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Preparation of Nitrided Titanium Alloys using Bipolar-Pulse Plasma

for Doctor of Philosophy (Physics)

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The examining committee has unanimously approved this Thesis, submitted by Miss Suninad Kaewnisai, as a partial fulfillment of the requirements for the Doctor of Philosophy Physics at Mahasarakham University



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ABSTRACT

In this study, the Ti-6Al-4V alloy, widely employed in biomedical implant applications, underwent plasma nitriding treatment. One investigation focused on varying the frequency of the power supply in bipolar pulse plasma, while the other examined the effect of the H_2/N_2 gas ratio on the surface properties of plasma-nitrided Ti-6Al-4V alloy. The nitriding process utilized an N_2 - H_2 plasma, with hydrogen flow rates ranging from 100 (duty cycle of 20%) to 500 sccm at a duty cycle of 10%, and a nitriding temperature of 650±5 °C for 4 hours. Bipolar pulse frequencies ranged from 25 to 200 kHz. Samples subjected to a 20% duty cycle exhibited a matte surface, possibly due to disparities in ion bombardment energy levels. Grazing incidence X-ray diffraction spectrometry (GI-XRD) analysis revealed the presence of δ -TiN and ϵ -Ti₂N phases in all nitrided samples, with increased ε -Ti₂N formation observed at a 20% duty cycle. Results indicated a surface hardness approximately three times greater than that of the unnitrided sample, with maximum hardness observed in samples subjected to a 20% duty cycle. Glow discharge emission spectroscopy (GD-OES) confirmed higher surface nitrogen content in samples with a 20% duty cycle, suggesting deeper nitrogen penetration. Post-plasma nitriding, surface roughness slightly increased, particularly under the 20% duty cycle condition, resulting in elevated water contact angles and reduced work of adhesion. The specific wear rate of all nitrided samples decreased, notably at a bipolar pulse frequency of 50 kHz, aligning with stable coefficients of friction after 6000 sliding cycles. Additionally, samples nitrided at 50 kHz exhibited the lowest corrosion current density in artificial saliva, as determined by the Tafel potential polarization method.

Keyword : Low temperature plasma nitriding, Bipolar-pulsed frequency, Ti-6Al-4V alloy, Surface properties, Corrosion resistance, Wear resistance

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CHAPTER I

Introduction

1.1 Rationale and background

Nowadays, medical technology has made rapid progress so that human life has become longer and the quality of human life has also become more important. One of the medical technologies is the use of biomaterials to replace organs in the human body or to restore and improve the internal organs of the body. Currently, there are various types of medical materials and devices that can be used as implants in the human body for both dental and medical applications, such as dental implants, small orthodontic screws, orthodontic screws, artificial bone, etc. When selecting the metal to be used for manufacturing implants, it is necessary to consider properties that are favorable for the function of the parts, such as hardness, stiffness, flexibility, elongation, tarnish resistance, unit weight, casting properties, as well as cost factors [1].

There are many types of implant metals, including grade 4 gold alloys, cobaltchromium alloys, nickel-chromium alloys, stainless steel, and titanium alloys. Currently, pure titanium and titanium alloys are used to make dental frameworks because it has good properties such as high strength, light weight, and high corrosion resistance. The most popular titanium alloy in dentistry is Ti-6Al-4V, it consists of 90 wt.% Ti, 6 wt.% Al and 4 wt.% V [2]. At room temperature, there are two phases: α phase and β -phase, also known as α + β -Ti alloy. The added aluminum stabilizes the α phase and gives the metal higher strength and lower weight, while the vanadium stabilizes the β -phase at room temperature. It has the potential to be used in dentistry, and the use of this alloy has been shown to be biologically acceptable [3]. However, titanium parts have some limitations, such as permanent deformation, discoloration of the titanium surface, and the problem of tribological properties of titanium metal [4], [5]. In addition, this alloy releases both aluminium and vanadium, both of which can cause biological problems [3], [6]. Aluminium affects bone mineralization [7], leading to structural deficiencies, and vanadium is both cytotoxic and capable of causing IV type allergic reactions [8]. Therefore, surface engineering methods have been improved to increase the wear resistance of titanium alloys, such as salt bath treatment [9], [10], gas nitriding [11], [12] and plasma nitriding [13]–[17].

In a typical plasma nitriding process, an external voltage is used to ionize the nitriding gas and provide an active nitrogen flux for surface modification between the nitriding furnace (anode) and the workpiece (cathode) [4], [5]. In addition to the power supply from DC and AC, the plasma can also be generated by radio frequency (RF) excitation [5], [18]. When the applied voltage is provided by a DC power supply, the continuous voltage supply can cause localized heating, overheating of thin sections, arcing, and other surface damage. These problems can be avoided by using a bipolar pulsed DC power supply in which the heat input is controlled by duty cycles and frequency. A duty cycle is defined as the ratio of the pulse on-time to a full on-off cycle time [19] and is typically on the order of 10-50% of the period without disturbing the nitriding time [20]. Bipolar pulse discharges with sufficiently low duty cycles can be used for such low-temperature processes, especially when arcing at the edge shape of the sample must be avoided. Discharges generated by various short-pulse waveforms have found applications in plasma nitriding through the generation of reactive species at ambient pressure and temperature [21]. Plasma nitriding improves the tribological properties of titanium alloys by forming a thin surface compound layer consisting mainly of TiN and Ti₂N. The microstructure of the nitride layer also consists of a region α -case (nitrogen-stabilized α -titanium) and a diffusion layer. This results in increased surface hardness and better tribological and fatigue properties [22]-[26]. The parameters of plasma nitriding have a significant effect on the microstructure, such as the duration time, temperature, pressure, and gas ratio. Plasma nitriding of titanium alloys is usually performed at temperatures between 700 and 1100 °C [27]-[29] for 6 to 80 hours in an environment containing nitrogen (N₂, N₂-Ar, N₂-H₂, or N₂-NH₃) [30]-[34]. The high temperatures in the nitriding process lead to grain growth, overaging, and microstructural transformations in titanium substrates that reduce fatigue, strength, and ductility [34]-[36]. In addition, the significant stiffness differences between the compound layer and the titanium substrate, as well as the brittleness of the compound

layer and α -case, lead to early failure originating from the surface. For this reason, lowtemperature plasma nitriding is used to improve the mechanical properties of titanium alloys. [35], [37], [38]. The slow nitriding kinetics of titanium alloys at low temperatures can be enhanced by surface treatment (plasma cleaning) before the nitriding process [39], [40]. This deepens the nitrogen diffusion and increases the loadbearing capacity of the plasma-nitrided surfaces [41].

The aim of this study is to investigate the plasma parameters used in the nitriding process, including H_2/N_2 ratio, temperature, time, and bipolar pulse frequency which can improve the mechanical, wear and corrosion resistance of Ti-6Al-4V alloys. The expected outcome of this research should be useful for dental applications.

1.2 Objectives of the study

- 1.1.1 Investigate plasma parameters used in the nitriding process, including H_2/N_2 ratio and bipolar pulse frequency.
- 1.1.2 Improvement of mechanical properties and wear resistance of Ti-6Al-4V alloys by plasma nitriding.
- 1.1.3 Investigate the corrosion behavior of Ti-6Al-4V alloys in artificial saliva.

1.3 Scope and limitations of the study

The scope of research for Ti-6Al-4V alloy parts is listed below. This work focuses on the fabrication of nitrided titanium alloys by bipolar pulse plasma using the following important parameters.

- 1. Bipolar pulse frequency is varied in the range of 25, 50, 100, 150, and 200 kHz, respectively with a duty cycle of 10%.
- Hydrogen content (%H₂/N₂) is varied in the range of 10, 20, 30, 40, and 50%, respectively, hydrogen content of 10% using a duty cycle of 20% and hydrogen content of 20, 30, 40, and 50% using a duty cycle of 10%.

All conditions mentioned above are operated under the same pressure of about 3-5 Torr, the nitriding temperature of 650±5 °C, and the nitriding time of 4 hours. After plasma nitriding, the samples are investigated with the parameter below.

- The depth of nitrogen diffusion into the surface of the Ti-6Al-4V alloy.
- Mechanical properties and corrosion resistance of nitrided Ti-6Al-4V alloy.

In this work, nitrided samples are characterized using the following techniques.

- Environmental scanning electron microscopy (ESEM) is used to study the morphology and cross-section of the samples before and after plasma nitriding.
- Glow discharge optical emission spectroscopy (GD-OES) is used to analyze the elemental composition of surface samples after plasma nitriding.
- Atomic force microscope (AFM) is used to study the roughness and morphology of the samples before and after plasma nitriding.
- Grazing incidence X-ray diffraction spectrometer (GI-XRD) is used to investigate the structural properties of the samples after plasma nitriding.Contact angle measurement using a static sessile drop method was used to estimate the work of adhesion.
- Nanoindentation technique is used to study the hardness value corresponding to the depth, based on an enhanced stiffness procedure (ESP) of the samples after nitriding.
 - Ball-on-disk test is used to study the coefficient of friction (CoF) and wear resistance the samples after nitriding.

- Potentiodynamic polarization based on a three-electrode system in artificial saliva is used to compare the corrosion resistance of the samples after nitriding.

1.4 Location of research conduction

Technological Plasma Research Unit, Department of Physics, Faculty of Science, Mahasarakham University, Mahasarakham, 44150, Thailand.

1.5 Anticipated outcomes

The plasma nitriding titanium alloys prepared at the Technological Plasma Research Unit (Department of Physics, Faculty of Science, Mahasarakham University) are expected to be useful in clinical dentistry as new Ti alloys with high corrosion resistance and mechanical strength.



CHAPTER II

Literature reviews and theoretical background

This chapter is divided into four sections as following. In the first section, plasma nitriding on the titanium alloys was reviewed. The classification of titanium alloys and its structure were described in the second section. In the third section, the theoretical background and mechanism of plasma nitriding were given in more detail. The last section gives an explanation of the microstructure, mechanical, tribological, and corrosion properties of plasma-nitrided titanium alloys.

2.1 Literature reviews

Titanium and its alloys have been used by in medical industry since the end of the 20th century due to their high specific strength and good corrosion resistance [42], [43]. Pure titanium is lightweight and has a high modulus of elasticity. However, the strength of pure titanium still is relatively low. Therefore, titanium alloys that have higher mechanical properties than pure titanium are used in dentistry [44]. They are formed by mixing of pure titanium with certain elements in certain proportions. There are many types of titanium alloys, depending on the alloying elements. The production of titanium alloys aims to increase strength and creep resistance and improve thermal properties [1]. The most popular titanium alloy in the biomedical industry is Ti-6AI-4V because this alloy has low density, high strength, light weight, high corrosion resistance, and biocompatibility [20], [45], [46]. However, the disadvantage of titanium alloys is poor tribological behavior and wear resistance due to low hardness [20], [45], [47]. Therefore, a way has been found to treat the surface to improve the tribological and mechanical properties, such as surface coating and so on, diamond-like carbon (DLC) coating [48]–[51] and metal carbide PVD/CVD metallic films coating [48], [52]–[55], acid and alkali treatment to improve biocompatibility [17], hydrogen peroxide treatment to enhance dense inner oxide layer [56]-[58], anodic oxidation

treatment to increase the thickness of TiO₂ [48], [59]–[62]. However, there are still concerns about factors such as adhesion and suitability for applications where thermal degradation may occur [48]. Therefore, there is an application of surface engineering is the production of a hard layer on the surface of the material. One of these methods is nitriding, which is widely used in industry. The basis of this method is the diffusion of atomic nitrogen into the surface of the material. [63], [64]. Many techniques can be used to nitride materials. The most commonly used technique is gas nitriding. This involves placing the sample in a furnace, to which ammonia (NH₃) is then added as a starting gas. This process typically uses a high nitriding temperature, which decreases the fatigue strength of the nitrided sample compared to that of non-nitrided [37] and decreases the core hardness of the workpiece [64]–[66]. Another nitriding method is liquid nitriding, in which surfaces are hardened by chemical heat treatment with cyanide solutions [9], [10]. Cyanide baths require aging and special mixtures, they yield greater case depths and consume less thermal energy than gas nitriding. However, cyanide baths are toxic and harmful to the environment and nature [67], [68]. To solve the problem of gas and liquid nitriding, the plasma-assisted thermochemical case hardening technique is used. This technique is called "plasma nitriding" and imparts a hard, wearresistant surface without embrittlement, abrasion, or spalling. This eliminates the need for costly cleaning or grinding to remove the brittle white layer that results from gas and salt bath nitriding.

Plasma nitriding is suitable for all ferrous materials, including sintered steels with higher porosity, cast irons and high-alloy tool steels even with chromium contents above 12%. Stainless steels and nickel-based alloys can be plasma nitrided and retain most of their corrosion resistance when low temperatures are applied. Special applications are plasma nitriding of titanium and aluminium alloys. When large machine parts such as shafts and spindles are subjected to high loads, the use of nitriding steels is of great advantage, as plasma nitriding achieves higher surface hardness and preserves the core properties of the material due to the lower processing temperatures (480-510 °C). In addition, plasma nitriding allows control the microstructure of the treated workpiece, phase and chemical composition, surface topography, morphology, and residual stresses [69], all of which are critical for determining surface properties,

especially if the workpiece is to be used as a part in the human body. In a typical plasma nitriding process, an external voltage is used to ionize the nitriding gas and provide an active nitrogen flux for surface modification between the nitriding furnace (anode) and the workpiece (cathode) [4], [5]. The plasma can also be generated by DC, pulsed-DC, radio frequency (RF) [5], [18], bipolar pulsed-DC power supply and others.

Krzysztof et al. [70] reported that the DCPN (direct current plasma nitriding) has a lower nitriding temperature compared to gas nitriding, but can produce composite and diffusion layers of similar thickness while maintaining the high mechanical properties of Ti-6Al-4V and Ti-6Al-7Nb core materials. However, this technique has some drawbacks, including "edge effects" that, contribute to preferential sputtering and overheating of the sharp edges. *Afsaneh E. and Khorameh F.* [20] reported that the applied voltage is provided by a DC power supply and that the continuous voltage and heat supply can lead to localized heating, overheating of thin sections, arcing and other surface damage.

Afsaneh E. and Khorameh F. [20] reported that the problems of DC can be conventionally avoided by using a pulsed DC power supply in which the heat input is controlled with duty cycles typically on the order of 10-50% of the total cycles [71] without affecting nitrogen activity or nitriding time. *M. Tarnowski et al.* [69] reported that the glow discharge nitriding processes can be used to produce higher thickness nitride layers with nanostructured titanium nitride at the cathode potential, which are characterized by good resistance to frictional wear and high hardness. However, the nitrided layers formed at the cathode potential are characterized by higher surface roughness. This results in a higher coefficient of friction and a higher density of the corrosion current. Which structural defects in the outer layer of the titanium nitride are caused by the sputtering effect.

Due to the DC plasma nitriding process sputtering effect and high nitriding temperature. Therefore, RF plasma nitriding is used because of the relatively low process temperature that does not change the microstructure and mechanical properties of the material [15], shorter process time compared to DC plasma [15], [72], [73], the possibility of machining workpieces with complex geometry [15], [18], [73], and high nitriding rates [73]. *Fouquet et al.* Reported on Ti-6Al-4V samples nitrided in a reactor

for plasma assisted heat treatment [74]. It was demonstrated that the RF plasma caused an increase in the nitriding effect at the top surface and accelerated the formation of the compound layer. However, the depth of nitrogen diffusion in the Ti-6Al-4V substrate did not increase significantly. In 2006, *El-Hossary et al.* [73] pointed out that the RF plasma nitriding process leads to an anomalously high nitriding rate. This high nitration rate of can be attributed to the high concentration of nitrogen species in the environment of the samples. The high nitrogen concentration and the precipitation of hard nitriding phases in the formed compound layer are the reasons for the microcracks on the surface. *Abd El-Rahman et al.* [75] reported that the thickness of the nitride layer increases with increasing plasma power and a maximum nitride layer thickness of only 720 nm is reached, which significantly increases the surface microhardness when a thick nitride layer is formed, and this growth occurs mainly in the high temperature region (800 to 900 °C) [74]

In the references listed below, the effects of plasma parameters, such as DC, pulsed DC, RF, and other related parameters such as temperature, nitriding time, pressure, and gas ratio on the surface properties of titanium alloys have been described. Table 2.1 shows the conditions and type of power supply used for the plasma nitriding process of titanium alloys. Based on the current investigation, the effect of bipolar pulse frequency on the mechanical properties and corrosion resistance of plasma nitrided Ti-6Al-4V alloy was studied. It has not been reported yet. Therefore, the aim of this study is to investigate the plasma parameters used in the nitriding process, including H₂/N₂ ratio, temperature, time, and bipolar pulse frequency, which can improve the anticipated outcomes of this research should be useful for medical implants placed inside or on the surface of the body.

Table 2.1 Plasma nitriding condition of titanium alloys

		Power supply	Pulsed DC	Pulsed DC	RF	Pulsed	DC	DC	RF	RF	Pulsed DC	
		Time (hours)	9	3-4	4	4, 8, 16	2 and 4	1	2-8	4-12	12	
	ondition	Temperature (°C)	730	500, 600, 700, 800, 900	600, 700, 800	500, 550, 600	700	700 -1020	600–1000	006-002	950	
		Pressure (torr)	1.42	2.2-3.3	1.05	0.97-7.5	2.6	3.7x10 ⁻²	0.75	0.075	2.25	
		Gas ratio	95%N ₂ +5%H ₂	$50\pm10\%$ Ar + $50\pm10\%$ N ₂	100% N ₂ 80N ₂ +20%H ₂	80% N ₂ + 20% H ₂	$\rm NH_3, N_2+\rm NH_3$	N_2	$80\% N_2 + 20\% H_2$	$N_2(50 \text{ sccm}) + H_2(50 \text{ sccm})$	$N_2 + H_2$	
WI		Sample	Ti6Al7Nb and grade 2 titanium	Ti5Al4V2Mo	Beta 21S	Ti-6Al-4V	CP-Ti	Pure titanium	Ti-6Al-4V	Ti-6Al-4V	Ti-6Al-4V	
		Name, Years	M.Tarnowski, 2021 [69]	Yu.V. Borisyuk, 2015 [13]	L. Mohan, 2013 [76]	Okan Unal, 2018 [77]	Hongyu Shen, 2020 [78]	A.V. Tyunkov, 2020 [79]	C. Fontoura, 2020 [80]	V.Fouquet, 2004 [74]	W. Kong, 2022 [45]	

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2.2 Titanium alloys and applications

Titanium (Ti) is a transition metal listed as a pure element in the periodic table with an atomic number of 22 and an atomic weight of 47.9. It is the ninth most abundant element and the fourth most abundant metallic element in the Earth's crust, after aluminum, iron, and magnesium [1], [2]. Titanium is a reactive element. Therefore, titanium does not occur in nature in pure elemental form, but in the form of titanium ores, including rutile (TiO₂), the most stable form of titanium oxides [1], [44] and ilmenite (FeTiO₃) [1]. Dr Wilhelm Kroll invented useful metallurgical processes for the commercial production of titanium metal [44]. It is produced by sintering titanium ores at 500 °C in the presence of carbon and chlorine until titanium tetrachloride (TiCl₄) is formed. The titanium tetrachloride can be obtained by reduction with magnesium or sodium at 850 °C in the form of a titanium sponge. This sponge is then melted into metal ingots under vacuum or argon atmosphere [1], [2], [44], [81]. Based on their atomic crystal structures, titanium alloys can be classified into four main groups: α -Ti alloy, near- α Ti alloy, α + β -Ti alloy, and β -Ti alloy [20], [82].

2.1.1 Commercially pure titanium

Commercially pure titanium (CP) has an allotropic phase transformation. The transformation temperature depends largely on the purity of the titanium; for commercially pure titanium it is in the range of 860-960 °C [83] At room temperature, commercially pure titanium has a hexagonal close-packed (HCP) structure called α -phase. At 883 °C (β -transus temperature [20]), titanium allotropically transforms from an HCP to a body-center cubic (BCC) structure , referred to as β -phase [2], [82]–[85], and the latter remains stable up to the melting point of 1670 °C [85].



Figure 2.1 (a) Hexagonal close-packed (HCP) structure referred to as α -phase, and (b) body-center cubic (BCC) structure referred to as β -phase [84]

Commercial high-purity titanium is a low- to medium-strength metal that is not well suited for aircraft structures or engines. The yield strength of high-purity titanium is in the range of 170-480 MPa [86]. However, the applications of high-purity titanium are limited due to its relatively low strength and wear resistance [87]. The composition and properties of various commercially available pure titanium alloys are listed in Romane! Islamumdan1561363. Commercially available pure titanium forms are classified according to the ASTM standard, which simply classifies metal types according to a numbering system, e.g., Grade 1, Grade 2, Grade 3, and others.

Types	Maximum impurity limits (wt.%)							
Types	Ν	С	Н	Fe	0			
ASTM Grad 1	0.03	0.1	0.15	0.20	0.18			
ASTM Grad 2	0.03	0.1	0.15	0.30	0.25			
ASTM Grad 3	0.05	0.1	0.15	0.30	0.35			

Table 2.2 Composition of commercially pure titanium alloys [86].

ASTM Grad 4	0.05	0.1	0.15	0.50	0.40

2.2.2 Alpha titanium alloys

Ti alloys are formed especially by CP -Ti and alloys with α -stabilizing elements, which have only one α -phase at room temperature. The families of α -Ti and near- α -Ti alloys are known for their microstructural stability at high temperatures and corrosion resistance; however, their microstructures cannot be altered by heat treatments. Some of the alloys in this family are commercial pure titanium, Ti-5Al-2.5Sn, Ti-3Al-2.5Sn, Ti-8Al-1Mo-1V, and Ti-6Al-2Sn-4Zr-2Mo and others [20]. Alloying elements have a strong influence on the allotropic transformation, e.g., aluminum increases the β -transus temperature and is called an α -stabilizer. Conversely, β -stabilizing elements lower the β -transus temperature and stabilize the β -phase at room temperature either by eutectoid transformations (iron, hydrogen) or solid solutions (V, Mo, and Nb) [20]. Such alloys exhibit high creep resistance and are therefore suitable for high temperature service [85].

2.2.3 Beta titanium alloys

β-Ti alloys are formed when a high amount of β-stabilizer elements (Mo, V, W, and Ta) are added to titanium, lowering the temperature of the allotropic transformation of titanium. When the content of β-stabilizer is high enough to lower the martensitic starting temperature (Ms) to temperatures below room temperature [85]. A large number of alloying elements can be used as β-stabilizers, although only V, Mo, Nb, Fe, and Cr are used in appreciable amounts (typically 10-20 wt.%) [86]. This type of titanium alloy can be hardened by heat treatment processes. In some cases, this depends on the composition and heat treatment parameters [85]. The strength and fatigue resistance of β-Ti alloys are generally higher than those of α-Ti alloys. However, due to their low creep resistance at high temperatures, the proportion of Ti alloys is very small and

accounts for less than a few percent of the total titanium used by the aerospace industry [86].

2.2.4 Alpha+Beta titanium alloys

The $\alpha+\beta$ -Ti alloys are by far the most important group of titanium alloys used in aerospace [86] and dental implants [2]. They are lightweight, strong, and highly resistant to fatigue and corrosion. The most common of these alloys contains 6 wt.% aluminum and 4 wt.% vanadium or Ti-6Al-4V [2], [20], [86]. The popularity of $\alpha+\beta$ - Ti alloys is due to their excellent high-temperature creep strength, ductility, and toughness (due to the β -Ti phase) [86]. These alloys are prepared by adding α -stabilizers and β -stabilizers to promote the formation of both α -Ti and β -Ti grains at room temperature. The amounts of α -stabilizers and β -stabilizers are typically in the range of 2-6 wt.% and 6-10 wt.%, respectively [86].

