Ti-6Al-4V alloy determined based on (a) mass loss measurements, (b) volumetric wear measured using optical profilometry compared with those calculated from mass loss measurements. The wear tests were carried out against AISI 52100 steel counterface at 0.1 m/s sliding speed for a total sliding distance of 200 m (5000 cycles).
Figure 4.9 (a) Variation of coefficient of friction with the sliding distance during ball-on-disk wear tests at different applied loads of 0.8 N, 1.2 N, 2 N, 3.5 N, and 5 N. (b) The average value of coefficient of friction in the steady state region decreased with the applied normal load.
Figure 4.10 (a) Three-dimensional and (b) two-dimensional optical profilometry images from the wear track at 0.8 N applied load. (Sliding speed: 0.1 m/s, sliding distance: 200 m, AISI 52100 steel counterface).

Figure 4.11 A back-scattered electron SEM image showing the typical morphology of wear track on Ti-6Al-4V alloy surface tested against AISI 52100 steel counterface at 0.8 N normal load, 0.1 m/s sliding speed after 200 m. The enclosed area is the location where higher magnification images in Figure 4.12 were taken.
Figure 4.12 Back-scattered SEM micrographs of the wear track on the surface of Ti-6Al-4V alloy at the applied load of 0.8 N. (a) The wear track consisted of dark grey patches of accumulated material (flat plateaus) as well as ploughing grooves. (b) A higher magnification view of location “I” showing the morphology of wear debris particles surrounding the plateaus. (c) A higher magnification view of location “II” showing the microcracks frequently observed within the plateaus. (d) A higher magnification view of location “III” showing the abrasive grooves on the wear track and some fine debris particles embedded inside the grooves. (Sliding speed: 0.1 m/s, sliding distance: 200 m, counterface material: AISI 52100 steel).
Figure 4.13 EDS analysis of the dark grey plateau marked as “c” on the SEM image shown in Figure 4.12-a showing the presence of oxygen and iron in this region in addition to titanium, aluminum and vanadium elements of the Ti-6Al-4V alloy.

Figure 4.14 (a) Back-scattered electron SEM image (BSI) showing the wear scar on the steel counterpart after sliding against Ti-6Al-4V at an applied load of 0.8 N (Sliding speed: 0.1 m/s, sliding distance: 200 m). The enclosed area is the location where higher magnification image in “b” was taken. (b) The accumulated material on one side of the worn surface on the counterface.
Figure 4.15 (a) Secondary electron SEM image of (a) the platelet debris which were approximately 20 µm long and 10 µm wide, (b) the fine equiaxed debris particles ranging from 0.3 µm to 3 µm in diameter, both generated during wear tests at an applied normal load of 0.8 N. (c) A typical EDS spectrum of the wear debris particles showing the presence of titanium, aluminum and vanadium as well as iron and oxygen. (Sliding speed: 0.1 m/s, sliding distance: 200 m, AISI 52100 steel counterface).
Figure 4.16 (a) Three-dimensional and (b) two-dimensional optical profilometry images of the wear track at 5 N applied load. (Sliding speed: 0.1 m/s, sliding distance: 200 m, AISI 52100 steel counterface).

Figure 4.17 A back-scattered electron SEM image showing the typical morphology of wear track on Ti-6Al-4V alloy surface tested against AISI 52100 steel counterface at the 5 N normal load, 0.1 m/s sliding speed after 200 m. The enclosed area is the location where higher magnification images shown in Figure 4.18 were taken.
Figure 4.18 Back-scattered SEM micrographs of the wear track on the surface of Ti-6Al-4V alloy at the applied load of 5 N. (a) The wear track consisted of dark grey patches of accumulated material as well as ploughing grooves. (b) A higher magnification view of location “I” showing the abrasion grooves on the wear track and some fine debris particles scattered on the grooves. (c) A higher magnification view of location “II” showing the fragmentation of the plateaus. (Sliding speed: 0.1 m/s, sliding distance: 200 m, counterface material: AISI 52100 steel).
Figure 4.19 EDS analysis of the region marked as “c” on the SEM image shown in Figure 4.18-a showing the presence of oxygen and iron in this region in addition to titanium, aluminum and vanadium elements of the Ti-6Al-4V alloy. A higher intensity peak of iron was observed at this loading condition (5 N) compared to lower loads (0.8 N).

Figure 4.20 (a) Secondary electron SEM image (SEI) of the cutting chip-like debris, (b) SEI of the platelet debris with sliding marks, (c) SEI of the loose fine debris particulates, all generated during wear tests at 5 N applied load. The enclosed areas are the locations were EDS analyses were performed. (d) EDS analysis of the enclosed area shown in “a” indicating that the cutting chip-like was composed of the same elements as the Ti-6Al-4V alloy. (e) EDS analysis of the enclosed area shown in “b” indicating that the wear debris was composed of the same elements as the Ti-6Al-4V alloy in addition to oxygen and iron. (Sliding speed: 0.1 m/s, sliding distance: 200 m, AISI 52100 steel counterface).
Figure 4.21 (a) Back scattered electron SEM image (BSI) of the wear scar on the steel counterface after wear test at 5 N against Ti-6Al-4V alloy (Sliding speed: 0.1 m/s, sliding distance: 200 m). The enclosed area is the location where the higher magnification image shown in “b” was taken. (b) Formation and fragmentation of the mechanically mixed layer (MML) on the worn surface of the counterface.
Figure 4.22 Back-scattered SEM micrographs showing the focused ion beam (FIB) milling location on the wear track of Ti-6Al-4V alloy after the ball-on-disk wear test at 0.8 N applied load. (a) A plateau on the wear track where FIB trench was milled, the enclosed area is the location where EDS analysis was performed. (b) A high magnification view of the image shown in (a). (Sliding speed: 0.1 m/s, sliding distance: 200 m, counterface material: AISI 52100 steel).

Figure 4.23 EDS spectrum obtained from the enclosed area in Figure 4.22-a showing presence of oxygen and iron in addition to titanium, vanadium and aluminum on the wear track. (Applied normal load: 0.8 N, sliding speed: 0.1 m/s, sliding distance: 200 m, counterface material: AISI 52100 steel).
Figure 4.24 Back-scattered SEM images showing the ion milled cross section of worn surfaces of Ti-6Al-4V alloy at 0.8 N applied load. (a) General view of the subsurface region showing the mechanically mixed layer (MML) and the subsurface region. The enclosed areas are the locations where higher magnification images in (b), (c) were taken. (b) A high magnification view of the enclosed area in (a) showing that MML layer consisted of agglomerated particles, and (c) a high magnification view of the enclosed area in (a) showing that delamination occurred within the MML layer.
Figure 4.25 (a) A back-scattered electron SEM image from the ion milled cross section of wear track showing the mechanically mixed layer (MML) and the location where EDS mapping was performed. The distribution of (b) oxygen, (c) aluminum, (d) titanium, (e) vanadium, (f) iron obtained by EDS elemental analysis. (Applied normal load: 0.8 N, sliding speed: 0.1 m/s, sliding distance: 200 m, counterface material: AISI 52100 steel).
Figure 4.26 Back-scattered electron SEM images showing the location of FIB milling on the wear track of Ti-6Al-4V alloy after the ball-on-disk wear test at 5 N applied load. (a) A plateau on the wear track before ion milling, (b) the location of FIB trench on the plateau, (c) a high magnification view of the image shown in (a), and (d) a high magnification view of the location where FIB milling for cross-sectional analysis of the wear track was performed. (Sliding speed: 0.1 m/s, sliding distance: 200 m, counterface material: AISI 52100 steel).
Figure 4.27 Back-scattered SEM images showing the ion milled cross section of worn surfaces of Ti-6Al-4V alloy at 5 N applied load. (a) General view of the subsurface region showing the mechanically mixed layer (MML) and the subsurface region. Occasional white streaks where observed in the MML layer as marked by the arrows. The enclosed area marks the location observed at higher magnification in (b). (b) A high magnification view of the enclosed area in (a) showing the white streaks inside the mechanically mixed layer, and (c) a higher magnification image showing plastic deformation in the subsurface region evidenced by the elongation of grains parallel to the sliding direction (as indicated by the arrows).
Figure 4.28 A back-scattered electron SEM image from the ion milled cross section of wear track showing the mechanically mixed layer (MML) and the location where EDS mapping was performed. The distribution of (b) oxygen, (c) aluminum, (d) titanium, (e) vanadium, (f) iron obtained by EDS elemental analysis. It was observed that the white streaks in the MML were rich in iron. (Applied normal load: 5 N, sliding speed: 0.1 m/s, sliding distance: 200 m, counterface material: AISI 52100 steel).
Figure 4.29 XRD spectra of the plasma nitrided surfaces after 24- and 45-h treatments at 600°C.
Figure 4.30 Secondary electron SEM images of the cross section of plasma nitrided Ti-6Al-4V alloy at 600°C for (a) 24 h and (b) 45 h.
Figure 4.31 Microhardness-depth profiles in the near-surface region of plasma nitrided samples at 600°C for 24- and 45-h durations indicating a deeper diffusion zone after 45 hours of nitriding.
Figure 4.32 The variation of coefficient of friction with sliding distance during microscratch tests on untreated and plasma nitrided Ti-6Al-4V alloy at 600°C for 24 and 45 hours. The microscratch tests were performed under constant loading conditions (a) 5 N, (b) 20 N.
Figure 4.33 XRD pattern of the plasma nitrided surface treated in an atmosphere containing 3% and 6% N₂ -balance H₂ for 24 hours at 600°C.
Figure 4.34 XRD pattern of the plasma nitrided surface treated in an atmosphere containing 3% N₂-balance Ar for 24 hours at 600°C.
Figure 4.35 Scanning electron SEM images of the cross section of plasma nitrided alloy at a total pressure of 400 Pa. (a) overall view in the near-surface region, (b) an image acquired at a higher magnification indicating the formation of compound layer and \( \alpha \)-case.
Figure 4.36 Scanning electron SEM image of the cross section of plasma nitrided alloy treated in a 3%N₂-balance Ar atmosphere, the presence of microvoids underneath the compound layer is likely due to the sputtering effect of heavy Ar atoms in the plasma.

Figure 4.37 Scanning electron SEM image of the cross section of plasma nitrided alloy treated in a 6%N₂-balance H₂ atmosphere.
Figure 4.38 Microhardness-depth profiles for plasma nitrided alloy in nitriding atmospheres containing 3% and 6% N$_2$ showing that increasing the nitrogen content inversely affected the hardness and depth of nitrogen diffusion.

Figure 4.39 Microhardness-depth profiles for plasma nitrided alloy treated in nitriding atmospheres containing H$_2$ and Ar as carrier gas.
Figure 4.40 Microhardness-depth profiles for plasma nitrided alloy treated in nitriding atmospheres with different pressures (67 Pa, 400 Pa).

Figure 4.41 (a) Secondary electron SEM image from the surface topography of plasma nitrided Ti-6Al-4V after a 24-hour treatment at 500˚C, (b) a higher magnification view of the image shown in (a). (Tilt angle: 45˚)
Figure 4.42 (a) Secondary electron SEM image from the surface topography of plasma nitrided Ti-6Al-4V after a 24 hr treatment at 600˚C. (b) a higher magnification view of the image shown in (a). (Tilt angle: 45˚)

Figure 4.43 An atomic force microscopy (AFM) image from the surface of plasma nitrided Ti-6Al-4V after a 24-hour treatment at 600˚C.
Figure 4.44 (a) Secondary electron SEM image from the surface topography of plasma nitrided Ti-6Al-4V after a 24 hr treatment at 900°C, (b) a higher magnification view of the image shown in (a). (Tilt angle: 45°)
Figure 4.45 The XRD spectra of the plasma nitrided Ti-6Al-4V surfaces treated at (a) 500°C showing presence of Ti$_2$N, TiN$_{0.3}$ and traces of TiN in the compound layer, (b) 600°C showing abundance of TiN and Ti$_2$N and TiN$_{0.3}$ in the compound layer, (c) 900°C showing the abundance of TiN and presence of Ti$_2$N in the compound layer. A higher contribution of α-Ti peaks (reflections from the substrate) in the XRD spectrum of the plasma nitrided alloy at 500°C and fewer number of titanium nitride peaks indicated the thin nature of the compound layer formed at this temperature.
Figure 4.46 A typical secondary electron SEM image of the cross section of plasma nitrided Ti-6Al-4V alloy at 500°C for 24 hours showing the formation of a thin compound layer and a shallow diffusion zone. The diffusion zone was differentiated by dissolution of fine recrystallized $\beta$ particles inside the $\alpha$ grains.

