# We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,900
Open access books available

185,000
International authors and editors

200M
Downloads

Our authors are among the

154
Countries delivered to

TOP 1%
most cited scientists

12.2%
Contributors from top 500 universities




WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index in Web of Science™ Core Collection (BKCI)

## Interested in publishing with us?
## Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com



Chapter 3

# Plasma Nitriding of Titanium Alloys

Afsaneh Edrisy and Khorameh Farokhzadeh

Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/61937

**Abstract**

Titanium alloys are found in many applications where weight saving, strength, corrosion resistance, and biocompatibility are important design priorities. However, their poor tribological behavior is a major drawback, and many surface engineering processes have been developed to enhance wear in titanium alloys such as nitriding. Plasma (ion) nitriding, originally developed for ferrous alloys, has been adopted to address wear concerns in titanium alloys. Plasma nitriding improves the wear resistance of titanium alloys by the formation of a thin surface layer composed of TiN and $Ti_2N$ titanium nitrides (e.g., compound layer). Nonetheless, plasma nitriding treatments of titanium alloys typically involve high temperatures (700–1100°C) that promote detrimental microstructural changes in titanium substrates, formation of brittle surface layers, and deterioration of mechanical properties especially fatigue strength. This chapter summarizes the previous and ongoing investigations in the field of plasma nitriding of titanium alloys, with particular emphasis on the authors' recent efforts in optimization of the process to achieve tribological improvements while maintaining mechanical properties. The development of low-temperature plasma nitriding treatments for $\alpha + \beta$ and near-$\beta$ titanium alloys and further wear improvements by alteration of near-surface microstructure prior to nitriding are also briefly reviewed.

**Keywords:** Titanium alloys, plasma nitriding, compound layer, nitrogen diffusion zone, fatigue crack initiation, severe plastic deformation, surface failure mechanisms

## 1. Introduction

Titanium alloys are attractive candidates for aerospace, automotive, and biomedical industries due to their many advantages including, but not limited to, high strength-to-weight ratio, excellent corrosion/oxidation resistance, biocompatibility, and high fatigue resistance. However, their poor tribological behavior, for example, high and unstable coefficient of friction, high wear rate, and susceptibility to galling and scuffing, restricts their use for

INTECH
open science | open minds

© 2016 The Author(s). Licensee InTech. This chapter is distributed under the terms of the Creative Commons Attribution License (http://creativecommons.org/licenses/by/3.0), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

applications where sliding is inevitable. Nitriding is a surface hardening process in which nitrogen atoms are utilized for surface modification and has been practiced for wear improvement in titanium alloys for many years. In conventional nitriding techniques such as salt bath treatments, gas nitriding, and hot isostatic pressing (HIP), nitrogen atoms are provided by liquid, gas, or solid media [1, 2]. In plasma nitriding, also known as ion nitriding and glow discharge nitriding, active nitrogen is provided by an ionized nitrogen-containing atmosphere [3–7].

The growing interest in this process is due to its high efficiency, cost-effectiveness for mass production, absence of pollution, and ease of process control [8–11]. Also, it is preferred over other nitriding technologies due to feasibility at lower temperatures, dimensional control, retention of surface finish, and versatility for achieving desired properties through modification of process parameters [8–13].

Plasma nitriding improves the tribological properties of titanium alloys through the formation of a thin surface layer mainly consisting of TiN and $Ti_2N$, that is, the compound layer. The nitrided microstructure also consists of a region of nitrogen-stabilized $\alpha$-titanium, that is, $\alpha$-case, and a nitrogen diffusion zone (typically 15–25 μm deep) underneath the compound layer [14, 15]. The plasma-nitrided microstructure is strongly correlated with the composition of titanium substrate and the nitriding process parameters such as duration, temperature, pressure, and composition of the nitriding medium, among which temperature has the most significant influence [12, 15–17].

Plasma nitriding of titanium alloys is typically carried out in the temperature range of 700–1100°C for 6–80 hours in a nitrogen-containing medium ($N_2$, $N_2$–Ar, $N_2$–$H_2$, or $N_2$–$NH_3$) [18–22]. The high temperatures involved in the process lead to grain growth, overaging, and microstructural transformations in titanium substrates that decrease the fatigue strength and ductility [10, 22, 23]. Moreover, the brittle nature of the compound layer and $\alpha$-case and the high stiffness mismatch between the compound layer and the titanium substrate lead to premature failure initiation from the surface. As such, improvements in mechanical properties have been reported by practicing plasma nitriding at lower temperatures [10, 24–26]. The slow nitriding kinetics of titanium alloys at low temperatures can be enhanced by alteration of the microstructure in the surface vicinity via thermochemical (e.g., laser-assisted treatments and electron beam (EB) melting) and mechanical (e.g., mechanical attrition and shot peening) pretreatment processes [27, 28]. As a result, the depth and hardness of nitrogen diffusion will increase and thus the load bearing capacity of the plasma-nitrided surfaces will be improved [29]. Duplex treatments have also been introduced and developed in surface engineering of titanium alloys. Duplex treatments combine the positive effect of deep hardened layers achieved in the diffusion zone with low friction and high wear resistance of surface coatings leading to significant enhancements in load bearing capacity and wear resistance [30–36].

This chapter is organized into seven sections as follows. After the introduction, Section 2 gives a brief description of the fundamentals of plasma nitriding and the nitriding process parameters for titanium alloys. Section 3 presents a review of the literature on the effect of plasma nitriding on the microstructure of titanium alloys. The tribological and mechanical properties of plasma-nitrided titanium alloys are discussed in Section 4 and Section 5, respectively. Recent

http://dx.doi.org/10.5772/61937

developments in the modification of plasma nitriding treatment via the introduction of duplex treatments and surface pretreatments are presented in Section 6, followed by a summary of the main findings in Section 7.

## 2. Fundamentals of plasma nitriding

In a conventional plasma nitriding treatment, an external voltage applied between the nitriding furnace (anode) and the workpiece (cathode) ionizes the nitriding gas and provides active nitrogen flux for surface modification [3, 4]. The nitriding atmosphere is generally composed of a buffer gas (e.g., Ar or $H_2$) and the reactant gas (e.g., $N_2$). A schematic illustration of voltage versus current density characteristic for glow discharge is shown in Figure 1. Plasma nitriding is conducted in the abnormal glow region where a uniform, stable glow covers the workpiece, and the current density is directly proportional to voltage drop and thus is easily controlled [13, 37]. As the applied voltage is provided by a direct current (DC) power supply, the continuous voltage and heat input may result in localized heating, overheating of thin sections, hollow cathode effect[1], arcing, and other damages to the surface. These problems can be avoided by utilizing a pulsed power supply where the heat input is controlled with duty cycles, usually in the order of 10–50% of the total cycles, without affecting the nitrogen activity or nitriding time [38]. In addition to DC and alternating current (AC) power supplies, plasma may be generated by radio frequency (r.f.) excitation [4, 39], microwaves, electromagnetic induction [4, 40], and electron emission configurations [4]. Some of the recent advances include intensifying the glow discharge using thermionically assisted triode glow discharge, plasma immersion ion implantation, electron cyclotron resonance, etc. The intensified plasma-assisted processes (IPAP) generate a higher density of energetic ions and increase the kinetics and efficiency of nitriding, making plasma nitriding feasible at low temperatures (less than 500°C), pressures, and durations. As a result, significant improvements in surface hardness, depth of nitrided layers, and tribological and fatigue properties have been reported [41–46].

Under the influence of the applied electric field, electrons accelerating from the cathode (workpiece) toward the anode collide with gas molecules of the nitriding atmosphere and generate an environment of positive and negative ions, electrons, and neutral and energetic atoms (e.g., plasma) within a few millimeters from the cathode. Subsequently, the positive ions accelerate toward the cathode over a comparatively short distance and cause a number of phenomena such as sputtering, diffusion to bulk, heating by radiation and collision, surface diffusion, plasma reaction, etc. As a result of these phenomena, surface modification takes place and the generated secondary electrons maintain the abnormal glow. This mechanism eliminates expensive precleaning operations and enhances nitriding kinetics at temperatures lower than those of the conventional nitriding techniques [47, 48].

1 Localized heating at narrow channels, holes, closely located workpieces, etc. where the generation of charge carriers is faster than their annihilation and the glow discharges contact each other or overlap, leading to a rise in current density and temperature.

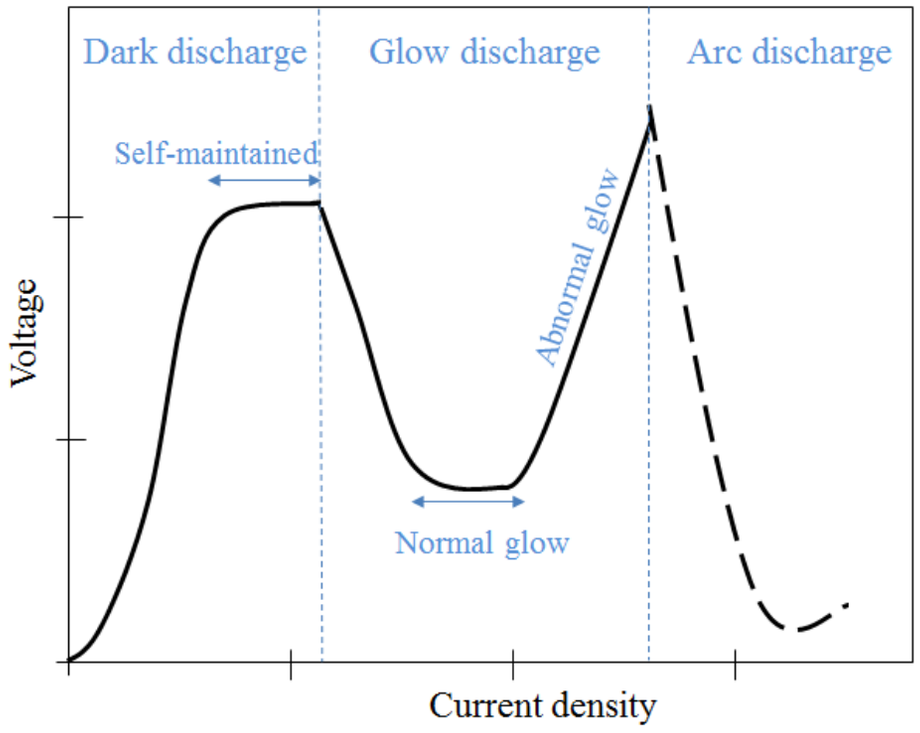



**Figure 1.** A schematic illustration of voltage vs. current density relationship for an electric glow discharge

Several mechanisms have been proposed to explain the mass transfer mechanism during plasma nitriding including the adsorption of atomic nitrogen model, ion adsorption model, nitrogen implantation model, Kölbel's model, and the $NH^+$ bombardment model. According to Kölbel's model, plasma nitriding initiates with sputter cleaning of the surfaces, followed by the reaction of sputtered atoms with nitrogen and subsequent deposition of nitride compounds on the surface. The $NH^+$ radical model is based on the generation of $N_mH_n^+$ molecular ions and radicals in the presence of hydrogen in the nitriding gas mixture. It is proposed that the adsorbed $NH^+$ radicals on the surface of workpiece dissociate and liberate nitrogen atoms that diffuse into the structure [4, 12, 13, 18].

Plasma nitriding treatments for titanium alloys are typically carried out at 700–1100°C for 6–80 hours. The atmosphere is composed of a nitrogen containing mixture, for example, $N_2$, $N_2$–Ar, $N_2$–$H_2$, or $N_2$–$NH_3$ mixtures, with pressures that vary in the range of 0.5–1.3 kPa [18–22]. In addition to the nitriding time and temperature, the pressure and composition of the nitriding gas also have a significant effect on the microstructure of plasma-nitrided titanium alloys [15, 17]. For instance, the presence of hydrogen in the nitriding mixture enhances nitrogen diffusivity by removing the inherent oxide layer on the surface of titanium alloy that interferes with the nitriding process. In another mechanism suggested by Tamaki et al. [18], the presence of hydrogen in the nitriding medium results in the formation of $H^+$, $NH^+$, and $NH^{2+}$ radicals that have a catalytic effect on nitriding kinetics. Conversely, the presence of Ar in the nitriding

mixture reduces the depth of nitrogen diffusion and causes random formation of $Ti_2N$ and TiN through sputtering/re-deposition reactions or homogeneous reactions in the plasma [4, 18, 49, 50]. The following sections review the previous investigations on the microstructure and properties of plasma-nitrided titanium alloys focusing especially on the authors' recent work in the field.

## 3. Microstructure of plasma-nitrided titanium alloys

### 3.1. Classification of titanium alloys

Titanium has an allotropic phase transformation from its low-temperature hexagonal close-packed (HCP) crystal structure ($\alpha$-phase) to body-centered cubic (BCC) crystal structure ($\beta$-phase) at 882°C, that is, $\beta$-transus temperature. Alloying elements have a strong influence on this allotropic transformation; elements such as aluminum, boron, nitrogen, and oxygen increase the $\beta$-transus temperature and are referred to as $\alpha$-stabilizers. Conversely, $\beta$-stabilizing elements decrease the $\beta$-transus temperature and stabilize the $\beta$-phase at room temperature through either eutectoid transformations (iron, hydrogen) or solid solutions (vanadium, molybdenum, and niobium). Thus, depending on the type and content of their alloying elements, titanium alloys can have a single-phase $\alpha$-structure ($\alpha$-Ti alloys), $\alpha$ phase with a small (2–5 vol.%) $\beta$-phase content (near-$\alpha$ Ti alloys), single-phase $\beta$-structure ($\beta$-Ti alloys), or a combination of both phases ($\alpha + \beta$ alloys). The families of $\alpha$- and near-$\alpha$ titanium alloys are famous for their microstructural stability at high temperatures 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 of this family. In contrast, a wide range of microstructures and properties can be achieved in $\alpha + \beta$ and $\beta$-titanium alloys by heat treatments and thermomechanical routes. Ti–6Al–4V, Ti–3Al–2.5V, Ti–6Al–2Sn–4Zr–6Mo, Ti–6Al–6V–2Sn, and Ti–4Al–4Mo–4Sn–0.5Si are some of the popular $\alpha + \beta$ titanium alloys. The class of $\beta$ (and near-$\beta$) titanium alloys contains a high concentration of $\beta$-stabilizing elements to retain a fully $\beta$-phase microstructure at room temperature. These alloys offer good hardenability and formability and resistance to corrosion and hydrogen embrittlement. 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 among commercially used $\beta$-Ti alloys [1-7].

The behavior of Ti–6Al–4V ($\alpha + \beta$ titanium alloy) and Ti–10V–2Fe–3Al (near-$\beta$ titanium alloy) alloys during plasma nitriding were investigated by the authors. The extra-low interstitial (ELI) grade Ti–6Al–4V had a mill-annealed microstructure consisting of equiaxed $\alpha$-grains with retained $\beta$-particles at $\alpha$-grain boundaries and fine $\beta$-particles inside the $\alpha$-grains (Figure 2a). The Ti–10V–2Fe–3Al microstructure consisted of elongated primary $\alpha$-plates in various orientations and aspect ratios inside $\beta$-grains with the occasional presence of $\alpha$-phase at $\beta$-grain boundaries (Figure 2b). The chemical composition, average grain size, and $\beta$-phase content of the as-received alloys are presented in Table 1.