The alloy Ti-6Al-4V is the most popular alloy of the α + β -type. It is widely used, very easy to process, and has high corrosion resistance. It is still widely applied as a biomaterial, especially for orthopedic implants [85] and dental implants [2]. However, the applications of pure titanium are limited due to its relatively low strength [87], low wear resistance, and low hardness [78]. The properties of these alloys can be improved by heat treatment to adjust the amount and type of β -phase elements [20], [82]. The yield strength of annealed Ti-6Al-4V is about 925 MPa [86], which is higher than most near- α Ti alloys (~800 MPa) but lower than many β -Ti alloys (1150-1400 MPa) [86]. Similar comparisons can be made for other properties, including fatigue strength, creep resistance, ductility, fracture toughness, and tensile strength [86]. Despite all these outstanding advantages, Ti-6Al-4V still has problems with low wear resistance, release of aluminium and vanadium ions, and hydrophobic surface [80], which is a major problem in osseointegration. All in all, the main problems of Ti-6Al-4V in medical implants are surface related. Surface modification is widely used to improve the properties of the alloy [88], and plasma nitriding is a leading surface hardening process consisting of a complex composite layer [80], [89], [90]. The surface hardening process is industrially recognized and has been performed for decades [73], [80], [91], [92], but is not widely used in medical substrates compared to surface modification processes such as physical vapor deposition (PVD) and chemical vapor deposition (CVD). Titanium nitride (TiN) coatings encountered problems with delamination of the layers [93], while the plasma nitriding process forms the nitride layers in the surface substrate by a diffusion process that is well bonded to the base material [80].

2.3 Plasma nitriding

In plasma nitriding, nitrogen atoms are brought to the surface of workpieces to diffuse into the microstructure. The nitriding atmosphere generally consists of a buffer gas, e.g., Ar or H₂, and the reactive gas, e.g., N₂, NH₃. The plasma can be generated by inputting an external voltage to ionize the nitriding gas and provide an active nitrogen flux for surface modification between the nitriding furnace (anode) and the workpiece (cathode) [4], [5]. The appropriate value of voltage and current density for plasma nitriding, called "glow discharge", is shown in Figure 2.2, where a uniform, stable glow covers the workpiece and the current density is directly proportional to the voltage drop and thus can be easily controlled [20], [64]. Under the influence of the applied electric field, free electrons accelerated from the cathode to the anode collide with gas molecules of the nitrided atmosphere, ionizing them and creating an environment of positive and negative ions, electrons, neutral and energetic atoms. Subsequently, the positive ions are accelerated toward the cathode, causing phenomena such as sputtering, diffusion into the bulk, heating by radiation and collision, surface diffusion, plasma reaction [20], [23], [64], [94], and so on. These mechanisms eliminate the need for expensive pre-cleaning operations, resulting in a significant increase in nitriding rates, and the nitrogen species are accelerated by the bombardment, heating the workpieces and improving nitriding kinetics at lower temperatures than conventional nitriding processes [64].



Figure 2.2 The plot of voltage versus current density for formation of discharges in argon [20]

Several mechanisms have been proposed to explain the nitrogen diffusion mechanism in plasma nitriding, such as the atomic nitrogen adsorption model, the ion adsorption model, the nitrogen implantation model, the NH⁺ bombardment model, and the Kölbel's model [20], [30]. According to the Kölbel's model, the first step of plasma nitriding begins with the sputter cleaning of the surfaces, followed by the reaction of the sputtered atoms with nitrogen, where TiN molecules are formed in gaseous form and redeposited on the substrate, and then the nitrogen atoms diffuse into the titanium matrix [95]. The adsorbed NH⁺ radicals are assumed to dissociate on the surface of the workpiece and release nitrogen atoms, which diffuse into the structure [20]. The solubility of nitrogen in titanium (22 to 25 at.%) for high temperature (above 882 °C [96] or β -transus temperature) and for a low temperature (below 880 °C [95]), the formation of titanium nitride requires at least 33 at.% N atoms to obtain the compound TiN_{0.42} [95], [96]. The phase diagram is shown in heavenal "luwuwatannationa". *A. Gicquel et al.* [95] reported that when nitrogen atoms diffuse in a polycrystalline substrate, diffusion occurs mainly along the grain boundaries. This lowers the activation barrier

and increases the diffusion coefficient. Due to the nitrogen concentration profiles in the matrix, nitride formation first occurs at the substrate surface. Then, the crystal lattice changes towards the cubic centered faces (FCC or NaCl crystal). Since some titanium nitride layers (δ and ϵ phases) have formed, nitrogen must diffuse through these layers for the nitriding process to continue. Since the nitrogen atoms in the titanium matrix adopt the octahedral structure [95], the titanium nitride provides a diffusion barrier for the nitrogen into the surface titanium, and the diffusion coefficients in the titanium nitride are expected to be lower than those in the titanium [95].



Figure 2.3 Titanium-nitrogen phase diagram [96]

Plasma nitriding of titanium alloys is usually carried out at temperatures between 700 and 1100 °C [20], [27]–[29] for 6 to 80 hours in a nitrogen-containing environment (N₂, N₂-Ar, N₂-H₂, or N₂-NH₃) [30]–[34], with pressures varying between 3.8 and 9.8 Torr [30]–[34]. Diffusion kinetics, which depend on the temperature, pressure, nitriding time, and composition of the nitriding gas, have a significant effect on the microstructure of plasma-nitrided titanium alloys [20], [35], [97]. For example, the presence of hydrogen in the gas mixture increases the nitrogen diffusivity by removing the sodium oxide layer on the surface, which hinders the nitriding process from the titanium alloy. *Tamaki et al.* [30] reported that another mechanism, the presence of hydrogen in the nitriding medium, leads to the formation of H^+ , NH^+ , and NH_2^+ radicals, which have an impulse effect on the nitriding kinetics [98]. On the other hand, the presence of Ar in the gas mixture decreases the nitrogen diffusion depth and causes random formation of Ti₂N and TiN by sputtering reactions or homogeneous reactions in the plasma [30], [98]–[100]. In addition, nitrogen concentration also has a significant effect on the diffusion rate of plasma nitrided titanium alloys [95]. The nitrogen density can be generated by the action of the high frequency electric field, which increases the nitrogen species, which is a precursor for the formation of a nitride layer. The following sections provide an overview of the previous studies on the microstructure and properties of plasma nitrided titanium alloys, focusing on the plasma nitriding of titanium alloys.

2.4 Properties of plasma nitrided titanium alloys

The Ti-6Al-4V alloy extra low interstitial (ELI) grade had a annealed microstructure consisting of α -grains with retained β -particles at α -grain boundaries and fine recrystallized β -particles inside the α -grains. The α -grains were delineated by the different orientation of fine recrystallized β -particles inside the α -grains (etched in Kroll's solution) [20], [101], is shown in Romano! ไม่พบแหล่งการอ้างอิง.



Figure 2.4 Scanning electron microscopy (SEM) images of Ti-6Al-4V had an annealed microstructure [20], [101].



Figure 2.5 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 [20], [102]

2.4.1 Microstructure of plasma-nitrided titanium alloys

After Plasma nitriding, the surface of the samples had a golden color. The actual color tone depended on the treatment atmospheres and temperatures employed for example, a gold-brown color was produced in high purity nitrogen and a pale straw color in cracked ammonia. The intensity of the gold coloration increased at higher temperatures [102]. Plasma nitriding of titanium alloys results in the formation of a "compound layer" and "diffusion zone". The compound layer on the surface that consists of TiN is called δ -phase, with FCC crystal structure ($Fm\overline{3}m$ space group) and Ti₂N is called ε -phase, with tetragonal crystal structure (P4₂-mnm space group), as shown in Figure 2.7 [20]. The TiN is stable over a wide range of nitrogen contents, TiN_x (0.43<x<1.08), and has a typical hardness of 2500 HV [103], [104]. The Ti₂N is stable over a small composition of nitrogen contents ~33.3 at.% and has a maximum hardness of 1600 HV [103], [104]. Raveh et al. [105], reported that the compound layer was composed of a TiN layer on top of a mixture of randomly polycrystalline TiN and highly Ti₂N. They also reported the clusters of fine (50-100 A°) precipitates consisting of Al, V, Cr, and Fe elements under the compound layer. The compound layer has a typical thickness of 1-4 μ m and may contain traces of Ti₄N_{3-x}, TiN_{0.26}, and TiO₂ in addition to TiN and Ti₂N [97], [103], [106]– [109].

Underneath the compound layer a continuous layer of the " α -case" and diffusion zone, respectively. The α -case is the formation of nitrogen stabilized α -titanium structure, with commonly hardness of 800-1000 HV [99], [100], [104], [105], which is a brittle layer, the formation of α -case is not desired due to its negative effect on the ductility and fatigue strength of titanium alloys [20]. Finally, the diffusion zone which is an interstitial solid solution of nitrogen atoms in the titanium structure called α' -(Ti,N) [20], [38], [99], [104], [105]. When α + β titanium alloys are nitrided at high temperatures (typically higher than 800 °C) [20], α -case is formed underneath the compound layer as shown in Figure 2.5

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 -phase and β -phase, for example, for temperature 950 °C solubility of nitrogen 17.5 at.% in α -phase against 0.75 at.% in β -phase [96], as shown in Romane! Inmundants and β . However, nitrogen diffuses three times faster in β -titanium alloys compared with α -titanium alloys but has limited solubility in the β -phase [20], [110]. 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 -titanium alloys that possess a combination of high nitrogen solubility and diffusivity [20].

The effect of plasma nitriding process parameters on the microstructure and properties of titanium alloys was studied. According to *da Silva et al.* [111] reported that the composition of plasma-nitrided Ti-6Al-4V surfaces was a very complex function of the nitriding parameters, for example, time, temperature, gas mixture, and pressure, which the temperature had the most significant influence. The XRD studies on plasma nitrided surfaces revealed that increasing

the pressure of nitrogen in the mixture gas resulted in preferential orientation of Ti₂N and promoted the formation of TiN. Which interpreted that the shift observed in β -phase XRD reflections corresponded to lattice distortions in this phase and likely residual strains induced by nitriding. Figure 2.6 is show X-ray diffraction (XRD) spectrum obtained from the plasma-nitrided surface. Peak analyses identified TiN, Ti₂N, and TiN_{0.3} nitrides as well as peaks corresponding to α -Ti from the substrate. The peaks corresponding to α -Ti appear in the spectrum due to X-ray depth of penetration the average penetration depth is 5 μm and increases with diffraction angle. It appears that Ti₂N is the dominating nitriding compound [20], [104], [111]. In addition to TiN and Ti₂N, they also reported XRD reflections of V_2O_2 , orthorhombic TiO₂, and nitrogen-deficient ζ - Ti_4N_{3-x} nitride in the compound layers formed at certain nitriding conditions. The 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 high nitriding temperature [20], [30]. However, the nitriding gas pressure had a minor influence on the nitrided microstructure. Yildiz et al. [112] reported that the nitriding time and temperature were directly correlated with the surface hardness, 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. In addition, the 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 α -grains. It has also been reported that the Ar+H₂ sputtering increased the nitriding kinetics in ferrous alloys by providing easy diffusion paths for nitrogen interstitials and eliminating inherent surface oxides [99], [113]



Figure 2.6 X-ray diffraction (XRD) spectrum obtained from the plasma-nitrided surface [20], [104], [111].




Figure 2.7 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: $Fm\overline{3}m$) and Ti₂N (space group: P4₂-mnm) nitrides in the compound layer [104].

2.4.2 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 [114]–[117]. Although it is well established that plasma nitriding improves the wear resistance of titanium alloys, but the tribological behavior of plasma nitrided titanium surfaces is a function of the surface hardness, surface roughness, the presence of brittle

nitriding microstructural features, and the depth of nitrogen diffusion zone. Thus, the wear resistance of plasma nitrided titanium surface is dependent on the process parameters, microstructure, and chemical composition of the titanium substrate.

Bell et al. [102] reported that the high wear rate and high coefficient of friction of Ti-6Al-4V (COF=0.3) were effectively improved by plasma nitriding at 800 °C, nitriding time for 12 hours, under the N₂ atmosphere. Found that the coefficient of friction decreased (COF=0.05), low wear rate, and anti-scuffing characteristics of the plasma nitrided surfaces to the hardness of the compound layer.

Taktak S. and Akbulut H. [118] 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 un-nitrided. *Shashkov* [119] reported that the plasma nitriding at high temperature (900, 1000, and 1100 °C) in different titanium alloys for different durations in N₂ atmosphere. Found that the reduction of wear resistance for nitrided alloys at higher temperatures and durations. They clarified that plasma nitriding of titanium alloys at high temperatures was accompanied by embrittlement due to the formation of brittle nitride layers and microstructural changes in the bulk such as coarse grain.

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.* [120], they reported that the scuffing and high friction coefficients, observed in the un-nitrided sample 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.* [103]. The plasma nitriding was 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 hr. 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 speed (0.3 m/s), nitriding inhibited oxidation-dominated wear in Ti-6Al-4V and decreased wear by providing resistance against adhesion and microfragmentation. 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. 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 hr.) was related to the inadequate depth of nitriding and lack of support for the compound layer. On the other hand, a longest duration (24 hr.) promoted a deeper diffusion zone that retained the compound layer on the surface under sliding conditions.

The positive effect of a diffusion zone on tribological behavior of plasma nitrided titanium alloys was also investigated by *Nolan et al.* [121], when comparing plasma nitriding and physical vapor deposition (PVD) coated surfaces. The plasma nitrided Ti-6Al-4V sample has lower mass loss was observed, with a 2 μ m compound layer on top of an about 40 μ m diffusion zone compared with the PVD-coated surface with a 2 μ m 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.

The results indicated that failures initiated by the formation of micro voids within the compound layer likely at grain boundaries. Increasing the applied load led to the formation of microcracks that propagated intergranular 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 [104]. 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, as shown in $\hat{\mu}_{0}$ was and $\hat{\eta}_{1}$ by the spale of the spale of the diffusion of the diffusion states and prevented by ductile β -particles in the diffusion zone, as shown in $\hat{\mu}_{0}$ was an $\hat{\eta}_{1}$ by the spale of the spale of the diffusion states and prevented by ductile β -particles in the diffusion zone and prevented by the diffusion zone in the diffusion zone and prevented by ductile β -particles in the diffusion zone.



Figure 2.8 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 [104] Surface roughness of plasma nitrided titanium alloys is another influential factor on their sliding behavior. *Salehi et al.* [122] 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 counter face 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.

2.4.3 Mechanical properties of plasma nitrided titanium alloys

Plasma nitriding is the most effective methods for hardening the surface of titanium alloys, which improve the mechanical properties and wear resistance, and corrosion resistance in some cases. Nitriding improves friction and wear properties of titanium alloys by the formation of a compound layer [107]. Numerous works have been considered to the effect of nitriding on the mechanical properties of titanium alloys. However, the obtained data often deviate from one another because of the different purity of the initial materials and conditions of the nitriding process. However, due to its brittle nature and accumulation of residual stresses, the compound layer can promote initiation of microcracks from the surface and lead to premature failures. Moreover, the plasma nitriding at high temperature result in the formation of a brittle " α stabilized layer" [107] or α -case a continuous layer of α -phase titanium enriched or α' -(Ti,N) with interstitial nitrogen atoms and unfavorable phase transformations in the substrate which impair the fracture toughness, ductility, and fatigue properties [99], [105], [107], [119], [123]. 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 mechanisms [20] and also leads to inevitable adverse effects on the toughness and fatigue properties [20], [37], [102], [124], [125].

The kinetics of nitrogen diffusion in titanium alloys was slowly, therefore requires high temperature (higher than 700 °C) for produce sufficient depth of nitriding. Typical plasma nitriding treatments, performed in the temperature range of 700-1100 °C [20], [27]–[29] for several hours, cause bulk microstructural changes such as grain growth and over-aging that negatively affect the fatigue behavior [34], [36], [102]. Moreover, plasma nitriding at high temperature it has been reported that the formation of brittle feature in the near surface and bulk microstructural changes are the main contributing factors in premature failure initiation and deterioration of mechanical properties of titanium alloys after plasma nitriding [99], [100], [102], [103], [105], [126]–[128].

According to *Nishida and Hattori* [37] after plasma nitriding of Ti-6Al-4V. They reported that the fatigue strength of plasma nitrided titanium alloys were lower than the untreated alloy but similarly to or even slightly better than that of the vacuum-annealed alloy with the same heating. 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. It has been reported that the impaired fatigue properties of titanium alloys after plasma nitriding to the thickness of the α -case. The α -case is a brittle layer (typical hardness 800-1000 HV [99], [100], [104], [105]) formed underneath the compound layer at high nitriding temperatures (\geq 800 °C), and its formation has proven to be detrimental for ductility and fatigue strength of titanium alloys [99], [100], [102], [103], [105], [126].

Raveh et al. [100] believed that in addition to the surface hardness, the 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 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.

A plasma nitriding treatment at 500°C for 6 hours in nitrogen and hydrogen (3:1) gas mixture in the work of *Rajasekaran and Raman* [129] also resulted in improvements in uniaxial plain fatigue and fretting fatigue behavior of Ti-6Al-4V alloy. Lower surface roughness, 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 of 390 $HV_{0.2}$ was slightly higher than the untreated material (330 $HV_{0.2}$), and the surface roughness was reduced (R_a decreased from 0.80 to 0.55) μ m) due to smoothing of the pretreatment grinding 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. Contradictory results were reported by Ali and Raman [125] which, carried out plasma nitriding on Ti-6Al-4V alloy at 520°C for 4 and 18 hours and found that both normal and fretting fatigue lifes were reduced by plasma nitriding. The samples that were nitrided in a nitrogen and 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.

A low temperature plasma nitriding at 600 °C was used to achieve a microstructure consisting of a thin compound layer (lower than $2 \mu m$) supported by a diffusion zone (higher than 40 μm) without any significant changes in the substrate (the average grain size increase only ~40%). 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. 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 μ m thick compound layer and a 19.3 μ m α -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 Romano! "Jul wuundan1201300.



Figure 2.9 Typical cross-sectional SEM micrographs of the microstructure of plasma nitrided Ti-6Al-4V at 900 °C [38].

2.4.4 Corrosion properties of plasma-nitrided titanium alloys

Metal corrosion is an ongoing natural process that can cause significant damage to both property and the economy. Assessing potential damage from corrosion in advance can help mitigate future losses. Various methods are available for evaluating the corrosion rate of metals. These methods include testing their resistance in different environmental conditions, such as atmospheric and salt spray environments, employing corrosion coupons, and utilizing electrochemical techniques to analyze polarization curves. These techniques can help preempt potential issues.

One effective and efficient method for assessing corrosion rates is through the use of electrochemical techniques. These methods simulate the corrosion process and typically involve the physical interaction of metals with their surrounding environment. This interaction occurs as a result of the flow of electrical charges or electron exchange in solutions, known as electrochemical reactions. Corrosion's electrochemical reaction involves oxidation and reduction. To accelerate corrosion, an electrical bias is applied using a potentiostat/galvanostat device in an electrolyte solution. This solution serves as the ion pathway and connects to an electrochemical cell, as shown in Figure 2.10. Through this process, we can calculate the corrosion rate.





Figure 2.10 Diagram of corrosion cell (Potentiodynamic polarization test)

The electrochemical cell used for testing metal corrosion consists of:

- 1. Working electrode (or specimen electrode): An anode, which is the test specimen. It is the electrode where oxidation reactions occur, releasing electrons.
- 2. Reference electrode: A cathode where reduction reactions occur, accepting electrons. Example Ag/AgCl, which have constant electrical potentials.
- 3. Counter electrode: Often made of a stable metal such as platinum, graphite, or stainless steel.
- 4. Electrolyte: The pathway for ions.

The value obtained from testing is the polarization curve, which shows the relationship between electrical potential and electrical current when applying a potential until the metal starts to corrode. This is called the corrosion potential (E_{corr}). At this point, the corrosion current density (i_{corr}) is also

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determined, which is used to calculate the corrosion rate, as shown in Figure 2.11.



Log current density, mA/cm²

Figure 2.11 Hypothetical cathodic and anodic Tafel polarization diagram [130]

Meanwhile, if the metal has a passive film, such as stainless steel, that resists corrosion, applying a potential may result in the formation of a passive film to protect against corrosion, leading to a constant or decreased electrical current density. However, when the potential is increased to a certain level, causing an increase in electrical current density, it indicates the breakdown of the passive film into pits. This is known as the pitting potential (E_{pp}) and the passive current density (i_p), as shown in Figure 2.12.



Figure 2.12 Hypothetical polarization diagram for an active/ passive/active system with anodic and cathodic branches [130]

The characteristics of the polarization curve, which depict the corrosion behavior of metals, are detailed as follows:

- Corrosion potential (E_{corr}) is the electrical potential at which the metal begins to corrode. Metals with lower corrosion potentials are more susceptible to corrosion compared to those with higher corrosion potentials.
- Corrosion current density (i_{corr}) is the density of electrical current that occurs at the E_{corr} point. i_{corr} represents uniform corrosion and can be used to calculate the annual corrosion rate of the test sample.

Corrosion resistance was assessed by measuring i_{corr} and E_{corr} . The corrosion rate (CR) can also be estimated based on the ASTM Standard G 102-89 using the following formula [131]

$$CR = K \frac{EW}{\rho} i_{corr} \qquad \dots (1)$$

where CR is the corrosion rate in mm/year (mmpy), K is 3.272×10^{-3} mm·g/(μ A·cm·yr), *i*_{corr} is the self-corrosion current density in μ A·cm⁻², ρ is the density in g·cm⁻³, and EW is the equivalent weight. For the Ti-6Al-4V alloy, the equivalent weight and density are 11.89 and 4.43 g·cm⁻³, respectively.

Plasma nitriding of titanium was generally carried out at high temperatures (900-1100 °C) [27]–[29], [132] which over the phase transformation temperature of α -phase to β -phase and maybe cause an deformation of plasma nitrided sample. Liu at el. [27] reported that the Ti-N layer obtained by plasma nitriding of titanium at 900 °C for 4 h in N₂ atmosphere did not improve the corrosion resistance of titanium. *Shen and Wang* [132] was carried out the plasma nitriding of titanium at 700 °C for different processing times in an ammonia (NH₃) atmosphere to prepare a continuous and dense Ti₂N layer with various thicknesses. Shen and Wang reported that the thin Ti₂N compound layer about 0.7-2.1 µm was formed on pure titanium (TA1) sample by low temperature plasma nitriding at 700 °C for 2 h, 3 h and 4 h. With increase in the process time, the corrosion resistance was greatly improved. The corrosion potential and the current density of nitrided samples are much lower than the corresponding value for un-nitrided titanium. The formation of Ti_2N compound layer not only causes the improvement of corrosion resistance but also remains the high electronic conductivity due to its high corrosion resistance. The investigation by the same author [78], was carried out the plasma nitriding of commercially pure titanium (CP) at 700 °C and 750 °C for 4 h in a NH₃ gas and a N₂+NH₃ mixture gas with a ratio of 2:1. Reported that the maximum hardness of nitride layer reached about 1320 Hv_{0.1} approximately 7 times higher than that of un-nitrided sample. The wear and corrosion resistance of titanium were simultaneously improved by plasma nitriding at 750 °C due to forming a thicker Ti-N compound layer.

2.4.5 Biocompatibility

Cell adhesion and spreading are crucial parameters in implant engineering. Poor integration of implants with surrounding tissue often leads to low biomaterial efficiency [133]. Tissue integration hinges on the adhesion and spreading capabilities of cells, particularly fibroblasts, on implant surfaces. The behavior of cells on biomaterial surfaces is contingent upon interactions with the implant, which are in turn correlated with surface properties such as hydrophilicity, roughness, texture, chemical composition, and morphology [134]. Numerous studies have demonstrated that the success of implants is not only reliant on physicochemical properties like surface free energy or interfacial free energy but also on surface roughness.