Figure 4.47 (a) A typical secondary electron SEM image of the cross section of plasma nitrided Ti-6Al-4V alloy at 600°C for 24 hours showing the formation of a thin compound layer and a deep diffusion zone. The diffusion zone was differentiated by dissolution of fine recrystallized $\beta$ particles inside the $\alpha$ grains. (b) A higher magnification view from the near-surface microstructure showing a well-bonded interface between the compound layer and the diffusion zone. (c) A higher magnification view of the substrate.
Figure 4.48 A back-scattered electron SEM image (BSI) of the FIB-milled cross section of the plasma nitrided microstructure (600°C, 24 hours). The compound layer/diffusion zone interface was not clearly distinguished indicating a well-bonded interface between the compound layer and diffusion zone. A layer of Pt was deposited on the surface prior to the milling as a protection layer to avoid the ion milling damage.

Figure 4.49 (a) A typical secondary electron SEM image of the cross section of plasma nitrided Ti-6Al-4V alloy at 900°C for 24 hours showing the formation of a thin compound layer, an α-case (β-free zone), and a deep diffusion zone. The diffusion zone was differentiated by dissolution of fine recrystallized β particles inside the α grains. (b) A higher magnification view showing the presence of an α-case at the interface between the compound layer and the diffusion zone. (c) A higher magnification view of the α-case region showing the presence of a distinct layer underneath the compound layer, according to the EDS line-scans this layer had a high concentration of aluminum and it is thus called the “Al-rich” layer.
Figure 4.50 EDS analysis showing the distribution of N, O, Al, Ti, and V elements in the region underneath the compound layer in the plasma nitrided Ti-6Al-4V alloy at 900˚C for 24 hours. The white line is the location where the EDS line scan was performed. A higher concentration of Al was found in the region underneath the compound layer (Al-rich layer).

Figure 4.51 A back-scattered electron SEM image showing the ion milled cross section of plasma nitrided Ti-6Al-4V alloy at 900˚C. A platinum layer was deposited on the surface to protect surface features from milling damage. Grains (approximately 1-3 µm in size) that were differentiated on account of their different contrasts were TiN grains according to the XRD results. (Tilt angle: 54°)
Figure 4.52 Secondary electron SEM images of the substrate microstructure after plasma nitriding treatment at 900°C (for 24 hours). (a) Substantial grain growth, (b) microstructural transformation from equiaxed mill-annealed microstructure to bimodal microstructure consisting of equiaxed α grains and grains composed of α/β lamellae.

Figure 4.53 Microhardness-depth profile for plasma nitried Ti-6Al-4V at different temperatures. The depth of diffusion zone was estimated at the distance from the compound layer interface where the hardness value reached that of the substrate.
Figure 4.54 (a) Scanning TEM (STEM) image of the cross section of plasma nitrided Ti-6Al-4V alloy showing the locations where the electron energy loss spectroscopy (EELS) analyses were performed. (b) EELS spectrum collected from locations marked as “1” in (a) falls within the compound layer and contains a nitrogen peak at 401 eV as well as two α-titanium peaks at 456 eV and 461 eV. (c) The grain marked as “2” in (a) falls within the diffusion zone and only shows α-titanium peaks. (d) EELS line scan confirming that the thickness of compound layer was around 2 µm.
Figure 4.55 Bright-field TEM image of cross section of plasma nitrided Ti-6Al-4V alloy (600°C for 24 hours). The enclosed areas are the locations where closer observation at higher magnifications was performed.
Figure 4.56 Higher magnification bright-field TEM images of locations marked as “a” and “b” in Figure 4.55 showing a distinct grain structure in the compound layer within the size range of 480 ± 20 nm, easy to distinguish from that of the diffusion zone whose grain size was around 4 µm. A 5-6 nm thick layer was also revealed on the surface which was characterized by x-ray photoelectron spectroscopy (XPS) analysis.
Figure 4.57 Bright-field TEM image of the location marked as “c” in Figure 4.55 showing a couple of grains in the compound layer and the corresponding selected area electron diffraction pattern (SAD) indicating presence of TiN (Fm-3m) in the marked region.

Figure 4.58 A bright-field TEM image of the surface vicinity of the plasma nitrided Ti-6Al-4V alloy and the corresponding selected area electron diffraction pattern (SAD) indicating presence of Ti$_2$N (P4$_2$/mnm) in the marked region.
Figure 4.59 (a) a typical high resolution TEM (HRTEM) image obtained from the compound layer, the enclosed areas are the locations where fast Fourier transform (FFT) patterns were derived. (b), (c) FFT diffraction patterns showing the presence of Ti$_2$N (P4$_2$/mnm) in the marked regions.
Figure 4.60 A typical bright-field TEM image of the region marked as “d” in Figure 4.55, showing a well bonded compound layer/diffusion zone interface that could not be clearly delineated.

Figure 4.61 Bright-field TEM image of the region marked s “e” in Figure 4.55 and corresponding electron diffraction pattern of α-Ti crystal structure (P63/mmm).
Figure 4.62 XPS survey scan with a wide energy range of 0-1100 eV acquired from the plasma nitrided Ti-6Al-4V surface.

Figure 4.63 Glow discharge optical emission spectroscopy (GDOES) atomic concentration profile obtained on plasma nitrided Ti-6Al-4V after a 24 hour treatment at 600°C in a dilute nitrogen atmosphere (3% N₂) showing a high concentration of nitrogen in the compound layer and a slightly higher amount of aluminum at the interface between the compound layer and the diffusion zone.
Figure 4.64 Stress-strain curves of the plasma nitrided and untreated alloys comparing the tensile properties before and after plasma nitriding treatments at two different temperatures of 600°C and 900°C. The yield strength (0.2% offset yield) was obtained based on the slope of the elastic region. It was found that the tensile and yield strength of the alloy were not affected by plasma nitriding at 600°C, however, the ductility (tensile elongation, %) decreased from 13.9 to 7.8. Conversely, plasma nitriding at 900°C resulted in substantial degradation of strength and ductility of the alloy.
Figure 4.65 Secondary electron images showing the fracture surface of the plasma nitrided Ti-6Al-4V alloy. (a) general morphology showing a cup and cone type of failure, the enclosed areas are the locations where higher magnification images in (b) and (d) were taken, (b) a brittle type of fracture in the surface vicinity, the enclose area is where a higher magnification image in (c) was taken, (c) cleavage surfaces and the formation of microcracks close to the surface, (d) dimpled rupture area indicated in (a).
Figure 4.66 (a) Secondary electron image showing circumferential (secondary) cracks on the surface of plasma nitrided alloy (marked by the arrows), the enclosed area is where the higher magnification image in (b) was taken, (b) a higher magnification SEI from the location indicated in (a) showing that the secondary cracks were connected at a 45° angle.
Figure 4.67 (a) A typical secondary electron SEM image of the cryogenic fracture microstructure of plasma nitrided Ti-6Al-4V (600°C, 24 hours). The enclosed area is the location where higher magnification image shown in “b” was taken. (b) A secondary electron fractograph revealing the brittle fracture of the compound layer and the presence of lateral microcracks underneath the compound layer. The microcracks propagated parallel to the surface into the diffusion zone. These microcracks were deflected (c) or stopped (d) at $\beta$ particles in the diffusion zone.
Figure 4.68 S-N curves illustrating the fatigue behaviour of Ti–6Al–4V alloy before and after plasma nitriding treatment at two different temperatures of 600°C and 900°C. The high cycle and low cycle fatigue regions were designated based on $10^5$ cycles of loading and the fatigue endurance limit was determined at $10^7$ cycles.
Figure 4.69 (a) A secondary electron SEM images (SEI) of the fatigue fracture surface of plasma nitrided alloy at 600°C tested at 569 MPa, the enclosed areas show the locations where higher magnification images were taken. The fracture surface consisted of a crack initiation site, a smooth area of crack propagation (Region I) followed by a rough propagation area (Region II) and the final rupture. (b) The fatigue crack initiation site on the surface associated with fragmentation and crack formation in the compound layer, (c) higher magnification image of the enclosed area in Figure 4.69-b illustrating striations and signs of plastic deformation in the compound layer, (d) fatigue crack propagation at the location indicated in Figure 4.69-a; a relatively smooth area with striations and microcracks perpendicular to the crack propagation direction, (e) a higher magnification view of striations at the location indicated in Figure 4.69-d, (f) the dimpled morphology observed in Region II prior to the final rupture.
Figure 4.70 Acoustic emission (AE) signal recorded during the microscratch test was used to study failure phenomena (angular, tensile and transverse cracks) as each and cracking event on the scratch path has an acoustic emission peak associated with it. Angular cracks initiated close to the edges of scratch path at 0.75 N, the tensile cracks formed a second critical normal load of 8 N, and at 15 N angular and tensile cracks combined into semi-circular cracks.
Figure 4.71 (a) Variation of the coefficient of friction (COF) with sliding distance for untreated and plasma nitrided Ti-6Al-4V at 600°C for 24 h. (b) The average COF value for plasma nitrided and untreated Ti-6Al-4V alloy at different applied normal loads.
Figure 4.72 Back-scattered electron SEM images of the scratch track on the surface of plasma nitrided alloy at 600°C under 0.5 N applied load showing (a) a general view of the scratch track, (b) a high magnification micrograph of a flattened asperity located in the area enclosed in (a) where FIB milling was carried out for cross-sectional analysis.
Figure 4.73 Back-scattered electron SEM images of the FIB-milled cross section of scratch track at 0.5 N load at the location indicated in Figure 4.72. (a) A general view of the cross section, (b) a high magnification image of the area enclosed in (a) showing the formation of microvoids in the surface vicinity within the compound layer likely at grain boundaries.
Figure 4.74 Back-scattered electron images of the scratch track on the surface of plasma nitrided alloy at 600°C under 1 N applied load showing (a) a general view of the scratch track, (b) a high magnification micrograph of a flattened asperity located in the area enclosed in (a) where FIB milling was carried out for cross-sectional analysis.
Figure 4.75 Back-scattered electron SEM images of the FIB-milled cross section of scratch track at 1 N load at the location indicated in Figure 4.79 showing that the microcracks that initiated from the surface or subsurface microvoids appear to have grown intergranularly in the Compound Layer.
Figure 4.76 Back-scattered electron images of the scratch track on the surface of plasma nitrided alloy at 600°C under 10 N applied load showing (a) a general view of the scratch track, (b) a high magnification micrograph of the area enclosed in (a) where FIB milling was carried out for cross-sectional analysis. The tensile cracks within the scratch track have been marked by arrows.
Figure 4.77 Back-scattered electron SEM images of the FIB-milled cross section of scratch track at 10 N load at the location indicated in Figure 4.78. (a) A general view of the cross section, (b) a high magnification image of the area enclosed in (a) showing the propagation of microcracks within the compound layer and into the diffusion zone.
Figure 4.78 Back-scattered electron images of the scratch track on the surface of plasma nitrided alloy at 600°C under 20 N applied load showing (a) a general view of the scratch track, (b) a high magnification micrograph of the area enclosed in (a) where FIB milling was carried out for cross-sectional analysis. The semi-circular cracks within the scratch track have been marked by arrows.
Figure 4.79 SEM observations from surface and FIB-milled cross section showed that even at the highest applied load of 20 N in microscratch tests, plasma nitrided Ti-64 surface at 600°C did not experience any spallation. The cracks were stopped at β particles in the diffusion zone.
Figure 4.80 Acoustic emission (AE) output combined with SEM observations of the scratch track on the plasma nitrided surface (900°C, 24 h) showing the onset of asperity fracture at 0.4 N, the formation of tensile cracks at 1.5 N, and buckling at 5.5 N.
Figure 4.81 Comparison of coefficient vs. sliding distance curves during microscratch tests performed at a constant normal load of 5 N on surfaces that were plasma nitrided at 600°C and 900°C. It can be observed that higher nitriding temperature resulted in higher coefficient of friction value with larger fluctuations. The average coefficient of friction values were 0.05 ± 0.005 and 0.06 ± 0.02 and for 600°C and 900°C treatments, respectively.
Figure 4.82 Back-scattered electron images of the scratch track on the surface of plasma nitrided alloy at 900°C under 1 N applied load showing (a) a general view of the scratch track, (b) a high magnification micrograph of the area enclosed in (a) where FIB milling was carried out for cross-sectional analysis. The microcracks on the surface asperities have been marked by arrows. (Tilt angle: 54°)
Figure 4.83 SEM observations of the FIB-milled cross section at the location indicated in Figure 4.82 showing the formation of microcracks parallel to the sliding direction in the compound layer (tilt angle: 54°).
Figure 4.84 Back-scattered electron SEM images of the scratch track on the surface of plasma nitrided Ti-6Al-4V alloy at 900°C after a microscratch test at an applied load of 20 N.
Figure 4.85 SEM observations of the FIB-milled cross section at the location indicated in Figure 4.84 showing the propagation of microcracks perpendicular to the sliding direction in the compound layer likely along grain boundaries (tilt angle: 54°).
Figure 4.86 Secondary electron SEM images from wear evolution as the applied normal load was increased: (a) 0.5 N, (b) 1 N, (c) 2 N, and (d) 3 N. Sliding direction and width of wear tracks are marked by arrows in the micrographs. (Sliding velocity: 0.1 m/s, sliding distance: 200 m, tilt angle: 50°)
Figure 4.87 Secondary electron SEM image of the wear track on the surface plasma nitrided coupon after a couple of hundreds of cycles (10 m) at 0.5 N. The insert shows the overall view of the wear track developed (Tilt angle: 50°).