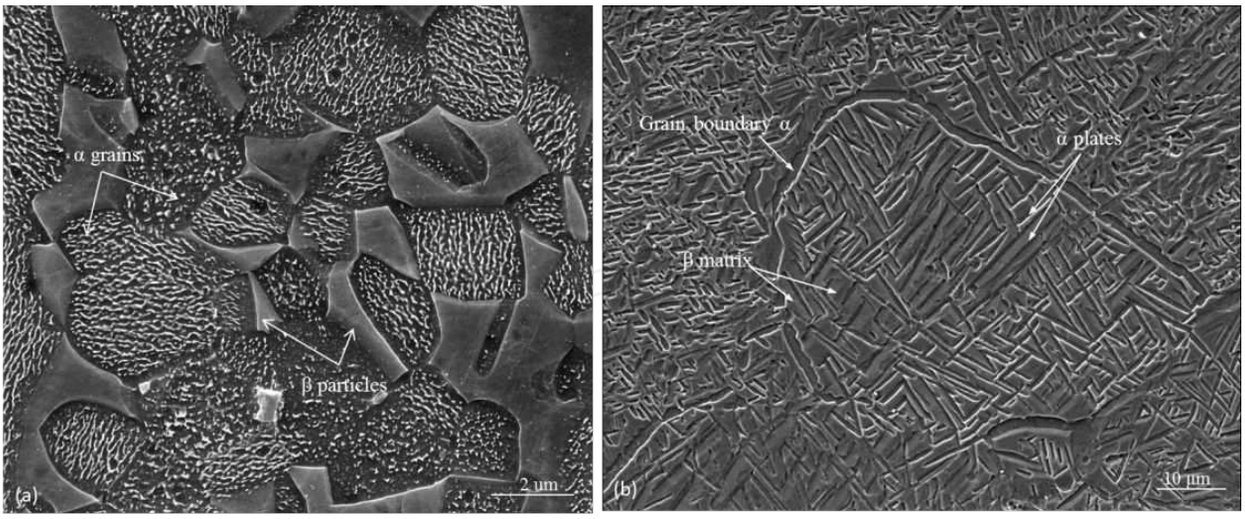



**Figure 2.** Scanning electron microscopy (SEM) images showing the typical microstructure of the as-received titanium alloys used in plasma nitriding investigations. (a) Ti–6Al–4V had a mill-annealed microstructure consisting of equiaxed $\alpha$-grains, retained $\beta$-particles at $\alpha$-grain boundaries, and fine recrystallized $\beta$-particles inside the $\alpha$-grains. $\alpha$-grains were delineated by the different orientation of fine recrystallized $\beta$-particles inside the $\alpha$-grains (etched in Kroll's solution) [51]. (b) Ti–10V–2Fe–3Al microstructure consisted of elongated primary $\alpha$-plates in various orientations and aspect ratios inside $\beta$-grains (marked by arrows) with the occasional presence of $\alpha$-layers at $\beta$-grain boundaries (etched in glycerol + hydrofluoric acid (1:1) solution) [52].

| | Chemical Composition (Wt. %) | | | | | | | | Hardness (HV) | Grain size (μm) | β content** (Vol. %) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | **Fe** | **V** | **Al** | **C*** | **O*** | **N*** | **H*** | **Ti** | | | |
| **Ti-6Al-4V (ELI)** | 0.17 | 4.10 | 5.98 | 0.007 | 0.13 | 0.012 | 0.009 | balance | 381.5 ± 22.8 | 3.8 | 24 |
| **Ti-10V-2Fe-3Al** | 1.73 | 10.65 | 2.99 | - | - | - | - | balance | 359.3 ± 15.4 | 42.4 | 63.5 |

* H, O, and N contents were determined by inert gas fusion and the C content by combustion

** The β phase content was determined following a procedure adopted from Tiley et al. [53] by overlaying a regular grid of points on the SEM images and dividing the number of points within the β phase by the total number of points.

**Table 1.** Properties of the as-received Ti-6Al-4V and Ti-10V-2Fe-3Al alloys used in the plasma nitriding experiments. Chemical compositions were measured using inductively coupled plasma optical emission spectrometry (ICP-OES).

### 3.2. Effect of plasma nitriding on microstructure of titanium alloys

Plasma nitriding of titanium alloys results in the formation of a *compound layer* on the surface that mainly consists of TiN, δ phase, with FCC crystal structure ($Fm\bar{3}m$ space group) and $Ti_2N$, ε phase, with tetragonal crystal structure ($P4_2$-mnm space group). TiN is stable over a wide range of nitrogen contents, $TiN_x$ ($0.43 < \times < 1.08$), and has a typical hardness of 2500 HV. $Ti_2N$ is stable over a small composition of ~33.3 at.% N and has a maximum hardness of 1500 HV [49, 50, 54–56]. In plasma nitriding investigations of Raveh et al. [14], the compound layer was composed of a TiN layer on top of a mixture of randomly oriented polycrystalline TiN and

http://dx.doi.org/10.5772/61937

highly oriented $Ti_2N$. They also reported clusters of fine (50–100 A°) precipitates consisting of Al, V, Cr, and Fe elements underneath the compound layer. The compound layer has a typical thickness of 1–4 μm and may contain traces of $Ti_4N_{3-x}$, $TiN_{0.26}$, and $TiO_2$ in addition to TiN and $Ti_2N$ [6, 14, 15, 52, 57].

Underneath the compound layer, a region of nitrogen-stabilized α-titanium, that is, *α-case* and a nitrogen *diffusion zone* form by interstitial solid solution of nitrogen atoms in the titanium structure. The formation of α-case, with typical hardness of 800–1000 HV, is not favorable due to its negative effect on the ductility and fatigue strength of titanium alloys. When α + β and β-titanium alloys are nitrided at high temperatures (typically higher than 800°C), α-case forms a continuous α-Ti layer underneath the compound layer as shown in Figure 3; however, at lower temperatures (< 800°C), coarse and columnar α-stabilized grains were reported underneath the compound layer [10, 49, 50, 54, 55, 58]. Similarly, α-case may be formed during plasma nitriding of α-titanium alloys; however, it is more difficult to distinguish unless hydride precipitation in the substrate creates contrast against the α-case [10].

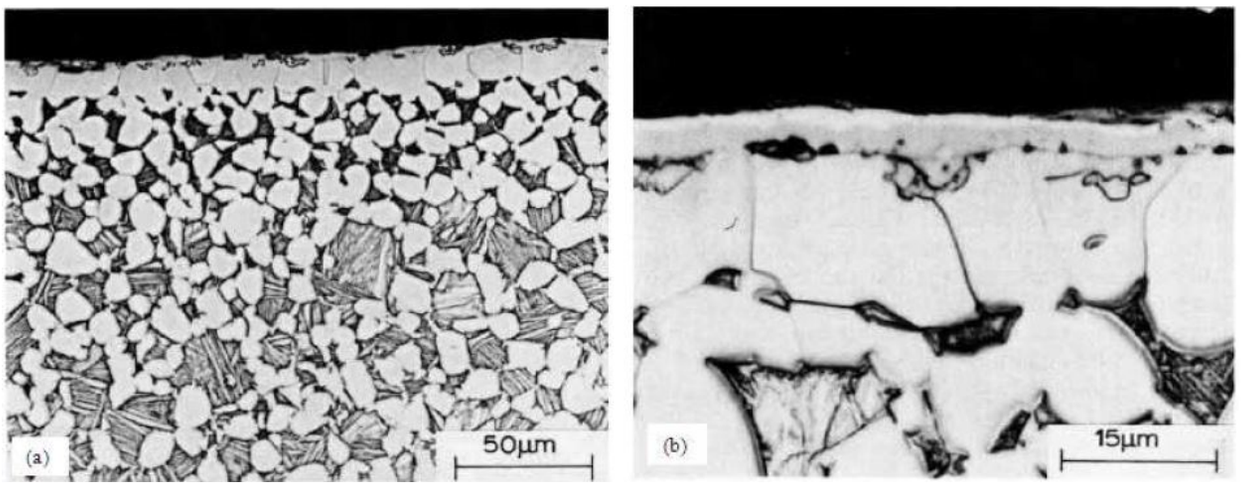



**Figure 3.** Optical micrographs of Ti–6Al–4V alloy after plasma nitriding in nitrogen for 3 hours at 1000°C showing the formation of an α-case underneath the compound layer at (a) low magnification and (b) high magnification [10].

Nitrogen atoms harden the diffusion zone with a profile that has its maximum at the near surface and gradually decreases toward the bulk. The depth of nitrogen diffusion is dependent on the process parameters as well as the phase composition of titanium alloys due to different solubility limits and diffusion rates of nitrogen in α- and β-titanium [5, 7, 59]. Nitrogen diffuses three times faster in β-Ti compared with α-Ti but has limited solubility in the β-phase [60, 61]. A study conducted by Il'in et al. [59] revealed that the addition of α-stabilizing elements such as Al slowed down the diffusion of nitrogen in α-titanium alloys. Conversely, β-titanium alloys had a shallow diffusion zone due to inadequate solubility of nitrogen in the β-phase. A higher depth of diffusion zone was achieved in α + β Ti alloys that possess a combination of high nitrogen solubility and diffusivity.

The effect of plasma nitriding process parameters on the microstructure and properties of titanium alloys was studied by several researchers [6, 16, 57, 62]. According to da Silva et al.

[16], the composition of plasma-nitrided Ti–6Al–4V surfaces was a very complex function of the nitriding parameters, for example, time, temperature, gas mixture composition, and pressure, among which temperature had the most significant influence. The x-ray diffraction (XRD) studies on plasma-nitrided surfaces revealed that nitriding gas pressure had a minor influence on the nitrided microstructure; however, increasing the partial pressure of nitrogen in the mixture resulted in preferential orientation of $Ti_2N$ and promoted the formation of TiN. They interpreted that the shift observed in β-Ti XRD reflections corresponded to lattice distortions in this phase and likely residual strains induced by nitriding. In addition to TiN and $Ti_2N$ titanium nitrides, they also reported XRD reflections of $V_2O$, orthorhombic $TiO_2$, and nitrogen-deficient ζ-$Ti_4N_{3-x}$ nitride in the compound layers formed at certain nitriding conditions. Yildiz et al. [62] found that time and temperature of nitriding were directly correlated with the surface hardness and roughness, thickness of the compound layer, TiN content in the compound layer, and depth of the diffusion zone. They also reported that Al atoms from the Ti–6Al–4V substrate tend to segregate underneath the compound layer and form an Al-enriched layer, which impedes the inward diffusion of nitrogen during plasma nitriding. The presence of an Al-enriched layer underneath the compound layer was also confirmed by other researchers [6, 57].

The authors' investigations on optimizing the plasma nitriding process parameters were aimed at preventing the formation of $\alpha$-case and microstructural changes in titanium substrates which are detrimental to some mechanical properties for example fatigue [52, 63]. Plasma nitriding treatments were performed in an industrial unit[2] consisting of a DC power supply and control console, nitriding chamber and base assembly, hydraulic lifting system for lifting the chamber from the base, temperature measurement system, evacuation system, gas supply, inlet/outlet, and pressure gauges. A schematic illustration of the nitriding set-up is given in Figure 4. No auxiliary heat source was utilized, and the heat was generated by the glow discharge.

Titanium coupons were placed at the geometric center of a cathodic cage in order to avoid common problems associated with DC plasma nitriding such as arcing damage, hollow-cathode, and edging effect. Prior to each run, the chamber was cleaned through a couple of filling/evacuation steps using Ar-$H_2$ (1:1) mixture. Subsequently, the coupons were sputter-cleaned at the process temperature in an Ar-$H_2$ (1:1) atmosphere for a few hours after a stable glow discharge was maintained. The nitriding gas mixture was purged into the chamber and the nitriding cycle was completed. Consequently, the coupons were cooled down to ~150°C inside the furnace under vacuum. Plasma nitriding was carried out at different temperatures (500–800°C), durations (4–87 hours), and pressures (67–533 Pa) in $N_2$/Ar and/or $N_2/H_2$ mixtures with nitrogen contents ranging between 1.5% and 75%. After each plasma nitriding treatment, microstructural and chemical analyses were performed and the samples were subjected to analytical microscopy examinations.

Phase constituents of the nitrided surfaces were identified using a Rigaku DMAX-1200 x-ray diffractometer and a Rigaku MiniFlex x-ray diffractometer equipped with Cu $K_\alpha$ tubes. The

2 Exactatherm Ltd., 2381 Anson Dr., Mississauga, ON, Canada

http://dx.doi.org/10.5772/61937

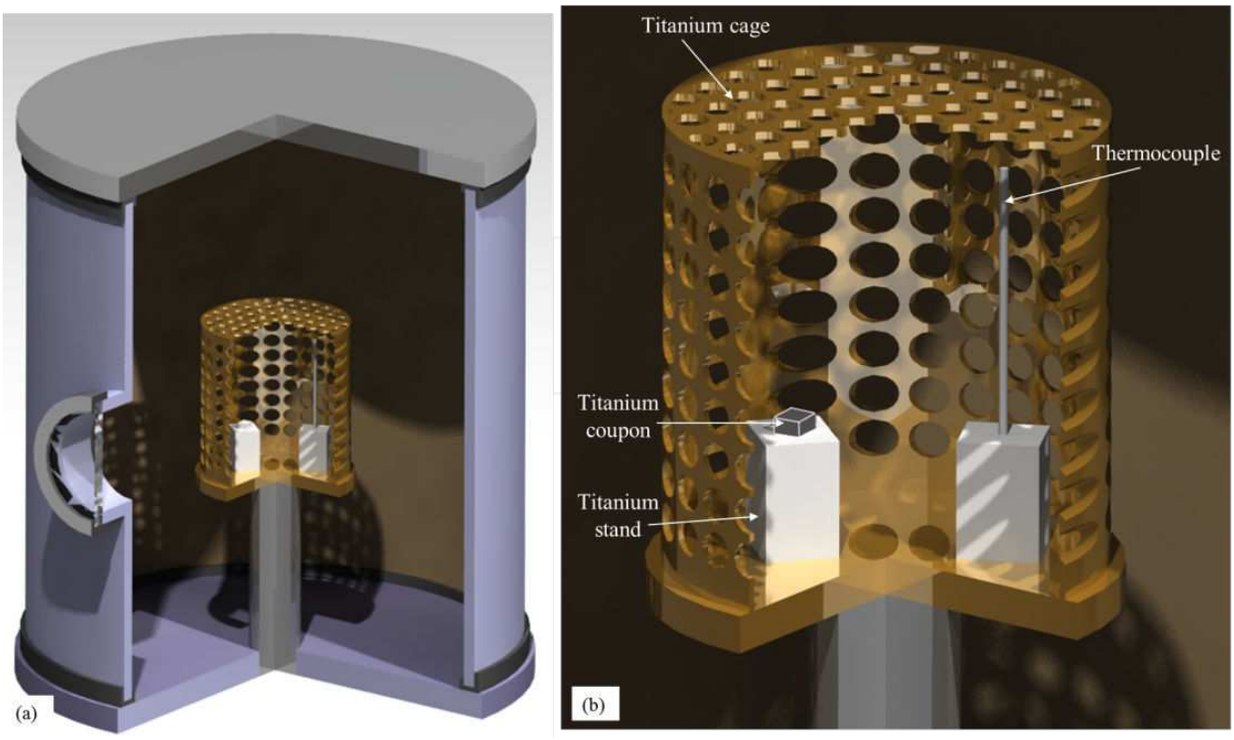



**Figure 4.** (a) A schematic illustration of the plasma nitriding set-up, no external heating source was used and (b) titanium coupons were placed at the geometric center of a cathodic cage (the cage was also made of Ti alloy to minimize contamination) [51].

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[3]. Surface morphology and cross-sectional microstructure of the nitrided alloys were examined under an FEI Quanta 200 Field Emission Gun (FEG) scanning electron microscope (SEM) equipped with an x-ray energy dispersive spectroscopy (EDS) detector. For cross-sectional study of microstructures, the nitrided surfaces were plated using an electroless nickel coating treatment prior to metallographic preparation to protect the near-surface microstructure against mechanical damage. The cross sections were then cut using a low-speed diamond saw and mounted in epoxy. The metallographic procedure began with serial wet grinding with silicon carbide abrasive papers in successive steps, followed by polishing with diamond. Ti–10V–2Fe–3Al surfaces had an additional fine polishing step using 0.06 μm colloidal silica suspension. The polished samples were cleaned in an ultrasonic bath of ethanol prior to microscopic examinations.

A scanning/transmission electron microscope (S/TEM) equipped with an energy dispersive x-ray spectrometer (Titan 80–3000) was used to investigate the microstructure of nitrided titanium alloys in the surface vicinity. Moreover, x-ray microanalysis coupled with electron diffraction patterns and electron energy-loss spectroscopy (EELS) was used to obtain structural information and chemical composition of the nitrided microstructures. TEM thin-foil speci-

3 Proto Manufacturing Ltd., 2175 Solar Crescent, OldCastle, ON, Canada

mens were prepared using focused ion beam (FIB) milling lift-out technique [64] (dual-beam Zeiss NVision 40[4]) with thicknesses of around 50 nm suitable for high-resolution TEM (HRTEM) imaging and EELS. Ion milling was performed using a gallium ion source at 30 kV and a thin (1–2 μm) layer of platinum was deposited on the milling location to protect the surface features from the milling damage.

The microstructure of plasma-nitrided Ti–6Al–4V consisted of a 1.9-μm compound layer on the surface followed by a 44.4-μm-deep nitrogen diffusion zone (Figure 5). The compound layer consisted of $Ti_2N$, TiN, and $TiN_{0.3}$ nitrides (Figures 6 and 7). Plasma-nitrided Ti–10V–2Fe–3Al had a 0.5-μm compound layer consisting of TiN ($Fm\bar{3}m$), $Ti_2N$ ($P4_2$-mnm), $V_2N$ ($P\bar{3}1m$), with the possibility of $Fe_8N$ (I4-mmm) (Figures 8 and 9). Vanadium nitride, rarely reported in the literature, was observed along titanium nitride grain boundaries possibly due to faster diffusion of vanadium along grain boundaries (acting as short-circuit paths) at the nitriding temperature [18, 36-37].