Ponsonnet et al. [135] stated that considering roughness, it was demonstrated that there might be a roughness threshold (between 0.08 and 1 μ m) beyond which cell proliferation became challenging, with higher roughness leading to lower proliferation rates. Captive bubble measurements revealed that all surfaces were enveloped by a hydrogel, which aided in reducing the theoretical high surface free energy of the metallic surfaces examined. In summary, while numerous factors influence cell adhesion and proliferation, surface free energy emerges as a dominant factor; however, roughness has the potential to significantly disrupt the relationship between surface free energy and cell proliferation.

Hallab et al. [136] showed that surface free energy took precedence over surface roughness in determining cellular adhesion strength and proliferation. They also found a correlation between the surface energy components of the various tested materials and cellular adhesion strength.

Schakenraad et al. [137] found that, despite numerous parameters affecting cellular adhesion and spreading, solid surface free energy remained a dominant factor in cellular attachment to a polymer surface. This dominance persisted even when the solid surface was covered by a protein layer.

Ruardy et al. [138], they observed that the spread area of human fibroblasts increased with wettability along a surface composed of a wettability gradient, moving from hydrophobic to hydrophilic. Georgi et al. [7] demonstrated increased cell proliferation with increasing material surface wettability using the water sessile drop method.

Webb et al. [139] examined the relative importance of surface wettability on fibroblast spreading. They found that cell attachment and spreading were significantly greater on hydrophilic surfaces compared to hydrophobic ones, with moderately hydrophilic surfaces promoting the highest level of cell attachment.

Groth and Altankov [140] investigated the role of tyrosine phosphorylation during fibroblast spreading on surfaces with varying wettability values. They concluded that the effect of a hydrophobic substrate on cells regarding adhesion and proliferation is due to a transfer of signals via integrins from the substrate to the cell interior. Pre-adsorption of fibronectin on a hydrophobic substrate may offer better initial conditions, thus improving the material's tissue compatibility.

Redey et al. [141] explored osteoclast adhesion and activity on synthetic hydroxyapatite, carbonated hydroxyapatite, and natural calcium carbonate and their relationship to surface free energies. They found surface energy to be crucial in osteoclast adhesion, while osteoclast spreading depended on surface chemistry, particularly on protein adsorption and newly formed apatite layers.

Den Braber et al. [142] evaluated the effect of parallel surface microgrooves and surface energy on cell growth. They concluded that physicochemical parameters such as wettability and surface free energy influence cell growth but do not measurably affect the shape and orientation of cells on microtextured surfaces.

CHAPTER III

Experimental procedure

This chapter is divided into three sections. The first section is the experimental setup, describing all the components used for plasma nitriding. The second section deals with the plasma nitriding procedure, explaining step by step the process of sample preparation, substrate cleaning, preheating, and nitriding. In the last section, the characterization techniques such as grazing incidence X-ray diffraction spectrometer (GI-XRD), glow discharge optical emission spectroscopy (GD-OES), environmental scanning electron microscopy (ESEM), nanoindentation test, atomic force microscope (AFM), wear test, contact angle measurement using a static sessile drop method was used to estimate the work of adhesion, corrosion resistance based on electrochemical, and biocompatible tests are explained.

3.1 Experimental setup

In this work, a plasma nitriding system as shown in Figure 3.1 was developed in the Technological Plasma Research Unit of the Faculty of Science, Mahasarakham University. It consisted of the vacuum chamber, evacuation system, asymmetric bipolar pulsed power supply in the frequency range of 25-250 kHz, gas supply of Ar, N₂ (99.995% purity) and H₂, mass flow controller, pressure gauges, cooling system and temperature monitoring. The vacuum system, base and operating pressure, and gas flow rate were set with a PXI controller on the monitor. The electrode temperature was measured with a type K thermocouple. Since there is no additional external heater, the substrate is heated by ion bombardment in the plasma. Figure 3.2 shows a schematic diagram of an actual experimental setup for plasma nitriding. The thermocouple is inserted into the power electrode to monitor the substrate temperature. In the vacuum chamber, the sample is placed on the power electrode, which is electrically connected to the bipolar pulse generator. Ti-6Al-4V alloy is used as the substrate. The details of each part are described in sections 3.1.1 to 3.1.4.



Figure 3.1 Photograph of a plasma nitriding system





Figure 3.2 Schematic diagram of the plasma nitriding system

3.1.1 Substrate preparation

In this study, the Ti-6Al-4V wafers were used as the substrate to fabricate the nitride layer. The ultrasonic cleaner (UC-5180L) with a frequency of 40 kHz, was used to remove the oils and impurity residues that appear on the substrates. The Ti-6Al-4V wafers with size of 30×35 mm² and a thickness of 1 mm were polished. The cleaning procedure for Ti-6Al-4V wafers is described below.

- The Ti-6Al-4V wafer was placed in the glass box, then acetone was poured over it, and the glass box was placed in the ultrasonic bath. The Ti-6Al-4V wafer was first immersed in acetone and shaken in the ultrasonic bath for 10 minutes.
- Remove the acetone, then pour out the methanol and place the glass box in the ultrasonic bath. The Ti-6Al-4V wafer was ultrasonically cleaned a second time, vibrating the methanol for 10 minutes to remove the acetone, and then this step was repeated once.

- Remove the methanol, pour in deionized water, and place the glass box in the ultrasonic bath. The Ti-6Al-4V wafer was ultrasonically cleaned a third time and shaken with deionized water for 10 minutes to remove the acetone.
- 4. Finally, the Ti-6Al-4V wafer was dried with dry air and then blown out with warm air to remove the moisture.

3.1.2 Electrode configuration

The power electrode is used to generate the plasma and is used as a substrate holder. The power electrode is made of stainless steel to which a titanium alloy plate is attached. The electrode has an overall diameter of 170 mm and a height of 15 mm. The type K thermocouple is mounted on to the side and separated from the power electrode by a ceramic tube. The ceramic plate with dimensions $200 \times 200 \text{ mm}^2$ and height 20 mm serves as an insulator to separate the power electrode from the ground, and everything is placed on the stainless steel support. The power electrode is connected to the bipolar pulse power supply. The details of the power supply are described in the topics of 3.1.4.

3.1.3 Vacuum components

The vacuum system is a central part of the plasma nitriding system, which is very necessary. The vacuum system consists of the vacuum chamber, vacuum pump, wide range gauge, capacitance gauge, and cooling system. The vacuum chamber is a double-layer cylindrical chamber with a volume of 0.16 m³. Cold water circulated around the vacuum chamber and kept the temperature constant at 20 °C. The electrical power was connected to the power electrode via the vacuum feedthrough. This part is described in more detail in section 3.1.2. The pumping speed at the vacuum chamber can be controlled by the gate

valve for maintaining the operating pressure, which is installed between the chamber and the pump. The vacuum pump includes two pumps: (i) a rotary pump (Edwards, E2M40 PFPE) and (ii) a mechanical booster pump or Root Pump (Edwards, EH250 PFPE 50 Hz, EH250FX 220-240/380-415V, 3-ph, 50Hz, 1.5kW). The primary pump is a rotary pump with a pumping speed of 37 m^{3}/h and a typical ultimate pressure of 7.7x10⁻⁴ Torr [143] to achieve the pressure required to operate the booster pump operation. The rotary vane vacuum pump is a mechanically oil-sealed pump. When the pump is switched off, the spring loaded distributor valve provides oil and air suck-back protection to the vacuum chamber. This rotary pump was connected to the booster pump and vacuum chamber to serve as a backing pump. A booster pump serves as a secondary pump or high vacuum pump for the base pressure of this plasma nitriding system of about $2x 10^{-3}$ Torr with a pumping speed of 310 m³/h [144]. It was connected between the vacuum chamber and the rotary pump. The booster pump is ideal for use at high differential pressures, so the booster pump can be started simultaneously with the rotary pump. The two pressure gauges for monitoring the pressures in the vacuum chamber consist of the wide range gauge (Pfeiffer, PKR361) and the capacitance gauge (Inficon, CDG100D). The wide range gauge is used to measure the base pressure. This gauge has two sensors in one housing, consisting of Pirani and cold cathode modes, and can measure pressure from atmosphere or 760 Torr to 1×10^{-8} Torr with an accuracy of $\pm 5\%$ [145]. The capacitance gauge is used to measure the operating pressure in the plasma cleaning, preheating, and plasma nitriding process. This gauge can measure the pressure from 9.7×10^{-4} Torr to 9.7×10^{-8} Torr [146].

The vacuum control system in the form of a control panel shown in Figure **3. 3** The schematic diagram shows the control panel of the plasma nitriding system. Figure **3. 3** is used to control the plasma nitriding system. This control system has been developed with many advanced features in the LabVIEW program. It is used together with the National Instrument (PXI-1042), as shown in Figure **3. 4**. The National Instrument control unit was installed with the main module NI PXIe-8133, as shown in Figure **3.5**. It

consists of the DVI-to-HDMI adapter, using to connect with the monitor via the HDMI port and the USB port, using to support USB devices such as a mouse, keyboard, and an external flash drive. The Ethernet port was connected to the Lane line for online data access and control.



Figure 3. 3 The schematic diagram shows the control panel of the plasma nitriding





Figure 3. 4 A photo of the National Instruments (PXI-1042)



Figure 3.5 The panel of NI PXIe-8133 module [147]

The flow rate of argon gas can be controlled with a digital mass flow controller (Yamatake Corporation, CMQ-V MQV9500BSSN0000), as shown in Figure 3.6. The Yamatake CMQ-V was used as a 24 VDC power supply for mass flow controllers and was used for setpoint control and flow indication. The current signal of 5 mA maximum from the Yamatake CMQ-V was converted to the flow rate in the range of 0-500 sccm for Ar. The flow rate of N₂ and H₂ gases can be controlled by the analogue output card (NI PXI -6281). The flow rates of these gases were calibrated for the mass flow controllers for N₂ (MKS instrument, GV50A013103GMV020) and H₂ (MKS instrument, GF040) according to the flow range of 0-1000 sccm and 0-500 sccm, respectively. For gases N₂ and H₂, the voltage signal from the analogue output card was used to control the setpoint controller. The voltage signal in the range of 0-24 VDC from the analogue output card was converted to the flow rate in the range of 0-1000 sccm for N₂ and 0-500 for H₂. In addition, the external 24 V DC power supply was used to drive the mass flow controllers for N₂ and H₂.



Figure 3.6 Mass flow controller for Ar gas (Yamatake Corporation, CMQ-V)

The pneumatic valves including the gate valve, the capacitance gauge, and the individual gas inputs for N_2 and H_2 are controlled by the relay module card (NI PXI-2564). The relay module card was used to switch gate valve, the capacitance gauge, and gas input. The external power supply of 24 VDC was connected to the load (solenoid valve) to close and open the relay. When the relay is closed, the relay switch is connected to the load and then the valve is opened. When the relay is opened, the relay switch is disconnected, and the valve is closed.

3.1.4 Power supply

The power supply (Advanced energy, DC pinnacle plus) can deliver up to 10 kW, 800 Vmax, in the 0-250 kHz frequency range. This DC pinnacle plus power supply can be used in continuous operation and in pulsed operation. For DC pinnacle plus in bipolar pulse mode, the duty cycle and pulse frequency can be adjusted from 0-100 % and 0-250 kHz respectively.

3.2 Plasma nitriding processes

In this work, the preparation of the nitride layer is divided into three processes, including the plasma cleaning process, the preheating process, and the plasma nitriding process, respectively. Figure 3.7 shows the substrate temperature as a function of time during plasma nitriding processes. The chamber was pumped down to a base pressure of about 10^{-3} Torr for about 60 minutes. After that, the substrate was cleaned by Ar-H₂ plasma for 20 minutes, as a result the temperature of substrate increases to 350 ± 5 °C. Then, the preheating process is continue operated for about 45 minutes until the substrate temperature up to 650 ± 10 °C. Next, the nitriding process is performed with N₂-H₂ plasma. This process the substrate temperature is maintained at 650 ± 5 °C, with a holding time of 4 h. Finally, the nitrided Ti-6Al-4V alloy is leaved under vacuum environment for cooling down to room temperature. This process take time around 10 h before taking the nitrided sample out of the vacuum chamber. Each of process is explained in more detail below.



Figure 3.7 A Schematic of the preparation of the nitride layer processes.

3.2.1 Plasma cleaning

Prior to the plasma nitriding procedure, the substrate holder and chamber were cleaned with sandpaper and methanol using a clean room wiper to remove all adherent contaminants. Then the current electrode and the previously cleaned workpieces were loaded into the chamber. These workpieces were placed on the titanium plate, which serves as the substrate holder (see Figure 3.8). The substrate holder was connected to the thermocouple on the left side and the power supply on the right side. In the next step, the chamber was pumped down to a pressure of about 3×10^{-2} Torr for about 30 minutes with the rotary pump and to a base pressure of about 10^{-3} Torr for about 30 minutes with the booster pump. The plasma cleaning process is necessary to remove the impurities and oxide layer on the top of the workpiece surface. The workpieces

were physically and chemically cleaned by bombardment with the argonhydrogen plasma mixture. A bipolar pulse power of about 500 W was used to generate the Ar-H₂ plasma, with a frequency of 50 kHz, a duty cycle of 20% (negative voltage), a self-bias of about 625-800 V, and currents of 0.6-0.8 A. During plasma cleaning, argon and hydrogen are used with a flow rate of 500 sccm, an operating pressure of 2.5×10^{-1} Torr, and a process time of 20 minutes at a temperature of 350 ± 5 °C. The photo of the Ar-H₂ plasma during the cleaning process of the Ti-6Al-4V alloy wafer is shown in Figure 3.9. After the plasma cleaning process is completed, the preheating process is started immediately.



Figure 3.8 A photo of the inside of the chamber and the power electrode.



Figure 3.9 A photo of the Ar-H₂ plasma during the cleaning process of the Ti-6Al-4V alloy

3.2.2 Preheating

The purpose of the preheating process is to eliminate residual moisture and oxygen gases that may adhere to the surface of the workpiece, and to avoid a high temperature rate that can cause cracks in the workpiece due to rapid expansion. After the plasma cleaning process was completed, the pump speed was reduced to increase the operating pressure. The flow rates of argon and hydrogen were 500 sccm at an operating pressure of 3.5 Torr. A bipolar pulse power supply with a current regulation of 2.5 A was used to generate the Ar-H₂ plasma, with a DC self-bias of 500-580 V and 800-1100 W for power consumption and hold time until the temperature reached 650 ± 10 C, which took about 45 minutes. The photo of the Ar-H₂ plasma during the preheating process of the Ti-6Al-4V alloy wafer is shown in Figure 3.10. After the completion of the preheating process, the plasma nitriding process is started immediately.



Figure 3.10 A photo of the Ar-H₂ plasma during the preheating process of the Ti-6Al-4V alloy

3.2.3 Plasma nitriding

After completion of the preheating process, the current was decreased by 0.5 A and then the pumping speed was increased to remove the impurities remaining from the preheating process. Then, the conversion of argon gas to nitrogen gas at a flow rate of 1000 sccm, but still hydrogen gas, was facilitated due to the presence of hydrogen in the reactive gases formed from the formation of atomic hydrogen under process conditions removing the surface layer of titanium oxides naturally formed during the preparation of the workpiece. Other effects of the hydrogen gases were used for the stability of the operating pressure and the maintenance of the plasma. In the next step, the pump speed was decreased to increase the operating pressure. The operating pressure for plasma nitriding was maintained at about 6.5 Torr. A bipolar pulse power supply with a current regulation of about 1.6-1.8 A was used to generate the N₂-H₂ plasma (1000:100, 200, 300, 400, and), with a DC self-bias voltage of about 490-515 V and a power consumption of 800-900 W. Nitriding temperature was maintained at 650 ± 5 °C, with a holding time of 4 h. After the plasma nitriding process was completed, the nitrided Ti-6Al-4V was cooled to room temperature in the vacuum chamber. The photo of the N₂-H₂ plasma during plasma nitriding of Ti-6Al-4V sample is shown in Figure 3.11, and the photo of the Ti-6Al-4V sample after plasma nitriding is shown in Figure 3.12.





Ti-6Al-4V sample



Figure 3.12 A photo of the Ti-6Al-4V samples before and after plasma nitriding

3.3 Experimental conditions and characterization techniques

In terms of experimental conditions, they will be divided into two sets of experiments: one studying the frequency of the power supply of bipolar pulse plasma and the other studying the H_2/N_2 gas ratio on the surface properties of plasma-nitrided Ti-6Al-4V alloy.

Table 3.1 shows the experimental conditions used to study the effect of pulsed frequency in the range of 25-250 kHz on the properties of nitride layer. In this step, the H₂:N₂ gas ratio and nitriding time are fixed. Table 3.2 shows the experimental conditions used to study the effect of H₂/N₂ gas ratio on the properties of nitride layer. In this step, the nitriding time and pulsed frequency are fixed. The above conditions are operated under the nitriding temperature of 650 °C.

Based on Figure 3.13 and Figure 3.14, the recording the potential difference every 10 minutes throughout a 4 hour plasma nitriding process. It was observed that the

potential difference exhibited a slight upward trend. This phenomenon arises from the formation of a nitride layer, which renders the sample surface more insulating. Consequently, electrical resistance decreases, impeding the flow of current. In response, the power supply endeavors to uphold the preset current level, leading to an attempt to provide higher electric potential, as depicted in Figure 3.13.





Table 3.1 Parameters used to study the effect of pulsed frequency on the surface

 properties of plasma-nitrided Ti-6Al-4V alloy.

Figure 3.13 Relationship between electric potential from bipolar pulse power supply and time during plasma nitriding at different frequencies, nitriding time of 4 hours



Table 3.2 Parameters used to study the effect of H_2/N_2 ratio on the surface propertiesof plasma-nitrided Ti-6Al-4V alloy.

Figure 3.14 Relationship between electric potential from bipolar pulse power supply and time during plasma nitriding at different hydrogen ratio, nitriding time of 4 hours

CHAPTER IV

Results and discussion

This research aims to improve the mechanical properties and study the corrosion behavior of Ti-6Al-4V by plasma nitriding with bipolar pulsed plasma. The study investigates the variables in the plasma nitriding process through two sets of experiments:

1.) Experiment studying the bipolar-pulse frequency of the power supply. Frequencies of 25, 50, 100, 150, and 200 kHz are investigated. The gas ratio of $H_2:N_2$ is maintained at 500:1000 sccm.

2.) The experiment investigates the optimal gas ratio by employing nitrogen gas at 1000 sccm and hydrogen gas at varying flow rates: 100, 200, 300, 400, and 500 sccm. Hydrogen at 100 sccm (H100) operates with a duty cycle of 20%, while hydrogen at 200, 300, 400, and 500 sccm (H200, H300, H400, and H500) operates with a duty cycle of 10%. The experiment selects the most suitable frequency for bipolar pulsed plasma based on the findings of the initial experiment, which is determined to be 50 kHz.

Both sets of experiments are conducted at a controlled temperature of 650 °C by adjusting the power supply current and last for 4 hours. The results of the experiments will be reported in two main sections as follows:

4.1 Bipolar-pulse frequency (1st experiment) Surface morphology

As depicted in Figure 4.1, the color of the Ti-6Al-4V samples undergoes a discernible shift from metallic grey to a golden hue. This alteration arises from the heightened atomic ratio of nitrogen to titanium, leading to an overall enhancement in reflectivity, thereby imparting a golden-like appearance [93], [148], [149]. Notably, a lighter coloration is observed around the edges of all nitride samples. This edge defect

is attributed to the elevated electric field, resulting in heightened energy levels of ion bombardment and consequent increased sputtering within this region.

Prior to the examination of surface morphology, all specimens underwent immersion in a solution comprising 98% H_2SO_4 and 37% HCl acids, with a volume ratio of 1:1, for a duration of 20 hours. Subsequently, the surface morphology of the etched samples was scrutinized utilizing the ESEM technique.

The Ti-6Al-4V alloy consisted of two phases before the treatment, the first phase was alpha phase and presented a hexagonal close-packed crystal structure (HCP) and the microstructure appeared brighter in this phase. The second phase was a beta phase and presented a body-center cubic (BCC), and this phase was darker than the alpha phase and lamellar arrangement, which is in agreement with the results of previous studies. However, the volume fraction of the alpha phase appeared in greater quantity than beta, which leads mainly making the phase in alloy, as shown in Figure 4.3.

Figure 4.2 (a) illustrates the surface morphologies of the unnitrided sample both pre- and post-etching. Evidently, the unnitrided specimen exhibits pronounced signs of corrosion, leading to the obliteration of discernible grain boundaries. In contrast, upon comparison of the surfaces of the nitrided samples before and after etching, minimal traces of corrosion are discernible. This outcome underscores the efficacy of the plasma nitriding process in bolstering the corrosion resistance of titanium alloys through the formation of a protective barrier.



Figure 4.1 The surface physical appearance of unnitrided and nitrided samples



Figure 4.2 Surface morphology of unnitrided and nitrided samples before and after 20-hour immersion in 98% H₂SO₄ and 37% HCl acids in a 1:1 volume ratio


Figure 4.3 Surface morphology of Ti-6Al-4V alloy

Phase identification

The Ti-6Al-4V alloy is classified as an α + β -type alloy, predominantly composed of the α -phase with a smaller proportion of the β -phase. The α -phase possesses a hexagonal close-packed (HCP) structure, while the β -phase exhibits a body-centered cubic (BCC) structure. The Ti-6Al-4V alloy extra low interstitial (ELI) grade had a annealed microstructure consisting of α -grains with retained β -particles at α -grain boundaries and fine recrystallized β -particles inside the α -grains. The α -grains were delineated by the different orientation of fine recrystallized β -particles inside the α grains (etched in Kroll's solution) [20], [101],

Plasma nitriding of titanium alloys leads to the development of a compound layer on the surface primarily composed of the TiN- δ phase, exhibiting a face-centered cubic (FCC) crystal structure ($Fm\overline{3}m$ space group), and the Ti₂N- ε phase, characterized by a tetragonal crystal structure (P4₂-mnm space group). TiN demonstrates stability across a broad spectrum of nitrogen contents, denoted as TiN_x (0.43 < × < 1.08) [20].

The phase composition and microstructural properties of the samples after plasma nitriding were analyzed by grazing incidence X-ray diffraction spectrometer (GI-XRD) (BRUKER, D8 Advance). A Cu Kα source with a wavelength of 0.15418 nm was used as the X-ray source. Tests were performed at a fixed incidence angle of 0.7° and with slit widths of 0.1 mm for both the input and output beams to the detector. The sampling rate of the diffractometer was set to 0.1° per second, with a 2 θ diffraction angle of 20°-80°. The phases α -Ti, β -Ti, δ -TiN, and ϵ -Ti₂N were identified from the JCPDS files using databases 01-1198, 44-1288, 65-0565, and 76-0198. Figure 4.4 shows the diffraction patterns of the sample before and after nitriding. The unnitrided sample contains the α -Ti and β -Ti phases. The diffraction peaks observed correspond to the Table 4.1.

Figure 4.5 shows the phase content of the Ti-6Al-4V alloy calculated from the semi-quantitative analysis based on the XRD patterns before and after plasma nitriding. It is obvious that the Ti-6Al-4V alloy before plasma nitriding consists of a mixture of α and β phases. After plasma nitriding, the formation of the ϵ -Ti₂N phase increases with increasing of bipolar pulsed frequency. However, as can be seen in Figure 4.5, the δ -TiN phase is highest (up to ~23%) at an excited frequency of 50 kHz.

In addition, the effect of hydrogen in the plasma cleaning and plasma nitriding processes in this study also accelerated nitrogen diffusion by forming multiple dislocations within the α -grains. It has also been reported that Ar-H₂ sputtering increases the nitriding kinetics in alloys by forming simple diffusion paths for nitrogen interstitials and eliminating inherent surface oxides [99], [113]. Therefore, no titanium oxide formation was observed. Based on the XRD results, the correlation between the intensity of phase formation and the bipolar pulse frequencies used during the nitriding process is still not clear.