Figure 4.88 Three-dimensional optical profilometry image showing severe deformation and smearing of transferred material from the steel counterface to the plasma nitrided surface.
Figure 4.89 Cutting chip-like wear debris particles found around the wear track of 0.5 N wear test after 10 m. According to EDS analysis these particles were rich in Fe and Cr.

Figure 4.90 Secondary electron SEM images showing examples of (a) severe deformation as evidenced by abrasion grooves, (b) spallation of the transfer layers formed on the surface of plasma nitrided Ti-6Al-4V alloy during wear tests against AISI 52100 steel counterface at 0.5 N after 200 m. (Sliding speed: 0.1 m/s, tilt angle: 50°)
Figure 4.91 (a) Secondary electron SEM image showing patches of transferred material on the surface of plasma-treated sample after wear test under an applied load of 2 N (tilt angle: 50°). (b) Typical EDS analysis taken from the transferred layers showing that Fe and O were the main constituents of the transfer layers.

Figure 4.92 Back-scattered electron SEM images of (a) cutting chip-like debris, (b) platelets and fine debris particles generated during wear tests at 2 N. (sliding speed: 0.1 m/s)
Figure 4.93 Secondary electron SEM images of (a) the oxide layers accumulated on the plasma nitrided surface at 3 N, (b) fine wear debris particles surrounding the oxide plateaus, (c) severe abrasion and fragmentation of the oxide plateaus. (The sliding direction (SD) is marked by an arrow)
Figure 4.94 (a) Three-dimensional optical profilometry image of a patch of oxide layer on the wear track of the plasma nitrided alloy tested at 2 N. (b) shows the same area after immersing the coupon in an aqueous solution containing hydrochloric acid. (c), (d) show secondary electron SEM images taken from the same locations shown in (a) and (b). (e) High magnification views of the locations shown in (c) and (d) indicating that most of the oxide layer was dissolved in the hydrochloric acid solution and the plasma nitrided surface underneath was unaffected by the sliding contact except for minor polishing of the asperity tips. (Sliding speed: 0.1 N, sliding distance: 200 m, tilt angle: 40°)
Figure 4.95 Optical micrographs of the wear scars on steel counterface balls tested against plasma nitrided Ti-6Al-4V alloy at (a) 0.5 N, (b) 1 N, (c) 2 N, and (d) 3 N. (sliding distance: 200 m, sliding speed: 0.1 m/s)

Figure 4.96 Area of wear scar on steel counterface balls as a function of applied load during wear tests of plasma nitrided Ti-6Al-4V alloy. (Sliding distance: 200 m, sliding speed: 0.1 m/s)
Figure 4.97 Variation of volumetric wear (volume of transferred material to the plasma nitrided surfaces during sliding) with applied load during wear tests. (Sliding speed: 0.1 m/s, sliding distance: 200 m)

Figure 4.98 Variation of the coefficient of friction with the sliding distance at different applied loads for the plasma nitrided surfaces (600°C, 24 h) tested against AISI 52100 steel counterface balls at 0.1 m/s.
Figure 4.99 Variation in coefficient of friction with sliding distance for untreated and plasma nitrided Ti-6Al-4V alloy (600°C, 24 h) tested against AISI 52100 steel counterface balls at 2 N, 0.1 m/s.

Figure 4.100 Comparison of average coefficient of friction values in the steady state condition for untreated and plasma nitrided Ti-6Al-4V alloy (600°C, 24 h) tested against AISI 52100 steel counterface under different applied loads at 0.1 m/s.
Figure 4.101 Back-scattered electron SEM micrographs of the worn surface of plasma nitrided Ti-6Al-4V tested against alumina counterface balls at 2 N, 0.01 m/s for 200 m. (a) General morphology of the wear track, (b) a high magnification view showing that the worn surface consisted of dark grey patches in a light grey background and the formation of cracks perpendicular to the sliding direction. The EDS analysis indicated that presence of Al, Ti, N and O elements on the worn surfaces, however, the dark grey regions were richer in Al and O.
Figure 4.102 (a) Back-scattered and (b) secondary electron SEM micrographs of the wear track on the surface of plasma nitrided Ti-6Al-4V tested against alumina counterface balls at 10 N, 0.01 m/s for 200 m. The enclosed areas marked as “1” and “2” are the location were higher magnification images were taken.
Figure 4.103 Secondary electron SEM micrographs showing different features on the wear tracks of plasma nitrided Ti-6Al-4V tested at 10 N against alumina counterface. (a) Severe plastic deformation and abrasion in the region marked as “2” in Figure 4.102. (b) The formation and removal of plateaus on the surface in the region marked as “1” in Figure 4.102. (c) The formation of microcracks perpendicular to the sliding direction on the plateaus in the region marked as “1” in Figure 4.102.

Figure 4.104 Secondary electron SEM micrographs of the different wear debris morphologies generated after wear tests of plasma nitrided Ti-6Al-4V against alumina at 10 N, 0.01 m/s. (a) Platelet debris, (b) cutting chip-like and fine debris.
Figure 4.105 (a) Secondary and (b) back-scattered electron SEM micrographs of the wear track on the surface of untreated Ti-6Al-4V tested against alumina counterface balls at 10 N, 0.01 m/s for 200 m. The enclosed areas marked as “1” and “2” are the location were higher magnification images were taken.
Figure 4.106 Secondary electron SEM micrographs showing different features on the wear tracks of untreated Ti-6Al-4V tested at 10 N against alumina counterface. (a) Severe plastic deformation and abrasion in the region marked as “1” in Figure 4.105. (b) High magnification view of the enclosed area in (a) showing the formation of microcrack perpendicular to the sliding direction as well as fracture and removal of part of the surface. (c) The formation of plateaus on the surface in the region marked as “2” in Figure 4.105.

Figure 4.107 Secondary electron SEM micrographs showing different wear debris morphologies generated after wear tests of untreated Ti-6Al-4V against alumina at 10 N, 0.01 m/s. (a) Platelet debris, (b) cutting chip-like and fine debris.
Figure 4.108 Typical (a) Three-dimensional and (b) two-dimensional optical surface profilometry images of the worn surfaces on plasma nitrided Ti-6Al-4V tested at 5 N showing flattening and polishing wear of the surface asperities.

Figure 4.109 Typical (a) Three-dimensional and (b) two-dimensional optical surface profilometry images of the worn surfaces on plasma nitrided Ti-6Al-4V tested at 10 N showing removal of the compound layer and some part of the diffusion zone.
Figure 4.110 Typical two-dimensional profiles of the worn surfaces on plasma nitrided and untreated Ti-6Al-4V tested at 10 N showing a deeper and wider wear track on the surface of the untreated alloy.

Figure 4.111 Variation of coefficient of friction (COF) with sliding distance during ball-on-disk wear tests on plasma nitrided surfaces against sapphire counterface at 0.01 m/s.
Figure 4.112 Variation of coefficient of friction (COF) with sliding distance during ball-on-disk wear tests on plasma nitrided and untreated Ti-6Al-4V surfaces against alumina counterface at 10 N and 0.01 m/s.

Figure 4.113 Secondary electron SEM micrographs of the cross section of wear track on plasma nitrided Ti-6Al-4V alloy tested at 10 N. (a) A general view of the cross section, (b) a higher magnification view of the location shown in (a) exhibiting the formation of a mechanically mixed layer (MML) on the surface after the wear test and severe plastic deformation underneath the MML as evidenced by the elongation of $\beta$ particles.
Figure 4.114 A secondary electron SEM micrograph of the cross section of the wear track on the plasma nitrided Ti-6Al-4V tested at 10 N. A mechanically mixed layer (MML) was formed on the surface after the wear tests. Underneath the MML, the Ti-6Al-4V substrate was severely deformed as evidenced by the elongation of the beta particles. Another notable feature are the microvoids nucleation and coalescence in the subsurface region likely evidence of the formation of shear bands during the wear test.
Figure 4.115 Secondary electron images (SEI) from the surface of a Ti-6Al-4V coupon (a) before and (b) after shot peening. (a) The as-received microstructure contains equiaxed α grains with fine recrystallized β particles and retained β particles at grain boundaries (marked by the arrows). The α grains can be differentiated by the different orientation of recrystallized β particles inside each grain. (b) The surface of shot peened samples after polishing contained no remnant oxide phases or contaminants. The severe plastic deformation was evidenced by the abundance of deformation bands and twins inside the α grains as marked by the arrows (Etched in glycerol + HF (1:1) solution).

