Low-Temperature Nitriding of Pure Titanium by using Hollow Cathode RF-DC Plasma

J M Windajanti¹,², D J Djoko H S¹ and Abdurrouf¹
¹Physics Department, University of Brawijaya, Jl. Veteran Malang, 65145, Indonesia
²SMAK Santa Maria, Jl. Raya Langsep 41 Malang, 65116, Indonesia
Email: abdurrouf@ub.ac.id

Abstract. Pure titanium is widely used for the structures and mechanical parts due to its high strength, low density, and high corrosion resistance. Unfortunately, titanium products suffer from low hardness and low wear resistance. Titanium’s surface can be modified by nitriding process to overcome such problems, which is commonly conducted at high temperature. Here, we report the low-temperature plasma nitriding process, where pure titanium was utilized by high-density RF-DC plasma combined with hollow cathode device. To this end, a pure titanium plate was set inside a hollow tube placed on the cathode plate. After heating to 450 °C, a pre-sputtering process was conducted for 1 hour to remove the oxide layer and activate the surface for nitriding. Plasma nitriding using N₂/H₂ gasses was performed in 4 and 8 hours with the RF voltage of 250 V, DC bias of -500 to -600 V, and gas pressure of 75 to 30 Pa. To study the nitriding mechanism as well as the role of hollow cathode, the nitrided specimen was characterized by SEM, EDX, XRD, and micro-hardness equipment. The TiN compound was obtained with the diffusion zone of nitrogen until 5 µm thickness for 4 hours nitriding process, and 8 µm for 8 hours process. The average hardness also increased from 300 HV in the untreated specimen to 624 HV and 792 HV for 4 and 8 hours nitriding, respectively.

Keywords: Low-temperature, nitriding, titanium, RF-DC plasma.

1. Introduction
Titanium is a lightweight metal representing some exceptional properties such as high strength, low density, high corrosion resistance, and stable properties at high temperature. Titanium and its alloys are widely used for structural and mechanical parts in the construction of industrial equipment such as heat exchanger, piping system in petrochemical and offshore industries. They can also be found in aircraft constructions and sports goods. They are also a bio-compatible material for medical implants [1-2]. However, the low surface hardness and the poor wear resistance of their products limit their usage life, especially if there is a friction on contact with other materials [3-4].

Recently, there has been an increasing interest in enhancing the surface properties of pure titanium for wider and more significant applications. To improve the wear resistance of pure titanium, the surface modification, such as nitriding process, is a crucial process in modern manufacturing. The nitriding process can increase the wear resistance of metals by surface hardening. The plasma nitriding is one of the promising nitriding processes, due to its shorter process time and reduced growth of the nitrided parts. In addition, it also saves gasses and keeps the environment clean. Titanium is a metal suitable for nitriding, but previously it needs high-temperature processing. Typically, the nitriding process of titanium has been conducted at a temperature above 700 °C. For example, plasma nitriding...
process for titanium alloy at a temperature of 1000 °C for 10 hours could be increased the hardness up to 1365 HV [4]. The increasing of surface hardness after nitriding is caused by the increase of nitrogen concentration as a solid solution and the formation of TiN and Ti2N on the metal surface [3].

The thermo-chemical process for titanium at high temperature causes a degradation of fatigue strength and a detrimental of microstructural changes in titanium substrates. Therefore, we need a method to perform the nitriding process at lower temperatures. In this present paper, a plasma nitriding process at a low temperature of 450 °C is introduced for increasing the surface hardness of pure titanium. A high-density RF-DC plasma with an addition of the hollow cathode tube was conducted for nitriding process. The use of hollow cathode device increases the electric field inside the tube, improves the number of ions and electrons trapped, and therefore increases the plasma density [5]. As a consequence, the specimen was effectively bombarded by the high plasma ion density, giving a higher nitrogen concentration in the surface of the nitried specimen.

2. Experimental Method

Figure 1 shows the RF-DC plasma system utilized for the present low-temperature plasma nitriding. This system consists of a vacuum chamber, a computerized control unit, a plasma generator, a gas supply sub-system and a vacuum pump system. The vacuum reactor consists of the RF dipole electrodes, the DC bias cathode plate, and the resistive heater is placed under the cathode plate where the temperature of the cathode and the samples on it can be control of the processing unit. At the low-pressure chamber, the glow discharge plasma can be generated independently by a DC bias generator and/or by RF generator with the frequency around of 2 MHz. The matching power condition is automatically adjusted around 2 MHz. The pressure processing and gas flow rate are controlled automatically. An addition of hollow cathode device made from stainless steel rectangular hollow tube was placed on the cathode plate. Setting up of the hollow cathode device is shown in Figure 2.