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Figure 4.4 Grazing incidence X-ray diffraction spectra obtained from the nitrided and unnitrided samples.

ICPDS file	Phase	2 Theta (deg),	2 Theta (deg),	[h k l]
J CI DO IIIC	Flast	Databases	Experiment	
01-1198	Titanium	35.308	35.280	100
- 11		<mark>40</mark> .416	40.280	101
		<mark>53</mark> .212	53.160	102
		<mark>63</mark> .204	63.500	110
		70.785	70.980	103
44-1288	β-Τί	<mark>38.</mark> 482	38.440	110
65-0565	TiN	<mark>36.6</mark> 73	36.460	111
		42.601	42.620	200
76-0198	ε-Ti ₂ N	25.452	25.480	110
		34.657	34.660	101
		39.282	39.320	111
		40.767	40.640	210
		51.063	51.120	211
		52.281	52.360	220
		61.027	61.200	002
		64.256	64.040	301
		67.305	67.440	311
W28.	0	73.125	73.280	202
2	6 91	76.099	76.140	321

Table 4.1 The phases α -Ti, β -Ti, δ -TiN, and ϵ -Ti₂N were identified from the JCPDS files.



Figure 4.5 Phase content from semi-quantitative analysis based on the XRD patterns of Ti-6Al-4V alloy before and after plasma nitriding.

Chemical composition

The elemental composition in the depth profile of the surface before and after plasma nitriding was investigated using the glow discharge optical emission spectroscopy (GD-OES). The GD-OES (model: GD PROFILER HR) with the polychromator mode was operated at a pressure of 600 Pa and a power of RF of 20 W with an anode size of 4 mm. The argon ion etch rate was set at about 1 µm per minute.

Figure 4.6 The output data underwent adjustments to account for background ionization and surface adsorption of residual atomic nitrogen, potential sources of the emission lines detected by the spectrometer. It is evident that the nitrogen content on the surface reaches approximately 45% and gradually diminishes with prolonged etching time. Additionally, the aluminum content adjacent to the surface diminishes as nitrogen diffuses from the surface towards the core. At a depth of one micrometer from

the surface, the aluminum content exhibits a greater increase compared to the unnitrided sample, likely due to the precipitation of AlN.

Furthermore, the vanadium curve initially declines to nearly zero due to the diffusion of nitrogen atoms from the surface, resulting in a reduction in the relative vanadium concentration. However, upon closer examination, the vanadium content is found to exceed 5%, consistent with typical levels observed in most titanium alloys.



Figure 4.6 Elemental composition of Ti-6Al-4V before and after plasma nitriding from surface to bulk, including (a) titanium, (b) aluminium, (c) vanadium, and (d) nitrogen concentrations.

Mechanical properties

The surface hardness in the depth profile of the sample was analyzed using the nanoindentation technique with a nanoindentor (FISCHERSCOPE® HM2000) based on an enhanced stiffness procedure (ESP). This method is particularly suitable for depth-dependent measurement, which allows the hardness of the nitride layer to be determined at very low forces without being affected by the bulk. As the force increases, with loading and unloading increased at intervals from 0.1 mN to 2000 mN, the transition from the surface to the base material can also be analyzed. The value of the hardness depth profile can be used to estimate the thickness of the nitride layer.

In general, the compound layer consists of phases δ -TiN and ϵ -Ti₂N, with δ -TiN phase having a hardness of approximately 2500 HV and ϵ -Ti₂N reaching a maximum hardness of 1500 HV. Underneath the compound layer, there forms a region of nitrogen-stabilized α -titanium, known as the α -case, and a nitrogen diffusion zone created by the interstitial solid solution of nitrogen atoms within the titanium structure. Analysis of hardness from Figure 4.7 reveals that the specimens subjected to plasma nitriding exhibit increased surface hardness ranging from 1100-1250 HV. This increase is predominantly attributed to the hardness characteristics of the Ti₂N phase, as indicated by the majority presence of ϵ -Ti₂N formation shown in the results of GI-XRD analysis when compared to δ -TiN phase.

Figure 4.7, it can be seen that all nitrided samples have higher surface hardness than the unnitrided sample. The nitrided samples have the highest surface hardness of about 1250 HV at bipolar pulse frequencies of 50, 150, and 200 kHz, which is close to a hardness value of the ε -Ti₂N phase [20], [150], which can be clearly seen in the results of GI-XRD. Based on the hardness depth profile, the thickness of the nitride layer can be roughly estimated at 5 μ m. Due to its lower processing temperatures, plasma nitriding is able to achieve high surface hardness while maintaining the high mechanical properties of the core material. In addition, plasma nitriding allows control the microstructure of the treated workpiece, phase and chemical composition, surface topography, morphology, and residual stresses [69], all of which are critical for

determining surface properties, especially if the workpiece is to be used as a part in the human body.



Figure 4.7 Nanoindentation test (ESP mode) indicates hardness of surface of nitrided samples.

Surface roughness and work of adhesion

The roughness and topography of the samples before and after plasma nitriding were documented using an atomic force microscope (AFM) (XE 70 model, Park systems, Korea). Surface topography was investigated in a tapping mode by scanning an area of $5\times5 \ \mu\text{m}^2$. Three regions of each sample were selected for roughness measurements. The roughness profiles and surface geometry parameters were determined based on the AFM data in non-contact mode.

Contact angle measurement (OCA 15EC, DataPhysics, Germany) using a static sessile drop method was used to estimate the work of adhesion between water droplets and the surface of titanium alloys. It can be calculated based on the Young-Dupré equation by measuring the contact angle of the water on the surface. [151]. 1 μ L of deionized water was dropped onto the surface of the sample. The drop was backlighted with LEDs and immediately photographed by a camera. The drop was left *in situ* for one minute, then the contact angle was measured at three locations on each sample. The environmental conditions were constant throughout the experiment at a temperature of 25-26 °C, and a relative humidity of 69-72%.

In this work, root mean square roughness (R_{rms}) was measured using atomic force microscopy, which is more sensitive to peaks and valleys than average roughness because of the squaring of the amplitude in its calculation. Figure 4.8 shows the surface topography corresponding to the scan area of 25 μ m² of the unnitrided and plasma nitrided samples. The surface roughness of the nitrided samples prepared with bipolar pulse frequencies of 25, 50, 100, 150, and 200 kHz is 33.6±1.0, 25.5±1.2, 31.0±0.6, 28.8±1.7, and 38.1±3.6 nm, respectively. It can be seen that the surface roughness of the nitrided samples is higher than that of the unnitrided samples (20.8±3.7 nm). This result can be attributed to the formation of the compound layer. Typically, the compound layer is rough and porous, which leads to the reformation of material that could cause the formation of whiskers (TiN nanoparticles) [47]. No significant improvement in surface topography when bipolar pulse frequency was increased. However, the bipolar pulse frequency of 200 kHz tends to give the highest surface roughness. Increasing the frequency enhances the plasma density, which increases the probability of nitrogen ions colliding with the surface of the workpiece. These highenergy ion collisions usually lead to an increase in surface roughness. In addition, the modulation caused by the bipolar pulse frequency affects the energy distribution of the sputtered Ti atoms by allowing them to redeposit in the substrate. This modulation increases the atomic mobility on the surface and facilitates the epitaxial replication of the crystallography found in the seed layer. Consequently, this modulation contributes to variations in surface roughness [152].

Figure 4.9 shows the contact angle, work of adhesion, and surface roughness of Ti-6Al-4V before and after plasma nitriding. For each sample, the measurement was repeated three times in different positions. The contact angle of the unnitrided sample was 86.39°±3.18°. For the nitrided samples with bipolar pulse frequencies of 25, 50, 100, 150, and 200 kHz, the contact angles increase slightly to about 94.65°±1.05°, 92.75°±0.93°, 91.61°±2.12°, 93.42°±1.71° 93.28°±0.87°, and respectively, corresponding to a slight increase in surface roughness. The work of adhesion between water droplets and the surface of titanium alloys can be calculated based on the Young-Dupré equation [151]. The work of adhesion at the bipolar pulse frequencies of 25, 50, 100, 150, and 200 kHz was 76.30, 65.96, 68.34, 69.76, and 67.50 mJ/m², respectively. In general, a surface is considered hydrophobic if the contact angle is greater than 90° [153], [154]. It is observed that the contact angle of the nitrided samples is higher than that of the unnitrided sample. This could be due to the Cassie-Baxter wetting model [88], where air is trapped in the pockets below the droplet during the measurement of the advancing contact angle. The micropores formed after nitriding and the surface roughness lead to a more hydrophobic surface. Therefore, the corrosion rate should be reduced for nitrided samples with increased hydrophobic properties, since water accumulation on the surface can accelerate corrosion. Therefore, a hydrophobic surface is desirable to prevent water from adhering. Plasma nitriding can improve the hydrophobic property of Ti-6A1-4V, making it more suitable for human applications.





Figure 4.8 Surface topography obtained using AFM of (a) unnitrided, (b) 25 kHz, (c) 50 kHz, (d) 100 kHz, (e) 150 kHz, (f) 200 kHz nitrided samples.



Figure 4.9 The surface roughness, contact angle and work of adhesion of unnitrided and nitrided samples.

Coefficient of friction and wear rate

The tribological tests were performed at room temperature. The size of wear samples with a dimension of $30 \times 35 \times 1$ mm³. A 6 mm in diameter of stainless steel ball (SUS440C) was slid over the surface of the samples under a normal applied load of 0.98 N, a rotational speed of 100 rpm, and 6000 frictional revolutions. The tests were repeated three times for each sample at the rotation radius of 3, 5, and 7 mm, corresponding to a total sliding distance of 113.04, 188.40, and 263.76 m, respectively. After the test, the average specific wear rate of the sample was calculated using the profiles of the wear track (three points in each rotation radius) measured by a color 3D laser scanning microscope (KEYENCE VK-9710). Morphology of the wear track was also characterized by an optical microscope.

Figure 4.10 shows the coefficient of friction (CoF) of unnitrided and nitrided samples at a rotation radius of 5 mm as a function of the number of sliding cycles. It

can be seen that the CoF of the unnitrided sample is about 0.1 during the interval of 1000 cycles, which is due to the behavior of the natural titanium oxide layer. Thereafter, the CoF increases to about 0.3, which is consistent with the surface of the titanium alloy [155]. For the plasma nitrided samples, the CoF is 0.5-0.6 during the interval of 2500 cycles. The increase in CoF is likely related to the higher surface roughness of the nitride layer. As the number of sliding cycles increases, the CoF of the nitride samples decreases sharply to the titanium alloy surface value at the bipolar pulse frequencies of 25 kHz, 100 kHz, 150 kHz, and 200 kHz. This behavior indicates detachment of the brittle nitride layer. However, the nitrided sample at 50 kHz maintains a stable coefficient of friction of about 0.6 throughout the test period and remains intact without flaking off. This can be attributed to the formation of the δ -TiN phase, which has a higher hardness compared to the ϵ -Ti2N phase. Moreover, this stability of the nitride layer is likely due to the lowest surface roughness seen on the AFM image. Consequently, the nitride layer exhibits better mechanical properties, is scratch resistant and leads to a lower wear rate.

Figure 4.11 shows the wear tests after a test with 6000 sliding cycles and dry sliding conditions. The left column shows the photo of all worn samples with rotation radius of 3, 5 and 7 mm, the middle column shows the wear tracks with sliding width and the right column shows the three-dimensional (3D) profilometer images (radius 5 mm). As can be seen in Figure 4.11 (a) for the unnitrided sample, the sliding width of the worn track is about 0.72 mm, which is consistent with the sliding width of the worn track determined from the 3D profilometer image. The average depth and width of the worn tracks with a rotation radius of 5 mm were used to calculate the specific wear rate. It can be seen that the worn surfaces of the unnitrided sample have the highest specific wear rate after sliding. The nitrided sample at 50 kHz, as shown in Figure 4.11 (c), still has a gold-colored surface indicating the lowest specific wear rate of 0.27×10^4 mm³/Nm. This outcome is attributed to the creation of a δ -TiN phase characterized by superior hardness, surpassing that of other conditions. This result is consistent with the stability of the CoF of the nitride layer.

Figure 4.12 shows the average specific wear rate of unnitrided and nitrided samples prepared with different bipolar pulse frequencies. For each sample, the specific

wear rate was determined at three positions with a rotation radius of 5 mm. All nitrided samples with higher surface roughness have lower wear rates than the unnitrided sample. This reduction in wear rate can be attributed to the higher surface hardness achieved by the plasma nitriding process.



Figure 4.10 Coefficient of friction of unnitrided and nitrided samples as a function of number of sliding cycles.



(a) Unnitrided



(e) 150 kHz



Figure 4.11 Photo of all worn samples, wear tracks, and three-dimensional (3D) profilometer images (radius of 5 mm) with (a) unnitrided and nitrided samples prepared using different bipolar pulse frequencies (b) 25 kHz, (c) 50 kHz, (d) 100 kHz, (e) 150 kHz, (f) 200 kHz.





Figure 4.12 Average specific wear rate at the rotation radius of 5 mm of unnitrided and nitrided samples prepared at different bipolar pulse frequencies.

Corrosion resistance

The interaction between saliva and Ti-6Al-4V alloy surfaces can directly affect their corrosion behavior. Artificial saliva serves as an important test medium for evaluating the performance and biocompatibility of dental materials. Therefore, in this work, the nitrided samples were corroded in an artificial saliva solution with a pH of 5.5 under simulated oral environment before they are placed in the human oral cavity. An electrochemical test (GAMRY, Reference3000) was performed using a potentiodynamic polarization method with a three-electrode configuration, consisting of reference (E *vs.* Ag/AgCl), counter (Pt), and working electrodes (nitrided sample). An immersion time of 180 minutes was applied to the open circuit potential of the alloy in all electrolytes before starting the tests, then a potential range of -1000 mV to 1500 mV was applied with a sampling rate of 1 mV/s. Tafel extrapolation was used to estimate self-corrosion current density (i_{corr}) and self-corrosion corrosion potential (E_{corr}) in an electrochemical cell. Corrosion resistance was assessed by measuring i_{corr} and E_{corr} . The corrosion rate (CR) can also be estimated based on the ASTM Standard G 102-89 using the following formula [131]

$$CR = K \frac{EW}{\rho} i_{corr} \qquad \dots (2)$$

where CR is the corrosion rate in mm/year (mmpy), K is 3.272×10^{-3} mm·g/(μ A·cm·yr), *i*_{corr} is the self-corrosion current density in μ A·cm⁻², ρ is the density in g·cm⁻³, and EW is the equivalent weight. For the Ti-6Al-4V alloy, the equivalent weight and density are 11.89 and 4.43 g·cm⁻³, respectively.

Figure 4.13 shows the potentiodynamic polarization curve of unnitrided and nitrided samples, which was generated in an artificial saliva solution with a potential (E vs. Ag/AgCl) of -1000 mV to 1500 mV, using a sampling rate of 1 mV/s. Lower i_{corr} values and more positive E_{corr} values indicate better corrosion resistance; therefore, all nitrided samples have higher corrosion resistance compared to the unnitrided sample. Although the surface of the unnitrided sample has a robust oxide layer, there is a possibility that metastable processes will occur if a film breakdown and re-passivation process is initiated. This process leads to the formation of grain boundaries and more open pathways within the oxide. Once a crevice is formed, it spreads rapidly and leads to corrosion [156]. The nitrided sample prepared at a frequency of 50 kHz exhibits the highest corrosion resistance. This is evident from the highest values of self-corrosion potential E_{corr} and the lowest self-corrosion current density i_{corr} , as shown in Figure 4.14. A low *i*corr value means a lower amount of ions released into the human body, which can serve as an indicator of better biocompatibility. This result is probably related to the lowest roughness and the highest wear resistance. When the bipolar pulse frequency is higher than 50 kHz, the self-corrosion current density tends to be higher. This phenomenon is probably related to the fact that the molecular nitrogen ions and the nitrogen ions tend to react more slowly at the higher excitation frequency during the nitriding process. In conjunction with the wear test, there may be a strong selfdetachment in the compound layer leading to the formation of a larger porosity, resulting in a string that separates the upward growing crystallites from the downward growing ones [16].

Assuming that the nitrided and unnitrided samples have similar equivalent weight and density, the changes in corrosion rates are proportional to the changes in self-corrosion current density. Figure 4.15 shows the corrosion rate of the samples after nitriding at different bipolar pulse frequencies. The nitrided sample prepared at a frequency of 50 kHz has the lowest corrosion rate of 0.51×10^{-4} mmpy, while the CR of the unnitrided sample is 1.4×10^{-4} mmpy. This means that the corrosion rate is reduced by three times compared to that of the unnitrided sample. This suggests that titanium nitride might mitigate the release of metal ions into the body.





Figure 4.14 Self-corrosion potentials (E_{corr}) and self-corrosion corrosion current (i_{corr}) of unnitrided and nitrided samples.



Figure 4.15 Corrosion rate of the samples after nitriding at different bipolar pulse frequencies

4.2 Effect of Hydrogen gas ratio (2nd experiment)

In the second experimental phase, the study investigates the optimal gas ratio using nitrogen gas at 1000 sccm and hydrogen gas at 100, 200, 300, 400, and 500 sccm. The frequency selected for bipolar pulsed plasma from the first experiment, which is 50 kHz, is utilized. The condition with hydrogen gas at 100 sccm employs a duty cycle of 20%, while conditions with hydrogen gas at 200, 300, 400, and 500 sccm utilize a duty cycle of 10%. This results in the specimen codes being designated as H100 (duty cycle 20%), H200, H300, H400, and H500, respectively. The experiments are conducted at a controlled temperature of 650±5 °C by adjusting the power supply current and last for 4 hours. The outcomes of the experiments will be presented as follows:

Surface morphology

As illustrated in Figure 4.16, the color of the Ti-6Al-4V samples undergoes a noticeable transition from metallic grey to a golden hue. This change is attributed to an increased atomic ratio of nitrogen to titanium, leading to an overall enhancement in reflectivity and imparting a golden-like appearance [93], [148], [149]. Additionally, upon visual inspection, the H100 specimen, which utilizes a duty cycle of 20%, exhibits a difference compared to other conditions with a duty cycle of 10%. Specifically, it is observed that the surface of the H100 specimen appears matte in comparison to other conditions. Notably, a darker and lighter coloration is observed around the edges of all nitride samples. This edge defect is attributed to the elevated electric field, resulting in heightened energy levels of ion bombardment and consequent increased sputtering within this region.



Figure 4.16 The surface physical appearance of unnitrided and nitrided samples

Phase identification

The phase composition and microstructural properties of the samples after plasma nitriding were analyzed by grazing incidence X-ray diffraction spectrometer (GI-XRD) (BRUKER, D8 Advance). A Cu K α source with a wavelength of 0.15418 nm was used as the X-ray source. Tests were performed at a fixed incidence angle of 3° and with slit widths of 0.1 mm for both the input and output beams to the detector. The sampling rate of the diffractometer was set to 0.1° per second, with a 20 diffraction angle of 20°-80°.

The diffraction pattern was characterized by grazing incidence X-ray diffraction (GI-XRD) at an angle of incidence of 3°. The phases α -Ti, β -Ti, δ -TiN, and ϵ -Ti₂N were identified from the JCPDS files using databases 01-1198, 44-1288, 65-0565, and 76-0198. Figure 4.17 shows the diffraction patterns of the sample before and after nitriding. The unnitrided sample contains the α -Ti and β -Ti phases. The diffraction peaks observed correspond to the Table 4.2. All nitrided samples show the formation of a nitride layer consisting of δ -TiN and ϵ -Ti₂N. However, under the condition of H100 with a duty cycle of 20%, there is a clear increase in the formation of the ϵ -Ti₂N phase observed at a bending angle position of 61.12°.

From all plasma nitriding conditions, the peak with the highest intensity is the peak of the ε -Ti₂N phase, which surface properties will be mainly represented by the ε -Ti₂N phase. Under the condition of H100 with a duty cycle of 20%, the quantity of ε -

Ti₂N phase formation is the highest. This may result in differences in surface hardness, surface roughness, work of adhesion, and other properties compared to other conditions, which will be further explained in the next section.

From Figure 4.18, the phase content from semi-quantitative analysis is depicted. Following plasma nitriding, phase formation was observed. The presence of δ -TiN and ϵ -Ti₂N phases within the compound layer under conditions H100, H200, H300, and H400 exhibited a tendency to decrease with an elevated proportion of hydrogen gas. Conversely, under condition H500, there was an increase in the quantities of δ -TiN and ϵ -Ti₂N phases. This phenomenon could be attributed to the heightened availability of hydrogen, which facilitates its reaction with nitrogen gas to produce ammonia gas. This reaction consequently reduces the hydrogen content within the system, leading to a decreased rate of oxide layer removal. Consequently, this diminishes the rate of compound layer formation. Furthermore, under condition H100 with a duty cycle of 20%, the highest compound class, consisting of δ -TiN and ϵ -Ti₂N phases, was observed. This occurrence is a direct consequence of the increased duty cycle, which results in denser plasma. While this enhances the rate of TiN formation and subsequent surface hardness, it also escalates the risk of microcracking and delamination due to the inherently brittle nature of the δ -TiN phase.





unnitrided samples.

Table 4.2 The phases α -Ti,	β-Ti, δ-TiN, and ε-Ti ₂ N	were identified from the JCPDS
files.		

JCPDS	Dhasa	2 Theta (deg),	2 Theta (deg),	[h k	
file	Fliase	Databases	Experiment	1]	
01-1198 Titanium		35.308	35.320	100	
		40.4 <mark>1</mark> 6	40.440	101	
		53.2 <mark>1</mark> 2	53.300	102	
		70. <mark>785</mark>	71.060	103	
		76.084	76.820	112	
		77 <mark>.549</mark>	78.040	-	
44-1288	β-Τί	38 <mark>.482</mark>	38.520	110	
65-0565	TiN	36 <mark>.673</mark>	36.600	111	
		42.601	42.680	200	
76-0198	76-0198 ε-Ti ₂ N	25.452	25.420	110	
	34.657	34.660	101		
	39.282	39.300	111		
	51.063	51.060	211		
	61.027	61.120	002		
	64.256	64.160	301		
		67.305	67.420	311	
		73.125	73.240	202	
N	800	76.099	76.080	321	
	54	ปญ สกา	6		



Figure 4.18 Phase content from semi-quantitative analysis based on the XRD patterns of Ti-6Al-4V alloy before and after plasma nitriding.

Chemical composition

The elemental composition of the surface was examined both before and after plasma nitriding through GD-OES.

Figure 4.19, it was observed that samples subjected to plasma nitriding under the conditions of H200, H300, H400, and H500 with a duty cycle of 10% displayed the highest average surface nitrogen content, approximately 17%wt, which decreased with depth. However, under the condition of H100 with a duty cycle of 20%, a higher surface nitrogen content of 23.74%wt was noted compared to other conditions. Furthermore, at the same depth (

Figure **4.20**), the nitrogen content of H100 remained consistently higher than other conditions throughout the GD-OES testing, suggesting that nitrogen can penetrate

deeply, beyond 40 μ m. This GD-OES analysis indicates that the %duty cycle significantly influences the nitrogen diffusion rate. Increasing the %duty cycle extends the duration of nitrogen ion bombardment, thereby enhancing the likelihood of TiN formation and subsequently increasing nitrogen diffusion throughout the material.



Figure 4.19 Elemental composition of Ti-6Al-4V before and after plasma nitriding from surface to bulk, including (a) titanium, (b) aluminium, (c) vanadium, and (d)

nitrogen concentrations.