Figure 4.116 The distribution of α grain size on the surface of Ti-6Al-4V coupons before and after shot peening. The measurements were made based on SEM observations.
Figure 4.117 (a) Cross-sectional secondary electron image (SEI) of the shot-peened alloy. The severe plastic deformation (SPD) and twinning regions have been marked in the image. The bulk microstructure consisted of equiaxed $\alpha$ grains with fine recrystallized $\beta$ particles and retained $\beta$ particles at grain boundaries. The enclosed areas are the locations where higher magnification images in (b)-(d) have been taken. (b) Extensive plastic deformation in the SPD layer (~ 5 $\mu$m thick) was evidenced by elongation of the intergranular $\beta$ particles parallel to the shot peened surface. (c) Below the SPD layer, plastic deformation was dominated by multiple twinning to a depth of ~ 20 $\mu$m. (d) Farther from the surface only single-system twinning was observed.
Figure 4.118 A secondary electron image (SEI) from surface morphology of untreated Ti-6Al-4V coupon after plasma nitriding (600°C, 24 h, 6% N₂-balance H₂). Conical features were developed on the surface after the nitriding treatment (tilt angle: 45°).
Figure 4.119 Cross-sectional secondary electron images (SEI) images after plasma nitriding at 600˚C, for 24 h in a 6%N₂-balance H₂ atmosphere (a) with the shot peening pretreatment and (b) without the shot peening pretreatment. A compound layer was formed on top of a diffusion zone by the nitriding treatment. The diffusion zone was delineated by the dissolution of fine recrystallized β particles inside the α grains. A deeper DZ was formed in the SP-PN sample and the mechanical twins were also observed in this sample. An electroless Ni coating was applied to protect the surface features from mechanical damage during the metallographic preparation of cross sections.
Figure 4.120 Microhardness-depth profiles for the plasma nitrided Ti-6Al-4V with the shot peening pretreatment (SP-PN) and without the shot peening pretreatment (PN). A deeper diffusion zone with higher hardness values in the SP-PN sample indicated that shot peening pretreatment resulted in enhanced diffusion of nitrogen interstitial atoms. The microhardness values were obtained by microindentations made at a maximum normal load of 245 mN using a diamond Vickers indenter.
Figure 4.121 (a) A cross-sectional bright field (BF) TEM micrograph showing the near-surface microstructure of plasma nitrided Ti-6Al-4V alloy with the shot peening pretreatment. The enclosed area shows the region where high magnification TEM images in have been taken. (b) A cross-sectional scanning transmission electron micrograph (STEM) from the same location in (a) showing the compound layer/diffusion zone interface. The compound layer was distinguished by its distinctive texture and finer grain size.
Figure 4.122 (a) Across-sectional bright field (BF) TEM micrograph showing subgrains and dislocations in the diffusion zone of the pretreated plasma nitrided alloy. The grain marked by “x” is the location where selected area electron diffraction pattern (SAD) was taken. (b) SAD pattern from the marked region in (a) indicating reflections from the α-Ti structure. (c) BF TEM micrograph from micro-twinning inside one of the grains in the diffusion zone. The images were taken from approximately 5 µm below the nitrided surface.
Figure 4.123 (a) A cross-sectional bright field (BF) TEM micrograph from the near surface of pretreated plasma nitrided alloy; the marked regions show the locations where higher magnification images were taken, (b) grain morphology of the compound layer inner layer, (c) nanograins in the compound layer outer layer, (d) a selected area electron diffraction (SAD) pattern corresponding to tetragonal Ti2N phase in the compound layer inner layer shown in (b), (e) SAD pattern corresponding to the FCC rings of TiN structure in the compound layer outer layer shown in (c).
Figure 4.124 A cross-sectional bright field (BF) TEM micrograph illustrating the grain morphology of the compound layer and diffusion zone in the plasma nitrided alloy without shot peening pretreatment (PN sample). The compound layer/diffusion zone interface has been delineated based on corresponding electron energy loss spectroscopy (EELS) maps. The present phases were identified by electron diffraction patterns from the marked location. (b) A selected area electron diffraction pattern from the marked region in (a) showing reflections from both TiN and Ti$_2$N crystals.
Figure 4.125 X-ray diffraction (XRD) spectra from the plasma nitrided surfaces with the shot peening pretreatment (SP-PN) and without the pretreatment (PN). A higher contribution of Ti$_2$N and α-Ti phases was observed in the SP-PN sample. The lower intensity of TiN peaks may be due to their nano-scale grain size.
Figure 4.126 Two dimensional optical profiles from scratch tracks on the plasma nitrided Ti-6Al-4V surface with the shot peening pretreatment (SP-PN) and without the pretreatment (PN) after single-pass microscratch tests at 10 N. Wider and deeper scratches were formed on the plasma nitrided surfaces without the pretreatment (PN) under the same testing conditions.

Figure 4.127 Scratch hardness values for plasma nitrided surfaces with the shot peening pretreatment (SP-PN) and without the pretreatment (PN) as a function of applied load measured by microscratch tests. The results are based on single-pass microscratch tests performed at 5 N, 10 N, and 20 N at a loading rate of 10 N/min and sliding speed of 1 mm/min. The shot peening pretreatment resulted in higher scratch hardness values especially at lower loads (e.g., 5 N) where the contribution of subsurface deformation on the hardness value is minimal.
Figure 4.128 Acoustic emission signals plotted against sliding distance during the microscratch tests on (a) plasma nitrided surface without the shot peening pretreatment (PN), (b) plasma nitrided surface with the shot peening pretreatment (SP-PN). The large pulses of acoustic emission that are observed in the PN sample after two sliding passes indicate damage to the coating and coating failure. The results are based on multiple pass (five sliding passes) microscratch tests performed at 20 N at a loading rate of 10 N/min and sliding speed of 1 mm/min.
Figure 4.129 (a) A secondary electron image (SEI) from the scratch track on the surface of plasma nitrided alloy with the shot peening pretreatment (SP-PN) after multiple-pass (five sliding passes) microscratch test at 20 N. Angular and transverse microcracks were the only failures observed and no delamination was detected. The marked regions at the rim and in the middle of the scratch track are the locations where higher magnification images were taken, (b) a SEI from angular cracks at the rim of the scratch track at the location indicated in (a), (c) a SEI from transverse cracks in the middle of the scratch track at the location indicated in (a).
Figure 4.130 (a) A secondary electron image (SEI) from the scratch track on the surface of plasma nitrided alloy without the pretreatment (PN) after multiple-pass (five sliding passes) microscratch test at 20 N. In addition to angular and transverse microcracks, occasional chipping of the compound layer was detected around the scratch track rims. The marked regions are the locations where higher magnification images were taken, (b) a SEI showing cracks in the compound layer in the direction parallel to the scratch direction at the location indicated in (a), (c) a SEI from chipping of the compound layer at the scratch track rim at the location indicated in (a).
Figure 4.131 (a) A typical back-scattered electron SEM image of the wear track on the surface of plasma nitrided Ti-6Al-4V alloy at 2 N, 0.005 m/s showing generation of patches of material on the surface, (b) A high magnification image of one of these patches at the location marked on (a), (c) energy dispersive spectroscopy (EDS) pattern obtained from the location marked on (c) showing the presence of Al, O, Ti, and N elements.
Figure 4.132 (a) Back-scattered electron SEM micrograph of the wear track on the surface of SP-PN sample (plasma nitrided with the shot peening pretreatment) tested against alumina counterface at 5 N, 0.005 m/s for 10 m (2000 cycles), the enclosed area is the location where higher magnification image was taken, (b) a higher magnification view of the area marked in (a) showing the occasional formation of microcracks inside the wear tracks (Tilt angle: $45^\circ$). (c) Energy dispersive x-ray spectroscopy (EDS) spectrum obtained from the location marked as “1” in (b) showing that the light grey areas on the wear track consisted of Ti, N and Al elements. (d) EDS spectrum obtained from the location marked as “2” in (b) showing the abundance of O in the dark grey areas on the wear track in addition to Ti, N and Al elements.
Figure 4.133 A secondary electron SEM micrograph showing the debris generated on the surface of SP-PN sample (plasma nitrided with the shot peening pretreatment) during wear test against alumina counterface at 5 N, 0.005 m/s for 10 m (2000 cycles) (Tilt angle: 45°). The debris particles were infrequently observed after the wear test and the EDS analysis showed presence of Ti, Al, N and O elements in these particles.

Figure 4.134 (a) Secondary electron, (b) back-scattered electron SEM micrographs of the wear track on the surface of PN sample (plasma nitrided without the shot peening pretreatment) tested against alumina counterface at 5 N, 0.005 m/s for 10 m (2000 cycles). The enclosed areas are the locations were higher magnification images were taken. (Tilt angle: 45°)
Figure 4.135 Secondary electron SEM micrographs of the locations marked in Figure 4.134-a showing (a) the delamination of the mechanically mixed layer and (b) the abrasion grooves on the worn surface of PN (plasma nitrided without shot peening) sample tested against alumina counterface at 5 N, 0.005 m/s for 10 m (2000 cycles)(Tilt angle: 45°).
Figure 4.136 (a) A secondary electron SEM micrograph of the worn surface on the PN (plasma nitrided without the shot peening pretreatment) sample tested against alumina counterface at 5 N, 0.01 m/s for 10 m (2000 cycles). (b) The abrasion grooves (marked by arrows) and wear debris particles (enclosed area) on the wear track (Tilt angle: 45˚). (c) Energy dispersive x-ray spectroscopy (EDS) pattern obtained from wear debris showing presence of N, O, Ti and V elements.
Figure 4.137 (a) A typical secondary electron SEM micrograph of the worn surface on the SP-PN (plasma nitrided with the shot peening pretreatment) surface tested against alumina counterface at 5 N applied load, 0.01 m/s sliding distance for 10 m (2000 cycles). (b) A back-scattered electron SEM micrograph of the wear track at a higher magnification showing existence of a mechanically mixed layer. The enclosed area is the location were the energy dispersive x-ray spectroscopy (EDS) pattern shown in “c” was taken. (c) The EDS pattern obtained from the enclosed area in “b” indicating a high contribution of O and the presence of N, Ti and V elements.
Figure 4.138 Variation of coefficient of friction (COF) with applied load obtained by ball-on-disk wear tests on plasma nitrided Ti-6Al-4V alloy with and without shot peening pretreatment against alumina counterface balls (3 mm diameter) at 0.005 m/s.
CHAPTER 5: DISCUSSION OF THE RESULTS

The following section discusses the results obtained in this investigation and is divided into two different sections that cover the experimental design for optimization of the plasma nitriding process. In the first and second sections, the results will be interpreted in terms of achieving simultaneous improvements of wear and fatigue properties by a low temperature nitriding treatment. In the third section the role of shot peening pretreatment in enhancing the performance of plasma nitrided Ti-6Al-4V surfaces will be discussed.

5.1 The Effect of Plasma Nitriding Microstructure on the Sliding Performance of Ti-6Al-4V Alloy

With the aim of improving the poor wear resistance of Ti-6Al-4V alloy without degradation of its mechanical properties especially the fatigue strength, the plasma nitriding treatment was optimized in this research. As it is established that coatings supported by deep diffusion hardened boundaries are more resistant to spallation and delamination under sliding motion compared with those with discrete boundaries to their substrates [122], the optimization was aimed at enhancing the nitrogen diffusion. This was achieved through a low temperature (600°C) treatment that led to the formation of a thin compound layer (< 2 μm) on the surface supported by a deep diffusion zone (~ 44 μm).