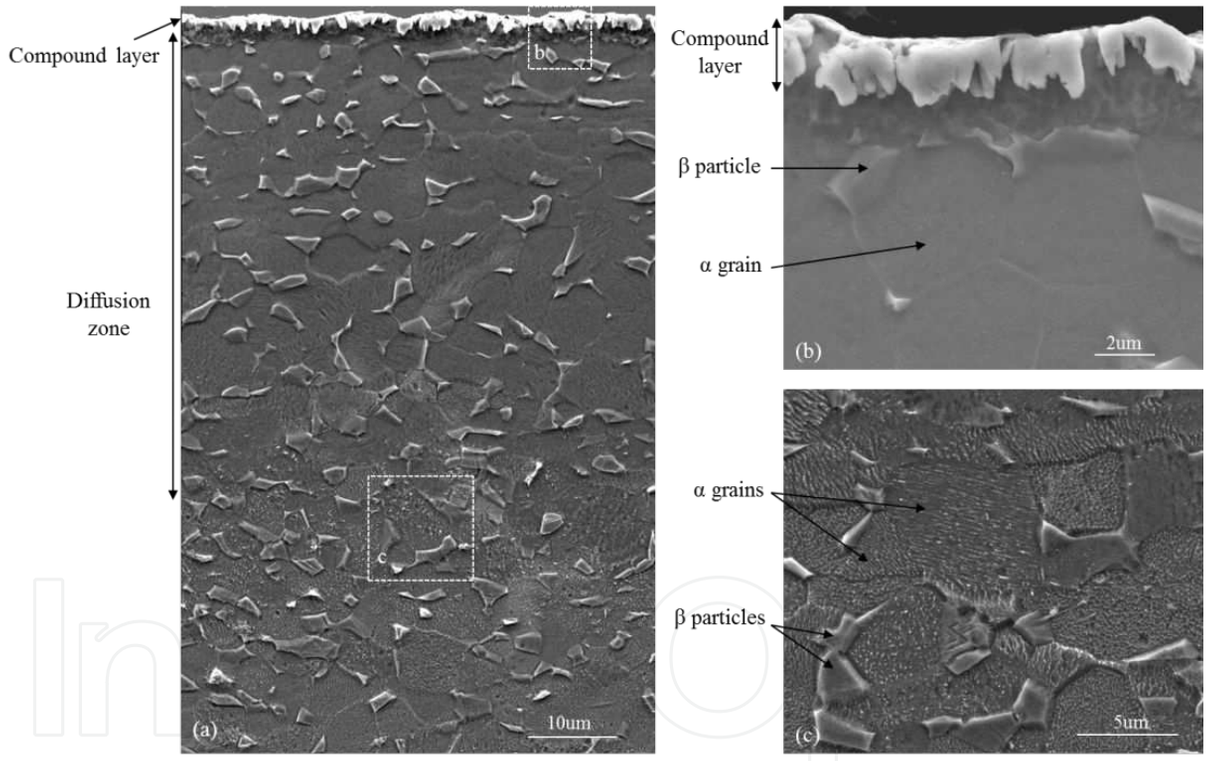



**Figure 5.** Typical cross-sectional SEM images of plasma-nitrided Ti–6Al–4V microstructure at 600°C consisting of a thin compound layer (1.9 ± 0.5 μm) and a deep (44.4 ± 5.6 μm) diffusion zone. Diffusion zone was delineated by the dissolution of fine recrystallized β-particles inside the α-grains (because nitrogen is an α-stabilizing element) and confirmed with the microhardness-depth profile measurements. (b) Higher magnification image of the enclosed area marked as "b" in Figure 5a confirming the absence of α-case underneath the compound layer. (c) Higher magnification image of the enclosed area marked as "c" in Figure 5a confirming that no phase transformations were observed in the titanium substrate [26].

4 The Canadian Centre for Electron Microscopy (CCEM), Brockhouse Institute for Materials Research, B161 A. N. Bourns Building, 1280 Main Street West, Hamilton, ON, Canada

http://dx.doi.org/10.5772/61937

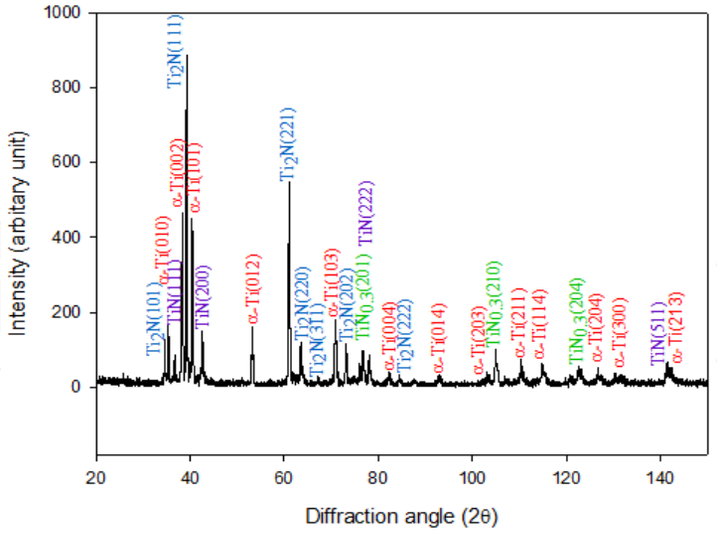



**Figure 6.** X-ray diffraction (XRD) analysis showing the presence of TiN, $Ti_2N$, and $TiN_{0.3}$ in the compound layer [63].

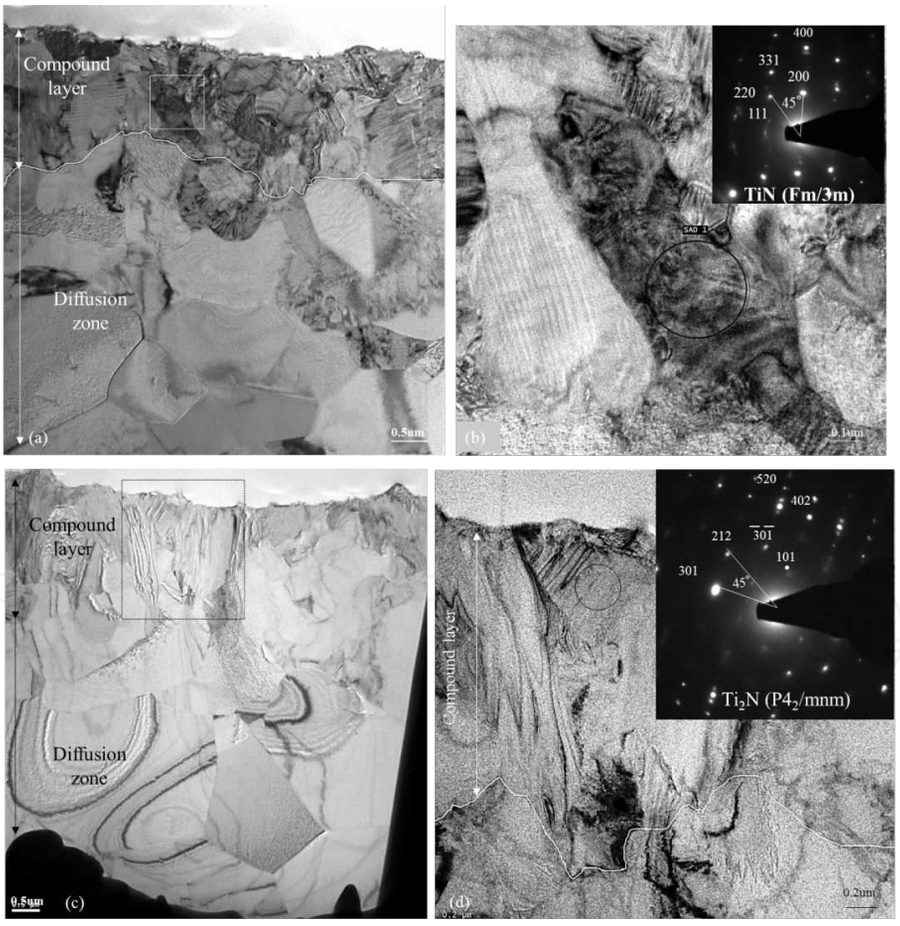



**Figure 7.** Bright-field TEM images and the corresponding selected area electron diffraction patterns of the plasma-nitrided Ti–6Al–4V microstructure showing the formation of TiN (space group: $Fm\bar{3}m$) and $Ti_2N$ (space group: $P4_2$-mnm) nitrides in the compound layer [63].

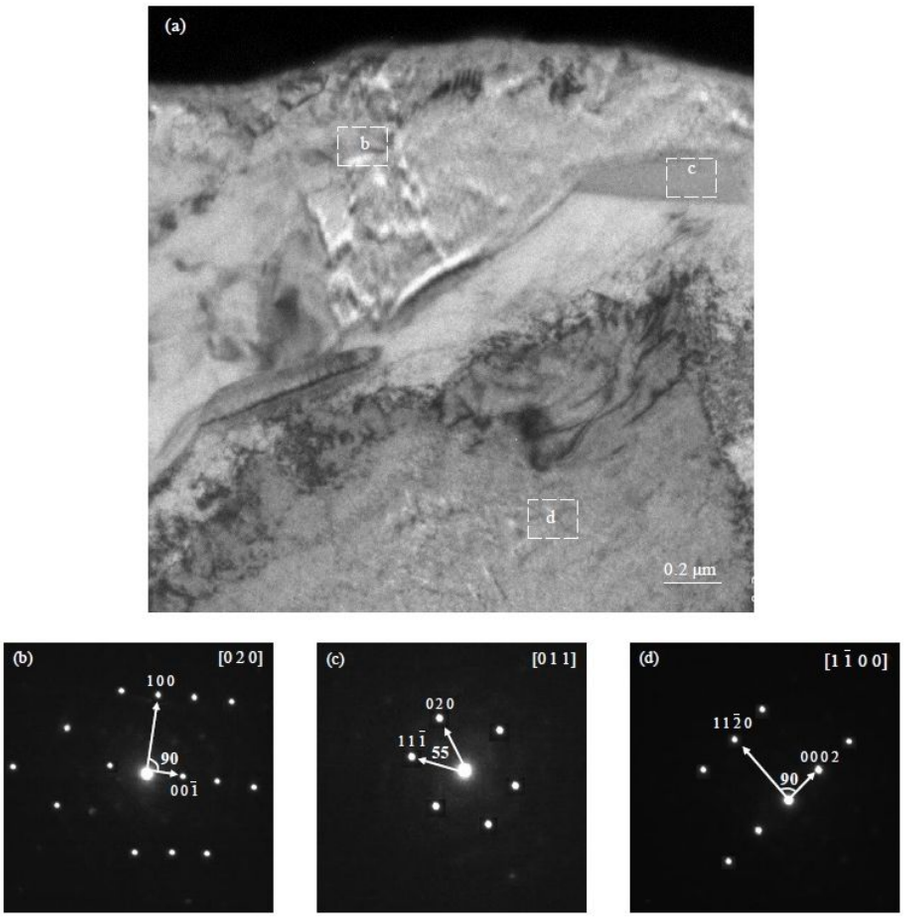



**Figure 8.** A bright-field TEM image of the plasma-nitrided Ti–10V–2Fe–3Al microstructure and the corresponding convergent beam electron diffraction (CBED) patterns confirming the formation of $Ti_2N$ (space group: $P4_2$-mnm) and $V_2N$ (space group: $P\bar{3}1m$) in the compound layer. $V_2N$ nitrides were located at the grain boundaries [52].

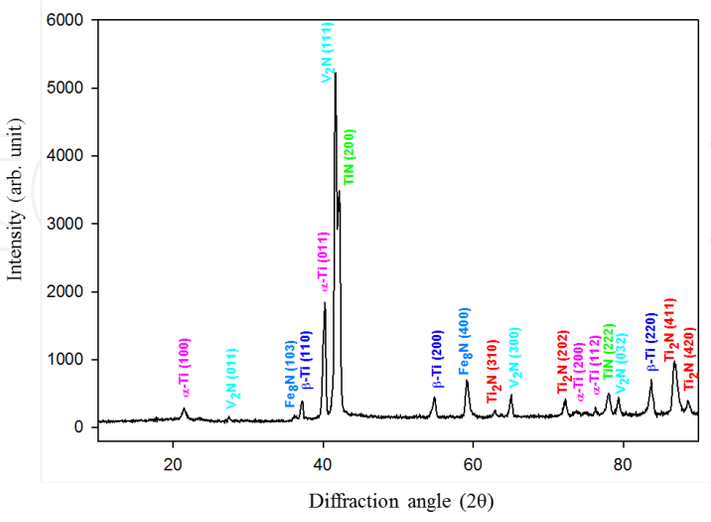



**Figure 9.** X-ray diffraction (XRD) pattern of the surface of plasma-nitrided Ti–10V–2Fe–3Al indicating the presence of titanium nitrides (TiN, $Ti_2N$), vanadium nitride ($V_2N$), and the possibility of iron nitride ($Fe_8N$) [52].

The depth of nitrogen diffusion was confirmed by microhardness versus depth profiles due to the solid-solution strengthening effect of interstitial nitrogen atoms in titanium structure. Microhardness profiles were obtained by microindentations at a maximum load of 245 mN (25 grf) using a diamond Vickers tip on tapered cross sections (CSM Instruments Micro-Combi Tester) and the microhardness values were determined based on load-penetration depth curves [65]. A deep nitrogen diffusion zone (35 ± 5 μm) in Ti–10V–2Fe–3Al after an 8-hour treatment (Figure 10) was attributed to the high β-phase content of the alloy with high nitrogen diffusivity [18, 22, 30, 47]. The prolonged sputtering of the surfaces prior to the nitriding process in this research also has accelerated the nitrogen diffusion by formation of several dislocations inside the $\alpha$-grains. It has also been reported that the Ar+$H_2$ sputtering increased the nitriding kinetics in ferrous alloys by providing easy diffusion paths for nitrogen interstitials and eliminating inherent surface oxides [48, 49].

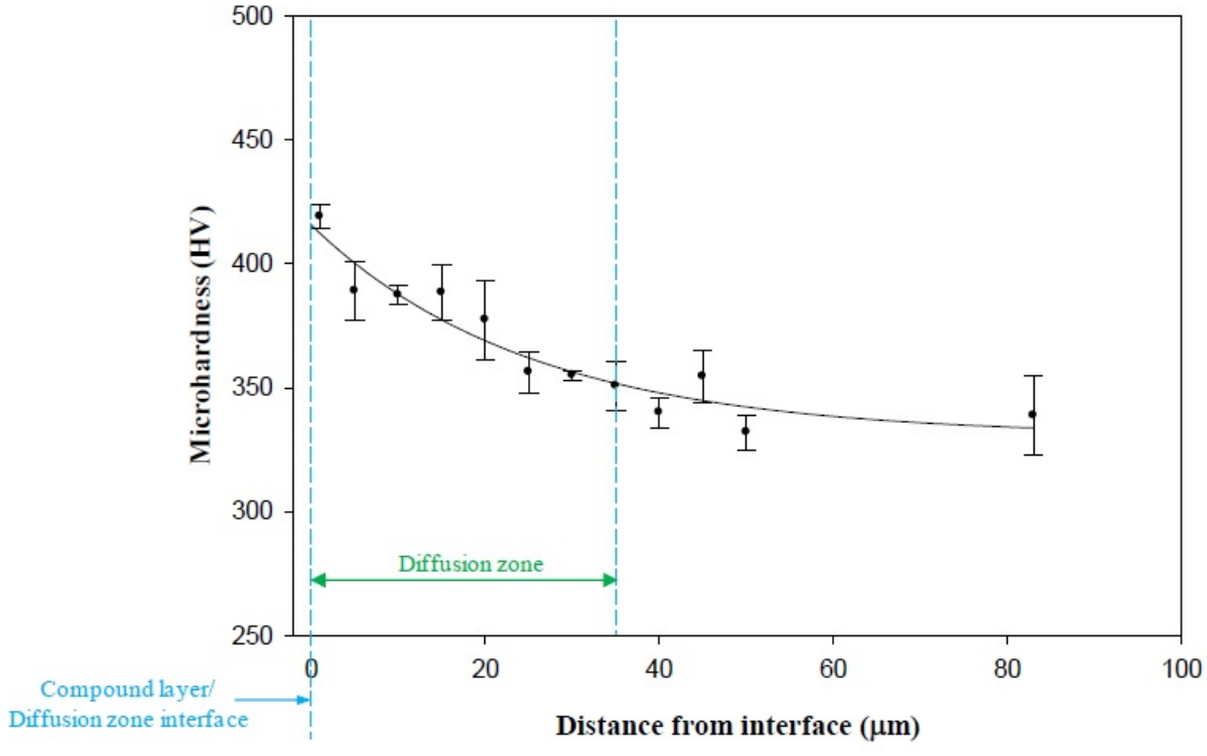



**Figure 10.** The microhardness-depth profile of the plasma-nitrided Ti–10V–2Fe–3Al. The diffusion zone extended to a depth of ~35 ± 5 μm underneath the compound layer [52].