313



Figure 4.20 Nitrogen concentration of Ti-6Al-4V before and after plasma nitriding from surface to bulk

Mechanical properties

The surface hardness in the depth profile of the sample was analyzed using the nanoindentation technique with a nanoindentor based on an ESP mode. As the force increases, with loading and unloading increased at intervals from 0.1 mN to 2000 mN.

When considering the processing of samples subjected to plasma nitriding under the conditions of H200, H300, H400, and H500 with a duty cycle of 10%, they exhibit the highest surface hardness ranging from about 1400-1800 HV, as shown in Figure 4.21. However, samples under the condition of H100 have a maximum surface hardness of up to 2500 HV before rapidly decreasing to levels close to other conditions. This is attributed to the formation of the δ -TiN, and ϵ -Ti₂N phases, which are higher than those under other conditions. In other words, it is also a result of the formation of certain compound layers. The formation of these compound layers may occur due to the increase in %duty cycle, which increases the duration of nitrogen ion bombardment, thereby increasing the likelihood of TiN formation. Simultaneously, nitrogen at the surface may not diffuse rapidly enough, leaving nitride compounds at the surface, forming thin compound layers.



Figure 4.21 Nanoindentation test (ESP mode) indicates hardness of surface of nitrided samples.

Surface roughness and work of adhesion

Figure 4.22 shows the surface topography corresponding to the scan area of 25 μ m² of the unnitrided and plasma nitrided samples. Before plasma nitriding, the surface roughness of Ti-6Al-4V was prepared to be approximately 20.8 nm. However, when the samples underwent plasma nitriding under the conditions of H200, H300, H400, and H500 with a duty cycle of 10%, it was found that the surface roughness slightly increased to 29.0±0.8, 23.6±3.2, 18.9±6.0, and 28.3±6.1 nm, respectively. Comparing at the same duty cycle, it can be observed that increasing the amount of hydrogen gas

in the plasma nitriding process may contribute to a minor reduction in surface roughness insignificantly. However, when considering the condition of H100 with an increased duty cycle of 20%, although the proportion of hydrogen gas is significant, the %duty cycle has a clear effect on the increased surface roughness (60.9 ± 5.7 nm). This is attributed to the increase in %duty cycle, which increases the ion bombardment, as evidenced by the GI-XRD results showing that the H100 condition exhibited the highest quantity of the ε -Ti₂N phase. This result can be attributed to the formation of the compound layer. Typically, the compound layer is rough and porous [47].

Figure 4.23 illustrates the contact angle, work of adhesion, and surface roughness of Ti-6Al-4V before and after plasma nitriding. Each sample underwent three measurements at different positions. The contact angle of the unnitrided sample measured $85.1^{\circ}\pm2.2^{\circ}$. After plasma nitriding under H200, H300, H400, and H500 conditions with a duty cycle of 10%, the contact angles increased slightly to around $97.8^{\circ}\pm2.0^{\circ}$, $96.8^{\circ}\pm0.1^{\circ}$, $97.9^{\circ}\pm2.1^{\circ}$, and $98.6^{\circ}\pm0.1^{\circ}$, respectively, correlating with a slight rise in surface roughness. However, the sample treated under H100 conditions with a duty cycle of 20% exhibited notably higher contact angle compared to the other conditions, likely due to significantly elevated surface roughness.

It is noteworthy that the contact angle of H100 surpassed that of all other nitrided samples, possibly because of the Cassie-Baxter wetting model stemming from the whisker formation mechanism, which could result in material reformation and the formation of whiskers (TiN nanoparticles).

The work of adhesion between water droplets and the titanium alloy surface can be determined using the Young-Dupré equation. Under H100 (duty cycle 20%), H200, H300, H400, and H500 conditions, the work of adhesion measured 54.50, 62.04, 63.32, 61.91, and 61.03 mJ/m², respectively, while it was 77.93 mJ/m² for the unnitrided sample. Micropore formation post-nitriding and surface roughness contribute to a more hydrophobic surface. Consequently, the corrosion rate is anticipated to decrease for nitrided samples exhibiting enhanced hydrophobic properties, as water accumulation on the surface may accelerate corrosion. Therefore, a hydrophobic surface is desirable to prevent water adhesion. Plasma nitriding has the potential to enhance the hydrophobic characteristics of Ti-6Al-4V, making it more suitable for biomedical applications.





Figure 4.22 Surface topography obtained using AFM of (a) unnitrided, (b) H_2/N_2 10%, (c) H_2/N_2 20%, (d) H_2/N_2 30%, (e) H_2/N_2 40%, and (f) H_2/N_2 50% nitrided samples.



Figure 4.23 The surface roughness, contact angle and work of adhesion of unnitrided and nitrided samples.

Nitride layer

To examine the structure and characteristics of the nitride layer, the workpiece undergoes a cutting process. The resulting sample is then mounted onto a substrate using epoxy resin to ensure stability for subsequent steps. Following mounting, the sample undergoes grinding and polishing procedures to attain a smooth, flat surface, eliminating any irregularities introduced during cutting and ensuring a perpendicular cross-section to the area of interest. Subsequently, the sample is etched using Nital solution to reveal the internal structure of the nitride layer. Finally, the cross-sectional samples were gold-plated before being analyzed using ESEM at $1500 \times$ and $10000 \times$ magnification.

Figure 4.24 presents a cross-section of the workpiece, revealing the structure of the nitride layer. Figure 4.25 delineates the separation of each area within the nitride

layer, comprising: The δ -TiN layer, resembling a white stripe at the top. The ϵ -Ti₂N layer, characterized by a high grain density. These layers collectively form the compound layer. Finally, the α' -Ti(N) diffusion layer situated below. This layer consists of α -Ti with interstitially inserted nitrogen atoms, inducing structural stress. Consequently, the diffusion layer is harder than the substrate but not as hard as the compound layer. Together, these areas constitute the nitride layer.

From Figure 4.26, measurements of compound layer and diffusion layer, are presented. It is observed that under conditions H100, H200, H300, and H400, the compound layer tends to decrease with higher proportions of hydrogen gas. However, at condition H500, a slightly higher compound layer thickness is noted. This may be attributed to the increased presence of hydrogen, facilitating its combination with nitrogen gas to form ammonia gas, thereby reducing the amount of hydrogen in the system. Consequently, the rate of oxide layer removal decreases, leading to accelerated compound layer formation. Additionally, under condition H100 with a 20% duty cycle, the thickest compound layer is observed, along with the thickest δ -TiN layer. While this results in higher surface hardness, it also elevates the risk of micro-cracking and detachment due to the brittle nature of the δ -TiN phase. Moreover, a higher proportion of hydrogen correlates with an increased tendency for diffusion layer formation. The diffusion layer acts as a supportive, hard layer, preventing cracks from propagating into the metal core and reducing workpiece breakage.

Figure 4.27 depicts the overall thickness of the nitride layer. Notably, at condition H100 with a 20% duty cycle, the highest nitride layer thickness is observed due to the rapid TiN formation rate facilitated by high nitrogen density in the plasma at higher duty cycle. Conversely, under conditions H200, H300, H400, and H500 with a 10% duty cycle, increasing hydrogen proportions coincide with increase nitride layer thickness.

(a) Unnitrided





Figure 4.24 Cross-section show the morphology of the nitride layer of unnitrided and nitrided samples.


Figure 4.25 Cross-sectional morphologies of nitrided sample (H100)



Figure 4.26 Thickness of compound layer and diffusion layer



Figure 4.27 Thickness of nitride layer

Coefficient of friction

The tribological tests (Tribometer, TRB 12-170, Nanotec Corporation, Japan) were performed at room temperature and humidity is 15-31%. The wear samples measured $30\times35\times1$ mm³ in size. Before testing, the samples were cleaned with an acetone wipe. A 6 mm in diameter of stainless steel ball (SUS440C) was slid over the surface of the samples under a normal applied load of 1 N, a linear speed of 5.25 cm/s, and 6000 frictional revolutions, and rotation radius of 5 mm.

Figure 4.28 shows the coefficient of friction (CoF) of unnitrided and nitrided samples at a rotation radius of 5 mm as a function of the number of sliding cycles. It can be seen that the CoF of the unnitrided sample is about 0.45 during the interval of 2000 cycles, which is due to the behavior of the natural titanium oxide layer.

Thereafter, the CoF increases to about 0.56, which is consistent with the surface of the titanium alloy [155].

If we consider the duty cycle10% conditions at H200, H300, H400, and H500 for sliding cycles fewer than 500 cycles, the coefficients of friction are 1.2, 0.8, 0.6, and 1.1, respectively. It can be observed that the coefficient of friction is consistent with the reported roughness values in Figure 4.22. The surface roughness measures 29.0 ± 0.8 , 23.6 ± 3.2 , 18.9 ± 6.0 , and 28.3 ± 6.1 nm, respectively, indicating that the coefficient of friction shown in Figure 4.28 is the coefficient of friction of the formed nitride layer.

For nitride plasma samples H200, H300, and H400, it was found that the nitride layer peeled off relatively quickly, starting after approximately 500-700 sliding cycles, as observed from the rapid decrease in CoF to the friction coefficient of the unnitrided workpiece. The initial friction coefficient is probably related to the rise of the nitride layer's surface roughness. This behavior indicates the removal of the brittle nitride layer. However, from Figure 4.28, two conditions stand out. The nitrided samples H100 and H500 have an initial coefficient of friction in the range of 0.9-1.1 before decreasing to the coefficient of friction of the unnitrided specimen after approximately 1800-2200 sliding cycles. This initial behavior is characteristic of the nitride layer. From the test results, it can be said that at the conditions H100 duty cycle 20% and H500 duty cycle 10%, this results in the formation of a nitride layer that exhibits the best mechanical.





Figure 4.28 Coefficient of friction of unnitrided and nitrided samples as a function of number of sliding cycles.





Figure 4.29 Photographs were taken of wear tracks (radius of 5 mm) on samples that were both unnitrided and nitrided. The nitrided samples were prepared using different hydrogen ratios: (a) H100 with a duty cycle of 20%, (b) H200, (c) H300, (d) H400, and (e) H500, each with a duty cycle of 10%.



CHAPTER V

Conclusions

The aim of this study is to investigate the effects of different bipolar pulse frequencies and H_2/N_2 gas ratio on the surface properties of Ti-6Al-4V alloy.

In the first set of experiments, to investigate the frequency of the bipolar pulse power supply, the Ti-6Al-4V alloy was nitrided using an N₂-H₂ plasma (1000:500 sccm) at an operating pressure of 6.5 torr, and a nitriding temperature of 650 ± 5 °C for 240 minutes. The bipolar pulse frequency was varied between 25 and 200 kHz. The results from GD-OES show that the nitrogen atom can diffuse up to 45% into the surface and gradually decreases with depth. The results of GI-XRD show the formation of the phases δ -TiN and ϵ -Ti₂N. Atomic force microscopy shows that the plasma nitriding process leads to an increase in surface roughness, which is probably due to the formation of the compound layer. The increase in water contact angle after plasma nitriding is likely due to the higher surface roughness. The hardness depth profile of a nitrided Ti-6Al-4V alloy was investigated by nanoindentation in the mode of enhance stiffness procedure. The results show that all nitrided samples have higher surface hardness (about 1260 HV) compared to the unnitrided sample (450 HV). The hardness values tended to decrease with increasing depth but did not affect the bulk hardness. The thickness of the nitride layer was estimated to be about 5 µm. The coefficient of friction and wear rate were determined by a ball-on-disk test. The nitrided sample with the bipolar pulse frequencies of 50 kHz gives an average COF of about 0.6, which is higher than the unnitrided sample due to the higher surface roughness of the nitride layer. For the other nitride samples, the COF decreases rapidly with increasing number of sliding cycles, indicating detachment of the brittle nitride layer during the test. This result is consistent with the specific wear rate, where the nitrided sample has the highest wear resistance and the lowest self-corrosion current density, indicating the highest corrosion resistance at 50 kHz.

In the second set of experiments, to investigate the H₂/N₂ gas ratio, Ti-6Al-4V alloy underwent plasma nitriding using nitrogen gas at 1000 sccm and hydrogen gas at various flow rates (100, 200, 300, 400, and 500 sccm), with a bipolar pulsed plasma frequency of 50 kHz. The condition with hydrogen at 100 sccm employed a 20% duty cycle, while other conditions used a 10% duty cycle. Experiments were conducted at 650°C for 4 hours. Notable transitions in Ti-6Al-4V sample colors from metallic grey to golden were observed, attributed to increased nitrogen-titanium atomic ratio. The H100 specimen with a 20% duty cycle displayed a matte surface, possibly due to ion bombardment energy differences. Darker and lighter colorations around nitride sample edges indicated edge defects. Phase composition analysis revealed α -Ti, β -Ti, δ -TiN, and ε -Ti₂N phases, with enhanced ε -Ti₂N formation observed under the H100 condition. GD-OES analysis showed higher surface nitrogen content in H200, H300, H400, and H500 samples with a 10% duty cycle, while H100 displayed the highest nitrogen content. Nanoindentation revealed maximum surface hardness in H100 samples. Increased duty cycle led to thin compound layer formation impacting surface hardness. Surface roughness slightly increased, with H100 showing the highest increase due to elevated ion bombardment. Contact angle measurements indicated increased hydrophobicity post-nitriding, with H100 displaying the highest angle possibly due to whisker formation. Work of adhesion measurements suggested decreased corrosion rates for nitrided samples. Nitride layer thickness varied; H100 exhibited the highest thickness, enhancing surface hardness but increasing micro-cracking risk, while H200, H300, H400, and H500 led to thicker layers with slightly higher thickness in H500, attributed to hydrogen's increased presence aiding in ammonia formation, reducing the system's hydrogen content. The unnitrided sample had a coefficient of friction (CoF) of approximately 0.56. Coefficients of friction for H200, H300, H400, and H500 nitride plasma samples aligned with reported roughness values, indicating representative nitride layer properties. Nitride layer peeling was observed in H200, H300, and H400 samples, suggesting brittle nitride layer removal. Nitrided samples H100 and H500 exhibited an initial CoF ranging from 0.9 to 1.1, characteristic of the nitride layer. Under H100 with a 20% duty cycle and H500 with a 10% duty cycle, the formation of a nitride layer resulted in the best mechanical properties.

Upon examining both experiments, it becomes evident that augmenting the duty cycle exerts a more pronounced influence on the surface characteristics of Ti-6Al-4V alloy compared to elevating the frequency of the power supply. Furthermore, these effects exhibit substantial disparities when juxtaposed with alterations in the H_2/N_2 gas ratio.





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การชุบแข็งที่ผิวของเหล็กกล้า SKD61 โดยการทำพลาสมาในไตร ดิงที่อุณหภูมิต่ำ

Surface Hardening of SKD61 Steel using Low-Temperature Plasma Nitriding

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บทคัดย่อ

งานวิจัยนี้ได้ทำการสังเคราะห์ชั้นในไตรด์บนเหล็กกล้าเครื่องมือ โดยการใช้พลาสมาช่วยให้เกิด กระบวนการในไตรดิงที่อุณหภูมิต่ำ เหล็กกล้าเครื่องมือ SKD61 ถูกทำความสะอาคโดยใช้พลาสมาไฮโดรเจนเป็น เวลาครึ่งชั่วโมง จากนั้นถูกทำให้ร้อนในสภาวะสุญญากาศที่อุณหภูมิ 450 °C เป็นเวลาครึ่งชั่วโมง และทำพลาสมาใน ไตรดิงต่อเป็นเวลา 4 ชั่วโมง โดยใช้อัตราการไหลของแก๊สในโตรเจนคงที่ เท่ากับ 1000 sccm ผสมกับแก๊ส ไฮโดรเจนที่อัตราการไหลต่างกัน คือ 0 300 และ 500 sccm ที่ความดันขณะทำงานเท่ากับ 149 Pa พลาสมาถูกจุดโดย ใช้แหล่งจ่ายไฟความถึ่ 10 kHz และกำลังไฟฟ้าเฉลี่ย 53 W ได้ทำการตรวจวิเคราะห์สเปกตรัมทางแสงในระหว่าง การทำพลาสมาในไตรดิง พบการคายพลังงานของอะตอมในโตรเจนที่ความยาวคลื่น 427.33 และ 585.57 nm และ อะตอมไฮโดรเจนที่ความอากสิ่น 434.05 486.14 และ 656.28 nm ได้ใช้เทคนิคการวัดการกระจายพลังงานของรังสี เอกซ์เพื่อตรวจสอบการมีอยู่ของในโตรเจน พบว่าปริมาณในโตรเจนมีก่าลดลงเมื่อใช้อัตราการไหลของแก๊ส ไฮโดรเจนเพิ่มขึ้น และได้ใช้เทคนิคการเลี้ยวเบนรังสีเอกซ์เพื่อตรวจสอบโครงสร้างผลึก พบว่าขึ้นงานที่ผ่านการทำ พลาสมาในไตรดิงสามารถตรวจพบเฟส ะ-Fe₃N ที่มุม 20 เท่ากับ 41.17 องศา และเฟส γ'-Fe₄N ที่มุม 47.97 และ 70.2 องสา นอกจากนั้นยังพบเฟส CrN ที่มุม 63.30 องสา ความหนาของชั้นในไตรค์ถูกตรวจสอบด้วยกล้องจุลทรรสน์ อิเล็กตรอนแบบส่องกราด พบว่าเมื่อใช้แก๊สไฮโดรเจนที่ 0 300 และ 500 sccm เกิดการก่อตัวของชั้นในไตรด์หนา เท่ากับ 184±9.51 µm 93±7.96 µm และ 77±5.56 µm ตามลำดับ ซึ่งทำให้ผิวขึ้นงานมีความแข็งเพิ่มขึ้นจาก 5.43±0.63 GPa เป็น 11.36±1.20 12.17±0.35 และ 7.42±0.62 GPa ตามลำดับ

คำสำคัญ: พลาสมาในไตรดิงอุณหภูมิต่ำ; เหล็กกล้าเครื่องมือ; SKD61

Abstract

In this research, a nitride layer on tool steel was synthesized using a plasma-assisted nitriding process at low temperatures. Before nitriding, the SKD61 tool steel was cleaned with a hydrogen plasma for half an hour. Then, it was heated in a vacuum with 450 °C for half an hour and followed by plasma nitriding for 4 hours. The nitrogen flow rate was kept at 1000 sccm and mixed with the hydrogen as a different flow rate of 0, 300, and 500 sccm. The operating pressure was held at 149 Pa. The plasma was generated using a 10 kHz power supply with an average power of 53 W. The optical emission spectra during the plasma nitriding process were analyzed. The atomic nitrogen species were detected at the wavelengths of 427.33 and 585.57 nm. The atomic hydrogens at the wavelengths of 434.05, 486.14, and 656.28 nm also were founded. The energy-dispersive X-ray spectroscopy was used for the elemental analysis of a sample. The atomic nitrogen concentration decrease with the increase of hydrogen flow rate. The structural property of the nitrided specimens was examined using the X-ray diffraction technique. The ϵ -Fe₄N phase was found corresponding to the 2 θ of 41.17, and the γ' -Fe₄N phase was also detected at 47.97 and 70.2. Moreover, the CrN phase arising from the precipitation was identified at 63.30. The thickness of the nitrided layer was estimated from the SEM image. It appears that the nitrogen can diffuse into the specimens up to 184, 93, and 77 µm. The Vicker hardness of the nitrided samples was increased from 5.43±0.63 GPa to 11.36±1.20, 12.17±0.35, and 7.42±0.62 GPa that is corresponding to the hydrogen flow rate of 0, 300, and 500 sccm, respectively.

Keywords: Low-temperature plasma nitriding; Tool steel; SKD61

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ບກນຳ

เหล็กกล้าเครื่องมือ ถูกผลิตขึ้นเพื่อใช้ทำเครื่องมือ ส่วนมากใช้ทำเป็นแม่พิมพ์หรือเครื่องมือสำหรับคัด เฉือนวัสดุอื่น ดังนั้นเหล็กกล้าเครื่องมือจึงต้องมีสมบัติทางด้านความแข็งที่สูง ทนต่อแรงกระแทก และคงความแข็ง ที่อุณหภูมิสูงได้ เป็นต้น การจำแนกประเภทของเหล็กกล้าเครื่องมือตามมาตรฐาน AISI สามารถแบ่งออกเป็น 6 ประเภท คือ เหล็กกล้าเครื่องมือขึ้นรูปเซ็น (W, O, A, D) เหล็กกล้าเครื่องมือทนแรงกระแทก (S) เหล็กกล้าเครื่องมือ ขึ้นรูปร้อน (H) เหล็กล้าเครื่องมือความเร็วสูง (M, T) เหล็กกล้าแม่พิมพ์ (P) และเหล็กกล้ากลุ่มพิเศษ (L) (Thammachot, 2017)

H13 หรือ SKD61 เป็นเหล็กกล้าเครื่องมือขึ้นรูปร้อนในกลุ่มโครเมียม ที่มีส่วนผสมของชาตุคาร์บอน 0.4 wt.% ชิลิกอน 1 wt.% โครเมียม 5.3 wt.% โมลิบดินัม 1.4 wt.% และวาเนเดียม 1 wt.% โดยประมาณ (Speciality Metals LLC, n.d.) นิยมนำไปใช้ทำเครื่องมืองานร้อนต่าง ๆ เช่น แม่พิมพ์อัดขึ้นรูป หรือแม่พิมพ์ฉีดพลาสติก เป็นต้น การเดิมชาตุผสมจำพวก โครเมียม โมลิบดินัม และวาเนเดียม จะช่วยทำให้เกิดเฟสคาร์ไบด์ขึ้นขณะทำเทมเพอร์ (tempering) ซึ่งเป็นเฟสที่จะช่วยลดความอ่อนตัวเนื่องจากอุณหภูมิที่สูงถึง 430 °C (Thammachot, 2017) ถึงแม้ว่า เฟสคาร์ไบด์จะสามารถคงความแข็งไว้ได้ที่อุณหภูมิสูง แต่ถ้าต้องอยู่ภายใต้ความร้อนสูงมากและเป็นระยะเวลานาน จะส่งผลให้เฟสคาร์ไบด์นั้นละลายจนหมดและเกิดการอ่อนตัวของวัสดุได้ และในบางสภาวะงานที่ต้องรองรับแรง กระแทก ขึ้นส่วนเหล่านั้นมักจะเกิดการแตกร้าวและเสื่อมประสิทธิภาพในที่สุด ดังนั้นจึงมีความคิดที่จะเพิ่มความ แข็งให้กับ SKD61 เพื่อเพิ่มขอบเขตการประยุกต์ใช้งานให้กว้างขึ้นและเพื่อยึดอายุการใช้งานด้วยการชุบแข็งที่ผิว (surface hardening)

ในงานวิจัยนี้จึงต้องการที่จะเพิ่มความแข็งเชิงผิวให้กับ SKD61 ด้วยกรรมวิธีพลาสมาไนไตรดิง เพื่อสร้าง ชั้นแข็งที่ผิวของวัสดุในช่วงเฟอร์ไรท์ (Paa-rai, 2005) เนื่องจากเป็นกรรมวิธีที่ใช้พลาสมาเป็นด้วช่วยในการแตกด้ว ของไนโตรเจน และสร้างชั้นไนไตรด์ได้ที่อุณหภูมิด่ำกว่าการชุบแข็งที่ผิวแบบอื่น ๆ ที่ด้องใช้อุณหภูมิใน กระบวนการอยู่ในช่วง 600 ถึง 1000°C (Pantil et al., 2017; Thammachot, 2017; Wu et al., 1999) ถ้าวัสดุได้รับ ความร้อนที่สูงต่อเนื่องเป็นระยะเวลานาน จะส่งผลให้โครงสร้างผลึกของวัสดุทั้งก้อนเปลี่ยนเป็นเฟสมาร์เทนไซด์ที่ มีสมบัติที่แข็งแต่เปราะ (Liu et al., 2020) กระบวนการพลาสมาในไตรดิง คือการทำให้แก้สไนโตรเจนเกิดการแตก ด้วเป็นไนโตรเจนไอออนและไนโตรเจนอะตอมแล้วเข้าไปจับกับอะตอมของเหล็กที่ผิววัสดุที่อยู่ในเฟสเฟอร์ไรท์ (อุณหภูมิด่ำกว่า 590 °C) (Thammachot, 2017) ก่อนแพร่เข้าไปด้วยกระบวนการแพร่แบบแทรก (interstitial diffusion) ซึ่งเป็นกระบวนการแพร่ที่อะตอมของไนโตรเจนที่มีขนาดเล็กเคลื่อนที่ไปตามช่องว่างระหว่างอะตอม ของเหล็กที่มีขนาดใหญ่ (Callister, 1991) ก่อนจะสร้างพันธะและเกิดเป็นเฟสเหล็กไนไตรด์จนส่งผลให้ผิวขึ้นงานมี ความแข็งเพิ่มขึ้นถึง 10 GPa (Diaz-Guillén et al., 2020; Pinedo & Monteiro, 2004)