The diffusion of nitrogen during plasma nitriding treatment plays an important role in the surface microstructure and properties. In titanium alloys, the α phase has a high solubility limit for nitrogen (~ 33 atom.%) and incorporation of interstitial nitrogen
atoms in the Ti-6Al-4V microstructure results in the solid solution hardening of the $\alpha$ phase following a profile that gradually reaches the core hardness due to the parabolic nature of diffusion process [81, 131, 217]. The concentration profile of nitrogen can be estimated according to the Fick’s second law in which concentration is a function of both time and position. The general solution can be expressed by Equation 5.1:

$$
C(x,t) = A + B \cdot \text{erf} \left( \frac{x}{2\sqrt{Dt}} \right)
$$

(5.1)

where $A$ and $B$ are constants determined by the boundary conditions, $x$ is the distance from the interface, $t$ is the time of diffusion and $D$ is the diffusion coefficient [218]. According to the above-mentioned equation, the diffusion coefficient increases with the square of the diffusion distance ($x^2$) and is inversely related to the diffusion time. The experimental results of depth of nitrogen diffusion obtained at two different nitriding durations of 24 h and 45 h were used to estimate the diffusion coefficient of nitrogen in titanium alloy. The diffusivity of nitrogen in Ti-6Al-4V alloy during plasma nitriding experiments of this investigation was estimated at $D = 7.0 \times 10^{-11} \text{ cm}^2/\text{s}$ to comply with the results obtained by the microhardness measurements (Figure 5.1 is an illustration). However, according to the literature, the diffusion coefficient of nitrogen in $\alpha$-titanium within the temperature range of 450-700$^\circ$C is reported as $D[\text{cm}^2/\text{s}] = 0.21 \exp(-53500 [\text{cal/mole}]/RT)$ [219]. This would result in a diffusion coefficient of $8.5 \times 10^{-15} \text{ cm}^2/\text{s}$ at 600$^\circ$C which is four orders of magnitude lower than the estimated value based on the experiments. Thus it can be concluded that the diffusivity of nitrogen was enhanced in the plasma nitriding treatment possibly due to the presence of energetic species in the glow discharge compared to the thermal processes [137]. Furthermore, Raveh et al. [147] reported that the enhanced nitrogen diffusivity in the
plasma nitriding process stems from the interaction of N-H molecular ions with the 
titanium surface, while in the thermal processes diffusion of N\textsubscript{2} molecules is the 
responsible nitriding mechanism. It should be noted that the diffusitivity of β-titanium 
was neglected in the discussion above due to its low volume fraction in the alloy.

The incorporation of hydrogen instead of argon in the nitriding atmosphere was 
also another contributing factor in the enhanced diffusion of nitrogen in the titanium 
structure (Figure 4-39). Several mechanisms have been proposed for the positive role of 
hydrogen buffer gas in increasing the nitriding kinetics: (i) the hydrogen atoms/ions react 
with the oxide layer on the surface of titanium that would otherwise hinder the nitrogen 
diffusion, (ii) in the presence of hydrogen, the NH\textsuperscript{+} and NH\textsuperscript{2+} molecular radicals form in 
the plasma and their adsorption followed by dissociation on the surface provides nitrogen 
atoms for diffusion into the substrate [65, 113, 138, 144].

The diffusion of nitrogen was promoted further by increasing the nitriding 
duration and temperature. As for the nitriding duration, although the plasma nitriding for 
45 h resulted in a higher depth of diffusion zone (Figures 4.30, 4.31) compared with the 
24-h treatment, the 45-h nitried surfaces exhibited high and unstable coefficient of 
friction values compared with the surfaces treated for 24 hours at lower loads (Figure 
4.32-a) likely as a result of a higher surface roughness. In terms of the nitriding 
temperature, plasma nitriding at 500°C, led to insufficient depth of nitriding (Figure 
4.46) and those of higher temperatures (e.g., 900°C) resulted in several unfavorable 
microstructural changes such as substantial surface roughening (Figure 4.44), the 
formation of a thick compound layer and α-case (Figure 4.49), and considerable grain 
growth and microstructural transformations in the bulk (Figure 4.52).
The main advantage of the optimized treatment in this investigation (low temperature treatment of 600°C, 24 hours, dilute (3% N₂) nitriding atmosphere) was the development of a nitrided microstructure with a thin compound layer (1.9 µm) and deep diffusion zone (44.4 µm) in which the β particles at α grain boundaries and triple points were not dissolved due to the nitrogen diffusion (Figure 4.47). The resulting microstructure of the diffusion zone provided a good combination of mechanical properties. The α phase was effectively strengthened by the nitrogen interstitials (Figure 4.40) due to the higher solubility of N in α-Ti. This was accompanied by an inevitable reduction of ductility in this region as evidence by the brittle failure features under cryogenic loading (Figure 4.67-a) and tensile loading (Figure 4.65-b) conditions. However, the ductile β particles retained within the diffusion zone after nitriding had a positive role of arresting and stopping the microcracks in the near surface region (Figures 4.67-c and 4.67-d). The plasma nitrided surfaces also exhibited excellent scratch resistance and load bearing capacity under sliding conditions that will be explained below.

The SEM investigations showed that failure events during the microscratch tests initiated by the formation of microcracks on flattened surface asperities and subsurface microvoids that appeared to be at grain boundaries within the compound layer (Figures 4.72-a, 4.73-b). Upon increasing the applied load, the subsurface microcracks appear to have propagated intergranularly within the compound layer, and angular cracks developed at the rim of scratch paths (Figures 4.70 and 4.75). The formation of angular cracks was due to the concurrent action of tensile stresses. These tensile stresses developed in the compound layer as a result of plastic deformation and material pile-up.
The tensile stress component at the rear of the stylus led to the formation of another type of surface cracks, namely transverse (tensile) cracks. These cracks that were observed at loads higher than 8 N perpendicular to the sliding direction (Figures 4.70, 4.76), initiated from the surface and propagated through the compound layer (Figure 4.77). The formation of tensile cracks has been reported by many researchers during scratch tests on coated systems [221-223].

Increasing the applied normal load during the microscratch tests resulted in angular and tensile cracks connecting together and forming as transverse cracks (Figures 4.70, 4.78). At this stage subsurface crack propagation reached the diffusion zone and continued until a $\beta$ particle is encountered in this zone (Figure 4.79). The diffusion zone was effectively strengthened by incorporation of nitrogen interstitial atoms as was shown in Figure 4.53. Firstly, the substantial depth of the diffusion zone formed in this investigation helped to sustain the compound layer on the surface without any spallation under sliding contact. No delamination was observed, and the compound layer maintained its integrity with the underlying diffusion zone even at the highest applied load of 20 N ($p_n = 13.2$ GPA). Secondly, the ductile $\beta$ particles were maintained within this zone after the nitriding treatment and contributed well to improving the resistance to crack propagation by arresting and stopping of microcracks.

In order to confirm the effect of $\beta$ phase in crack propagation, plasma nitriding treatment (temperature: 600°C, time: 24 hr and nitrogen partial pressure: 3%) was performed on a near-$\beta$ Ti alloy, Ti-10V-2Fe-3Al with the initial microstructure consisting of 63.5 vol. % $\beta$ phase. Microscratch tests were performed on the nitrided alloy under the same conditions as the plasma nitrided Ti-6Al-4V alloy. The cross-sectional
microstructure investigations indicated that the cracks that originated from the surface were stopped at $\beta$ particles after passing through the compound layer (Figure 5.2). These observations confirm the benefit of maintaining these particles in the microstructure.

According to the microscratch tests results, irrespective of their initiation mechanism (tensile surface cracks and/or subsurface microvoids), once the microcracks were formed, they propagated likely through grain boundaries and surpassed the compound layer upon increasing the applied load. The absence of spallation/delamination of the compound layer during scratch tests can be attributed to the higher amount of Ti$_2$N according to the XRD spectrum (Figure 4.45-b). The tetragonal Ti$_2$N has a higher ductility than TiN [224]; therefore it accommodated plastic strains generated at the subsurface better than TiN that resulted in lower COF when compared to the untreated alloy (Figure 4.71). In summary, a thin compound layer supported by a thick diffusion zone consisting of $\beta$ particles at $\alpha$ grain boundaries provided an optimum microstructure and high resistance to crack propagation.

In comparison, a thick compound layer (5.9 µm) formed after plasma nitriding at 900°C (Figure 4.49) led to premature crack initiation at the surface; the formation of angular and tensile cracks began at applied loads of 0.4 N, 1.5 N (Figure 4.80), which are considerably lower compared to 0.75 N, 8 N applied loads for plasma nitrided surfaces at 600°C. The brittle nature of the compound layer formed at higher nitriding temperatures is also evident from brittle fragmentation and formation of lateral cracks at an applied load of 1 N (Figures 4.82, 4.83).

X-ray diffraction (XRD) analysis revealed that after nitriding at 900°C the compound layer mainly consisted of TiN and Ti$_2$N nitrides (Figure 4.45-c). The high
intensity of Ti$_2$N (002) peak in the XRD spectrum is likely due to the preferential orientation of the Ti$_2$N crystallites in this direction, which is in agreement with the observations of Raveh et al. [225] of a very thin layer of TiN crystallites randomly oriented on top of larger Ti$_2$N crystallites with (002) orientation. This can explain the buckling and spallation of the compound layer which initiated at a critical normal load of 5.5 N (Figure 4.80). It appears that the lateral cracks form at the interface between the TiN crystallites on the surface with the larger Ti$_2$N crystallites and then propagate along the Ti$_2$N grain boundaries (Figure 4.85).

Moreover, it was found that the conical features formed on the surface of the alloy after plasma nitriding increased the average surface roughness by 26% and 87% for treatments at 600°C and 900°C, respectively. This resulted in higher COF value with larger fluctuations of the surfaces plasma nitrided at 900°C (Figure 4.81). The detrimental effects of nitriding on fatigue behaviour of Ti-6Al-4V alloy were also minimized by the formation of a thin compound layer, a deep diffusion zone, and restricting changes in the bulk microstructure through a low temperature (600°C) plasma nitriding treatment.

### 5.2 The Effect of Plasma Nitriding on the Tensile Properties and Fatigue Behaviour of Ti-6Al-4V Alloy

A low temperature (600°C) treatment was utilized to improve the fatigue performance of plasma nitrided Ti–6Al–4V alloy by optimization of the microstructure. As explained in the experimental results, presented in Section 3.2, the tensile properties of the alloy were studied using uniaxial tensile tests; and in order to study the fatigue behaviour, rotation bending tests were conducted, the S-N curves were constructed, and finally the results were compared with those obtained by an elevated temperature
treatment (900°C). It was found that the detrimental effects of nitriding on the tensile strength and fatigue behaviour of Ti-6Al-4V alloy were minimized by optimization of the plasma nitriding treatment at a low temperature (600°C). The correlation between the microstructure and mechanical response of the nitried alloy and the micromechanisms of fatigue failures identified by the SEM examination of the fracture surfaces will be discussed in this section.

It has been reported by several researchers that the formation of brittle features in the surface vicinity, and bulk microstructural changes are the main contributing factors in deterioration of mechanical properties of titanium alloys after nitriding [147, 167, 171, 226]. In this study, it was found that plasma nitriding at an elevated temperature of 900°C led to a substantially lower tensile strength, toughness, and fatigue life compared with a low temperature treatment at 600°C. As presented in Table 4.15 and Figure 4.64, the 900°C plasma nitriding treatment was accompanied by a 13% reduction of tensile strength and a 78% reduction of ductility compared with the untreated alloy. Moreover, while the plasma nitried alloy at 600°C had an endurance limit of 552 MPa (Figure 4.68), plasma nitriding at 900°C resulted in the reduction of fatigue life by at least two orders of magnitude compared to the 600°C treatment.

A substantial decrease in tensile strength and fatigue life of the elevated temperature treatment are due to the premature failure of thick and brittle nitried surface layers – a 5.6 µm thick compound layer and a 19.3 µm α-case (Figure 4.49) – acting as stress risers and promoting a brittle type of failure in the alloy as well as substantial grain growth (370% increase in the average grain size compared to the untreated alloy) and microstructural transformations in the substrate. Conversely, plasma nitrided alloy at
600°C illustrated a ductile type of failure under uniaxial tensile loads (Figure 4.65) and the thin compound layer (1.9 µm) maintained its integrity with the underlying diffusion zone (Figure 4.66).

The periodic transverse cracks perpendicular to the loading direction without any signs of spallation confirmed a well-bonded interface between the compound layer and the substrate (Figure 4.66). The maximum shear stress that developed at a 45° angle and led to the cross-linking of these cracks was the result of a tensile stress component in the loading direction and a perpendicular compressive stress component induced by the Poisson’s effect. Similar observations were reported by Chen et al. [227] for TiN coatings on stainless steel substrates under tensile loads.