## 4. Tribological properties of plasma-nitrided titanium alloys

Titanium alloys are renowned for their poor tribological characteristics, their strong adhesion tendency, high wear rates, susceptibility to seizure and galling, and high and unstable coefficient of friction [66–71]. Severe material transfer occurs during sliding of titanium alloys

against themselves and other alloys[5], ceramics, or even polymers [72–75]. This behavior is attributed to their low resistance to plastic shearing, low work hardening, the brittle nature and low sliding resistance of their inherent surface oxides, and possibly microstructural embrittlement by oxygen dissolution [67, 76–78].

Although it is well established that plasma nitriding improves the wear resistance of titanium alloys, the tribological behavior of plasma-nitrided titanium surfaces is a function of the hardness of surface layers, surface roughness, the presence of brittle nitriding microstructural features, and the depth of nitrogen diffusion zone. Thus, the wear resistance of plasma-nitrided titanium surfaces is dependent on the process parameters, microstructure, and chemical composition of the titanium substrate and sliding conditions.

One of the earliest investigations on wear behavior of plasma-nitrided titanium alloys was performed by Bell et al. [10]. They reported that the high wear rate and high coefficient of friction of Ti–6Al–4V (COF = 0.3) were effectively improved by plasma nitriding (800°C, 12 hours, $N_2$ atmosphere). They attributed the low coefficient of friction (COF = 0.05), low wear rate, and anti-scuffing characteristics of the plasma-nitrided surfaces to the hardness of the compound layer.

Taktak and Akbulut [79] performed plasma nitriding at temperatures ranging from 700°C to 900°C for different durations and reported that the treatment performed at the highest temperature for the longest duration exhibited the best wear resistance and friction behavior. This was correlated with the compound layer thickness and hardness; however, the compound layer failure at high applied loads resulted in a transition to high wear rates, close to those of the untreated alloy. Higher plasma nitriding temperatures of 900°C, 1000°C, and 1100°C were studied by Shashkov [80] in different titanium alloys for different durations in $N_2$ atmosphere. They reported some wear resistance for plasma-nitrided titanium alloys at 900°C and reduction of wear resistance for nitrided alloys at higher temperatures and durations. They clarified that plasma nitriding of titanium alloys at elevated temperatures was accompanied by embrittlement due to the formation of brittle nitride layers and microstructural changes in the bulk such as grain coarsening.

The tribological behavior of Ti–6Al–4V alloy plasma-nitrided at temperatures ranging between 450°C and 520°C were studied by Yilbas et al. [81] against ruby counterpart in lubricated conditions. They reported that the scuffing and high friction coefficients, observed in the untreated alloy after a few sliding cycles, were avoided in the plasma-nitrided surfaces before the breakthrough of nitrided layers. This breakthrough was delayed when plasma nitriding was performed at 520°C due to a higher depth and hardness of the diffusion zone.

The wear mechanisms of plasma-nitrided Ti–6Al–4V alloy were studied by Molinari et al. [55]. The plasma nitriding treatments were carried out at different temperatures of 700°C, 800°C, and 900°C in a $N_2$–$H_2$ (4:1) gas mixture for 24 hours and tested against disks that had seen the same treatments. They found that the wear resistance was dependent on the microstructure and surface roughness of the nitrided surfaces and wear test conditions. At the lowest sliding

5 Except Ag–10Cu alloy and Babbitt metal (grade 2) that showed no galling against Ti–4Al–4Mn alloy

http://dx.doi.org/10.5772/61937

speed (0.3 m/s), nitriding inhibited oxidation-dominated wear in Ti–6Al–4V and decreased wear by providing resistance against adhesion and microfragmentation. However, compound layer failure that occurred at low-to-moderate loads for low-temperature (700°C) nitriding and at high loads for elevated temperature (800°C and 900°C) nitriding led to third-body abrasion and high wear rates. Plasma nitriding reduced wear at high sliding velocities (0.6 m/s and 0.8 m/s) by restricting the extensive plastic deformation and delamination wear of the titanium substrate. The elevated temperature plasma treatments exhibited better wear performance at high loads due to their higher thickness of the compound layer and depth of diffusion zone, but lower wear resistance at low loads possibly due to the increased residual stress level in the nitride layers and higher surface roughness.

The same authors also studied the wear mechanisms of Ti–6Al–4V alloy plasma nitrided at 800°C under lubricated rolling–sliding conditions [66]. Their findings indicated that the efficiency of lubricants was reduced by plasma nitriding, resulting in higher friction, possibly due to the better wettability and higher ionic character of the inherent titanium oxides compared with the titanium nitrides of the compound layer. However, the wear rates decreased by plasma nitriding and had an inverse relationship with the nitriding duration. The insufficient wear improvement after a short-duration process (8 hours) was related to the inadequate depth of nitriding and lack of support for the compound layer. On the other hand, an elongated nitriding treatment (24 hours) promoted a deeper diffusion zone that retained the compound layer on the surface under sliding conditions.

The positive role of a deep diffusion zone in tribological behavior of plasma-nitrided titanium alloys was also established by Nolan et al. [82], upon comparing plasma-nitrided and physical vapor deposition (PVD)-coated surfaces. Significantly lower mass loss was observed for plasma-nitrided Ti–6Al–4V with a 2-μm compound layer on top of an approximately 40-μm diffusion zone compared with the PVD-coated surface with a 2-μm TiN layer. Examination of worn surfaces and cross sections indicated that the compound layer endured the applied loads without significant subsurface plastic deformation. They proposed that the strengthening effect of the solid solution nitrogen atoms within the diffusion zone provided mechanical support for the compound layer and improved the wear resistance. Moreover, a gradual hardness profile decreased the chances of interfacial debonding due to a gradual change of elastic modulus and hardness from the surface toward the bulk.

The effect of nitriding microstructural features on the wear performance of plasma-nitrided titanium alloys was further elucidated by Cassar et al. [83]. They plasma-nitrided Ti–6Al–4V alloy using a triode set-up at low (200 V) and high (1000 V) voltages and evaluated the wear behavior against WC–Co and sapphire. The low-voltage treatment formed a thin compound layer on a deeply strengthened diffusion zone and despite the lower hardness of the compound layer, it provided better wear resistance compared with the high-voltage treatment especially at high loads. The thin compound layer could conform to the substrate deformation without experiencing spallations as the maximum shear stress was constrained within the diffusion zone. Bloyce et al. [30] explained that when the maximum applied stress during sliding exceeds the substrate yield strength, it experiences plastic deformation as evidenced by elongated

grains within the subsurface and material pile-up. However, the TiN/$Ti_2N$ surface layer cannot conform to the plastic deformation due to its low fracture toughness.

Recent studies by the authors investigate the failure micromechanisms of plasma-nitrided Ti–6Al–4V under dry sliding conditions using microscratch tests [63]. The tests were carried out using a diamond Rockwell tip with a 200-μm radius (CSM Instruments Micro-Combi tester) according to the ASTM C1624 standard [84]. Lateral displacement speed of 1 mm/min and loading rate of 10N/min were selected for the experiments. In addition to normal and tangential force (resolution of 0.3 mN), penetration depth (resolution of 0.3 nm) and acoustic emission signals were 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)). During the progressive tests, the applied load linearly increased from 0.03 to 20 N as the tip moved at a constant displacement speed on the surface. The critical loads corresponding to the onset of coating failure events were identified using acoustic emission signals and subsequent SEM observations. In-depth site-specific cross-sectional analysis of scratch paths was carried out using a LEO (Zeiss) 1540 XB dual-beam FIB/SEM fitted with an EDS detector[6]. A thin layer of osmium (~3 nm) was deposited on the surfaces prior to the milling process to increase conductivity, prevent charging, and enhance the secondary electron yield for imaging. After locating the region of interest, a 2-μm-thick layer of platinum was deposited on the selected area to prevent surface features from damage during the milling process. 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. All the FIB trenches were made parallel to the scratch direction of the scratch paths. The ion-milled trenches were imaged using a 1 kV electron beam located at a 54° angle.

The results indicated that failures initiated by the formation of microvoids within the compound layer likely atgrain boundaries. Increasing the applied load led to the formation of microcracks that propagated intergranularly within the compound layer and finally into the diffusion zone. The low resistance of nitrided surfaces to crack initiation and growth was correlated with the brittle nature and low damage tolerance of the compound layer [10]. However, it was observed that the deeply strengthened diffusion zone improved the adhesion of compound layer to the underlying substrate and prevented the spallation/delamination events under sliding contact. Moreover, subsurface crack propagation was retarded by ductile β-particles in the diffusion zone (Figure 11). The high resistance of β-phase to crack propagation in plasma-nitrided titanium alloys was confirmed by testing a plasma-nitrided near-β Ti–10V–2Fe–3Al alloy under the same conditions (Figure 12). It was proposed that the optimum microstructure consisted of a thin compound layer supported by a deep diffusion zone consisting of β-particles. Keeping that in mind, a low-temperature plasma nitriding treatment was developed for Ti–10V–2Fe–3Al alloy [52]. Evaluation of the tribological properties of the plasma-nitrided Ti–10V–2Fe–3Al surfaces using microscratch tests revealed that the coefficient of friction values were reduced by more than 72% and the nitrided surfaces exhibited an excellent load-bearing capacity. The compound layer did not experience any failures, for

6 Western Nanofabrication Facility, University of Western Ontario, London, ON, Canada

http://dx.doi.org/10.5772/61937

example, buckling or spallation, and maintained a good interfacial bonding to its substrate up to the high applied load of 17 N where partial chipping of the coating was observed at the scratch rims. Despite a low thickness, the compound layer suppressed the adhesion tendency and transfer of titanium due to high hardness and chemical inertness of TiN and $Ti_2N$ [32, 33], and high toughness and adhesion resistance of $V_2N$ [34, 35]. The deep diffusion zone (35 ± 5 μm) underneath the compound layer also contributed to high load-bearing capacity of the nitrided alloy by providing a good mechanical support for the compound layer [20, 39–42, 45-46]. The diffusion zone inhibited premature failures at the surface by mitigating the significant difference in the deformation behaviors of the compound layer and Ti–10V–2Fe–3Al substrate and acting like a "functionally-graded interface" [43, 44].

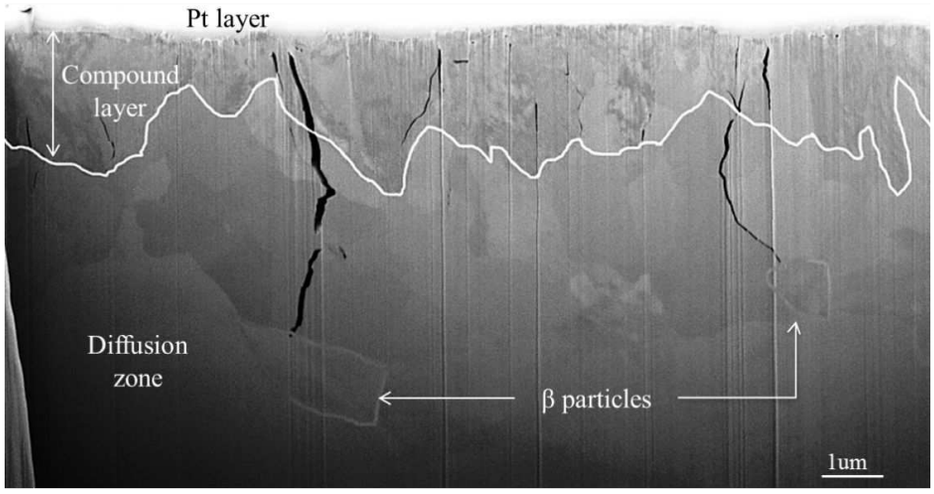



**Figure 11.** A typical SEM image of the FIB-milled cross section of the scratch track on the surface of plasma-nitrided Ti-6Al-4V at the highest load of 20 N showing that the microcracks initiating from the surface were stopped at β-particles in the diffusion zone [63].

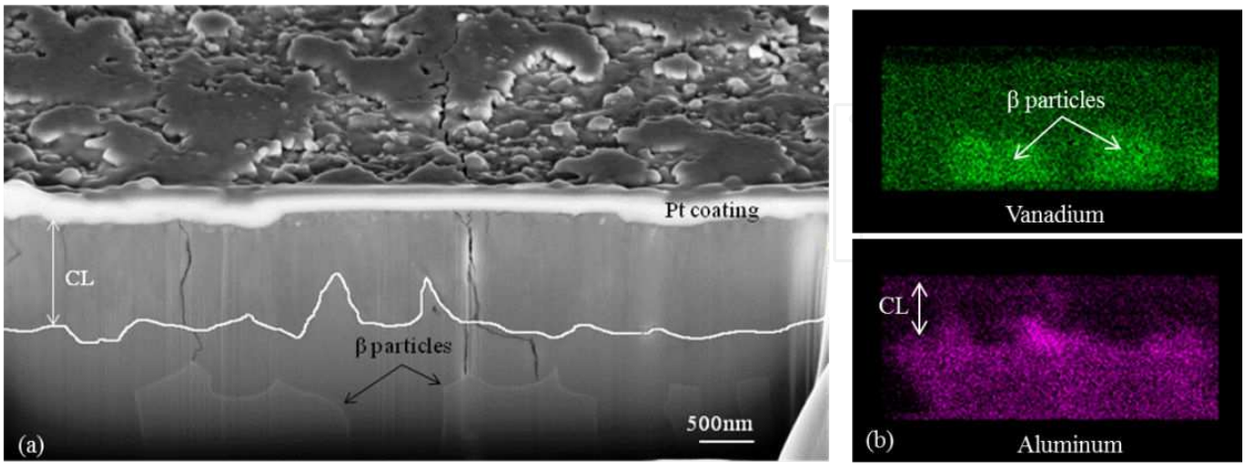



**Figure 12.** (a) A typical SEM image of the FIB-milled cross section of the scratch track on the surface of plasma-nitrided Ti-10V-2Fe-3Al and (b) the corresponding EDS mpas for aluminum and vanadium confirming that the β-particles inhibited further crack propagation in the subsurface region [63] (CL: compound layer, DZ: Diffusion zone).

Surface roughness of plasma-nitrided titanium alloys is another influential factor on their sliding behavior. Salehi et al. [85] investigated the effect of surface topography on the wear behavior of PVD TiN-coated and plasma-nitrided Ti–6Al–4V surfaces. They found that the compound layer thickness and surface roughness both increased with plasma nitriding-treatment temperature and proposed that sputtering is responsible for the changes in surface roughness. They reported that under self-mating conditions, oxidational wear dominated with significant mass loss for surfaces of higher roughness and thicker compound layers. Sliding wear tests against alumina counterface revealed that plasma nitriding at high temperatures (850°C and 950°C) yielded low wear rates at high loads due to thick compound layers but high wear rates at low loads due to high surface roughness. Plasma-nitrided surfaces at low temperatures (700°C and 750°C) improved the wear resistance below a critical load, above which the compound layer spalled off and the coefficient of friction increased abruptly. Similar observations were made by Yildiz et al. [62].

## 5. Mechanical properties of plasma-nitrided titanium alloys

Nitriding improves the fatigue strength of steels due to the precipitation of submicroscopic alloying element nitrides and compressive residual strains in the diffusion zone. Conversely, nitriding of titanium alloys does not promote precipitation strengthening mechanisms [86] and also leads to inevitable adverse effects on the toughness and fatigue properties [10, 24, 87–89]. In this section, the correlation between plasma nitriding and mechanical properties of titanium alloys is presented, and since the microstructural features of gas-nitrided Ti alloys affect fatigue properties in the same manner, gas nitriding investigations have been occasionally referred to in this section.

Due to the slow kinetics of nitrogen diffusion in titanium alloys, relatively high temperatures (>700°C) are used to produce sufficient depth of nitriding. Typical plasma nitriding treatments, performed in the temperature range of 700–1100°C for several hours, cause bulk microstructural changes such as significant grain growth and overaging that adversely affect the fatigue behavior [10, 22, 23]. Moreover, 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 premature failure initiation and deterioration of mechanical properties of titanium alloys after nitriding [10, 49, 50, 54, 55, 58, 90, 91].

According to Morita et al. [90] and Tokaji et al. [92], the formation of the compound layer and grain growth were equally responsible for the fatigue deterioration of gas-nitrided titanium alloys. Morita et al. [90] proposed that the high stiffness gradient between the compound layer and Ti substrate ($E_{\text{compound layer}}$ = 426 GPa, $E_{\text{Ti}}$ = 100 GPa) led to stress concentration at the surface. The resulting stress concentration cancelled the effect of compressive residual stresses and led to the premature fracture initiation at the surface due to the low fracture toughness of the compound layer. They also reported that the fatigue strength had a Hall–Petch relationship with the grain size of nitrided titanium and the negative effect of grain growth was more

pronounced for elongated treatments at high temperatures. Consequently, promising results were obtained by inhibiting grain growth through a low-temperature nitriding process.