ในงานวิจัยนี้จึงมีวัตถุประสงค์ที่จะนำเหล็กกล้าเครื่องมือมาทำพลาสมาในไตรดิงที่อุณหภูมิต่ำ เพื่อสร้าง ชั้นในไตรด์ และปรับปรุงสมบัติเชิงกลให้ดีขึ้น โดยใช้เตาเผาสุญญากาศ (vacuum fumace) โดยใช้อัตราการไหลของ

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แก็สในโตรเจนคงที่ เท่ากับ 1000 seem และศึกษาผลของการผสมแก็สไฮโดรเจนที่อัตราการใหลต่างกัน คือ 0 300 และ 500 seem ในระหว่างกระบวนการทำพลาสมาในไตรดิงได้ตรวจสอบสปีชีส์ที่อยู่ในพลาสมาโดยการตรวจ วิเคราะห์สเปกตรัมทางแสง (optical emission spectroscopy: OES) และ วัดความหนาของชั้นในไตรด์ด้วยกล้อง จุลทรรศน์อิเล็กตรอนแบบส่องกราด (scanning electron microscope: SEM) ตรวจสอบชนิดของธาตุด้วยเทคนิค วิเคราะห์การกระจายพลังงานรังสีเอกซ์ (energy dispersive X-ray spectroscopy: EDS) ตรวจสอบไดรงสร้างผลึก ด้วยเทคนิคการเลี้ยวเบนรังสีเอกซ์ (X-ray diffraction: XRD) และตรวจวัดความแข็งระดับจุลภาคแบบวิกเกอร์ (Vickers micro-hardness) และความแข็งตามความลึกระดับนาโนโดยใช้โหมด enhanced stiffness procedure (ESP)

วิธีการทดลอง

การติดตั้งอุปกรณ์

รูปที่ 1 แสดงแผนผังของระบบพลาสมาในไตรดิง ซึ่งประกอบด้วยภาชนะสุญญากาศทรงกระบอกความจุ 0.16 ถูกบาศก์เมตร ที่มีน้ำหล่อเย็นโดยรอบภาชนะสุญญากาศและสามารถควบคุมอุณหภูมิให้คงที่ เท่ากับ 15 °C ตลอดช่วงที่ทำการทดลอง ปื้มโรตารี (rotary pump: Edward, EH250 PFPE 50 Hz) และปื้มรูท (roots pump: Edward, E2M40 PFPE) ถูกใช้ในการสร้างสภาวะสุญญากาศ โดยค่าความดันภายในภาชนะสุญญากาศถูกอ่านด้วย เกจวัดความดันแบบคาปาชิแตนซ์ (Inficon AG, CDG100D) ที่สามารถอ่านความดันได้ในช่วง 0.13 Pa ถึง 1.3x10⁵ Pa



รูปที่ 1 แผนผังระบบพลาสมาในไตรดิง

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อัตราการไหลของแก๊สไนโตรเจนและแก๊สไฮโดรเจนถูกควบคุมโดยใช้ Mass flow controller โดยแก๊ส ในโตรเจน สามารถปรับอัตราการไหลได้ในช่วง 0-1000 sccm (MKS, GV50A) และแก๊สไฮโดรเจนสามารถปรับ อัตราการไหลได้ในช่วง 0-500 sccm (MKS, 2179A) ชิ้นงานถูกติดตั้งบนขั้วไฟฟ้าที่ใช้จุดพลาสมา โดยมีแผ่นให้ ความร้อน (heater) อยู่ด้านบน หัววัดเทอร์โมคับเปิลชนิด K (K-type thermocouple) ถูกหุ้มด้วยเซรามิกเพื่อป้องกัน การถูกรบกวนจากแหล่งจ่ายไฟที่ใช้จุดพลาสมา อุณหภูมิของชิ้นงานถูกควบคุมด้วยชุดควบคุมอุณหภูมิ (temperature controller) ขั้วไฟฟ้าได้รับกำลังไฟฟ้ามาจากแหล่งจ่ายไฟกระแสสลับความถี่ 10 kHz ซึ่งทำหน้าที่เป็น แหล่งให้พลังงานกับแก๊สในกระบวนการพลาสมาไนไตรดิง เลนส์รวมแสง (collimator lens) ความยาวไฟกัส 10 เซนติเมตร ถูกใช้สำหรับเก็บแสงที่เปล่งออกมาจากพลาสมาและส่งสัญญาณผ่านไฟเบอร์ออปติกเข้าสู้เครื่อง วิเคราะห์สเปกตรัมทางแสง (optical spectrometer, AvaSpec-ULS4096CL-EVO) ที่ถูกควบคุมโดยคอมพิวเตอร์เพื่อ แสดงและประมวลผลผ่านโปรแกรม AvaSoft 8 ก่อนการใช้งานสเป็กโตรมิเตอร์ความไวของซีซีดี (charge couple device) ในแต่ละพิกเซล จะถูกสอบเทียบ (calibrate) กับสเปกตรัมของแสงที่ปลดปล่อยออกมาจากวัตถุดำ (blackbody radiation) เส้นสเปกตรัมของแสงถูกบันทึกในช่วงความยาวกลิ่น 300-900 nm ใช้ระยะเวลาเก็บแสง 500 ms และเฉลี่ย 3 ครั้ง ลักษณะเส้นสเปกตรัมของแสงที่บันทึกได้จะถูกนำมาจำแนก (identified) เป็นชนิดของสปีซีส์ โดยใช้ฐานข้อมูลจากออนไลน์จาก NIST Atomic Spectra Database Lines Data (Kramida et al., 2020)

การทำพลาสมาในไตรดิง

ในงานวิจัยนี้ ได้ใช้เหล็กกล้าเครื่องมือในกลุ่ม SKD61 หรือ H13 ที่มีลักษณะเป็นเม็ดทรงกระบอก ขนาด เส้นผ่านศูนย์กลาง 15 มิลลิเมตร สูง 20 มิลลิเมตร เป็นตัวอย่างที่ใช้ในการทำพลาสมาไนไตรดิง ขึ้นงานถูกทำความ สะอาดด้วยสารละลายอะซิโตนโดยการสั่นในเครื่องอัลตราโซนิค เป็นเวลา 10 นาที และสารละลายเมทานอล 10 นาที 3 รอบ ที่อุณหภูมิ 50 °C จากนั้นขึ้นงานจะถูกเป่าให้แห้งด้วยลมร้อนทันที แล้วนำเข้าภาชนะสุญญากาศ ต่อมา จึงสูบอากาศออกจากภาชนะสุญญากาศให้ได้ความดันฐานที่ 0.13 Pa จากนั้นขึ้นงานจะถูกทำความสะอาดด้วย พลาสมาไฮโดรเจน เป็นเวลา 30 นาที ที่กำลังไฟฟ้า 75 W โดยใช้แก๊สไฮโดรเจนที่อัตราการไหล 500 secm ที่ความ ดัน 16 Pa ต่อด้วยการอุ่นร้อนขึ้นงานที่อุณหภูมิ 450 °C เป็นเวลา 30 นาที จึงเริ่มกระกวนการพลาสมาไนไตรดิงต่อที่ อุณหภูมิเดียวกัน โดยใช้แก๊สไนโตรเจนที่อัตราการไหล 1000 secm และใช้แก๊สไฮโดรเจนที่อัตราการไหลเตกต่าง กัน 3 ค่า คือ 0 300 และ 500 secm เป็นเวลา 240 นาที ที่กำลังไฟฟ้า 53 W ซึ่งจะใช้รหัสแทนเงื่อนไขการทำพลาสมา ในไตรดิงเป็น H0 H300 และ H500 ตามลำดับ ความดันขณะทำพลาสมาไนไตรดิงถูกควบคุมไว้ที่ 149 Pa ใน ขั้นตอนสุดท้ายขึ้นงานถูกทำให้เซ็นตัวลงอย่างช้า ๆ มาที่อุณหภูมิห้องจึงนำออกจากภาชนะสุญญากาศ เงื่อนไขการ ทำพลาสมาไนไตรดิงถูกวัดโดยใช้หัววัดแรงดันสูง (Keysight N2771B, CA 95403-1738) หลังจากนั้นสำหรับการ ดรวจวิเคราะห์กวามหนาโดยใช้หัววัดแรงดันสูง (Keysight N2771B, CA 95403-1738) หลังจากนั้นสำหรับการ

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ความเข้มข้น 10% เป็นเวลา 90 วินาที ในขณะที่ชิ้นงานอีกชุดหนึ่งจะถูกนำไปตรวจวิเคราะห์สมบัติความแข็ง วิเคราะห์การเกิดเฟสเหล็ก ในไตรด์ ต่อไป ชิ้นงานควบคุมและชิ้นงานที่ผ่านการทำพลาสมาไนไตรดิงได้ถูกตรวจ วิเคราะห์สัณฐานวิทยาของพื้นผิวโดยใช้กล้องจุลทรรศน์อิเล็กตรอนแบบส่องกราด (Hitachi, TM4000) ตรวจสอบ ชนิดของธาตุโดยใช้เครื่องวิเคราะห์การกระจายพลังงานรังสีเอกซ์ (FEI, Quanta 450) ตรวจสอบโครงสร้างผลึกด้วย เทคนิคการเลี้ยวเบนรังสีเอกซ์ (Bruker, D8 Advance) ตรวจวัดความแข็งระดับจุลภาคแบบวิกเกอร์ (Economical manual micro Vickers hardness tester, HV-1000 series) และตรวจวัดความแข็งตามความลึกโดยใช้เครื่อง Nanoindentor (Fischer, FISCHERSCOPE HM2000)

Parameters	Plasma cleaning	Preheating	Plasma nitriding	Cool down
Operate pressure (Pa)	16	0.7	149	0.7
Voltage (V _{ms})	475±15	-	220, 240, 340	-
Average power (W)	~ 75	-	~ 53	-
H2 flow rate (sccm)	500	-	0, 300, 500	-
N2 flow rate (sccm)	-	-	1000	-
Operated time (min)	30	30	240	240

ตารางที่ 1 ตัวแปรที่ใช้ในกระบวนการพลาสมาในไตรดิง

ผลการทดลองและการวิจารณ์

การวิเคราะห์สเปกตรัมทางแสงด้วยเทคนิค OES

การวิเคราะห์สเปกตร้มของแสงที่ปลดปล่อยออกมาจากพลาสมาเป็นเทคนิคที่ใช้ตรวจสอบชนิดของสปีชีส์ ที่อยู่ในพลาสมาในระหว่างขั้นตอนการทำพลาสมาในไตรดิง ทั้งนี้ยังสามารถนำข้อมูลที่วัดได้มาวิเคราะห์หา อุณหภูมิของอิเล็กตรอนได้โดยที่ไม่เป็นการรบกวนต่อระบบ (Chingsungnoen et al., 2007) เทคนิคการวิเคราะห์ สเปกตร้มอาศัยหลักการเปล่งแสงของอะตอมหรือโมเลกุลที่อยู่ในสถานะกระตุ้น ซึ่งเกิดจากการคายพลังงานของ อิเล็กตรอนที่อยู่ในระดับพลังงานสูงเปลี่ยนสถานะกลับมาที่ระดับพลังงานด่ำกว่า ความยาวคลื่นของโฟตอนที่คาย พลังงานออกมาสามารถนำไปจำแนกเป็นชนิดของสปีชีส์และความเข้มเส้นสเปกตร้มจะแปรผันโดยตรงกับความ หนาแน่นของสปีชีส์นั้น ๆ ดังแสดงตามรูปที่ 2 เส้นสเปกตร้ม (a) เกิดจากการเปล่งแสงของพลาสมาไฮโดรเจนใน ขั้นตอนการทำความสะอาดผิวและกำจัดขั้นออกไซด์ เส้นสเปกตร้มที่ความยาวคลื่น 434.05 486.14 656.28 nm สอดคล้องกับการเปลี่ยนสถานะของอิเล็กตรอนในอะตอมไฮโดรเจนจากระดับพลังงาน 5 4 3 กลับลงมาที่ระดับ พลังงาน 2 ตามลำดับ แสงพลาสมามีลักษณะเป็นสีชมพูเนื่องจากเส้นสเปกตรัมสีแดงความยาวคลื่น 656.28 nm มี ความเข้มมากกว่าเส้นอื่น ๆ นั่นเอง อะตอมไฮโดรเจนมีส่วนสำคัญอย่างมากในการลดความเข้มขึ้นของแก้ส

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วารสารวิทยาศาสตร์ประยุกต์ ออกซิเจนที่หลงเหลืออยู่ (residue oxygen gas) ในระบบสูญญากาศ เนื่องจากทั้งอะดอมไฮโดรเจนและออกซิเจนที่ เกิดจากการแตกตัวเป็นพลาสมา สามารถรวมด้วกันเป็นไอน้ำ (H,O) จึงถูกปั้มสุญญากาศดูดออกไปจากภาชนะ สุญญากาศ ปริมาณออกซิเจนที่อดองจะอดการเกิดขั้นออกไซด์ที่บริเวณผิวขึ้นงานในระหว่างการทำพอาสมาในไตร ดิง ทำให้อะตอมของในโตรเจนสามารถแพร่เข้าในในผิวขึ้นงานได้ง่ายขึ้น เนื่องจากไอออนถูกเร่งด้วยสนามไฟฟ้าที่ บริเวณชีสต์ ชิ้นงานที่วางอยู่ที่ขั้วกำลังจึงถูกระคมชนด้วยไอออนไฮโครเจน (H`) ขบวนการนี้สามารถทำให้อะตอม ของออกซิเจนที่อยู่ในชั้นโลหะออกไซด์ (metal oxide) หลุดออกเปลี่ยนเป็นสถานะแก๊สและถูกปั้มสูญญากาศดูด ออกไปในที่สด ตัวอย่างของสมการการกำจัดชั้นโลหะออกไซด์โดยใช้พลาสมาไฮโดรเจน แสดงได้ตามสมการที่ 1

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$$FeO + 2H \rightarrow H_{2}O + Fe$$
 ...(1)

ตามรูปที่ 2 เส้นสเปกตรัม (b) เกิดจากการเปล่งแสงของพลาสมาในโตรเจนในระหว่างขั้นตอนการทำ พลาสมาในไตรดิงของขึ้นงาน H0 จะเห็นว่าแสงพลาสมามีสีออกไปทางสีน้ำเงินเนื่องจากเส้นสเปกครัมส่วนใหญ่ที่ พบมีความขาวคลื่นน้อยกว่า 450 nm พบพีกของอะตอม ในโตรเจนที่อยู่ในสถานะกระคุ้น N I N II N III และ N V นอกจากนั้นยังพบพีคของโมเลกุลในโครเจนในสถานะกระคุ้น N₂ A(³ ∑₀⁺) ซึ่งเป็นอนุมูล (radical) ที่มักพบ จากการแตกด้วของแก๊สไนโตรเจน (Uhm, 2015) สปีชีส์เหล่านี้มีบทบาทสำคัญต่อการเกิดปฏิกิริยาของเหล็กไนไตร์ ที่ผิว (สมการที่ 2) ตามแบบจำลองของโกเบล (Koebel's model) (Bernal, 2006)



รปที่ 2 สเปกครัมของแสงที่เปล่งออกมาจาก (a) พลาสมาไฮโครเจน (b) พลาสมาในโครเจน และ (c) พลาสมา ในโครเจนผสมไฮโครเจน

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ตามรูปที่ 2 เส้นสเปกครัม (c) เกิดจากการเปล่งแสงของพลาสมาในโตรเจนผสมไฮโครเจนในระหว่าง ขั้นตอนการทำพลาสมาในไตรดิงของขึ้นงาน H500 (N₂ = 1000 sccm + H₂ = 500 sccm) จะเห็นว่าพบพึกของ อะตอมและโมเลกุลในโตรเจนที่อยู่ในสถานะกระตุ้น แสงพลาสมามีลักษณะเป็นสีม่วงอมชมพูเนื่องจากยังพบพึก ของอะตอมไฮโครเจนที่ความยาวคลื่น 656.28 nm ซึ่งเป็นแสงสีแคงแต่ความเข้มพึคน้อยมากเนื่องจากแสงที่เปล่ง ออกมาจากพลาสมาในโตรเจนมีความเข้มมากกว่า และเนื่องจากอะตอมไฮโครเจนมีขนาดเล็กและมีมวลน้อย จึงทำ ให้แก๊สไนโตรเจนสามารถพาอะตอมของไฮโครเจนออกไปจากระบบได้มาก ซึ่งส่งผลให้อะตอมของไฮโครเจน หลงเหลือภายในภาชนะสุญญากาศน้อยกว่าในกระบวนการทำความสะอาดด้วยพลาสมา

การวิเคราะท์สัณฐานวิทยาด้วยเทคนิค SEM และองค์ประกอบของชาตุด้วยเทคนิค EDS

เทคนิคสเปกโทรเมตรีรังสีเอกซ์แบบกระจายพลังงาน หรือเรียกสั้น ๆ ว่าเทคนิค EDS เป็นการวิเคราะห์ องค์ประกอบของชาตุที่ใช้ร่วมกับกล้องจุลทรรศน์อิเล็กตรอนแบบส่องกราค รูปที่ 3 (a) และ 3 (b) แสดงภาพถ่าย SEM ที่กำลังขยาย 300 และ 3000 เท่า ของผิวขึ้นงาน SKD61 ที่ไม่ผ่านการทำพลาสมาในไตรดิง (Pristine) ซึ่งจะ สังเกตเห็นความขรขระของผิวขึ้นงานที่เกิดจากการตัดและขัดขึ้นรูปขึ้นงานได้อย่างชัดเจน รูปที่ 3 (c) และ 3 (d) แสดงผิวขึ้นงานที่ผ่านการทำพลาสมาในไตรดิงโดยใช้แก๊ส N, 1000 sccm รูปที่ 3 (e) และ 3 (f) แสดงผิวขึ้นงานที่ ผ่านการทำพลาสมาในไตรดิงโดยใช้แก๊ส N, 1000 sccm และ H, 300 sccm และ รูปที่ 3 (g) และ 3 (b) แสดง ผิวขึ้นงานที่ผ่านการทำพลาสมาในไตรดิงโดยใช้แก๊ส N. 1000 sccm และ H. 500 sccm เมื่อเปรียบเทียบสัญขาน วิทยาของพื้นผิวขึ้นงาน H0 ที่ไม่มีส่วนผสมของแก๊สไฮโดรเจนในพลาสมา พบว่าผิวขึ้นงานมีเม็ดเกรนกระจายทั่ว ทั้งพื้นผิวชั้นนอก (รูปที่ 3 (d)) ซึ่งน่าจะเกิดจากการไม่มีไอออนไฮ โครเจนมาช่วยกำจัดชั้นออกไซค์ จึงทำให้อะตอม ของในโตรเจนแพร่เข้าไปที่ผิวขึ้นงานได้ช้าลง เกิดการออกันของอะตอมในโตรเจนที่ผิว ในขณะเดียวกันในโตรเจน ไอออนที่ระดมชนพื้นผิวทำให้อะตอมของเหล็กหลดออกและตกกลับไปที่พื้นผิว และฟอร์มด้วกับอะตอม ในโตรเจนเกิดเป็นอนุภาคนาโนไนไตรด์ (nitride nano-particle) (Diaz-Guillén et al., 2020) ที่สามารถรวมตัวกัน เป็นอนุภาคขนาดใหญ่ได้ง่ายภายใต้อุณหภูมิสูง (She et al., 2013) จะมีลักษณะเป็นชั้นสีขาว (white layer) ซึ่ง โดยทั่วไปจะประกอบไปด้วยเฟส ɛ-Fe,N และเฟส v'-Fe,N (Bemal, 2006) และเป็นชั้นที่มีสมบัติด้านทานการสึก หรอและมีความแข็งสูงแต่เปราะ (Aghajani & Behrangi, 2017) ในขณะที่ชิ้นงาน H300 และ H500 มีส่วนผสมของ แก้สไฮโดรเจนในพลาสมาจะพบว่าไม่มีเม็ดเกรนที่บริเวณผิว ซึ่งน่าจะเกิดขั้นสีขาวน้อยมาก (Diaz-Guillén et al., . 2020) เนื่องจากไฮโครเจนไอออนมีส่วนช่วยในกำจัดชั้นออกไซค์ทำให้อะตอมไนโครเจนสามารถแพร่เข้าไปในเนื้อ ชิ้นงานได้ดีขึ้น จึงไม่เกิดการรวมตัวกันของอนภาคนาโนไนไตรด์เป็นอนภาคขนาดใหญ่

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รูปที่ 3 ภาพถ่าย SEM ที่กำลังขยาย 300 และ 3000 เท่า ของขึ้นงาน SKD61 (a),(b) ควบคุม (Pristine) (c),(d) ทำ พลาสมาในไดรดิงโดยใช้แก๊ส N₂ 1000 sccm (H0) (e),(f) N₂ 1000 sccm และ H₂ 300 sccm (H300) (g),(h) N₂ 1000 sccm และ H₂ 500 sccm (H500)

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องค์ประกอบของชาตุเชิงผิวของแต่ละขึ้นงานแสดงได้ดังตารางที่ 2 โดยที่ปริมาณไนโตรเจนที่พื้นผิวมี แนวโน้มลดลงเมื่อปริมาณของแก๊สไฮโดรเจนเพิ่มขึ้น แสดงดังกราฟในรูปที่ 4 ซึ่งสามารถอชิบายได้ในเชิง พฤติกรรมของพลาสมา คือ แม้ว่าไอออนไฮโดรเจนจะมีบทบาทสำคัญในการกำจัดชั้นออกไซด์ แต่เมื่อปริมาณของ แก๊สไฮโดรเจนมากขึ้น ทำให้มีโอกาสมากขึ้นที่อะตอมไฮโดรเจนและไอออนไฮโดรเจนจะเกิดการก่อตัวกับอะตอม ในโตรเจนที่บริเวณผิวและเปลี่ยนเป็นแก๊สแอมโมเนีย (NH,) ทำให้สัดส่วนอะตอมไนโตรเจนลดลง ซึ่งจะส่งผลให้ อัตราการแพร่ของอะตอมไนโตรเจนเข้าไปในเนื้อชิ้นงานลดลง และส่งผลไปถึงการก่อด้วของเฟสไนไตรด์ที่ลดลง ไปด้วย โดยสังเกตได้จากภาพถ่ายภาคตัดขวาง SEM ที่กำลังขยาย 100 เท่า ในโหมด back scattered electron (BSE) บริเวณขอบของชิ้นงานที่ถูกขัดผิวหน้าออก ดังรูปที่ 5 จะพบว่าความหนาของชั้นไนไตรด์มีก่าลดลงจาก 184±9.51 µm เป็น 93±7.96 µm และ 77±5.56 µm เมื่อเพิ่มอัตราการไหลของแก๊สไฮโดรเจน เป็น 300 และ 500 seem ตามลำดับ