According to Agrawal and Raj [228] the inter-crack-spacing reaches a steady state (saturation) condition and the corresponding value can be used to estimate the interfacial shear stress at the coating/substrate interface, \( \tau \), according to Equation 5.2:

\[
\tau = \frac{\pi \delta \sigma}{\lambda}
\]

where, \( \tau \) is the interfacial shear strength, \( \sigma \) is the tensile (fracture) strength of the coating and \( \lambda \) is the inter-crack-spacing at the saturated stage. This estimation is sometimes referred to as “A-R model”. The compound layer also exhibited signs of plastic deformation under cyclic loading conditions (Figure 4.69-c). Nonetheless fragmentation of the compound layer and brittle failure features observed at the fatigue crack initiation sites of the plasma nitrided alloy (Figure 4.69-b) suggested that brittle fracture of the compound layer was the precursor to the fatigue failure and likely correlated with the surface roughness.
The average surface roughness ($R_a$) of the plasma nitrided surfaces was 0.58 ± 0.03 µm, four times higher than that of the polished Ti-6Al-4V (0.14 ± 0.05 µm). This could also account for a 23% loss of endurance limit after nitriding treatment observed in the S–N curves obtained by subjecting the samples to fully reversed bending fatigue tests (Figure 4.68). Similar results were reported by Cassar et al. [226] and Novovic et al. [229] for the fatigue behaviour of surfaces with average roughness values of 0.1 µm and higher.

In order to clarify the mechanism of crack initiation and the effect of surface roughening, the plasma nitrided surfaces were slightly polished using 3 µm diamond suspension to an average surface roughness of 0.23 ± 0.01 µm and tested under the same conditions. The results indicated substantial improvements in the fatigue strength and fatigue life of the nitrided alloy as the fatigue data of the plasma nitrided alloy fell into the corresponding S-N plot of the untreated Ti–6Al–4V alloy as shown in Figure 5.3. An integration of the Paris law [230] (Equation 5.3) was used to estimate the number of cycles elapsed during fatigue crack growth in the compound layer, (Table 5.1).

$$N_f = \frac{1}{A \sigma_{CL}^{m/2} \pi^{m/2}} \int_{a_0}^{a_f} \alpha(a)^{-m/2} a^{-m/2} da \quad (5.3)$$

where, $N_f$ is the number of cycles elapsed for fatigue crack growth, $A$ and $m$ are the Paris law parameters that were estimated by the corresponding values for TiN coating [231], $\sigma_{CL}$ is the effective stress in the compound layer that is the resultant of surface residual stress and stress concentration due to the compound layer/substrate stiffness mismatch (calculated using Equation 5.4 [232]). $a_0$ is the initial crack length approximated by the average valley depth measured on the optical profiles, $a_f$ is the final
crack length or thickness of the compound layer, $\alpha$ is a function of the crack geometry and loading conditions for rotation bending test configuration\textsuperscript{13} [233].

\[
\frac{\sigma_{CL}}{\sigma_{applied}} = \frac{E_{CL}(h_{CL} + h_{substrate})}{E_{CL}h_{CL} + E_{substrate}h_{substrate}}
\]

(5.4)

where, $h_{CL}$, $h_{substrate}$ are the thickness of the compound layer and the radius of the thinnest section of the beam, $E_{CL}$, $E_{substrate}$ are the elastic modulus of the compound layer and the substrate and $\sigma_{CL}$, $\sigma_{substrate}$ are the effective stress values within the compound layer and the substrate, respectively.

Subsequently, Equation 5.3 was used in order to find the number of cycles elapsed during fatigue crack growth in the Ti-6Al-4V substrate, $N_{f,substrate}$. Here the Paris parameters corresponded to titanium alloys [234], and $a_0$ was taken as the compound layer thickness. The $a_f$ value was determined using Equation 5.5 substituting the fracture toughness ($K_{IC}$) with that of the Ti-6Al-4V-ELI alloy (60 MPa$\sqrt{m}$ [2]). It should be noted that the stress intensity factor during the compression loading cycles is taken as zero in this equation [230].

\[
a_f = \frac{1}{\pi} \left( \frac{K_{IC}}{\alpha \sigma_{max}} \right)^2
\]

(5.5)

In order to verify the validity of the calculations, the crack length values were divided by the number of cycles dedicated to crack growth within the substrate to approximate the average crack extension rates ($\Delta a/\Delta N$) and the results obtained were

\[
\alpha = (1.222 - 4.365(a/b) + 10.364(a/b)^2 - 15.664(a/b)^3 + 12.667(a/b)^4 - 4.120(a/b)^5)(1 - a/b)^{3/2}
\]

where, $a$ and $b$ are the crack length and the diameter at the thinnest section of the beam, respectively.
compared to the average striations’ spacing values measured at different fatigue loads based on the SEM micrographs. The results (Table 5.1) indicated that the beneficial effect of the compressive residual stress in the compound layer (-530 MPa) was overshadowed by the stress concentration in this layer due to the modulus mismatch with the substrate. There was an acceptable agreement between the calculated and measured crack extension rate values for the plasma nitrided alloy.

After the reduction of the surface roughness by polishing, a higher fraction of cycles were dedicated to the formation of fatigue cracks compared to the as-treated condition resulting in an increase in the fatigue resistance and therefore improved fatigue life (Figure 5.3). The discrepancies between the measured and calculated crack extension rates for the polished nitrided surfaces and Ti-6Al-4V alloy indicate that the average valley depths were not a fair approximation of fatigue cracks and likely another micromechanism besides fracture of the compound layer dominated the fatigue crack initiation. This was confirmed with the fractographic observations, as no evidence of cleavage facets or brittle failure of the compound layer were detected at the crack nucleation sites (Figures 5.4-a, 5.4-b). In fact, observation of striation like features within the diffusion zone in the vicinity of the crack origin indicated the possibility that the crack formation was triggered by intrusions and extrusions and plastic deformation of the underlying diffusion zone. The fatigue cracks consequently propagated in the same manner as the untreated alloy (Figures 5.4-c, 5.4-d).

Nevertheless, it was found that the fatigue strength of the plasma nitrided alloy in this investigation was superior, at least 17% higher fatigue limit, to those achieved by conventional gas and plasma nitriding treatments (Figure 5.5). This was attributed to the
formation of a thin compound layer (<2 µm) on top of a deep diffusion zone (~45 µm) during the low temperature nitriding treatment at 600°C (Figure 4.30-a): the former restricted the level of brittle failure on the surface while the latter provided mechanical support and increased the load bearing capacity by acting as a graded interface between the compound layer and the Ti substrate [235]. On the other hand, a plasma nitriding at 600°C did not have any side effects on the tensile strength, toughness and microstructure of the alloy as the average grain size in the substrate showed only a 9% grain growth after a 24 h treatment.

Fractography analyses showed that in the low cycle region (N≤10⁵ cycles) fatigue failure in the nitrided alloy also initiated from the surface, accompanied by brittle failure and fragmentation of the compound layer at the initiation site (Figures 4.69). Interestingly, no failures were observed in the high cycle region (N>10⁵ cycles) and the nitrided samples endured cyclic loading until the tests were stopped at 10⁷ cycles. It appears that at corresponding stress amplitudes, the compressive residual stress induced by nitriding balanced the bending stress on the surface and transferred the maximum tensile stress to the subsurface region [230].
Table 5.1 The obtained results of the quantitative fatigue crack propagation analysis

<table>
<thead>
<tr>
<th>Maximum valley depth (µm)</th>
<th>σ (MPa)</th>
<th>σ_{CL} (MPa)</th>
<th>N_{f}^{C} (cycles)</th>
<th>a_{f} (mm)</th>
<th>N_{f}^{calc} (cycles)</th>
<th>Calculated Δa/ΔN (µm/cycle)</th>
<th>Measured Δa/ΔN (µm/cycle)</th>
<th>cycles to failure</th>
<th>cycles for crack initiation</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.73</td>
<td>723</td>
<td>1055</td>
<td>331</td>
<td>2.74</td>
<td>12699</td>
<td>0.22</td>
<td>0.25</td>
<td>18250</td>
<td>5220</td>
</tr>
<tr>
<td></td>
<td>569</td>
<td>717</td>
<td>1124</td>
<td>3.58</td>
<td>26181</td>
<td>0.14</td>
<td>0.15</td>
<td>106950</td>
<td>79645</td>
</tr>
<tr>
<td>0.29</td>
<td>728</td>
<td>978</td>
<td>809</td>
<td>2.85</td>
<td>15739</td>
<td>0.18</td>
<td>0.35</td>
<td>97400</td>
<td>80852</td>
</tr>
<tr>
<td></td>
<td>688</td>
<td>1065</td>
<td>1064</td>
<td>2.85</td>
<td>29196</td>
<td>0.10</td>
<td>0.33</td>
<td>650750</td>
<td>620490</td>
</tr>
<tr>
<td>0.12</td>
<td>816</td>
<td>-</td>
<td>2.33</td>
<td>47356</td>
<td>0.06</td>
<td>0.44</td>
<td>42800</td>
<td>3214</td>
<td></td>
</tr>
<tr>
<td></td>
<td>769</td>
<td>-</td>
<td>2.62</td>
<td>39583</td>
<td>0.05</td>
<td>0.41</td>
<td>75200</td>
<td>27847</td>
<td></td>
</tr>
</tbody>
</table>
The residual stress level induced in the plasma nitrided surfaces was estimated by Equation 5.6:

\[ \sigma_{th} = \frac{\Delta T(\alpha_{\text{surface}} - \alpha_{\text{Ti-6Al-4V}})}{1 - \nu} \]  

(5.6)

where, \( \Delta T \) is the temperature gradient between the plasma nitriding temperature and room temperature, \( \alpha_{\text{surface}} \) and \( \alpha_{\text{Ti-6Al-4V}} \) are the coefficient of thermal expansion for the plasma nitrided surface and Ti-6Al-4V substrate, respectively, and \( \nu \) is the Poisson’s ratio of the plasma nitrided surface. The coefficient of thermal expansion and Poisson’s ratio of the plasma nitrided surface were estimated by those of TiN coatings found in the literature (Table 5.2).

<table>
<thead>
<tr>
<th>Material</th>
<th>Coefficient of thermal expansion (K(^{-1}))</th>
<th>Elastic Modulus (GPa)</th>
<th>Poisson’s Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiN [142, 171, 236-241]</td>
<td>6.8 - 9</td>
<td>350-600</td>
<td>0.22-0.25</td>
</tr>
<tr>
<td>Ti-6Al-4V [1, 171, 242, 243]</td>
<td>8.5 - 9</td>
<td>110-114</td>
<td>0.33-0.36</td>
</tr>
</tbody>
</table>

The compressive residual stress in the nitrided surface can vary between 0-920 MPa and the tensile residual stress in the Ti-6Al-4V substrate can vary between 0-190 MPa. Thus the measured value of 530 MPa (compressive) in this investigation is consistent with the reported data in the literature. The formation of a deep diffusion zone with a well-bonded interface to the compound layer by low temperature nitriding decreased the likelihood of fatigue initiation at (or below) the compound layer interface.
Therefore, there appears to be a critical stress (between 569 and 552 MPa) for fatigue crack initiation. It is suggested that at high stress amplitudes (low cycle region), the compressive residual stress generated by nitriding was not sufficient to counteract the tensile bending stress on the surface resulting in crack initiation from the compound layer.

Considerable reduction of fatigue life (97% lower than 600˚C treatment) was observed when plasma nitriding was performed at a high temperature of 900˚C (Figure 4.68). Fractographic observations showed that the fatigue cracks initiated from the surface of plasma nitrided samples. The dimples observed in the middle of the fracture surfaces indicated that the cracks initiated circumferentially and propagated towards the center (Figure 5.7).