Tokaji et al. [92] separated the effect of nitriding on the substrate microstructure by subjecting the titanium alloys to the same heating cycle under vacuum. The results indicated a slight increase in the fatigue limit compared with the annealed Titanium alloys after a 4-hour nitriding treatment, but 15 hours of nitriding significantly reduced the fatigue strength. They believed that the compound layer and diffusion zone were both responsible for impaired fatigue properties and observed improvements in fatigue life by complete removal of the compound layer and partial removal of the diffusion zone (Figure 13). Similar results were found by Nishida and Hattori [24] and Rodriguez et al. [93] after plasma nitriding of Ti–6Al–4V. They reported that the fatigue strength of plasma-nitrided Ti alloys was lower than the untreated alloy but was similar to – or even slightly better than – that of the vacuum-annealed alloy with the same heating history. The fatigue endurance limit was found to be inversely related to the plasma nitriding temperature and increased by about 30 MPa when the brittle compound layer was removed after plasma nitriding. Rodriguez et al. [93] reported that the bulk microstructural changes from mill-annealed to Widmanstätten structure were caused by a reduction in low-cycle fatigue resistance. They proposed that imposed strains during cyclic loading at low loads were not sufficient for compound layer failure, and thus the residual compressive strains retarded the fatigue crack nucleation. However, the compound layer failed at high cyclic strains due to a high surface roughness and the different stiffness between Ti–6Al–4V and titanium nitrides.

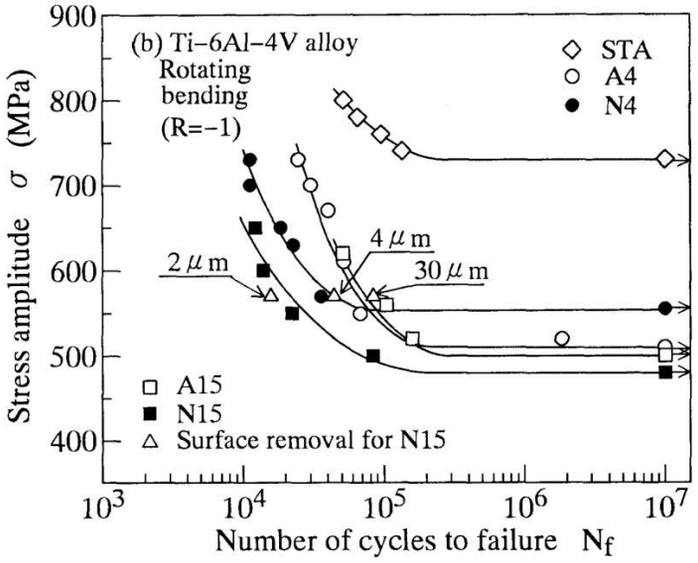



**Figure 13.** The S–N curve obtained by rotation bending fatigue tests on Ti–6Al–4V alloy. STA: solution treated at 950°C for 1 hour and aged at 540°C for 4 hours; A4 and N4: annealed and nitrided at 850°C for 4 hours; A15, N15: annealed and nitrided at 850°C for 15 hours [92].

Several researchers including Bell et al. [10, 25] and Guiraldenq et al. [94] correlated the impaired fatigue properties of titanium alloys after plasma nitriding to the thickness of the $\alpha$-case. The $\alpha$-case is a brittle layer (typical hardness 800–1000 HV) formed beneath the compound layer at high nitriding temperatures (≥ 800°C), and its formation has proven to be detrimental for ductility and fatigue strength [10, 49, 50, 54, 55, 58].

Raveh et al. [50] believed that in addition to the surface hardness, fatigue crack initiation was also a function of residual strains in the nitrided layers, crystallographic orientation of different phases, and segregation of alloying elements near the surface region. The fatigue crack initiation resistance decreased with TiN content of the compound layer and the surface hardness due to its brittle nature. Moreover, incorporation of Ar in the nitriding plasma also decreased the crack initiation resistance, possibly as a result of inducing microstrains in the nitrided layers.

Conversely, according to Sobiecki and Rudnicki [95], plasma nitriding (at 800°C for 3 and 12 hours) increased the fatigue strength of Ti–1Al–1Mn alloy from 350 to 390 MPa. A plasma nitriding treatment at 500°C for 6 hours in nitrogen–hydrogen (3:1) gas mixture in the work of Rajasekaran and Raman [96] also resulted in improvements in uniaxial plain fatigue and fretting fatigue behavior of Ti–6Al–4V alloy. Lower surface roughness, generation of compressive residual stresses on the surface, and higher surface hardness were considered the main factors responsible 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 by plasma nitriding ($R_a$ decreased from 0.80 to 0.55 μm) due to 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 Ali and Raman [88] 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.

In a recent investigation by the authors, a plasma nitriding treatment was designed for Ti–10V–2Fe–3Al β-titanium alloy to address its susceptibility to adhesion without any detrimental effects on bulk microstructure. Uniaxial tensile tests were conducted at room temperature on small-sized specimens (6 mm in diameter and 24 mm in length at the gauge section) conforming to the specifications outlined in the ASTM E8M standard [97]. The tensile tests were performed at a cross-head speed of 0.5 mm/min (MTS Criterion-43) and strain values were measured using a clip-on axial extensometer to an accuracy better than ± 0.5% of the applied strain. Subsequently, the engineering stress–strain curves were constructed and the offset yield strength, ultimate tensile strength (UTS), and ductility (tensile elongation) were determined. It was found that the modified nitriding process led to improvements in the tensile (from 881.0 to 922.5 MPa) and yield (from 821.5 to 873.0 MPa) strengths of the alloy with a minor decrease

in the elongation (from 18.9% to 15.9%). The reduction of tensile elongation was possibly due to the mutual influence of precipitation of $\alpha$-phase during age hardening and the solid-solution strengthening effect of nitrogen interstitials. Similar observations were made by Akahori et al. [98] after gas nitriding experiments on Ti–Nb–Ta–Zr (β-titanium) alloy. More importantly, as confirmed by TEM observations and tensile test results, the formation of brittle $\omega$ precipitates (forming in the range of 250–450°C [2, 4, 10, 12]) and $\alpha$-case was avoided by optimizing the nitriding parameters.

Rotation bending fatigue tests (fully reversed cyclic loading, $R = -1$) were utilized in another investigation to evaluate the performance of plasma-nitrided Ti-6Al-4V alloy under cyclic loading conditions [26]. The tests were conducted using an R. R. Moore fatigue tester (Instron) at a frequency of 3000 rpm. The first samples were tested at ~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. 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. The stress–life (S–N) curves were constructed and used to evaluate the resistance to fatigue crack initiation. The fracture surfaces were then analyzed under the SEM (Quanta 200 FEG-SEM) at an accelerating voltage of 10 kV to investigate the failure micromechanisms.

The fatigue tests were also performed on untreated Ti-6Al-4V alloy under the same conditions for the purpose of comparison. The gauge section of the untreated samples was mechanically polished using 1-μm diamond suspension in the last step to an average surface roughness ($R_a$) and root-mean-squared roughness (RMS) of 0.14 and 0.18 μm, respectively. The surface roughness measurements were obtained using an optical profilometer (Wyko, Veeco NT1100).

A low-temperature plasma nitriding (600°C) was exploited to achieve a microstructure consisting of a thin compound layer (<2 μm) supported by a deep diffusion zone (>40 μm) without any significant changes in the substrate (only a ~40% increase in the average grain size). It was found that the low-temperature plasma nitriding resulted in improvements in fatigue strength of plasma-nitrided Ti-6Al-4V compared with conventional nitriding treatments (Figure 14). Moreover, the plasma-nitrided Ti-6Al-4V alloy at 600°C illustrated a ductile type of failure under uniaxial tensile loads. Periodic transverse cracks observed on the plasma-nitrided surfaces perpendicular to the loading direction without any signs of spallation confirmed a well-bonded interface between the compound layer and the substrate. Similar observations were reported by Chen et al. [99] for TiN coatings on stainless steel substrates under tensile loads. Conversely, plasma nitriding at an elevated temperature of 900°C led to substantial deterioration of strength, toughness, and fatigue life. This was attributed to premature failure of thick and brittle nitrided surface layers – a 5.6-μm-thick compound layer and a 19.3-μm $\alpha$-case – 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 with the untreated alloy) and phase transformation in the bulk microstructure from equiaxed to coarse lamellar grains (~5 times higher average grain size value) as shown in Figure 15.

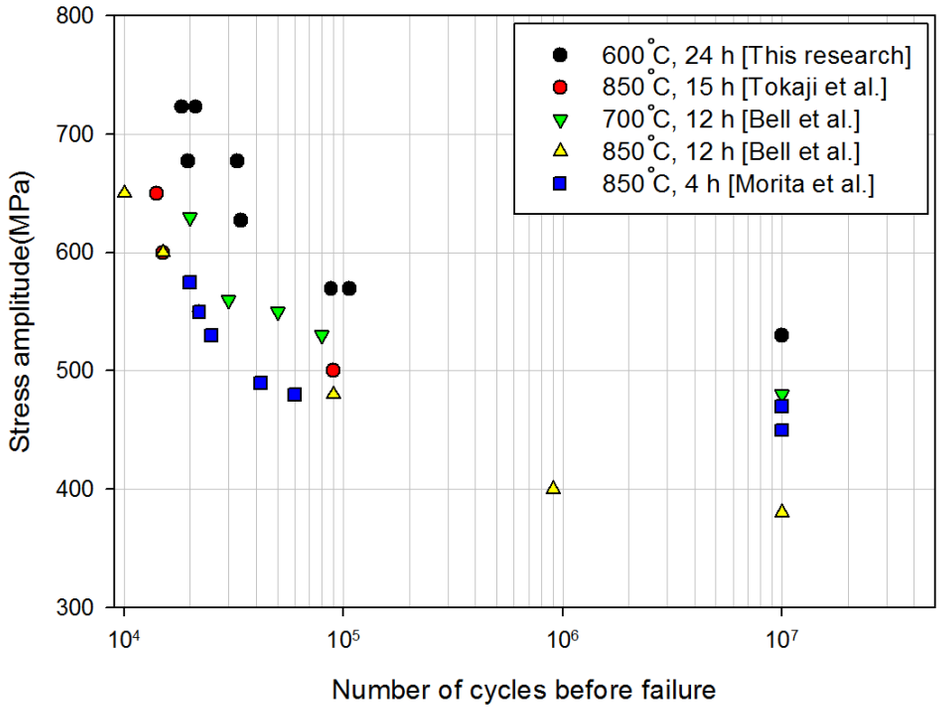



**Figure 14.** Comparison of the fatigue data obtained for plasma-nitrided Ti–6Al–4V with the conventional gas and plasma nitriding treatments in the literature [26].

According to fractographic investigations of the fatigue failures in low-temperature plasma-nitrided Ti-6Al-4V alloy, the fatigue failure initiated at the surface in the low cycle region ($N \leq 10^5$ cycles) and propagated in a ductile manner leading to the final rupture. No failures were observed in the high cycle region ($N > 10^5$ cycles) and the nitrided alloy endured cyclic loading until the tests were stopped at $10^7$ cycles. The thin compound layer restricted the extent of premature crack initiation from the surface, whereas the deep diffusion zone with a well-bonded interface decreased the likelihood of fatigue initiation at (or below) the compound layer interface. Although the compound layer exhibited signs of plastic deformation under cyclic loading conditions, fragmentation of the compound layer and brittle failure features observed at the fatigue crack initiation sites suggested that brittle fracture of the compound layer was the precursor to the fatigue failure (Figure 16). The 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. The beneficial effect of compressive residual stresses in the compound layer (−530 MPa) was overshadowed by the stress concentration in this layer due to the modulus mismatch with the substrate. Surface roughness was also an influential parameter on the fatigue strength of the nitrided alloy as by polishing the nitrided surfaces, a higher number of cycles were dedicated to the formation of fatigue cracks compared with the as-treated condition resulting in an improved fatigue life (Figure 17). Similar results were reported by Cassar et al. [91] and Novovic et al. [100] for the fatigue behavior of surfaces with average roughness values of 0.1 μm and higher.

http://dx.doi.org/10.5772/61937

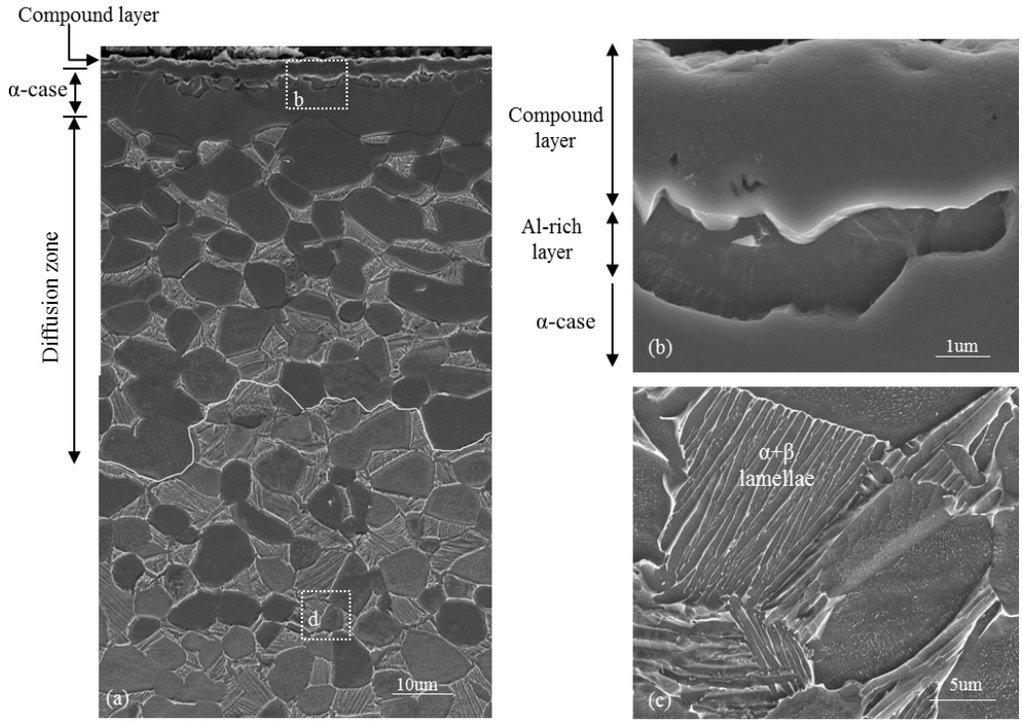



**Figure 15.** Typical cross-sectional SEM micrographs of the microstructure of plasma-nitrided Ti–6Al–4V treated at 900°C [26].

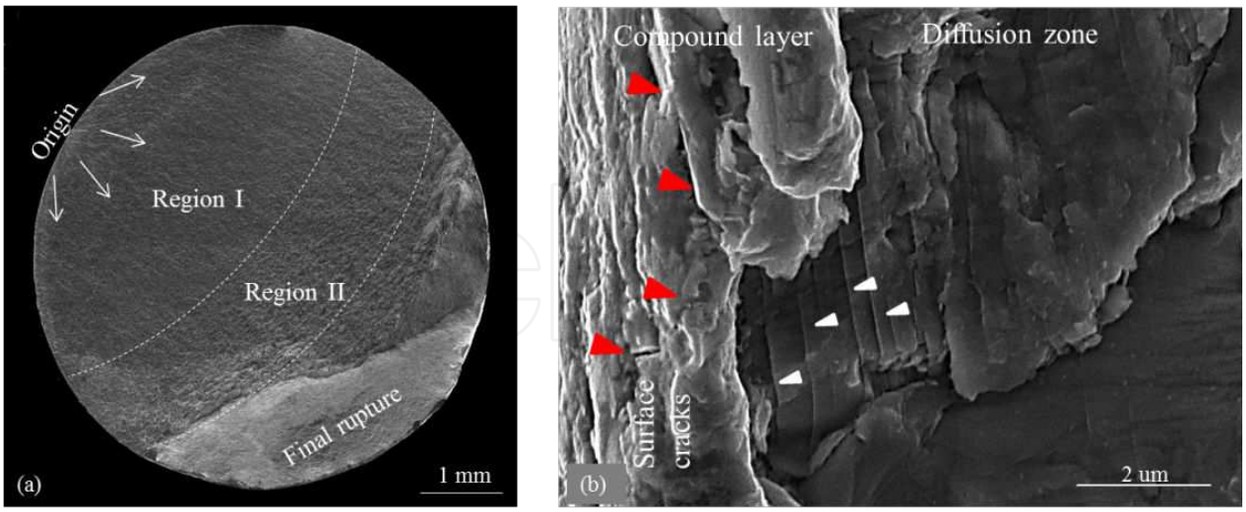



**Figure 16.** (a) A typical SEM image of the general view of the fatigue fracture surface of plasma-nitrided Ti–6Al–4V and (b) striation-like features and microcracks in the surface vicinity [26].