รหัส	Elementary concentration (wt.%)									
	Fe	С	Cr	Mo	Si	v	0	N		
Pristine	82.0±0.9	8.7±0.8	4.9±0.1	1.2±0.1	0.8±0.1	0.8±0.04	0.6±0.6	-		
H0	72.7±1.0	6.6±0.8	4.0±0.8	1.0 ± 0.04	0.6±0.1	0.7±0.04	4.2±0.3	9.0±1.5		
H300	80.9±1.0	5.5±0.5	4.9±0.04	1.4±0.1	0.8±0.1	0.8±0.04	0.8±0.8	4.0±0.7		
H500	82.8±1.1	5.8±1.2	4.7±0.1	1.6±0.2	0.8±0.1	0.8±0.1	1.9±0.1	0.7±0.7		







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รูปที่ 5 ภาพถ่ายภาคตัดขวางในโหมด BSE ที่กำลังขยาย 100 เท่า ของขึ้นงาน SKD61 (a) ควบคุม (Pristine) (b) H0 (c) H300 และ (d) H500

การวิเคราะท์โครงสร้างผลึกด้วยเทคนิค XRD

ในงานวิจัยนี้ได้ทำการศึกษาองก์ประกอบและโครงสร้างของ SKD61 ทั้งที่ผ่านและไม่ผ่านการทำพลาสมา ในไตรดิง เพื่อตรวจสอบการก่อตัวของชั้นไนไตรด์ ใช้มุม 20 ในช่วง 30 ถึง 80 องศา ได้รูปแบบการเลี้ยวเบนของ รังสีเอ็กซ์ ดังรูปที่ 6 เมื่อเปรียบเทียบคำแหน่งพีคกับฐานข้อมูล JCPDs ที่ปรากฏอยู่ในงานวิจัยของ Farghali & Aizawa, 2018; Huang et al., 2021; Keddam et al., 2005; Nascimento et al., 2009; Paa-rai, 2005; ILBE Xi et al., 2008 พบว่าชิ้นงานที่ไม่ผ่านการทำพลาสมาไนไตรดิงปรากฏพีคของเหล็กที่ดำแหน่งมุมเลี้ยวเบน 44.47 องศา พีค ของ Fe-Cr ดำแหน่งมุมการเลี้ยวเบน 65.1 องศา และพบการเกิดโครเมียมออกไซด์ (CrO) ที่ดำแหน่งมุมการเลี้ยวเบน 63.3 องศา ในส่วนของชิ้นงานที่ผ่านการทำพลาสมาไนไตรดิงปรากฏพีคของเหล็กที่ดำแหน่งมุมกลี่ยวเบน 44.47 องศา พีค ของ Fe-Cr ดำแหน่งมุมการเลี้ยวเบน 65.1 องศา และพบการเกิดโครเมียมออกไซด์ (CrO) ที่ดำแหน่งมุมการเลี้ยวเบน 63.3 องศา ในส่วนของชิ้นงานที่ผ่านการทำพลาสมาไนไตรดิงปรากฏพีคของเฟส E-Fe_sN ที่ดำแหน่งมุมการ เลี้ยวเบน 41.17 58.0 และ 77.0 องศา ซึ่งสอดคล้องกับโครงสร้างผลึกแบบ HCP (bexagonal close-packed) พบเฟส γ'-Fe_sN ที่เป็นโครงสร้างแบบ FCC (face-center cubic) ปรากฏที่ดำแหน่งมุมการเลี้ยวเบน 47.97 และ 70.20 องศา ซึ่งทั้งสองเฟสนี้แสดงถึงการเกิดชั้นสีขาวที่บริเวณพิวชั้นนอก นอกจากนั้นยังพบการตกตะกอนของเฟส CrN ที่ ดำแหน่งมุมการเลี้ยวเบน 43.9 องศา ดังแสดงตามภาพประกอบของรูปที่ 6 การตกตะกอนของโลหะไนไตรด์เหล่านี้ มักเกิดขึ้นที่บริเวณขอบเกรนในชั้นได้ชั้นสีขาว หรือเรียกชั้นนี้ว่าชั้นการแพร่ (diffusion layer) ซึ่งมีกวามสำคัญอย่าง มากในการเพิ่มความแข็งที่ผิวให้กับชิ้นงาน (Agbajani & Behrangi, 2017) และจะสังเกตเห็นว่ารูปแบบการเลี้ยวเบน รังสีเอ็กซ์ของ H0 จะพบชั้นโครเมียมออกไซด์ที่ผิวสูงขึ้นจากชิ้นงานกวบคุม (Pristine) ที่มุการเลี้ยวเบน 63.3 องศา ซึ่งนั้นน่าจะเกิดจากการที่เงื่อนไขการทำพลาสมาในไตรดิง H0 ไม่ได้ใช้แก้สไฮโดรเจนช่วยในการกำจัดชั้นออกไซด์ ดังกล่าว



รูปที่ 6 เปรียบเทียบรูปแบบการเลี้ยวเบนรังสีเอ็กซ์ของขึ้นงาน SKD61 ที่ไม่ผ่านและผ่านการทำพลาสมาในไตรดิง

การวิเคราะห์ความแข็งระดับจุลภาคแบบวิกเกอร์

ใต้ทำการวัดความแข็งของขึ้นงาน SKD61 ที่ไม่ผ่านและผ่านการทำพลาสมาไนไตรดิง รูปที่ 7 เป็นผลการ ทดสอบความแข็งระดับจุลภาค (microbardness) แบบวิกเกอร์ ใช้แรงกด 0.2 kgf หรือ 2 N กดผ่านหัวกดที่ทำด้วย เพชรรูปพีรามิดฐานสี่เหลี่ยมจัตุรัส มุมรวมที่ปลายหัวกด 136° โดยที่ชั้นงานหนึ่งขึ้นจะถูกวัดความแข็งในบริเวณที่ โดนพลาสมาไนไตรดิง (ด้านบน) และบริเวณที่ไม่โดนพลาสมาไนไตรดิง (ฐานด้านล่าง) แต่ละชั้นทำการวัดทั้งหมด 5 จุดที่แตกต่างกันแล้วหาค่าเฉลี่ย พบว่าขึ้นงานควบคุม (Pristine) มีก่าความแข็งเฉลี่ยเท่ากับ 5.43±0.63 GPa เมื่อทำ พลาสมาไนไตรดิงที่อุณหภูมิ 450 °C เป็นเวลา 4 ชั่วโมง โดยใช้แก๊สไนโตรเจนที่ยัตราการไหล 1000 sccm ความ แข็งเพิ่มขึ้นเป็น 11.36±1.20 GPa และเมื่อผสมแก๊สไฮโดรเจนที่ยัตราการไหล 300 sccm ความแข็งมีล่าเพิ่มขึ้น เล็กน้อยเป็น 12.17±0.35 GPa แต่เมื่อเพิ่มอัตราการไหลของแก๊สไฮโดรเจนเป็น 500 sccm ความแข็งมีล่าเพิ่มขึ้น เล็กน้อยเป็น 12.17±0.35 GPa แต่เมื่อเพิ่มอัตราการไหลของแก๊สไฮโดรเจนเป็น 500 sccm กำความแข็งกลับลดลง เหลือ 7.42±0.62 GPa ในขณะที่ฐานด้านล่างขึ้นงานควบคุมที่ไม่ได้ผ่านการทำพลาสมาไนไตรดิง ซึ่งแสดงให้เห็นว่า กายใน (bulk bardness) จึงมีก่าใกล้เคียงกับขึ้นงานควบคุมที่ไม่ได้ผ่านการทำพลาสมาไนไตรดิง ซึ่งแสดงให้เห็นว่า การทำพลาสมาไนไตรดิงสามารถเพิ่มความแข็งเริงพิภัล(surface bardness) ของขึ้นงานโดยที่ไม่ได้ไปทำให้ความแข็ง และความเหนียวภายในชิ้นงานเปลี่ยนแปลง การใช้แก๊สไฮโดรเจนที่มากเกินไป (ชั้นงาน H500) จะลดอัตราการแพร่ ของอะตอมในโตรเจนส่งผลให้ความหนาของชั้นในไตรด์ลดลง ความแข็งติงผิวของชิ้นงานจึงลดง

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รูปที่ 7 ความแข็งแบบวิกเกอร์ที่ผิวค้านบนและฐานค้านล่างของขึ้นงานที่ผ่านและไม่ผ่านการทำพลาสมาไนไตรคิง





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รูปที่ 8 แสดงความแข็งแบบวิกเกอร์ตามความลึกของขึ้นงานที่ผ่านและไม่ผ่านการทำพลาสมาไนไตรดิง วัคโดยการใช้โหมค ESP ซึ่งเป็นการเพิ่มแรงกค (load) และลดแรงกค (unload) เป็นช่วง ๆ จาก 0.1 N จนถึง 2.0 N ใช้การเพิ่มขึ้นครั้งละ 0.1 N ในทุกค่าแรงกดเครื่อง Nanoindentor จะแสดงก่าความแข็งที่สอดคล้องกับความลึก (depth) ออกมา ผลการทดลองพบว่าเมื่อใช้แรงกดถึงก่าสูงสุด 2 N ความแข็งของขึ้นงานที่ผ่านการทำพลาสมาไน ไตรดิง H0 และ H300 มีก่าใกล้เกียงกัน ในขณะที่ขึ้นงาน H500 มีก่าความแข็งลดลง ซึ่งสอดคล้องกับก่าความสึก ระดับจุลภาคในรูปที่ 7 และที่แรงกดเท่ากันผิวขึ้นงานที่อ่อนกว่าหัวกดจะลงไปได้ลึกมากกว่า ซึ่งจะเห็นว่าขึ้นงานที่ ไม่ผ่านการทำพลาสมาไนไตรดิง (Pristine) ที่ โหลด 2 N ตำแหน่งหัวกดจะลึกลงไปจากผิวถึงประมาณ 5.6 µm และ ความแข็งที่บริเวณผิวในช่วงความลึกน้อยกว่า 0.5 µm จะมีก่าสูงกว่าภายใน เป็นผลมาจากชั้นสีขาว (white layer) ที่ เกิดขึ้นบริเวณผิวโดยธรรมชาติระหว่างกระบวนการไนไตรดิง ซึ่งโดยทั่วไปแล้วชั้นสีขาวจะมีความแข็งมากกว่าชั้น การแพร่ (diffusion layer) เล็กน้อย และจะลดลงเรื่อย ๆ ตามความลึก (Bernal, 2006) ดังนั้นในช่วงแรงกดที่มีก่าน้อย ๆ ขึ้นงาน H0 จึงมีความแข็งมากกว่าชิ้นงาน H300 และ H500 ซึ่งเป็นผลมาจากความหนาของชั้นสีขาวที่มากกว่า ขึ้นงานอื่น ๆ นั่นเอง

สรุปผลการทดลอง

งานวิจัยนี้ได้ทำการเพิ่มความแข็งที่ผิวให้กับเหล็กกล้าเครื่องมือ SKD61 ด้วยการทำพลาสมาในไตรดิงที่ อุณหภูมิต่ำ (450 °C) เป็นเวลา 4 ชั่วโมง โดยใช้อัตราการไหลของแก๊สไนโตรเจนคงที่ เท่ากับ 1000 sccm ผสมกับ แก๊สไฮโครเจนที่อัตราการไหลต่างกัน คือ 0 300 และ 500 sccm พลาสมาถูกจุดโดยใช้แหล่งจ่ายไฟความถี่ 10 kHz ใต้ทำการตรวจวิเคราะห์สเปกตรับทางแสงใบระหว่างการทำพอาสบาใบไตรดิง พบอะตอบใบโตรเจบและ ไฮโครเจนที่สถานะกระดุ้น อะตอมในโตรเจนมีบทบาทสำคัญในการก่อตัวของเหล็กในไตรค์ ขณะที่ไอออน ไฮโครเจนมีส่วนสำคัญในการกำจัดชั้นโลหะออกไซด์ที่ผิวขึ้นงาน และสามารถจับกับอะตอมไนโตรเจนเกิดเป็น แก๊สแอมโมเนีย การใช้แก๊สไนโตรเจน 1000 sccm และแก๊สไฮโครเจน 300 sccm ทำให้ขึ้นงานที่ผ่านการทำ พลาสมาในไตรดิงมีความแข็งที่ผิวเพิ่มขึ้นสูงสุดถึงประมาณ 12.17 GPa โดยที่ไม่มีเม็ดเกรนขนาดเล็กกระจายทั่วทั้ง พื้นผิวขั้นนอก ผลการวัดความแข็งตามความลึก พบว่าความแข็งมีค่าสูงสุดที่ผิวด้านนอกและมีแนวโน้มลดลงเรื่อย ๆ ตามความลึก นั่นหมายถึง การทำพลาสมาไนไตรดิงมีผลทำให้ความแข็งที่ผิวเพิ่มขึ้นจริง แต่ยังคงสมบัติความเหนียว ของเนื้อขึ้นงานเดิมไว้ได้ และได้ทำการตรวจสอบการแพร่ของอะตอมไนโตรเจนโดยใช้เทคนิก EDS พบว่าที่ผิวมี ปริมาณในโตรเจนเพิ่มขึ้นอย่างชัดเจน ผลจากการตรวจสอบโครงสร้างผลึกโดยใช้เทคนิค XRD พบเฟส ɛ-Fe.N และ γ'-Fe,N และการตกตะกอนของ CrN ซึ่งเป็นการยืนยันการมีอยู่ของชั้นในไตรด์ และโดยทั่วไปแล้วความแข็งที่ ผิวจะสอดคล้องกับความหนาของชั้นในไตรด์ จึงมีการตรวจสอบความหนาของชั้นในไตรด์จากภาพถ่าย ภากตัดขวาง SEM พบกวามหนาของชั้นในใตรค์เป็น 184±9.51 µm เป็น 93±7.96 µm และ 77±5.56 µm สอดกล้องกับอัตราการไหลแก๊สไฮโดรเจน 0 300 และ 500 sccm ตามลำดับ ซึ่งความหนาของชั้นไนไตรด์มี

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แนวโน้มลดลงตามปริมาณแก๊สไฮโดรเจนที่เพิ่มขึ้น แต่ยังคงมีกวามแข็งสูงกว่าชิ้นงานที่ไม่ผ่านการทำพลาสมาไน ไตรดิง

กิตติกรรมประกาศ

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PAPER Effect of pulse frequency on the surface properties and corrosion resistance of a plasma-nitrided Ti-6AI-4V alloy

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Abstract

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Any further distribution of Keywords: low temperature plasma nitriding, bipolar-pulsed frequency, Ti-6Al-4V alloy, surface properties, corrosion resistance this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI.



In this work, Ti-6Al-4V alloy, commonly used as implant material in biomedical applications, was treated by plasma nitriding. The nitriding process was carried out using an N2-H2 plasma (1000:500 sccm) at an operating pressure of about 866 Pa. The current regulation was about 1.8 A, the negative voltage was about 480-500 V, and the power was 840-940 W. The nitriding temperature was maintained at 650 ± 5 °C, and the nitriding time was 240 min. Bipolar pulse frequencies were varied at 25, 50, 100, 150, and 200 kHz. Analysis by grazing incidence x-ray diffraction spectrometer (GI-XRD) revealed the presence of δ -TiN and ε -Ti₂N phases in all nitrided samples. The hardness depth profile was measured with a penetration depth of about 5 nm using the enhanced stiffness procedure (ESP). The results showed that all the nitrided samples had a surface hardness approximately three times that of the unnitrided sample. This result is consistent with that from glow discharge emission spectroscopy (GD-OES), which confirmed the diffusion distance of nitrogen atoms from the surface of about 5 µm. After plasma nitriding, the surface roughness tended to increase, resulting in an increase in the water contact angle (WCA) and a decrease in the work of adhesion. The specific wear rate (ball-on-disk) of all nitrided samples decreased and was significantly lower at a bipolar pulse frequency of 50 kHz. This result is consistent with the stability of the coefficient of friction (COF) after 6000 sliding cycles. Moreover, the nitrided sample at 50 kHz exhibited the lowest corrosion current density in artificial saliva based on the Tafel potential polarization method.

1. Introduction

Nowadays, medical technology has made rapid progress so that human life has become longer, and the quality of life has also become more important. One of these medical technologies is the use of biomaterials to replace organs in the human body or to restore and improve the internal organs of the body. Currently, there are various types of medical materials and devices that can be used as implants in the human body for both dental and medical applications, such as dental implants, small orthodontic screws, orthodontic screws, artificial bone, etc When selecting the metal to be used for manufacturing implants, it is necessary to consider properties that are favorable for the function of the parts, such as hardness, stiffness, flexibility, elongation, tarnish resistance, unit weight, casting properties, as well as cost factors [1].

There are many types of implant metals, including grade 4 gold alloys, cobalt-chromium alloys, nickelchromium alloys, stainless steel, and titanium alloys. Currently, pure titanium and titanium alloys are used to

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make dental frameworks because they have good properties such as high strength, light weight, and high corrosion resistance. The most popular titanium alloy in dentistry is Ti-6Al-4V, it consists of 90 wt% Ti, 6 wt% Al and 4 wt% V [2]. At room temperature, there are two phases: α -phase and β -phase, also known as $\alpha+\beta$ -Ti alloy. The added aluminium stabilizes the α -phase and gives the metal higher strength and lower weight, while the vanadium stabilizes the β -phase at room temperature. It has the potential to be used in dentistry, and the use of this alloy has been shown to be biologically acceptable [3]. However, titanium alloy parts have some limitations, such as permanent deformation, discoloration of the titanium surface, and the problem of tribological properties of titanium metal [4, 5]. In addition, this alloy releases both aluminium and vanadium, both of which can cause biological problems [3, 6]. Aluminium affects bone mineralization [7], leading to structural deficiencies, and vanadium is both cytotoxic and capable of causing type IV allergic reactions [8].

To overcome these problems, implant devices from Ti-6Al-4V alloy have been subject to various surface engineering methods to improve their surface properties and corrosion resistance in aggressive environments. Nitriding, a widely used process to improve the surface properties of titanium alloys. The nitride phase is chemically inert, meaning that it does not react with most chemicals or biological substances. This inertness is important in preventing chemical reactions with body fluids and ensuring the stability and safety of implants and medical devices over time, and it can coexist with living tissue without causing undesirable reactions. Some nitride phases, such as aluminum nitride (AlN) and titanium nitride (TiN, Ti-N), are highly corrosion resistant, so they do not degrade or deteriorate when exposed to body fluids or other corrosive environments in the human body. A widely used process to improve the surface properties of titanium alloys is gas nitriding, which is carried out in the gas phase in the temperature range of 800 °C-1050 °C [9, 10] in a nitrogenous environment $(N_2, N_2-Ar, N_2-H_2, or N_2-NH_3)$ [11–15] with a nitriding time of 6 to 80 h. However, gas nitriding requires high temperature for dissociation of bonds and leads to fatigue deterioration. The surface of the sample after gas nitriding usually has a high thickness compound layer, which needs to be polished, or surface finished before use. Plasma nitriding of titanium alloys with electric discharge is usually performed at lower temperatures and shorter nitriding times. This process can improve the tribological properties of titanium alloys by forming a thin compound layer mainly composed of δ -TiN and ε -Ti₂N. The microstructure of the nitride layer also consists of a region α -case (nitrogen-stabilized α -titanium) and a diffusion layer. This leads to higher surface hardness and better tribological and fatigue properties [16-20].

The high temperatures (>800 °C) in the nitriding process usually lead to grain growth, over-aging, and microstructural transformations in titanium substrates that reduce fatigue limit, strength, and ductility [15, 21, 22]. In addition, the significant stiffness differences between the compound layer and the titanium substrate, as well as the brittleness of the compound layer and α -case, lead to early failure originating from the surface and the over compound layer acts as a ceramic skin was a high hardness but which is brittle [23, 24]. For this reason, low-temperature plasma nitriding is used to improve the mechanical properties of titanium alloys [10, 21, 25]. The slow nitriding kinetics of titanium alloys at low temperatures can be enhanced by plasma cleaning before the nitriding process [26, 27]. This plasma cleaning deepens the nitrogen diffusion and increases the load bearing capacity of the plasma nitrided surfaces [28].

The important parameters of plasma nitriding include substrate temperature, gas mixture, plasma density, and ion bombardment energy. The substrate temperature is a crucial factor for the grain boundary expansion, which is responsible for the diffusion of nitrogen atoms from the surface into the base material. In addition, the substrate temperature also affects the phase formation between titanium and nitrogen. High nitriding temperatures can lead to the formation of brittle nitride layers and microstructural changes in the bulk [29]. The gas ratio between nitrogen and hydrogen is also important, because the increase of the nitrogen partial pressure directly affects the increase of the nitrogen concentration near the surface and the precipitation of hard TiN phases in the formed compound laver. This result can lead to microcracks on the surface [30]. Hydrogen content in plasma can remove inherent surface oxides and increase nitriding kinetics in titanium alloys by providing easy diffusion pathways for nitrogen interstitials [11, 21, 31]. Plasma density is the essential factor for plasma nitriding, which depends on the power input and the type of power supply. A higher plasma density corresponds to a higher ion flux bombarding the sample, resulting in rapid self-heating of the substrate. At the same time, a bias voltage, e.g. in the form of an asymmetric bipolar pulse, can increase the impulsive force to accelerate the ion bombardment of the sample. A small positive voltage can neutralize the positive charges that accumulate on the sample surface. This step helps to ensure that the ions are continuously impinging on the surface of the material. Increasing the high-energy ions and pulse frequency has a direct effect on increasing the sputtering rate, which can change the surface roughness and structure of compound layer. In a typical plasma nitriding process, an external voltage is used to ionize the nitriding gas and provide an active nitrogen flux for surface modification between the nitriding furnace (anode) and the workpiece (cathode) [4, 5]. In addition to the power supply from DC and AC, the plasma can also be generated by radio frequency (RF) excitation [5, 32]. When the applied voltage is provided by a DC power supply, the continuous voltage supply can cause localized heating, overheating of thin sections, arcing, and other form of surface damage. These problems can be avoided by using



an asymmetric bipolar pulsed power supply in which the heat input is controlled by duty cycles and frequency. A duty cycle is defined as the ratio of the pulse on-time to a full on-off cycle time [33] and is typically on the order of 10%–50% of the period without disturbing the nitriding time [31]. Bipolar pulse discharges with sufficiently low duty cycle can be used for such low-temperature processes, especially when arcing at the edge shape of the sample must be avoided. Discharges generated with different short pulse wavforms have found applications in plasma nitriding by generative species at ambient pressure and temperature [34]. However, the effects of pulse frequency on the surface properties and corrosion resistance of Ti-6Al-4V alloy in artificial saliva have not yet been investigated. The expected results of this research should be useful for dental applications.

2. Materials and methods

In this study, the Ti-6Al-4V plate was used as the substrate to fabricate the nitride layer. The Ti-6Al-4V plate with a dimension of $30 \times 35 \times 1$ mm³ was mirror polished on both sides by buffing cloth wheels. The sample was first cleaned with an ultrasonic cleaner in acetone for 10 min, then shaken in methanol for 10 min twice and rinsed with deionized water three times to remove the impurities present on the substrates. The experimental setup for the plasma nitriding system is schematically shown in figure 1, which consists of the vacuum chamber, the evacuation system, the asymmetric bipolar pulse power supply in the frequency range of 0 to 250 kHz, the gas supply with Ar, N₂ (99.995% purity), and H₂ (99.995% purity), and the cooling system. Since there was no additional external heater, the substrate was heated by ion bombardment in the plasma. The substrate holder was connected to the thermocouple on the left side and to the power supply on the right side. In the vacuum chamber, the sample was placed on the power electrode.