For the alloy that was treated at 900˚C, brittle fracture in the surface vicinity (evidenced by cleavage facets and microcracks) extended to approximately 50 µm below the surface (Figure 5.7-b). This is attributed to the detrimental role of a thick compound layer and a thick α-case. The α-stabilized layer (α-case) has been reported frequently during nitriding of titanium alloys at high temperatures [81, 173], because nitrogen is an alpha-stabilizing element that decreases the $\beta \leftrightarrow \alpha$ transformation temperature [192]. The presence of α-case promotes brittle fracture in the nitrided structures because of its low damage tolerance [81]. Furthermore, the Al-rich layer detected underneath the compound layer (Figure 4.50), likely contained brittle aluminum nitride compounds deleterious for fatigue properties [142]. The formation of an Al-rich layer was also reported in the electron microprobe line-scan results by Raveh et al. [225] and Magnan et al. [244].
The fatigue crack propagation of the alloy treated at 600˚C was evidenced by striations perpendicular to the growth direction and dimples (Figure 4.69-c) which are signs of a ductile fatigue crack growth. However, in the fatigue crack propagation of the alloy treated at 900˚C was evidenced by striations in different directions and planes which indicate rapid fatigue crack growth due to larger grain size (Figures 5.6-c, 5.6-d). The average α grain size in substrate was found to increase by 3.7 times after plasma nitriding at 900˚C.

Rotation bending fatigue test results indicated that the plasma nitrided alloy at 900˚C had a considerably lower fatigue life (more than 97% lower than the treated alloy at 600˚C). To sum up, these results indicated that the formation of a thin compound layer and relatively deep diffusion zone at 600˚C plasma nitriding treatment resulted in better fatigue performance and higher fatigue life compared to nitriding at a higher temperature of 900˚C. Increased thickness of brittle microstructural features (compound layer and α-case), average surface roughness and substrate grain size after plasma nitriding at 900˚C were known to be responsible for reduction of the fatigue life and fatigue strength of the alloy.

When tested against both steel and alumina counterface materials, it was found that the formation of the compound layer resulted in significant enhancement of the tribological properties. Similar to other titanium alloys, Ti-6Al-4V suffers from poor tribological behaviour characterized by high and unstable coefficient of friction and high wear rate (Figures 4.8, 4.9). The variation of coefficient of friction (COF) curve vs. distance at the initial stage of sliding during ball-on-disk tests against AISI 52100 steel is illustrated in Figure 5.7. It showed that under all of the tested applied loads, COF reached
a maximum value after a short sliding distance (< 0.1 m). This maximum friction force corresponds to the force needed to break the asperity junctions [245]. Therefore, it can be concluded that the adhesion of titanium to the steel counterface begins at an initial stage of sliding. The maximum force ranged from 0.3 N for the wear test at 0.8 N to 1.9 N for the wear test at 5 N, indicating that stronger asperity junctions were formed at higher applied normal loads. The sliding continues by the back transfer and oxidation of the transferred layers as evidenced by presence of oxygen in the plateaus on the worn surfaces (Figures 4.11, 4.12). After sliding for approximately 30 m, COF gradually increased to an average value of around 0.6 at the steady state condition with relatively large fluctuations as shown in Figure 4.8. The observed trend has been attributed to the formation and periodic, localized fracture of oxide islands (plateaus) on the wear tracks [56, 246].

The formation of these oxide plateaus, also referred to as mechanically mixed layers (MMLs), were reported during sliding of aluminum alloys as well as titanium alloys [247-249]. The MMLs form by intermixing and agglomeration of severely deformed particles detached from the surface and their oxides and may also contain elements from the counterface material [52]. In this research, the cross-sectional analysis of the worn surfaces using focused ion beam milling (FIB) technique elucidate the structure of the MMLs.

The layers that formed at a lower applied load of 0.8 N had a more dense structure and less Fe content compared to a higher load of 5 N (Figures 4.24, 4.25). Closer inspection of the interface between that MML and the deformed Ti-6Al-4V substrate (Figure 4.24-c) showed the formation of lateral cracks within the MML indicating that
this layer fractured and delaminated from the surface easily and was not protective during wear. The detachment of these layers and their fragmentation under the sliding contact results in the generation of hard oxide particles that contribute to wear by a third-body abrasion mechanism and subsequently new oxide plateaus form.

The MMLs formed at higher applied loads were found to be less tribologically-protective on account of substantially higher wear rates (Figure 4.8) which is likely a result of their porous and fragmented structure (Figure 4.27). The iron splats observed in the MML at 5 N (Figure 4.28) indicated more wear damage on the steel counterface possibly due to the severe abrasive action of abundant debris particles generated during wear (Figure 4.18).

The wear rate studies also revealed that the measured volumetric values were less than those estimated from the mass loss measurements (based on the density of the titanium alloy) at all tested loads except 5 N applied load (Figure 4.8-b). This indicated that the density of the mechanically mixed layer was higher than that of the Ti-6Al-4V alloy at applied loads lower than 5 N. This is consistent with the corresponding FIB observation of dense MML formation as shown in Figure 4.24. Conversely, the estimated volumetric wear value was less than that of the calculated value when the wear test was performed at an applied load of 5 N. Thus the density of the MML is lower than that of Ti-6Al-4V as expected from the porous and fragmented structure of this layer at 5 N applied load according to FIB observations (Figure 4.27).

The plasma nitrided surfaces were also covered with a layer after sliding against steel counterface (Figure 4.86). This layer was in the form of separate patches at lower loads (0.5 N, 1 N) and a continuous layer of accumulated material at higher applied loads.
(5 N) and mainly consisted of Fe and O elements (Figure 4.91). As the oxide layer was dissolved and removed from the worn surfaces, the plasma nitrided surface underneath was found to be intact and unaffected by the sliding contact except for minor polishing of the surface asperities (Figure 4.94). On the other hand, the steel counterface balls were severely abraded (Figure 4.95) and experienced considerable material loss (Figure 4.96). Thus, it was concluded that plasma nitrided surfaces experienced minor damage in the form of polishing wear of surface asperities, during ball-on-disk tests against steel counterface. The main wear mechanism was the transfer of iron to the nitrided surfaces followed by oxidation of this layer.

At low loads (≤ 1 N, corresponding to maximum Hertz pressure of 522 MPa), detection of cutting chip-like debris composed of Fe and Cr indicated that wear started off by abrasion of the steel counterface by hard surface asperities on the plasma nitrided surface (Figure 4.89). Upon increasing the number of cycles, the worn surfaces were gradually covered with patches of Fe which oxidized by the heat generated during sliding. When the oxide islands reached a critical thickness, they exfoliated from the wear tracks as shown in Figure 4.90. The delamination and fracture of the oxide islands resulted in generation wear debris (Figure 4.92) and promoted wear of the counterface by abrasion (Figure 4.95) which marked a transition from low to high COF values (Figure 4.98).

The oxide layers completely covered the wear tracks at higher applied loads (> 1 N) indicating extensive transfer and oxidation of Fe from the counterface balls. Microcracks frequently observed on the surface of these layers (Figure 4.93) revealed that they encountered extensive plastic deformation as a result of repetitive sliding cycles.
and abrasion. It can be concluded that the main wear mechanism after plasma nitriding was material transfer from the steel counterface followed by oxidation and abrasion of Fe the transferred layers [84, 250, 251]. The wear transition from adhesion and oxidation of Ti surfaces before the treatment, to wear of the counterface after the nitriding treatment is also evident by comparing the large fluctuation in COF vs. sliding distance for the untreated alloy with the small instantaneous fluctuations of the plasma nitrided surfaces (Figure 4.99).

Analysis of wear properties of plasma nitrided surface against alumina counterface showed that the main wear mechanisms were polishing wear and formation of a mechanically mixed layer composed of Al, Ti, N, and O at low loads (Figure 4.101). At high loads however, the compound layer failed and the Ti-6Al-4V substrate was exposed (Figure 4.102). Thus the main wear mechanisms at high loading conditions were delamination wear, oxidation wear and abrasive wear (Figure 4.103). However, wear tests performed under the same conditions on the untreated Ti-6Al-4V alloy resulted in deeper and wider wear tracks (Figure 4.110). This indicates that strengthening of the diffusion zone with nitrogen interstitial atoms had a beneficial effect in reducing the extent of wear in the plasma nitrided surface.

5.3 The Effect of Shot Peening Pretreatment on Plasma Nitriding of Ti-6Al-4V Alloy

In this study, shot peening was utilized as a pretreatment step for low-temperature (600°C) plasma nitriding of Ti-6Al-4V alloy to enhance the nitriding efficiency by introducing a severe plastic deformation (SPD) surface layer and subsurface microstructural defects, such as twins and grain boundaries. The microstructural analyses
showed that the high level of plastic strains induced by shot peening was accommodated by activation of both twinning and slip mechanisms. This shot peening pretreatment resulted in the formation of a 5 μm thick SPD layer on the surface of Ti alloy, characterized by microstructural features such as twins, deformation bands, and grain refinement (Figures 4.116, 4.117). This is in agreement with the 20% increase in the surface hardness value due to the work hardening of the SPD layer. Underneath the SPD layer, a twinned zone extended to a depth of 40 μm below the surface as shown in Figure 4.117. These features were also observed by Thomas et al. and Sheng et al. in Ti-4Al-2V alloy and pure titanium after shot peening [185, 187].

At the atomic level, the TEM investigations revealed micro-twinning and a high density of non-equilibrium crystal defects such as subgrain boundaries and dislocation pile-ups in the SPD layer (Figure 4.122). It has been previously reported that the \( \{11\overline{2}2\}/\{11\overline{2}3\} \) was the most common twinning system in α-Ti under compressive loads at room temperature [252, 253]. Therefore, compressive stresses developed during shot peening in the current study were expected to activate the same twinning systems. The unique structure of the SPD layer resulted in accelerated nitriding kinetics in the posterior plasma nitriding treatment for two main reasons. Firstly, grain boundaries, deformation bands, and twins act as diffusion shortcuts by providing easy diffusion paths for nitrogen interstitial atoms. Moreover, the higher density of non-equilibrium crystal defects increased the stored energy of the surfaces and their chemical reactivity especially by providing additional preferential nucleation sites for titanium nitrides [181, 254]. The accelerated nitriding kinetics resulted in the formation of a nanocrystalline TiN layer
(Figures 4.121 and Figure 4.123) in the compound layer and increased the depth of nitrogen diffusion by almost 50% (Figure 4.120).

The superior sliding performance of the shot peened surfaces after nitriding (SP-PN samples) is strongly correlated with their microstructure. They exhibited excellent scratch resistance after multiple sliding passes without experiencing any delamination or premature failures in the coating (Figures 4.128, 4.129). During the ball-on-disk tests against alumina counterface balls, these samples exhibited lower coefficient of friction values compared with the plasma nitrided surfaces that did not see the pretreatment, PN samples (Figure 4.138). The main wear mechanism at low loads ($\leq 5\,\text{N}$) was transfer of alumina from the counterface and the formation of MML composed of Ti, N, Al, and O elements on the plasma nitrided surfaces (Figures 4.131, 4.132). Occasional exfoliation and spallation of the MML observed on the wear tracks of PN surfaces (Figures 4.134). At higher loads ($> 5\,\text{N}$), the maximum shear stress (~$14\,\mu\text{m}$ in the subsurface at static conditions) was within the diffusion zone. At these conditions complete removal of the compound layer and wear of the diffusion zone took place in the PN sample (Figure 4.136). On the wear tracks of the pretreated surfaces, however, the MML remained on the surface without any signs of delamination (Figure 4.137).