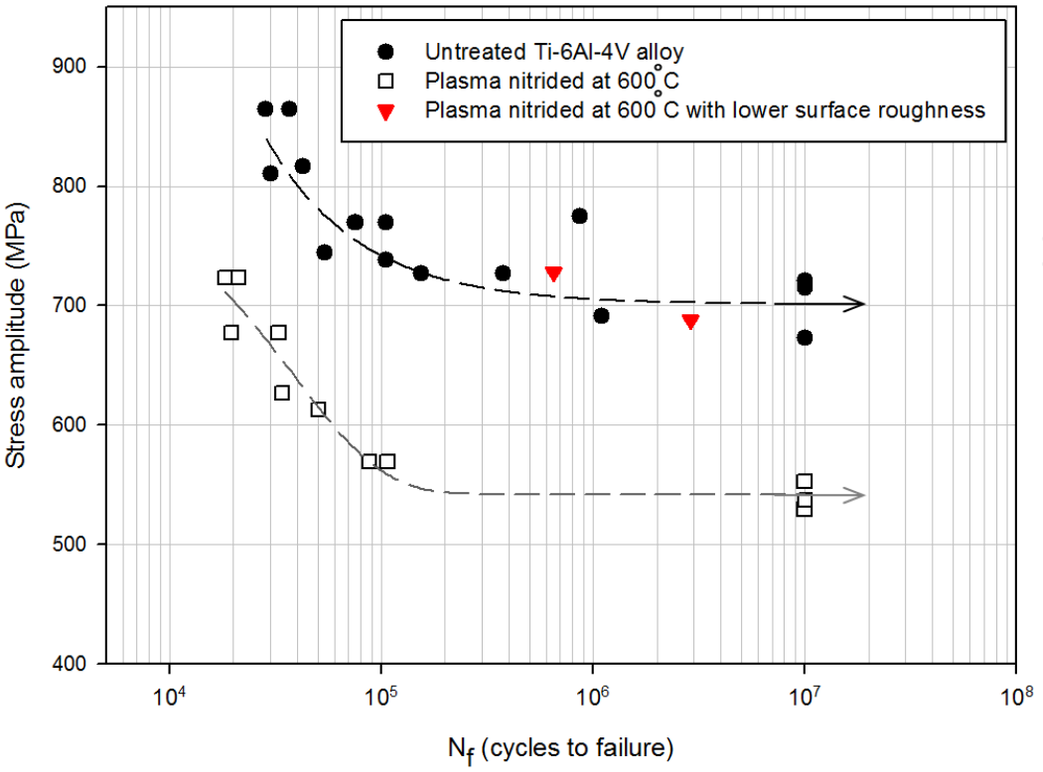



**Figure 17.** Stress–life (S–N) curves showing the effect of plasma nitriding on fatigue behavior of Ti–6Al–4V. It was found that decreasing the surface roughness with polishing resulted in an increase in the fatigue strength [26].

## 6. Recent development in plasma nitriding titanium alloys

As explained in Section 5, the main reasons for the initiation of premature failures in nitrided titanium alloys are the brittle nature of the compound layer and the $\alpha$-case, the incompatibility in deformation behavior of the compound layer and the substrate and lack of sufficient adhesion at their interface. As such, the compound layers cannot conform to the extensive plastic deformation of titanium substrates and eventually experience adhesive (from the interface) or cohesive (within the compound layer) failures. Thus, the mechanical response mismatch between the nitride layers and substrates should be minimized in order to enhance the load-bearing capacity of the nitrided surfaces. The effective practical measures are based on eliminating discrete nitride layer–substrate boundaries by the design and fabrication of multilayer coatings and coatings with gradient diffusion boundaries [29, 31, 36, 82, 83, 101]. A summary of recent investigations are presented in this section.

### 6.1. Duplex treatments

Duplex treatments were introduced to the field of surface engineering of titanium alloys to exploit the benefits of wear-resistant coatings and the deep hardening effect of diffusion

treatments [30–34, 102]. Significant improvements in wear resistance and long-term durability of titanium surfaces have been achieved by deposition of diamond-like carbon (DLC) coatings after diffusion hardening by plasma nitriding [103] or thermal oxidation [104, 105].

The beneficial role of plasma nitriding pretreatment in accommodating subsurface deformation and preventing premature failures in DLC-coated Ti–6Al–4V was confirmed in the work of Meletis et al. [103]. In their experiments, radio-frequency plasma nitriding treatment was utilized for substrate surface hardening, followed by deposition of DLC coatings with a silicon interlayer. In addition to substantial reduction of wear and coefficient of friction, it was found that the nitriding pretreatment retarded catastrophic failure of DLC coatings during sliding at high contact loads.

In another investigation by Dong [36], the combined effect of electron beam melting and plasma nitriding treatments resulted in significant improvements in wear resistance and load-bearing capacity of Ti–8.5Si titanium alloy. Electron beam melting generated a deep strengthened zone (800 HV to a depth of 600 μm) in the alloy before plasma nitriding that provided support for the nitride layer under sliding contact. As a result, the surface nitride layer endured the stresses applied during wear tests without spalling, leading to a three orders of magnitude reduction of wear rate compared with the untreated titanium alloy.

Several researchers also introduced duplex treatments that are composed of plasma nitriding and physical vapor deposition (PVD) or chemical vapor deposition (CVD) of nitride coatings. Rie et al. [106, 107] used plasma-assisted CVD (PACVD) technique to produce a thick TiN layer on top of plasma-nitrided substrates to enhance wear and corrosion resistance for biomedical applications. Their findings indicated that the duplex-treated surfaces were free of wear against ultrahigh-molecular-weight polyethylene under the tested conditions, and the corrosion resistance and biocompatibility of the untreated titanium alloy were preserved. Wear improvements were also confirmed by Ma et al. [108] through plasma nitriding and plasma-enhanced chemical vapor deposition (PCVD) of TiN coatings of Ti–6Al–4V substrates. They correlated the wear enhancement to higher surface hardness of PCVD coating and its strong adhesion to plasma-nitrided substrate. Other coatings, such as CrN, CrAlN, and WC/C, were also deposited on plasma-nitrided titanium alloys, in addition to TiN, by Cassar et al. [35, 91, 109]. Evaluation of the duplex-treated surfaces by impact tests, ball-on-disk wear tests, rotation bending fatigue tests, and microscratch tests revealed improvements in wear resistance, adhesion, and resistance to fatigue crack initiation. This was attributed to higher load support and adhesion strength offered by hard-coated surfaces and deeply strengthened substrates. It was noted that chromium aluminum nitride (CrAlN) coatings exhibited superior wear performance due to their high hardness and low elastic modulus (higher $H^3/E^2$ parameter).

### 6.2. Surface pretreatments

Alteration of the microstructure in the surface vicinity via thermochemical (e.g., laser-assisted treatments, electron beam melting, etc.) and mechanical (e.g., mechanical attrition, shot peening, etc.) pretreatment processes [27, 28] has been successfully used for increasing the nitriding efficiency of titanium alloys. Microstructural changes thus introduced, such as significant grain refinement and nonequilibrium defects, act as diffusion shortcuts and

enhance the nitriding kinetics and efficiency during the posterior plasma nitriding treatment even at low temperatures [110–115].

Shot peening, extensively used for fatigue improvement, is based on introducing compressive stresses in the surface layers via impingement of high-velocity shots, under controlled conditions. 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 addition to the development of a residual stress profile near the surface, shot peening results in surface roughening, strain hardening, and formation of a subsurface plastic deformation zone. Surface roughening favors early nucleation of fatigue cracks, whereas strain hardening and compressive residual stresses increase the resistance to plastic deformation and fatigue crack propagation by providing crack closure mechanism. Recently, improvements in the sliding wear behavior and tensile properties have been reported by shot peening due to its surface hardening effect [116].

Experimental studies showed that shot peening can introduce a severely deformed layer in the surface vicinity characterized by significant refinement of grains and generation of nonequilibrium defects [110–113]. The thickness of this severely deformed layer may 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 [117]. A high-energy shot peening treatment by Han et al. [27] resulted in the formation of a nanostructured layer on the surface of Ti–4Al–2V alloy. This treatment also introduced microstructural changes such as twinning and grain refinement that extended to ~230 μm below the surface. They proposed that the grain refinement occurs through various mechanisms such as "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. Mechanical twinning was recommended to have major contributions in grain refinement of Ti–4Al–2V alloy due to its HCP structure and high stacking fault energy (SFE > 300 mJ/m$^2$). 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 and Jackson [118] to understand the effect of temperature and alloy composition on the subsurface microstructure of shot-peened titanium alloys.

Alteration of surface microstructure by introducing high-diffusivity paths such as grain boundaries, dislocations, and atomic-level microstructural defects by shot peening can be used to accelerate the diffusion of interstitial atoms [112]. Thomas et al. [114, 115] reported that generation of a high density of twin boundaries and dislocations in the near-surface region of pure titanium and Ti–4Al–2V alloys after shot peening increased the oxygen uptake during the following thermal exposure in air. Moreover, the high stored energy associated with the higher density of these nonequilibrium defects increases chemical reactivity of surfaces and enhances the kinetics of surface reactions [113]. Several researchers have confirmed that

http://dx.doi.org/10.5772/61937

microstructural changes brought by severe plastic deformation (SPD) in ferrous alloys enhanced the nitrogen diffusion rate during the posterior nitriding treatments and increased the efficiency of nitriding at lower temperatures [110–113]. The effect of shot peening after diffusion treatments has also been studied in the literature. In a recent study, Bansal et al. [119] 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.

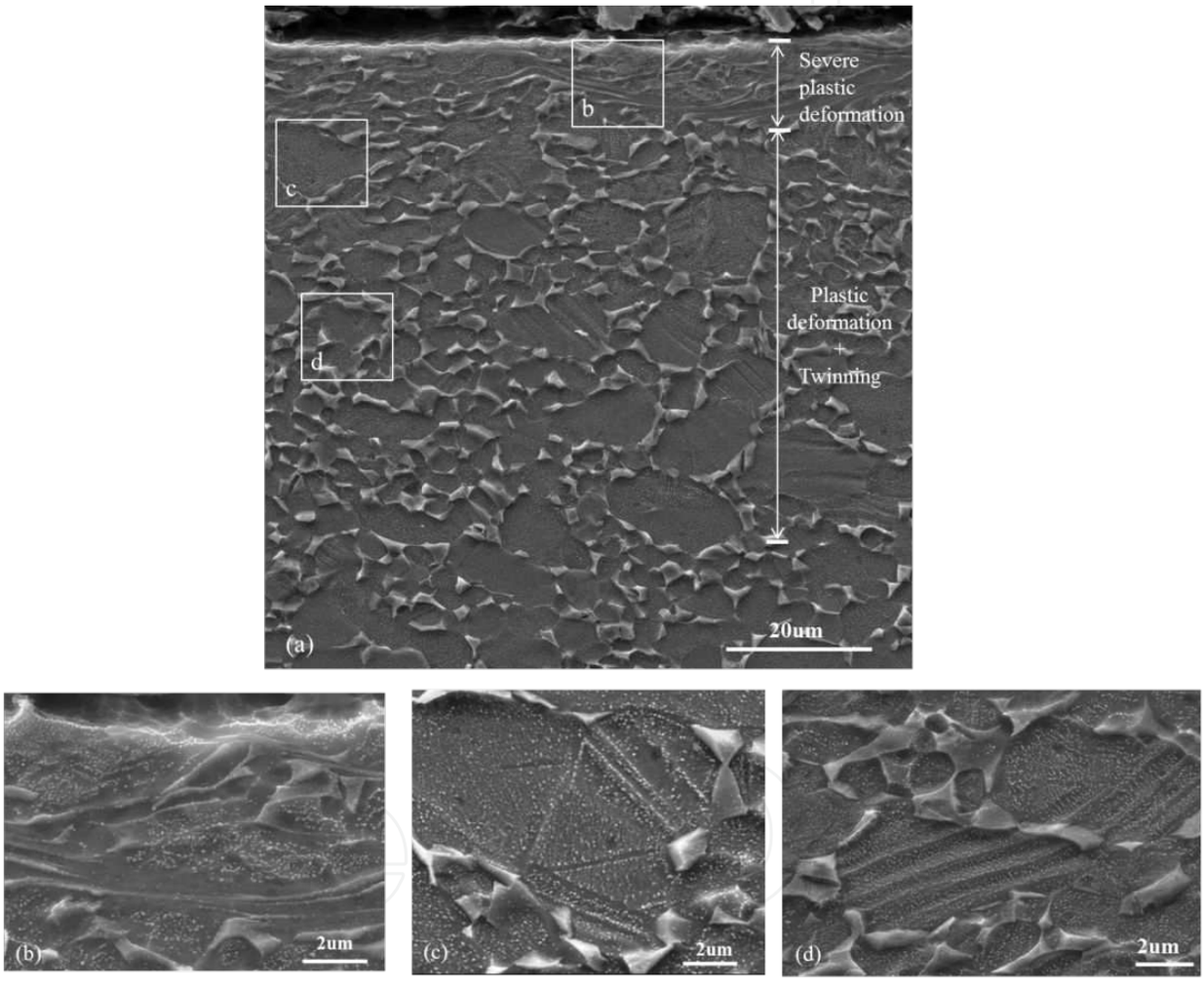



**Figure 18.** Typical cross-sectional SEM images showing the microstructure of Ti–6Al–4V after shot peening. A 5-μm deep severe plastic deformation (SPD) layer was formed on the surface characterized by elongation of intergranular β-particles parallel to the surface [28].

Severe plastic deformation surface layer introduced by shot peening pretreatment was found to enhance the plasma nitriding efficiency of Ti–6Al–4V alloy [28]. The high level of plastic strains induced by shot peening resulted in the formation of a 5-μm deep SPD layer on the surface characterized by twins, deformation bands, grain refinement, and a high density of

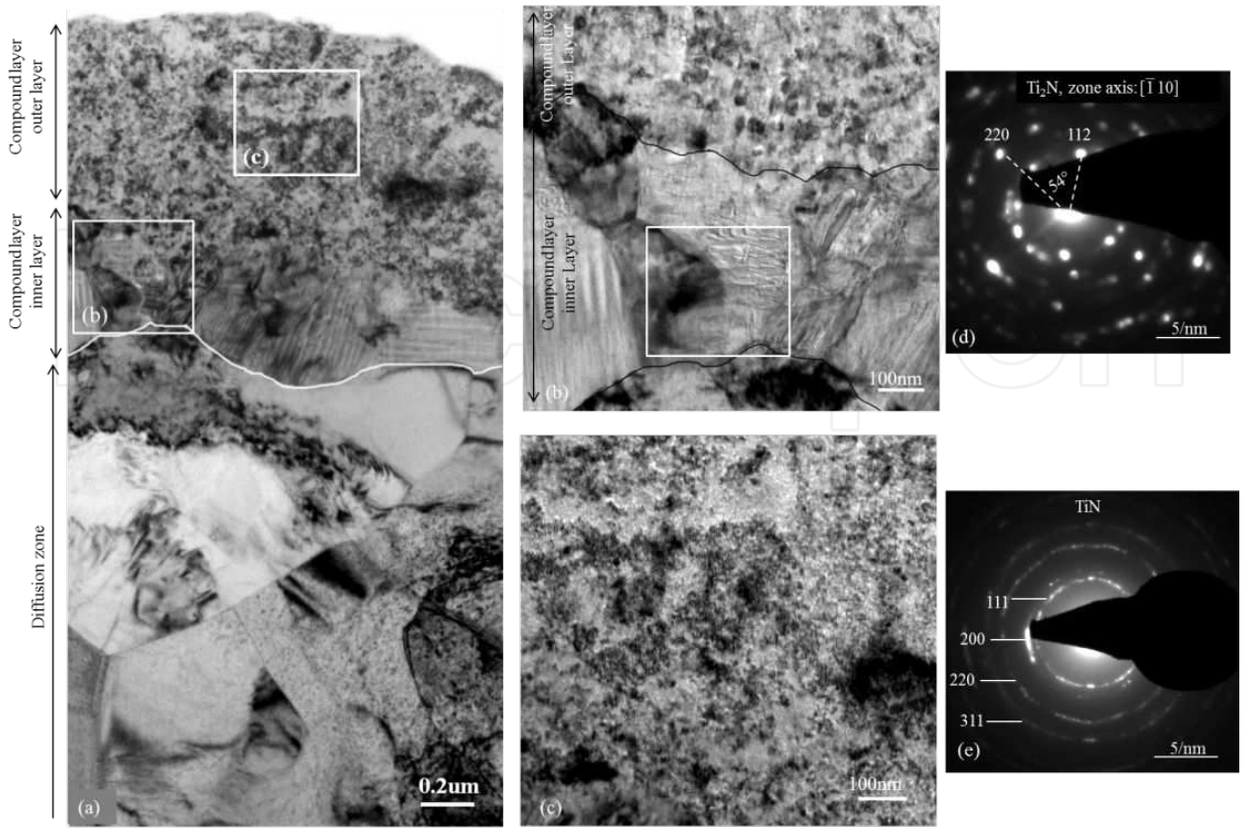



**Figure 19.** Typical cross-sectional bright-field TEM images of the near-surface microstructure of plasma-nitrided Ti–6Al–4V alloy with shot-peening pretreatment and the corresponding selected area electron diffraction (SAED) patterns [28].

nonequilibrium crystal defects such as subgrain boundaries and dislocation pile-ups (Figure 18 and Figure 19). This is in agreement with the 20% increase in the surface hardness value due to the work hardening of the SPD layer. The formation of the SPD layer resulted in accelerated nitriding kinetics during the plasma nitriding treatment that followed due to two main reasons: (i) grain boundaries, deformation bands, and twins provided easy diffusion paths for nitrogen interstitial atoms and (ii) high density of nonequilibrium crystal defects increased the stored energy of the surfaces and their chemical reactivity and offered additional preferential nucleation sites for titanium nitrides [111, 120]. The accelerated nitriding kinetics resulted in the formation of a 0.6-μm-thick nanocrystalline TiN layer in the compound layer (Figure 19) and increased the depth of nitrogen diffusion by almost 50% normally observed in high-temperature nitriding treatments (e.g., 900°C) [121]. As such, the plasma-nitrided surfaces that received the pretreatment step exhibited higher load-bearing capacity and better interfacial bonding compared with those without the pretreatment. The presence of nanoscale TiN grains increased the hardness and toughness of the compound layer and the compound layer endured high contact stresses for several sliding passes without chipping or spallation. In comparison, plasma-nitrided surfaces without the pretreatment experienced severe delamination and coating spallation after only two sliding passes in microscratch tests. The deep diffusion zone in the pretreated surfaces, strengthened by nitrogen interstitials, also

contributed to a well-bonded interface and diminished the incompatibility in plastic deformation of the compound layer ($E$ = 250–600 GPa [122, 123]) and substrate ($E$ = 110 GPa [124]) by providing a more homogenized stress distribution across the interface [30, 104, 125–127]. Thus, the shot-peening pretreatment improved the nitriding efficiency of low-temperature plasma nitriding without introducing detrimental microstructural changes in the substrate that would lead to sacrificing mechanical properties.