In this work, an asymmetric bipolar pulse power supply (Advanced Energy Pinnacle[®] Plus+) with peak voltages up to 800 V, a maximum power of 10 kW and an adjustable frequency range from 0 to 250 kHz was used to maintain the plasma. Preparation of the nitride layer was divided into three processes, plasma cleaning, preheating and plasma nitriding. For plasma cleaning, Ar and H₂ were used at a flow rate of 500 sccm and an operating pressure of about 33 Pa. By using the power control mode at low pressure corresponding to low plasma current and high discharge voltage, high ion energy can be generated to impinge on the substrate. Ar was chosen to generate plasma to promote ion bombardment and physical ablation of impurities, while H₂ plasma was necessary to remove the oxide layer on the surface of the sample. In this process, a power of about 500 W was controlled with a bipolar pulse frequency of 50 kHz, a duty cycle of 10%, a negative voltage of about 625–800 V, currents of 0.6–0.8 A, and a process duration of 20 min, raising the temperature of the substrate to 350 ± 5 °C. After the plasma cleaning was completed, the preheating process was immediately started by decreasing the pump speed to increase the operating pressure to about 466 Pa. At higher pressure, the plasma current ane adjusted up to 2.5 A, corresponding to 800–1100 W power, to increase the ion flux into the substrate. To avoid cracks in the sample due to rapid expansion, the temperature of the substrate was gradually increased until it reached 650 ± 5 °C, which took about 45 min. Then the nitriding process was performed with a

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Table 1. Process parameters used to study the effect of pulse frequency on the surface properties of plasma nitrided Ti-6Al-4V alloy.

Parameter	Plasma cleaning	Preheating	Plasma nitriding
Gas mixtures (sccm)	Ar:H ₂ = 500:500	Ar:H ₂ = 500:500	N ₂ :H ₂ = 1000:500
Operating pressure (Pa)	~33	~466	~866
Controlled mode	Power	Current	Current
Power (W)	500	800-1100	840-940
Current(A)	0.6-0.8	2.5	1.8
Bipolar pulse frequency (kHz)	50	50	25, 50, 100, 150, 200
Substrate temperature (°C)	350 ± 5	650 ± 5	650 ± 5
Time (min)	20	45	240

 N_2 - H_2 plasma (1000:500 sccm). The hydrogen mixture is the key to the presence of the atomic hydrogen, which can remove the titanium oxide layer formed during the preparation of the sample and stabilize the operating pressure. The higher operating pressure was maintained at about 866 Pa, which corresponds to a plasma current of about 1.8 A. In this step, the substrate temperature was maintained at 650 ± 5 °C with a holding time of 240 min. To investigate the effects of pulse frequency on the properties of the nitrided layer, the pulse frequency was varied at 25, 50, 100, 150, and 200 kHz. The process parameters of plasma cleaning, preheating and plasma nitriding are summarized in table 1.

After completion of the plasma nitriding process, the nitrided Ti-6Al-4V was cooled to room temperature in the vacuum chamber. The nitrided samples were characterized using the environmental scanning electron microscopy (ESEM) (Thermo Fisher Scientific, Quattro S) with the secondary electron mode to observe the surface morphology. Contact angle measurement (OCA 15EC, DataPhysics, Germany) using a static sessile drop method was used to estimate the work of adhesion between water droplets and the surface of titanium alloys. It can be calculated based on the Young-Dupré equation by measuring the contact angle of the water on the surface [35]. 1 μ l of deionized water was dropped onto the surface of the sample. The drop was backlighted with LEDs and immediately photographed by a camera. The drop was left in situ for one minute, then the contact angle was measured at three locations on each sample. The environmental conditions were constant throughout the experiment at a temperature of 25 °C-26 °C, and a relative humidity of 69%-72%. The roughness and topography of the samples before and after plasma nitriding were documented using an atomic force microscope (AFM) (XE 70 model, Park systems, Korea). Surface topography was investigated in a tapping mode by scanning an area of $5 \times 5 \mu m^2$. Three regions of each sample were selected for roughness measurements. The roughness profiles and surface geometry parameters were determined based on the AFM data in non-contact mode. The friction and wear behaviors were assessed using ball-on-disk friction testing (FPR-2100; RHESCA Co., Ltd, Tokyo, Japan). The tribological tests were performed at room temperature. The size of wear samples with a dimension of 30 × 35 × 1 mm³. A 6 mm in diameter of stainless steel ball (SUS440C) was slid over the surface of the samples under a normal applied load of 0.98 N, a rotational speed of 100 rpm, and 6000 frictional revolutions. The tests were repeated three times for each sample at the rotation radius of 3, 5, and 7 mm, corresponding to a total sliding distance of 113.04, 188.40, and 263.76 m, respectively. After the test, the average specific wear rate of the sample was calculated using the profiles of the wear track (three points in each rotation radius) measured by a color 3D laser scanning microscope (KEYENCE VK-9710). Morphology of the wear track was also characterized by an optical microscope. The elemental composition in the depth profile of the surface before and after plasma nitriding was investigated using the glow discharge optical emission spectroscopy (GDOES). The GDOES (model: GD PROFILER HR) with the polychromator mode was operated at a pressure of 600 Pa and a power of RF of 20 W with an anode size of 4 mm. The phase composition and microstructural properties of the samples after plasma nitriding were analyzed by grazing incidence X-ray diffraction spectrometer (GI-XRD) (BRUKER, D8 Advance). A Cu Kα source with a wavelength of 0.15418 nm was used as the X-ray source. Tests were performed at a fixed incidence angle of 0.7° and with slit widths of 0.1 mm for both the input and output beams to the detector. The sampling rate of the diffractometer was set to 0.1° per second, with a 2θ diffraction angle of $20^{\circ}-80^{\circ}$. The hardness value corresponding to the depth was measured with a nanoindentor (FISCHERSCOPE® HM2000) based on an enhanced stiffness procedure (ESP). This method is particularly suitable for depth-dependent measurement, which allows the hardness of the nitride layer to be determined at very low forces without being affected by the bulk. As the force increases, with loading and unloading increased at intervals from 0.1 mN to 2000 mN, the transition from the surface to the base material can also be analyzed. The value of the hardness depth profile can be used to estimate the thickness of the nitride layer. The interaction between saliva and Ti-6Al-4V alloy surfaces can directly affect their corrosion behavior. Artificial saliva serves as an important test medium for evaluating the performance and biocompatibility of dental materials. Therefore, in this work, the nitrided samples were corroded in an artificial saliva solution with a pH of 5.5 under simulated oral environment before they are placed in the human oral cavity. An electrochemical test (GAMRY, Reference3000) was performed using a potentiodynamic polarization method with a three-electrode configuration, consisting of reference (Ag/AgCl), counter (Pt), and working electrodes (nitrided sample). An immersion time of

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180 min was applied to the open circuit potential of the alloy in all electrolytes before starting the tests, then a potential range of -1000 mV to 1500 mV was applied with a sampling rate of 1 mV s⁻¹. Tafel extrapolation was used to estimate self-corrosion current density (i_{corr}) and self-corrosion corrosion potential (E_{corr}) in an electrochemical cell. Corrosion resistance was assessed by measuring i_{corr} and E_{corr} . The corrosion rate (CR) can also be estimated based on the ASTM Standard G 102–89 using the following formula [36]

$$CR = K \frac{EW}{\rho} i_{corr}$$
(1)

where CR is the corrosion rate in mm/year (mmpy), K is 3.272×10^{-3} mm g/(μ A cm yr), i_{corr} is the self-corrosion current density in μ A cm⁻², ρ is the density in g cm⁻³, and EW is the equivalent weight. For the Ti-6Al-4V alloy, the equivalent weight and density are 11.89 and 4.43 g cm⁻³, respectively.

3. Results and discussion

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3.1. Surface morphology

As can be seen in figure 2, the color of the Ti-6Al-4V samples changes from metallic grey to gold due to the increase in the atomic ratio of nitrogen to titanium, which causes the overall reflectivity of the gold-like color [37-39]. The lighter color appears around the edge of all nitride samples. This edge defect is due to the higher electric field resulting in higher energy of ion bombardment and more sputtering in this region. Prior to the determination of surface morphology, all samples were immersed in 98% H₂SO₄ and 37% HCl acids in a volume ratio of 1:1 for 20 h. The surface morphology of the samples after etching was then observed using the ESEM technique. The surface morphologies of the unnitrided samples before and after etching are shown in figure 3(a). It is obvious that the unnitrided sample shows clear signs of corrosion, so that the grain boundaries can no longer be seen. In contrast, if one compares the surface of the nitrided samples before and after etching, almost no traces of corrosion can be seen. This result shows that the process of plasma nitriding can improve the corrosion resistance of a titanium alloy by creating a protective barrier.

3.2. Phase identification

The diffraction pattern was characterized by grazing incidence x-ray diffraction (GI-XRD) at an angle of incidence of 0.70°. The phases α -Ti, β -Ti, δ -TiN, and ε -Ti₂N were identified from the JCPDS files using databases 44–1294, 44–1288, 38–1420, and 17–0386 [40–42]. Figure 4 shows the diffraction patterns of the sample before and after nitriding. The unnitrided sample contains the α -Ti and β -Ti phases. The diffraction peaks observed correspond to the α -Ti (100), (002), (101), (110), (112), (201), and (004) at 35.28°, 38.48°, 40.53°, 53.33°, 63.50°, 76.12°, 78.09°, and 82.55°, and β -Ti (110) at 40.08°. All nitrided samples show the formation of a nitride layer consisting of δ -TiN (111) and (200) at 36.32° and 42.56°, ε -Ti₂N at 39.30°, 51.24°, 61.14°, 67.20°, and 73.30°, and η -Ti₃N_{3-x} at 76.00° [41]. Figure 5 shows the phase content of the Ti-6Al-4V alloy before plasma nitriding consists of a mixture of α and β phases. After plasma nitriding, the formation of the ε -Ti₂N phase increases with increasing of bipolar pulsed frequency. However, as can be seen in figure 5, the δ -TiN phase is highest (up to ~23%) at an excited frequency of 50 kHz.

In addition, the effect of hydrogen in the plasma cleaning and plasma nitriding processes in this study also accelerated nitrogen diffusion by forming multiple dislocations within the α -grains. It has also been reported that Ar-H₂ sputtering increases the nitriding kinetics in alloys by forming simple diffusion paths for nitrogen interstitials and eliminating inherent surface oxides [43, 44]. Therefore, no titanium oxide formation was

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observed. Based on the XRD results, the correlation between the intensity of phase formation and the bipolar pulse frequencies used during the nitriding process is still not clear.

3.3. Chemical composition

Nitrogen diffusion and concentration were analyzed using the glow discharge optical emission spectroscopy technique (GD-OES) to measure the content of nitrogen and other elements (see figure 6). The argon ion etch rate was set at about 1 μ m per minute. The output data were subtracted with the background ionization and

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surface adsorption of residual atomic nitrogen, which could be the cause of the emission lines detected by the spectrometer. It can be seen that the nitrogen content on the surface is up to ${\sim}45\%$ and gradually decreases with increasing etching time. In addition, the aluminium content near the surface decreases with increasing nitrogen diffusion from the surface to the core. At a depth of one micrometer from the surface, the aluminium content increased more than that of the unnitrided sample, which is probably related to the precipitation of AlN. Moreover, the curve of vanadium initially drops to almost zero due to diffusion of nitrogen atoms from the surface, which reduces the relative vanadium concentration. However, upon closer inspection, the vanadium content is found to be above 5%, which is the same as in most titanium alloys.

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3.4. Mechanical properties

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The surface hardness in the depth profile of the sample was analyzed using the nanoindentation technique in the enhanced stiffness procedure mode (ESP), as shown in figure 7. It can be seen that all nitrided samples have higher surface hardness than the unnitrided sample. The nitrided samples have the highest surface hardness of about 1250 HV at bipolar pulse frequencies of 50, 150, and 200 kHz, which is close to a hardness value of the ε -Ti₂N phase [31, 45], which can be clearly seen in the results of GI-XRD. The TiN layer is generally slightly

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stiffer than the diffusion layer. Based on the hardness depth profile, the thickness of the nitride layer can be roughly estimated at 5 μ m. Due to its lower processing temperatures, plasma nitriding is able to achieve high surface hardness while maintaining the high mechanical properties of the core material. In addition, plasma nitriding allows control the microstructure of the treated workpiece, phase and chemical composition, surface topography, morphology, and residual stresses [46], all of which are critical for determining surface properties, especially if the workpiece is to be used as a part in the human body.

3.5. Surface roughness and work of adhesion

In this work, root mean square roughness (R_{rms}) was measured using atomic force microscopy, which is more sensitive to peaks and valleys than average roughness because of the squaring of the amplitude in its calculation. figure 8 shows the surface topography corresponding to the scan area of $25 \,\mu\text{m}^2$ of the unnitrided and plasma nitrided samples. The surface roughness of the nitrided samples prepared with bipolar pulse frequencies of 25, 50, 100, 150, and 200 kHz is $33.6 \pm 1.0, 25.5 \pm 1.2, 31.0 \pm 0.6, 28.8 \pm 1.7, and <math>38.1 \pm 3.6$ nm, respectively. It can be seen that the surface roughness of the nitrided samples is higher than that of the unnitrided samples (20.8 ± 3.7 nm). This result can be attributed to the formation of material that could cause the formation of whiskers (TiN nanoparticles) [47]. No significant improvement in surface topography when bipolar pulse frequency was

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increased. However, the bipolar pulse frequency of 200 kHz tends to give the highest surface roughness. Increasing the frequency enhances the plasma density, which increases the probability of nitrogen ions colliding with the surface of the workpiece. These high-energy ion collisions usually lead to an increase in surface roughness. In addition, the modulation caused by the bipolar pulse frequency affects the energy distribution of the sputtered Ti atoms by allowing them to redeposit in the substrate. This modulation increases the atomic mobility on the surface and facilitates the epitaxial replication of the crystallography found in the seed layer. Consequently, this modulation contributes to variations in surface roughness [48].





Figure 9 shows the contact angle, work of adhesion, and surface roughness of Ti-6Al-4V before and after plasma nitriding. For each sample, the measurement was repeated three times in different positions. The contact angle of the unnitrided sample was $86.39^{\circ}\pm 3.18^{\circ}$. For the nitrided samples with bipolar pulse frequencies of 25, 50, 100, 150, and 200 kHz, the contact angles increase slightly to about $94.65^{\circ}\pm 1.05^{\circ}$, $92.75^{\circ}\pm 0.93^{\circ}$, $91.61^{\circ}\pm 2.12^{\circ}$, $93.42^{\circ}\pm 1.71^{\circ}$ and $93.28^{\circ}\pm 0.87^{\circ}$, respectively, corresponding to a slight increase in surface roughness. The work of adhesion between water droplets and the surface of titanium alloys can be calculated based on the Young-Dupré equation [35]. The work of adhesion at the bipolar pulse frequencies of 25, 50, 100, 150, and 200 kHz was 76.30, 65.96, 68.34, 69.76, and 67.50 mJ/m², respectively. In general, a surface is considered hydrophobic if the contact angle is greater than 90° [49, 50]. It is observed that the contact angle of the nitrided sample. This could be due to the Cassie–Baxter wetting model [51], where air is trapped in the pockets below the droplet during the measurement of the advancing contact angle.

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The micropores formed after nitriding and the surface roughness lead to a more hydrophobic surface. Therefore, the corrosion rate should be reduced for nitrided samples with increased hydrophobic properties, since water accumulation on the surface can accelerate corrosion. Therefore, a hydrophobic surface is desirable to prevent water from adhering. Plasma nitriding can improve the hydrophobic property of Ti-6Al-4V, making it more suitable for human applications.

3.6. Coefficient of friction and wear rate

Figure 10 shows the coefficient of friction (COF) of unnitrided and nitrided samples at a rotation radius of 5 mm as a function of the number of sliding cycles. It can be seen that the COF of the unnitrided sample is about 0.1 during the interval of 1000 cycles, which is due to the behavior of the natural titanium oxide layer. Thereafter, the COF increases to about 0.3, which is consistent with the surface of the titanium alloy [52]. For the plasma nitrided samples, the COF is 0.5–0.6 during the interval of 2500 cycles. The increase in COF is likely related to

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the higher surface roughness of the nitride layer. As the number of sliding cycles increases, the COF of the nitride samples decreases sharply to the titanium alloy surface value at the bipolar pulse frequencies of 25 kHz, 100 kHz, 150 kHz, and 200 kHz. This behavior indicates detachment of the brittle nitride layer. However, the nitrided sample at 50 kHz maintains a stable coefficient of friction of about 0.6 throughout the test period and remains intact without flaking off. This can be attributed to the formation of the δ -TiN phase, which has a higher hardness compared to the ε -Ti₂N phase. Moreover, this stability of the nitride layer is likely due to the lowest surface roughness seen on the AFM image. Consequently, the nitride layer exhibits better mechanical properties,

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is scratch resistant and leads to a lower wear rate. Figure 11 shows the wear tests after a test with 6000 sliding cycles and dry sliding conditions. The left column shows the photo of all worn samples with rotation radius of 3, 5 and 7 mm, the middle column shows the wear tracks with sliding width and the right column shows the three-dimensional (3D) profilometer images (radius 5 mm). As can be seen in figure 11(a) for the unnitrided sample, the sliding width of the worn track is about 0.72 mm, which is consistent with the sliding width of the worn track determined from the 3D profilometer image. The average depth and width of the worn tracks with a rotation radius of 5 mm were used to calculate the specific wear rate. It can be seen that the worn surfaces of the unnitrided sample have the highest specific wear rate after sliding. The nitrided sample at 50 kHz, as shown in figure 11(c), still has a gold-colored surface indicating the lowest specific wear rate of 0.27×10^{-4} mm³/Nm. This outcome is attributed to the creation of a δ -TiN phase characterized by superior hardness, surpassing that of other conditions. This result is consistent with the stability of the COF of the nitride layer.

Figure 12 shows the average specific wear rate of unnitrided and nitrided samples prepared with different bipolar pulse frequencies. For each sample, the specific wear rate was determined at three positions with a rotation radius of 5 mm. All nitrided samples with higher surface roughness have lower wear rates than the unnitrided sample. This reduction in wear rate can be attributed to the higher surface hardness achieved by the plasma nitriding process.

3.7. Corrosion resistance

Figure 13 shows the potentiodynamic polarization curve of unnitrided and nitrided samples, which was generated in an artificial saliva solution with a potential (Eversus Ag/AgCl) of -1000 mV to 1500 mV, using a sampling rate of 1 mV s⁻¹. Lower icorr values and more positive Ecorr values indicate better corrosion resistance; therefore, all nitrided samples have higher corrosion resistance compared to the unnitrided sample. Although the surface of the unnitrided sample has a robust oxide layer, there is a possibility that metastable processes will occur if a film breakdown and re-passivation process is initiated. This process leads to the formation of grain boundaries and more open pathways within the oxide. Once a crevice is formed, it spreads rapidly and leads to corrosion [53]. The nitrided sample prepared at a frequency of 50 kHz exhibits the highest corrosion resistance. This is evident from the highest values of self-corrosion potential Ecorr and the lowest self-corrosion current density icorr, as shown in figure 14. A low icorr value means a lower amounts of ions released into the human body, which can serve as an indicator of better biocompatibility. This result is probably related to the lowest roughness and the highest wear resistance. When the bipolar pulse frequency is higher than 50 kHz, the selfcorrosion current density tends to be higher. This phenomenon is probably related to the fact that the molecular nitrogen ions and the nitrogen ions tend to react more slowly at the higher excitation frequency during the nitriding process. In conjunction with the wear test, there may be a strong self-detachment in the compound layer leading to the formation of a larger porosity, resulting in a string that separates the upward growing crystallites from the downward growing ones [54].

Assuming that the nitrided and unnitrided samples have similar equivalent weight and density, the changes in corrosion rates are proportional to the changes in self-corrosion current density. Figure 15 shows the corrosion rate of the samples after nitriding at different bipolar pulse frequencies. The nitrided sample prepared at a frequency of 50 kHz has the lowest corrosion rate of 0.51×10^{-4} mmpy, while the CR of the unnitrided sample is 1.4×10^{-4} mmpy. This means that the corrosion rate is reduced by three 3 times compared to that of the unnitrided sample.

4. Conclusions

The aim of this study is to investigate the effects of different bipolar pulse frequencies on the surface properties and corrosion resistance of Ti-6Al-4V alloy in artificial saliva. For this purpose, the Ti-6Al-4V alloy was nitrided with a N₂-H₂ plasma (1000:500 sccm) at an operating pressure of 866 Pa, a power of about 840–940 W, and a nitriding temperature of 650 \pm 5 °C for 240 min. The bipolar pulse frequency was varied between 25 and 200 kHz. The results from GD-OES show that the nitrogen atom can diffuse up to 45% into the surface and gradually decreases with depth. The results of GI-XRD show the formation of the phases δ -TiN and ε -Ti₂N.

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Atomic force microscopy shows that the plasma nitriding process leads to an increase in surface roughness, which is probably due to the formation of the compound layer. The increase in water contact angle after plasma nitriding is likely due to the higher surface roughness. The hardness depth profile of a nitrided Ti-6Al-4V alloy was investigated by nanoindentation in the mode of enhance stiffness procedure. The results show that all nitrided samples have higher surface hardness (about 1260 HV) compared to the unnitrided sample (450 HV). The hardness values tended to decrease with increasing depth but did not affect the bulk hardness. The thickness of the nitride layer was estimated to be about 5 μ m. The coefficient of friction and wear rate were determined by a ball-on-disk test. The nitride sample with the bipolar pulse frequencies of 50 kHz gives an average COF of about 0.6, which is higher than the unnitrided sample due to the higher surface roughness of the nitride layer. For the other nitride samples, the COF decreases rapidly with increasing number of sliding cycles, indicating detachment of the brittle nitride layer during the test. This result is consistent with the specific wear rate, where the nitride sample has the highest wear resistance and the lowest self-corrosion current density, indicating the highest corrosion resistance at 50 kHz.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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Article

The Modification of Activated Carbon for the Performance **Enhancement of a Natural-Rubber-Based Triboelectric** Nanogenerator

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Abstract: Increasing energy demands and growing environmental concerns regarding the consump-

tion of fossil fuels are important motivations for the development of clean and sustainable energy sources. A triboelectric nanogenerator (TENG) is a promising energy technology that harnes mechanical energy from the ambient environment by converting it into electrical energy. In this work, the enhancement of the energy conversion performance of a natural rubber (NR)-based TENG has been proposed by using modified activated carbon (AC). The effect of surface modification techniques, including acid treatments and plasma treatment for AC material on TENG performance, are investigated. The TENG fabricated from the NR incorporated with the modified AC using N2 plasma showed superior electrical output performance, which was attributed to the modification by N2 plasma introducing changes in the surface chemistry of AC, leading to the improved dielectric property of the NR-AC composite, which contributes to the enhanced triboelectric charge density. The highest power density of 2.65 mW/m² was obtained from the NR-AC (N₂ plasma-treated) TENG. This research provides a key insight into the modification of AC for the development of TENG with high energy conversion performance that could be useful for other future applications such as PM2.5 removal or CO2 capture.

Keywords: triboelectric nanogenerator; activated carbon; acid treatment; N2 plasma; natural rubber

1. Introduction

Due to a predominant reliance on limited and non-renewable energy sources, significant issues have arisen concerning energy shortages and environmental pollution. Consequently, clean and sustainable energy has received continuous attention and development. The triboelectric nanogenerator (TENG) is an innovative technology capable of harvesting mechanical energy and converting it into electrical energy, based on the principles of contact electrification and electrostatic induction [1]. TENG has been demonstrated to be highly efficient, environmentally friendly, low-cost, easy to manufacture, and suitable for large-scale applications. Its versatility extends to various applications, such as sensors [2], portable micro/nano power sources [3], raindrop energy harvesting [4], and air filtration systems [5].

Natural-based materials, such as leaves, wood, silk, and paper, have been developed for TENG applications. Most of them have shown promising energy production performance and potential applications. However, some of them experience difficulties in

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