The presence of nano-scale TiN grains increased the hardness (Figure 4.127) and toughness of the compound layer and eliminated the disadvantages associated with polycrystalline TiN coatings (e.g., poor ductility) through grain boundary sliding. It was observed that in the pretreated surfaces, the compound layer conformed well to the plastic deformation of the Ti substrate and endured high contact stresses for several sliding passes without chipping or spallation. In comparison, plasma nitrided surfaces without
the pretreatment experienced occasional chipping at the scratch track rims after two sliding passes during multiple-pass microscratch tests.

The deep diffusion zone in the pretreated samples also contributed to a well-bonded interface and the absence of compound layer decohesion. Strengthened by nitrogen interstitials, the diffusion zone compensated for the incompatibility in plastic deformation of the titanium nitride coating (E = 250-600 GPa [240, 241]) and the titanium substrate (E = 110 GPa [243]). Therefore, the diffusion zone provided a good mechanical support for the compound layer and normalized the stress concentration at the compound layer/diffusion zone interface and thus coating spallation was avoided [123, 128, 151, 255, 256].

Another notable feature during ball-on-disk wear tests was observation of shear bands in the plastically-deformed subsurface region of plasma nitrided alloy at high contact loads (Figure 4.113-b). The deformation shear bands, characterized by the coalescence of microvoids in the subsurface region as shown in Figure 4.114 have been reported for localized severe plastic deformation of titanium alloys at the contact areas. The maximum shear stress (at static conditions) was estimated by Equation 5.7,

\[ \tau_{\text{max}} = \frac{\sigma_1 - \sigma_2}{2} \]  

where, \( \sigma_1 \) and \( \sigma_2 \) are principal stresses calculated by the following equations:

\[ \sigma_i = -p_{\text{max}} \left[ (1 - \frac{e^2}{a^2}) \tan^{-1} \left( \frac{1}{\sqrt{a}} \right)(1 + \nu) - \frac{1}{2(1 + \frac{e^2}{a^2})} \right] \]  

\[ \nu \]
\[ \sigma_2 = -\frac{p_{\text{max}}}{1 + \frac{z^2}{a^2}} \]  
\[ p_{\text{max}} = \frac{3F}{2\pi a^2} \]  
\[ a = \sqrt{\frac{1}{8} \left( \frac{3F}{E_1} + \frac{1}{d_1} + \frac{1}{d_2} \right)} \]

where, \( a \) is the contact radius, \( p_{\text{max}} \) is the maximum Hertz Pressure and \( E_1, E_2, \nu_1, \nu_2 \) are the elastic modulus and Poisson’s ratio of the counterface and plasma nitrided surface, respectively [257, 258].

The maximum shear stress was estimated at 596 MPa and 1019 MPa for applied normal loads of 1 and 5 N, respectively. However, when the applied normal load was 10 N, the maximum shear stress was 1284 MPa at a depth of 16 µm from the surface. This severe plastic deformation and shear instability under sliding conditions at higher loads can be related to the slower heat dissipation at the contact areas relative to the heat generation due to plastic deformation, promoted by the low thermal conductivity (6.7 W/mK) and low strain hardening rate of Ti-6Al-4V alloy [259]. Thus, it can be concluded that the strength of the MML/substrate is higher than the cohesive strength of the alloy and the platelet particles delaminate by the formation and coalescence of microvoids at the shear bands as shown in Figure 4.121.

Although the plasma nitrided surface exhibited a better performance compared to the untreated Ti-6Al-4V, the shot peening pretreatment step resulted in the microstructural modification and improved sliding behaviour of plasma nitrided Ti-6Al-4V. The obtained microstructure consisted of a deep diffusion zone and a nanocrystalline...
titanium nitride surface layer, which is normally associated with fast nitriding kinetics in high temperature nitriding treatments (e.g., 900°C) [260]. Nonetheless, the exposure of Ti alloys to those temperatures results in the formation of a thick (up to 30 µm) α-case as well as substantial grain growth and microstructural transformation in the bulk material. Both of which are well-recognized to cause adverse effects on the mechanical properties (e.g., fracture toughness and fatigue strength) of the Ti substrate. None of these features were observed in the SP-PN microstructures in this research.
Figure 5.1 A schematic illustration indicated estimated nitrogen concentration in the surface vicinity based on the Fick’s law and microhardness measurements.
Figure 5. 2 A FIB cross-sectional view of a tensile crack formed on the surface of plasma nitrided Ti-10V-2Fe-3Al alloy (a near-β titanium alloy) during microscratch test at 10 N applied load. (b) Corresponding EDS maps used to identify the different phases present in “a”; the β particles were differentiated by abundance of vanadium and the compound layer by the absence of aluminum. The plasma nitriding was performed at 600°C for 24 h in an atmosphere of 3% N₂-balance H₂.
Figure 5. 3 Stress-life (S-N) curves showing the effect of plasma nitriding on fatigue behaviour of Ti–6Al–4V alloy. It was also found that the fatigue data of nitried samples fell into the S-N curve of untreated Ti–6Al–4V alloy after polishing the surfaces.
Figure 5. 4 Secondary electron SEM images (SEI) showing (a) a general view of the fatigue fracture surface (tested at 728 MPa) of the plasma nitried alloy after the compound layer was partially polished. (b) No evidence of cleavage facets or brittle failure of the compound layer were observed at the crack initiation site originating from the surface. The enclosed regions show the presence of slip steps inside the grains close to the crack initiation site. Crack propagation was accompanied by the formation of (c) striations and microcracks perpendicular to the crack growth direction which gradually transformed to (d) dimples close to the final rupture region.
Figure 5.5 Comparison of fatigue data obtained for plasma nitrided Ti–6Al–4V alloy in this investigation compared to the conventional plasma and gas nitriding of the alloy by several researchers [161, 261-263].
Figure 5. Secondary electron SEM micrographs of the fracture surface of Ti-nitrided at 900°C. (a) General morphology of the fracture surface, (b) brittle fracture and fragmentation of the compound layer at the crack initiation site, (c) far-spaced striations in the diffusion zone revealing fast crack propagation in this region, (d) striations in different orientations and planes indicating rapid fatigue crack growth due to large grain size, (e) dimples observed in the middle area indicating that the cracks initiated circumferentially and propagated towards the center.
Figure 5.7 Coefficient of friction variation with distance at the initial stage of sliding. Ball-on-disk tests on Ti-6Al-4V against AISI 52100 steel at different applied normal loads.
CHAPTER 6: CONCLUSIONS

In this investigation a modified plasma nitriding process was developed for Ti-6Al-4V alloy for wear and friction improvement without sacrificing the fatigue resistance. The main conclusions are as follows:

- **Optimized microstructure**: The optimized plasma nitrided microstructure consisted of a thin compound layer (< 2 µm) on top of a deep diffusion zone (~40 µm). The low nitriding temperature (600°C) utilized in this treatment restricted the bulk microstructural changes during nitriding and no signs of the formation of an \( \alpha \) stabilized layer (\( \alpha \)-case) were found underneath the compound layer.

- **Load bearing capacity**: The microscratch test results indicated that the deep diffusion zone provided mechanical support for the compound layer and increased the load bearing capacity of the surfaces. No delamination or chipping occurred in the compound layer even at the highest applied load of 20 N (corresponding to a Hertz pressure of 3.1 GPa). The findings also showed that the \( \beta \) particles within the diffusion zone acted as crack arrestor sites and deflected/stopped the microcracks that initiated from the surface/near surface region. The microscratch test results also indicated significant reduction of friction coefficient after the plasma nitriding treatment (at least 46% compared to the untreated alloy) especially at higher contact loads.

- **Wear resistance**: Significant improvement in the wear resistance was observed after the plasma nitriding treatment against AISI 52100 steel and alumina counterface
materials. When slid against the steel counterface, no damage was observed to the plasma nitrided surfaces even at the highest tested load and the main wear mechanism was oxidative and delamination wear of the counterface. When sliding against alumina, a mechanically mixed layer was formed on the wear tracks of plasma nitrided surfaces accompanied by polishing wear of the nitrided surfaces at low loads and removal of the compound layer and partial wear of the diffusion zone at high loads. The formation of shear bands in the subsurface region was a possible responsible delamination mechanism at high loads.

- **Fatigue strength**: No failures were observed in the high cycle fatigue region (N>10⁵ cycles, corresponding to lower stress amplitudes), where the tensile bending stress on the surface was balanced with compressive residual stress of nitriding. The fatigue strength of the alloy after the modified plasma nitriding, tested under rotation bending conditions, was superior to those of the conventional nitriding treatments. This was attributed to the formation of a thin compound layer that minimized the extent of brittle failure at the surface, a well-bonded interface that inhibited subsurface crack formation, as well as minor grain growth (~ 30%) and absence of bulk microstructural changes. However, despite the improvements observed in the cyclic load bearing capacity, the nitrided alloy still suffered from 23% loss of the fatigue endurance limit compared with the untreated Ti–6Al–4V, likely due to an increase in average surface roughness after the nitriding treatment and brittle fracture of the compound layer.

- **Novel pretreatment step**: Shot peening was introduced as a pretreatment step to promote the nitriding kinetics during low temperature plasma nitriding of Ti-6-Al-4V alloy. This pretreatment introduced a 5 µm thick severe plastic deformation (SPD)
surface layer and subsurface microstructural defects, such as twins, that extended to a depth of 40 µm. These surfaces exhibited higher load bearing capacity and interfacial bonding as the compound layer maintained its integrity with no incidence of chipping or delamination during multiple-pass microscratch tests. The improved performance of the pretreated nitrided samples during scratch tests was attributed to the formation of a nanocrystalline TiN surface layer, with higher hardness and toughness, and a 50% deeper diffusion zone.
CHAPTER 7: FUTURE DIRECTIONS

The research presented in this dissertation could form the foundation of future endeavours towards commercialization of plasma nitriding for extended application of titanium alloys in the aerospace and biomedical sectors, specifically for components encountering sliding motion and repeated loading cycles, e.g., flap tracks. However, a number of features need to be clarified along this path. The following future research directions for full implementation of the process are recommended:

• Comprehensive investigation of the fatigue performance of the plasma nitrided titanium alloy under a variety of testing conditions to simulate real-life service conditions of the components. For instance while high cycle and low cycle fatigue are equally important for aircraft engine application subjected to thermal cycles and rotational and vibrational stresses, components under high contact loads, e.g., flap tracks are normally tested at high stress regimes. Axial fatigue tests may be carried out at different stress ratios, peak stress values, and frequencies with additional contributions of high temperature and oxidizing media.

• Performing wear tests that reproduce the real life service conditions faced in potential industrial applications. The wear resistance and friction behavior of the plasma nitrided surfaces can be studied against a variety of different counterparts, test conditions and environments. Accordingly, wear mechanisms can be identified and wear maps constructed to facilitate predication of wear behaviour of plasma nitrided titanium surfaces for corresponding specific applications.
• As the results of this investigation indicated that there is room for improvement of the fatigue strength by the reduction of surface roughness and the enhancement of wear resistance by the formation of hard surface layers, introduction of duplex surface treatments is proposed for future works. One alternative is deposition of diamond like coatings (DLC)s on the plasma nitrided surfaces, which will likely result in reduction of coefficient of friction and wear rate while the nitrogen diffusion zone provides mechanical support for the DLC coating and increases the load bearing capacity of the surfaces.

• Despite the significant enhancement of plasma nitriding kinetics by the shot peening pretreatment step, there are yet many variables that can be optimized in this pretreatment such as duration, peening intensity, the material and size of shots.
BIBLIOGRAPHY


[181] W. P. Tong, Z. Han, L. M. Wang, J. Lu, and K. Lu, "Low-temperature nitriding of 38CrMoAl steel with nanostructured surface layer induced by surface mechancial


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