## 7. Summary

Plasma nitriding is a surface hardening treatment utilized to improve the tribological properties of titanium alloys by the formation of a compound layer mainly consisting of TiN and $Ti_2N$ titanium nitrides on the surface. However, plasma nitriding has a negative side effect on the mechanical properties of titanium alloys, especially fatigue strength, since the high temperatures involved in the treatment (700–1100°C) promote formation of brittle surface layers and detrimental microstructural changes in the bulk. Recent advancements in the field of plasma nitriding of titanium alloys are focused on the development of low-temperature (600°C or less) treatments as well as increasing the long-term durability of the nitrided surfaces through deposition of hard surface coatings such as diamond-like carbon and PVD/CVD nitride coatings. Furthermore, alteration of the surface microstructure by thermochemical and mechanical pretreatment steps is also successfully applied for increasing the nitriding efficiency during low-temperature plasma nitriding of titanium alloys.

## Acknowledgements

The authors acknowledge Exactatherm Ltd., Dr. P. Lidster, Mr. G. Pigott, and Mr. Simeon Simeonov, for their help in plasma nitriding. The appreciation is extended to Natural Science and Engineering Council of Canada (NSERC) Discovery Individual Grant Program for providing financial support and the Canadian Centre of Electron Microscopy (CCEM) for TEM experimental work.

## Author details

Afsaneh Edrisy* and Khorameh Farokhzadeh

*Address all correspondence to: edrisy@uwindsor.ca

Department of Mechanical, Automotive and Materials Engineering, University of Windsor, Windsor, ON, Canada

## References

[1] F. Preissner and P. Minarski, "Results on nitriding titanium and Ti6Al4V with a new thermochemical treatment under high gas pressure," in Titanium '92, Science and Technology, F. H. Froes and I. Caplan, editors, Cannes, France: The Mineral, Metals and Materials Society, 1993, pp. 1979–1987.

[2] V. M. Fedirko and I. M. Pohrelyuk, "Improvement of the wear resistance of titanium alloys by thermochemical treatment in nitrogen-containing media," Materials Science, vol. 30, pp. 66–71, 1994.

[3] A. Gicouel, N. Laidani, P. Saillard, and J. Amouroux, "Plasma and nitrides: Application to the nitriding of titanium," Pure Applied Chemistry, vol. 62, pp. 1743–1750, 1990.

[4] T. Spalvins, "Advances and directions of ion nitriding/carburizing," in Proceedings of ASM's 2nd International Conference on Ion nitriding and Ion Carburizing, T. Spalvins and W. L. Kovacs, editors, Cincinnati, OH, 18-20 September 1989, ASM International, pp. 1–4.

[5] T. Bacci, G. Pradelli, B. Tesi, C. Gianoglio, and C. Badini, "Surface engineering and chemical characterization in ion-nitrided titanium and titanium alloys," Journal of Materials Science, vol. 25, pp. 4309–4314, 1990.

[6] E. Rolinski, G. Sharp, D. F. Cowgill, and D. J. Peterman, "Ion nitriding of alpha plus beta alloy for fusion reactor applications," Journal of Nuclear Materials, vol. 252, pp. 200–208, 1998.

[7] K. C. Chen and G. J. Jaung, "D.C. diod ion nitriding behavior of titanium and Ti-6Al-4V," Thin Solid Films, vol. 303, pp. 226–231, 1997.

[8] H. Akbulut, O. T. Inal, and C. A. Zimmerly, "Ion nitriding of explosively-clad titanium/steel tandems," Journal of Materials Science, vol. 34, pp. 1641–1652, 1999.

[9] C. X. Li and T. Bell, "Principles, mechanisms and applications of active screen plasma nitriding," Heat Treatment of Metals, vol. 1, pp. 1–7, 2003.

[10] T. Bell, H. W. Bergmann, J. Lanagan, P. H. Morton, and A. M. Staines, "Surface engineering of titanium with nitrogen," Surface Engineering, vol. 2, pp. 133–143, 1986.

[11] R. Gunn, "Industrial advances for plasma nitriding," in Ion Nitriding and Ion Carburizing, Proceedings of ASM's 2nd International Conference on Ion Nitriding and Ion Carburizing, T. Spalvins and W. L. Kovacs, editors, Cincinnati, OH, 18-20 September 1989, ASM International, pp. 157–163.

[12] B. Edenhofer, "Physical and metallurgical aspects of ion nitriding," Heat Treatment of Metals, vol. 1, pp. 23–28, 1974.

[13] S. Dressler, "Plasma treatments," in Surface Modification Technologies: An Engineer's Guide, T. S. Sudarshan, editor, New York: Marcel Dekker, 1989, pp. 317–419.

[14] A. Raveh, P. L. Hansen, R. Avni, and A. Grill, "Microstructure and composition of plasma-nitrided Ti-6Al-4V layers," Surface and Coatings Technology, vol. 38, pp. 339–351, 1989.

[15] S. G. Lakshmi, D. Arivuoli, and B. Ganguli, "Surface modification and characterisation of Ti–Al–V alloys," Materials Chemistry and Physics, vol. 76, pp. 187–190, 2002.

[16] S. L. R. da Silva, L. O. Kerber, L. Amaral, and C. A. d. Santos, "X-ray diffraction measurements of plasma-nitrided Ti–6Al–4V," Surface and Coatings Technology, vol. 116–119, pp. 342–346, 1999.

[17] N. N. Koval, P. M. Schanin, Y. K. Akhmadeev, I. V. Lopatin, Y. R. Kolobov, D. S. Vershinin, and M. Yu. Smolyakova, "Influence of the composition of a plasma-forming gas on nitriding in a non-self-maintained glow discharge with a large hollow cathode," Journal of Surface Investigation: X-ray, Synchrotron and Neutron Techniques, vol. 6, pp. 154–158, 2012.

[18] M. Tamaki, Y. Tomii, and N. Yamamoto, "The role of hydrogen in plasma nitriding: Hydrogen behavior in the titanium nitride layer," Plasmas and Ions, vol. 3, pp. 33–39, 2000.

[19] X. Li, D. Q. Sun, X. Y. Zheng, and Z. A. Ren, "Effect of N2/Ar gas flow ratios on the nitrided layers by direct current arc discharge," Material Letters, vol. 62, pp. 226–229, 2008.

[20] H. Yilmazer, S. Yilmaz, and M. E. Acma, "Treatment of surface properties of titanium with plasma (ion) nitriding," Defect and Diffusion Forum, vol. 283–286, pp. 401–405, 2009.

[21] T. A. Panaioti and G. V. Solov'ev, "Ion nitriding of aging ($\alpha$+$\beta$) titanium alloys," Metal Science and Heat Treatment, vol. 38, pp. 216–219, 1996.

[22] H.-J. Spies, "Surface engineering of aluminum and titanium alloys: An overview," Surface Engineering, vol. 26, pp. 126–134, 2010.

[23] H.-J. Spies, B. Reinhold, and K. Wilsdorf, "Gas nitriding – Process control and nitriding non-ferrous alloys," Surface Engineering, vol. 17, pp. 41–54, 2001.

[24] S. Nishida and N. Hattori, "Fatigue strength of ion-nitrided Ti-6Al-4V alloy in high cycle region," Surface Treatment: Computer Methods and Experimental Measurements, vol. 17, pp. 199–208, 1997.

[25] J. Lanagan, P. H. Morton, and T. Bell, "Surface engineering of titanium with glow discharge plasma," in Designing with Titanium, London: Institute of Metals, 1986, pp. 136–147.

[26] K. Farokhzadeh and A. Edrisy, "Fatigue improvement in low temperature plasma nitrided Ti-6Al-4V alloy" Materials Science and Engineering A, vol. 620, pp. 435–444, 2014.

[27] J. Han, G. M. Sheng, and G. X. Hu, "Nanostructured surface layer of Ti–4Al–2V by means of high energy shot peening," ISIJ International, vol. 48, pp. 218–223, 2008.

[28] K. Farokhzadeh, J. Qian, and A. Edrisy, "Effect of SPD surface layer on plasma nitriding of Ti-6Al-4V alloy," Materials Science and Engineering A, vol. 589, pp. 199–208, 2014.

[29] H. Dong, T. Bell, and A. Mynott, "Surface engineering of titanium alloys for the motorsports industry," Sports Engineering, vol. 2, pp. 213–219, 1999.

[30] A. Bloyce, H. Dong, and T. Bell, "Design and performance of a titanium duplex surface engineering system," in Surface Performance of Titanium Alloys, J. K. Gregory, H. J. Rack, and D. Eylon, editors, Warrendale, PA: The Mineral, Metals & Materials Society (TMS), 1996, pp. 23–31.

[31] C. Kwietniewski, H. Dong, T. Strohaecker, X. Y. Li, and T. Bell, "Duplex surface treatment of high strength Ti metal 550 alloy towards high load-bearing capacity," Surface and Coatings Technology, vol. 139, pp. 284–292, 2001.

[32] Y. Fu, J. Wei, B. Yan, and N. L. Loh, "Characterization and tribological evaluation of duplex treatment by depositing carbon nitride films on plasma nitrided Ti-6Al-4V," Journal of Materials Science, vol. 35, pp. 2215–2227, 2000.

[33] B. S. Yilbas, M. S. J. Hashmi, and S. Z. Shuja, "Laser treatment and PVD TiN coating of Ti-6Al-4V alloy," Surface and Coatings Technology, vol. 140, pp. 244–250, 2001.

[34] H. Dong, A. Bloyce, and T. Bell, "Oxygen thermochemical treatment combined with DLC coating for enhanced load bearing capacity of Ti–6Al–4V," Surface Engineering, vol. 14, pp. 505–512, 1998.

[35] G. Cassar, S. Banfield, J. C. Avelar-Batista Wilson, J. Housden, A. Matthews, and A. Leyland, "Impact wear resistance of plasma diffusion treated and duplex treated/PVD-coated Ti–6Al–4V alloy," Surface and Coatings Technology, vol. 206, pp. 2645–2654, 2012.

[36] H. Dong, "Current status and trends in duplex surface engineering of titanium alloys," in Heat Treating: Proceedings of the 20th Conference – Volume 1, K. Funatani and G. E. Totten, editors, Materials Park, OH: ASM International, 2000, pp. 170–177.

[37] F. Schnabaum, "Materials selection and process control for plasma-diffusion treatment of PM materials," in ASM's 2nd International Conference on Ion Nitriding and Ion Carburizing, T. Spalvins and W. L. Kovacs, editors, Cincinnati, OH, 18-20 September 1989, ASM International, pp. 81–89.

[38] U. Huchel and S. Strämke "Pulsed plasma nitriding of titanium and titanium alloys," in Proceedings of the 10th World Conference on Titanium, Chichester: Wiley-VCH, 2003, pp. 935–939.

[39] M. Raaif, F. M. El-Hossary, N. Z. Negm, S. M. Khalil, and P. Schaaf, "Surface treatment of Ti–6Al–4V alloy by rf plasma nitriding," Journal of Physics: Condensed Matter, vol. 19, pp. 1–12, 2007.

[40] A. Brokman and F. R. Tuler, "A study of the mechanisms of ion nitriding by the application of a magnetic field," Journal of Applied Physics, vol. 52, pp. 468–471, 1981.

[41] E. Meletis, "Plasma nitrided titanium and titanium alloy products," United States Patent 5443663, 1995.

[42] E. I. Meletis, "Intensified plasma-assisted processing: Science and engineering," Surface and Coatings Technology, vol. 149, pp. 95–113, 2002.

[43] A. A. Adjaottor, "A study of the effect of energetic flux bombardment on intensified plasma-assisted processing," PhD dissertation, Louisiana State University, 1997.

[44] N. Kashaev, H.-R. Stock, and P. Mayr, "Nitriding of Ti-6%Al-4%V alloy in the plasma of an intensified glow discharge," Metal Science and Heat Treatment, vol. 46, pp. 294–298, 2004.

[45] N. Kashaev, H.-R. Stock, and P. Mayr, "Assessment of the application potential of the intensified glow discharge for industrial plasma nitriding of Ti-6Al-4V," Surface and Coatings Technology, vol. 200, pp. 502–506, 2005.

[46] T. Czerwiec, H. Michel, and E. Bergmann, "Low-pressure, high-density plasma nitriding: Mechanisms, technology and results," Surface and Coatings Technology, vol. 108–109, pp. 182–190, 1998.

[47] N. L. Loh, “Plasma Nitriding,” in Surface Engineering: Processes and Applications, K. N. Strafford, R. St. C. Smart, I. Sare, and C. Subramanian, editors, Pennsylvania: Technomic Publishing Company, Inc., 1995, pp. 157–178.

[48] C. Alves, O. F. de Araujo, and M. de Rômulo Ribeiro de Sousa, "Comparison of plasma-assisted nitriding techniques," in Encyclopedia of Tribology, Q. J. Wang and Y.-W. Chung, editors, New York: Springer, 2013, pp. 402–410.

[49] A. Grill, A. Raveh, and R. Avni, "Layer structures and mechanical properties of low pressure r. f. plasma nitrided Ti-6Al-4V alloy," Surface and Coatings Technology, vol. 43–44, pp. 745–755, 1990.

[50] A. Raveh, A. Bussiba, A. Bettelheim, and Y. Katz, "Plasma-nitrided $\alpha$-$\beta$ Ti alloy: Layer characterization and mechanical properties modification," Surface and Coatings Technology, vol. 57, pp. 19–29, 1993.

[51] K. Farokhzadeh, "Modification of Ion Nitriding of Ti-6Al-4V for Simultaneous Improvement of Wear and Fatigue Properties," PhD dissertation, Department of Me-

chanical, Automotive and Materials Engineering, University of Windsor, Windsor, ON, Canada, 2014.

[52] J. Qian, K. Farokhzadeh, and A. Edrisy, "Ion nitriding of a near-β titanium alloy: Microstructure and mechanical properties," Surface and Coatings Technology, vol. 258, pp. 134–141, 2014.

[53] J. Tiley, T. Searles, E. Lee, S. Kar, R. Banerjee, J. C. Russ, and H. L Fraser, "Quantification of microstructural features in $\alpha/\beta$ titanium alloys," Materials Science and Engineering A, vol. 372, pp. 191–198, 2004.

[54] A. Raveh, P. L. Hansen, R. Avni, and A. Grill, "Microstructure and composition of plasma-nitrided Ti-6Al-4V layers," Surface and Coatings Technology, vol. 38, pp. 339–351, 1989.

[55] A. Molinari, G. Straffelini, B. Tesi, T. Bacci, and G. Pradelli, "Effects of load and sliding speed on the tribological behaviour of Ti-6Al-4V plasma nitrided at different temperatures," Wear, vol. 203–204, pp. 447–454, 1997.

[56] H. A. Wriedt and J. L. Murray, "The N-Ti (nitrogen-titanium) system," Bulletin of Alloy Phase Diagrams, vol. 8, pp. 378–388, 1987.

[57] A. Nishimoto, T. E. Bell, and T. Bell, "Feasibility study of active screen plasma nitriding of titanium alloy," Surface Engineering, vol. 26, pp. 74–79, 2010.

[58] A. Fleszar, T. Wierzchon, S. K. Kim, and J. R. Sobiecki, "Properties of surface layers produced on the Ti-6Al-3Mo-2Cr titanium alloy under glow discharge conditions," Surface and Coatings Technology, vol. 131, pp. 62–65, 2000.

[59] A. A. Il'in, S. V. Skvortsova, L. M. Petrov, E. A. Lukina, and A. A. Chernysheva, "Effect of phase composition and structure of titanium alloys on their interaction with nitrogen during low-temperature ion nitriding," Russian Metallurgy, vol. 2006, pp. 400–405, 2006.

[60] R. J. Wasilewski and I. Kehl, "Diffusion of nitrogen and oxygen in titanium," Journal of the Institue of Metals, vol. 55, pp. 94–104, 1954.

[61] Z. Liu and G. Welsch, "Literature survey on diffusivities of oxygen, aluminum, and vanadium in alpha titanium, beta titanium, and in rutile," Metallurgical Transactions A, vol. 19A, pp. 1121–1125, 1988.

[62] F. Yildiz, A. F. Yetim, A. Alsaran, and A. Çelik, "Plasma nitriding behavior of Ti6Al4V orthopedic alloy," Surface and Coatings Technology, vol. 202, pp. 2471–2476, 2008.

[63] K. Farokhzadeh, A. Edrisy, G. Pigott, and P. Lidster, "Scratch resistance analysis of plasma-nitrided Ti–6Al–4V alloy," Wear, vol. 302, pp. 845–853, 2013.

[64] R. Wirth, "Focused Ion Beam (FIB) combined with SEM and TEM: Advanced analytical tools for studies of chemical composition, microstructure and crystal structure in geomaterials on a nanometre scale," Chemical Geology, vol. 261, pp. 217–229, 2009.

[65] W. C. Oliver and G. M. Pharr, "Measurement of hardness and elastic modulus by instrumented indentation: Advances in understanding and refinements to methodology," Journal of Materials Research, vol. 19, pp. 3–20, 2004.

[66] G. Straffelini, A. Andriani, B. Tesi, A. Molinari, and E. Galvanetto, "Lubricated rolling-sliding behaviour of ion nitrided and untreated Ti-6Al-4V," Wear, vol. 256, pp. 346–352, 2004.

[67] G. Straffelini and A. Molinari, "Dry sliding wear of Ti-6Al-4V alloy as influenced by the counterface and sliding conditions," Wear, vol. 236, pp. 328–338, 1999.

[68] H. Hong and W. O. Winer, "A fundamental tribological study of Ti/Al2O3 contact in sliding wear," Journal of Tribology, vol. 111, pp. 504–509, 1989.

[69] J. A. Ruppen, C. L. Hoffmann, V. M. Radhakrishnan, and A. J. McEvily, "The effect of environment and temperature on the fatigue behavior of titanium alloys," in Fatigue, Environment and Temperature Effects, J. J. Burke and V. Weiss, editors, New York: Springer, pp. 265-300, 1930.

[70] P. D. Nicolaou, E. B. Shell, and T. E. Matikas, "Microstructural and surface characterization of Ti-6Al-4V alloys after fretting fatigue," Materials Science and Engineering, vol. A269, pp. 98–103, 1999.

[71] J. Takeda, M. Niinomi, T. Akahori, and Gunawarman, "Effect of microstructure on fretting fatigue and sliding wear of highly workable titanium alloy, Ti-4.5Al-3V-2Mo-2Fe," International Journal of Fatigue, vol. 26, pp. 1003–1015, 2004.

[72] P. D. Miller and J. W. Holladay, "Friction and wear properties of titanium," Wear, vol. 2, pp. 133–140, 1958.

[73] H. Dong and T. Bell, "Tribological behavior of alumina sliding against Ti6Al4V in unlubricated contact," Wear, vol. 225–229, pp. 874–884, 1999.

[74] M. O. Alam and A. S. M. A. Haseeb, "Response of Ti-6Al-4V and Ti-24Al-11Nb alloys to dry sliding wear against hardened steel," Tribology International, vol. 35, pp. 357–362, 2002.

[75] J. Qu, P. J. Blau, T. R. Watkins, O. B. Cavin, and N. S. Kulkarni, "Friction and wear of titanium alloys sliding against metal, polymer, and ceramic counterfaces," Wear, vol. 258, pp. 1348–1356, 2005.

[76] S. Yerramareddy and S. Bahadur, "Effect of operational variables, microstructure and mechanical properties on the erosion of Ti-6Al-4V," Wear, vol. 142, pp. 253–263, 1992.

[77] K. G. Budinski, "Tribologial properties of titanium alloys," Wear, vol. 151, pp. 203–217, 1991.

[78] C. Feng and T. I. Khan, "The effect of quenching medium on the wear behaviour of a Ti-6Al-4V alloy," Journal of Materials Science, vol. 43 (2), pp. 788–792, 2008.

[79] S. Taktak and H. Akbulut, "Dry wear and friction behavior of plasma nitrided Ti-6Al-4V alloy after explosive shock treatment," Tribology International, vol. 40, pp. 423–432, 2007.

[80] D. P. Shashkov, "Effect of nitriding on mechanical properties and wear resistance of titanium alloys," Metal Science and Heat Treatment, vol. 43, pp. 233–237, 2001.

[81] B. S. Yilbaş, A. Z. Şahin, A. Z. Al-Garni, S. A. M. Said, Z. Ahmed, B. J. Abdulaleem and M. Sami, "Plasma nitriding of Ti-6Al-4V alloy to improve some tribological properties," Surface and Coatings Technology, vol. 80, pp. 287–292, 1996.

[82] D. Nolan, S. W. Huang, V. Leskovsek, and S. Braun, "Sliding wear of titanium nitride thin films deposited on Ti–6Al–4V alloy by PVD and plasma nitriding processes," Surface and Coatings Technology, vol. 200, pp. 5698–5705, 2006.

[83] G. Cassar, J. C. A.-B. Wilson, S. Banfield, J. Housden, A. Matthews, and A. Leyland, "A study of the reciprocating-sliding wear performance of plasma surface treated titanium alloy," Wear, vol. 269, pp. 60–70, 2010.

[84] ASTM C1624, "Standard test method for adhesion strength and mechanical failure modes of ceramic coatings by quantitative single point scratch testing," ASTM International, 2005.

[85] M. Salehi, T. Bell, and P. H. Morton, "Effect of surface topography on tribo-oxidation of titanium nitrided surfaces," Journal of Physics D: Applied Physics, vol. 25, pp. 889–895, 1992.

[86] P. A. Dearnley, T. Bell, and F. Hombeck, "Crafting the surface with glow discharge plasmas," in Surface Engineering: Processes and Applications, K. N. Strafford, R. St. C. Smart, I. Sare, and C. Subramanian, editors, Pennsylvania: Technomic Publishing Company, Inc., 1995, pp. 21–47.

[87] M. Y. P. Costa, M. L. R. Venditti, M. O. H. Cioffi, H. J. C. Voorwald, V. A. Guimarães, and R. Ruas, "Fatigue behavior of PVD coated Ti–6Al–4V alloy," International Journal of Fatigue, vol. 33, pp. 759–765, 2011.

[88] M. M. Ali and S. G. S. Raman, "Effect of plasma nitriding environment and time on plain fatigue and fretting fatigue behavior of Ti–6Al–4V," Tribology Letters, vol. 38 pp. 291–299, 2010.

[89] A. Bloyce, P. H. Morton, and T. Bell, "Surface engineering of titanium and titanium alloys," in Metals Handbook, vol. 5, Metals Park, Ohio: American Society for Metals, 1994, pp. 835–851.

[90] T. Morita, H. Takahashi, M. Shimizu, and K. Kawasaki, "Factors controlling the fatigue strength of nitrided titanium," Fatigue and Fracture of Engineering Materials, vol. 20, pp. 85–92, 1997.

[91] G. Cassar, J. C. Avelar-Batista Wilson, S. Banfield, J. Housden, M. Fenech, A. Matthews, and A. Leyland, "Evaluating the effects of plasma diffusion processing and duplex diffusion/PVD-coating on the fatigue performance of Ti–6Al–4V alloy," International Journal of Fatigue, vol. 33, pp. 1313–1323, 2011.

[92] K. Tokaji, T. Ogawa, and H. Shibata, "The effects of gas nitriding on fatigue behavior in titanium and titanium alloys," Journal of Materials Engineering and Performance, vol. 8, pp. 159–167, 1999.

[93] D. Rodriguez, J. M. Manero, F. J. Gil, and J. A. Panell, "Low cycle fatigue behavior of Ti6Al4V thermochemically nitrided for its use in hip prostheses," Journal of Materials Science, vol. 12, pp. 935–937, 2001.

[94] P. Guiraldenq, B. Haenggi, B. Cerati, and F. Gaillard, "Fretting wear and fatigue (in air and sea water) of Ti6Al4V alloy with different surface treatments," in Surface Modification Technologies VIII, T. S. Sudarshan and M. Jeandin, editors, London, UK: The Institute of Materials, 1995, pp. 17–27.

[95] T. W. J. R. Sobiecki, and J. Rudnicki, "The influence of glow discharge nitriding, oxynitriding and carbonitriding on surface modification of Ti–1Al–1Mn titanium alloy," Vacuum, vol. 64, pp. 41–46, 2002.

[96] B. Rajasekaran and S. G. S. Raman, "Plain fatigue and fretting fatigue behaviour of plasma nitrided Ti-6Al-4V," Materials Letters, vol. 62, pp. 2473–2475, 2008.

[97] ASTM E8/E8M-11, "Standard Test Methods for Tension Testing of Metallic Materials," ASTM International, 2011.

[98] T. Akahori, M. Niinomi, K. Fukunaga, and I. Inagaki, "Effects of microstructure on the short fatigue crack initiation and propagation characteristics of biomedical $\alpha/\beta$ titanium alloys," Metallurgical and Materials Transactions A, vol. 31A, pp. 1949–1958, 2000.

[99] B. F. Chen, J. Hwang, G. P. Yu, and J. H. Huang, "In situ observation of the cracking behavior of TiN coating on 304 stainless steel subjected to tensile strain," Thin Solid Films, vol. 352, pp. 173–178, 1999.

[100] D. Novovic, R. C. Dewes, D. K. Aspinwall, W. Voice, and P. Bowen, "The effect of machined topography and integrity on fatigue life," International Journal of Machine Tools and Manufacture, vol. 44, pp. 125–134, 2004.

[101] J. C. A. Batista, A. Matthews, and C. Godoy, "Micro-abrasive wear of PVD duplex and single-layered coatings," Surface and Coatings Technology, vol. 142–144, pp. 1137–1143, 2001.

[102] T. Bell, H. Dong, and Y. Sun, "Realising the potential of duplex surface engineering," Tribology International, vol. 31, pp. 127–137, 1998.

[103] E. I. Meletis, A. Erdemir, and G. R. Fenske, "Tribological characteristics of DLC films and duplex plasma nitriding/DLC coating treatments," Surface and Coatings Technology, vol. 73, pp. 39–45, 1995.

[104] H. Dong and T. Bell, "Designer surfaces for titanium components," Anti-Corrosion Methods and Materials, vol. 46, pp. 338–345, 1999.

[105] Z. X. Zhang, H. Dong, T. Bell, and B. S. Xu, "The effect of deep-case oxygen hardening on the tribological behaviour of a-C:H DLC coatings on Ti6Al4V alloy," Journal of Alloys and Compounds, vol. 464, pp. 519–525, 2008.

[106] K.-T. Rie and E. Broszeit, "Plasma diffusion treatment and duplex treatment – recent development and new applications," Surface and Coatings Technology, vol. 76–77, pp. 425–436, 1999.

[107] K.-T. Rie, T. Stucky, R. A. Silva, E. Leitao, K. Bordji, J. Y.-. Jouzeau, et al., "Plasma surface treatment and PACVD on Ti alloys for surgical implants," Surface and Coatings Technology, vol. 74–75, pp. 973–980, 1995.

[108] S. Ma, K. Xu, and W. Jie, "Wear behavior of the surface of Ti–6Al–4V alloy modified by treating with a pulsed d.c. plasma-duplex process," Surface and Coatings Technology, vol. 185, pp. 205–209, 2004.

[109] G. Cassar, S. Banfield, J. C. Avelar-Batista Wilson, J. Housden, A. Matthews, and A. Leyland, "Tribological properties of duplex plasma oxidised, nitrided and PVD coated Ti–6Al–4V," Surface and Coatings Technology, vol. 206, pp. 395–404, 2011.

[110] L. Shen, L. Wang, Y. Wang, and C. Wang, "Plasma nitriding of AISI 304 austenitic stainless steel with pre-shot peening," Surface and Coatings Technology, vol. 204, pp. 3222–3227, 2010.

[111] 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 mechanical attrition treatment," Surface and Coatings Technology, vol. 202, pp. 4957–4963, 2008.

[112] J. F. Gu, D. H. Bei, J. S. Pan, J. Lu, and K. Lu, "Improved nitrogen transport in surface nanocrystallized low-carbon steels during gaseous nitridation," Materials Letter, vol. 55, pp. 340–343, 2002.

[113] W. P. Tong, N. R. Tao, Z. B. Wang, J. Lu, and J. L. K. Lu, "Nitriding iron at lower temperatures," Science, vol. 299, pp. 686–688, 2003.

[114] M. Thomas, T. Lindley, D. Rugg, and M. Jackson, "The effect of shot peening on the microstructure and properties of near-alpha titanium alloy following high temperature exposure," Acta Materialia, vol. 60, pp. 5040–5048, 2012.

[115] M. Thomas, T. Lindley, and M. Jackson, "The microstructural response of a peened near-a titanium alloy to thermal exposure," Scripta Materialia, vol. 60, pp. 108–111, 2009.

[116] B. K. C. Ganesh, W. Sha, N. Ramanaiah, and A. Krishnaiah, "Effect of shot peening on sliding wear and tensile behavior of titanium implant alloys," Materials and Design, vol. 56, pp. 480–486, 2014.

[117] F. Appel, "Atomic level observations of mechanical damage in shot peened TiAl," Philosophical Magazine, vol. 93, pp. 2–21, 2013.

[118] M. Thomas and M. Jackson, "The role of temperature and alloy chemistry on subsurface deformation mechanisms during shot peening of titanium alloys," Scripta Materialia, vol. 66, pp. 1065–1068, 2012.

[119] D. G. Bansal, M. Kirkham, and P. J. Blau, "Effects of combined diffusion treatments and cold working on the sliding friction and wear behavior of Ti–6Al–4V," Wear, vol. 302, pp. 837–844, 2013.

[120] S. Hogmark, S. Jacobson, and M. Larsson, "Design and evaluation of tribological coatings," wear, vol. 246, pp. 20–33, 2000.

[121] A. Czyrska-Filemonowicz, P. A. Buffat, M. Lucki, T. Moskalweicz, W. Rakowski, J. Lekki, et al., "Transmission electron microscopy and atomic force microscopy characterization of titanium-base alloys nitrided under glow discharge," Acta Materialia, vol. 53, pp. 4367–4377, 2005.

[122] E. Torok, A. J. Perry, L. Chollet, and W. D. Sproul, "Young's modulus of TiN, TiC, ZrN and HfN," Thin Solid Films, vol. 153, pp. 37-43, 1987.

[123] W. Ziaja, "Finite element modelling of the fracture behaviour of surface treated Ti-6Al-4V alloy," Computational Materials Science and Surface Engineering, vol. 1, pp. 53–60, 2009.

[124] V. Fouquet, L. Pichon, M. Drouet, and A. Straboni, "Plasma assisted nitridation of Ti-6Al-4V," Applied Surface Science, vol. 221, pp. 248–258, 2004.

[125] C. X. Li, D. Horspool, and H. Dong, "Effect of ceramic conversion surface treatment on fatigue properties of Ti6Al4V alloy," International Journal of Fatigue, vol. 29, pp. 2273–2280, 2007.

[126] H. Dong, A. Bloyce, and T. Bell, "Design and the performance of a new titanium duplex surface engineering system," presented at the Symposium on Surface Performance of Titanium, Cincinnati, OH, 7-9 October 1996.

[127] A. D. Wilson, A. Leyland, and A. Matthews, "A comparative study of the influence of plasma treatments, PVD coatings and ion implantation on the tribological performance of Ti-6Al-4V," Surface and Coatings Technology, vol. 114, pp. 70–80, 1999.

IntechOpen

IntechOpen