![Figure 1. High-density RF-DC plasma systems [6].](image)

In this study, a pure titanium plate with a dimension of 18 x 40 x 0.3 mm³ was used as the substrate to investigate the nitriding process. In preparation, the specimen was cleaned with industrial soap (alkali solution) in the ultrasonic cleaner bath because it must be clean from oils and surface surfactants. After that, the titanium specimen was placed in the hollow cathode tube, and then the device was loaded into the chamber, and the system was pumped down to 0.7 Pa to remove oxygen gas from the chamber.

The series of the nitriding process begins by heating the specimen to 450 °C in a nitrogen atmosphere at a pressure of 300 Pa. After the target temperature had been reached, the chamber pressure was lowered back to the value of the set-up process pressure. Before the main nitriding process, a pre-sputtering was performed by applying a high voltage of -500 V DC plasma of nitrogen and hydrogen gas for 1 h. This process was used to remove the oxide layer and activate the surface. The main nitriding process followed
the activation process by using both RF and DC plasma. The RF voltage was fixed at 250 V while the DC bias was varied from -500 V to -600 V. The nitriding process was conducted for 4 hours and 8 hours by using a mixed gas with the flow rate of 160 mL/min of N₂ gas and 40 mL/min of H₂. The effect of gas pressure on the hardening process was studied by varying the pressure of the system. The gas pressure was adjusted at 75 Pa, 50 Pa, and 30 Pa, respectively. After the main process, the specimen was cooled down in a nitrogen atmosphere until the temperature of 300 °C.

![Image](figure2.jpg)

**Figure 2.** Setting up of the hollow cathode device, from a side view (a) and front view (b and c)

The surface of the nitrided specimen was observed by using SEM equipment, Shimadzu SSX-550M. The composition of elements of the nitrided subsurface of the specimen was obtained from EDX point analysis of the cross-sectional area. XRD measurements were carried out through Rigaku Ultima IV XRD system to identify the phases of nitrided materials with monochromated Cu Kα radiation (λ = 1.54598 Å). The diffraction angle (2θ) was controlled to vary from 3° to 90°. The surface hardness of the specimens was tested by means of Akashi MVK – H1 tester under an applied load of 0.5 N or 50 gf for 10 s for five different positions of surface area.

3. Results and Discussion

A diffusion of nitrogen atoms into pure titanium by the nitriding process causes a significant change of its surface morphology. Before the nitriding process, the SEM image at 1600× magnification of the surface morphology (Figure 3, left panel) showed a striped line structure. After 4 hours nitriding process by high-density RF-DC plasma at a temperature of 450 °C, a gas pressure of 30 Pa, and DC bias voltage of -600 V, a top surface of nitried specimens showed a pronounce of underlying granular structure morphology as seen in Figure 3, right panel.

![Image](figure3.jpg)

**Figure 3.** Top surface morphology of a nitried titanium before (left panel) and after subjecting to plasma nitriding (right panel).
Observation of cross section cutting by using SEM and EDX equipment showed a thin layer of the surface part with a thickness of few micrometers formed on the outermost surface of every nitrided specimen. Below the surface part, the darker parts were appeared, which is identified as nitride layers and followed by diffusion zone with a matrix of the pure titanium as shown in Figure 4. The increase of surface part thickness was obtained in the process with lower gas pressure and long-term process of 8 hours. At the outermost, a thin layer of the contaminant was identified. This element of Fe, Cr and Ni did not originally come from titanium alloys. These residues coated on the surface of pure titanium came from the stainless steel hollow via high-density plasma nitriding. The EDX point analysis result showed the maximum concentration of 18.55 at.% of nitrogen element detected at a depth of 2 μm for the nitrided sample after 4 hours treatment and amounted to 26.96 at.% detected at a depth of 3 μm on the nitrided sample for 8 hours. The nitrogen diffusion zone was detected up to a depth of 5 μm in the process for 4 hours and 8 μm in the process for 8 hours. Figure 5 shows nitrogen atom concentration from the surface to the nitriding depth of 8 μm in the specimen.

Figure 4. The microstructure of cross section nitrided specimen for 4 hours (left panel), and 8 hours (right panel). The nitriding process was conducted under DC bias of -600 V and at a gas pressure of 30 Pa.

Figure 5. Nitrogen concentration versus nitriding depth.

The nitrogen diffusivity depends on energy and ion flux. Correspondingly, the nitried layer thickness also depends on the energy and ion flux. Therefore, the higher the concentration of nitrogen
in the nitrided specimen leading to higher ion flux, so that the nitrogen diffusivity will increase as well. In this present study, the use of the hollow cathode device is proven to increase the plasma density, which is used to expose the titanium specimen. Then, the high-density plasma combined with the high energy of nitrogen ions causes the increase of nitrogen depth. The relationship between nitrogen concentration and hardness is an important subject of nitriding process. The incorporation of nitrogen increases, in general, the hardness of the material, so the physical result is an increase in the surface hardness of nitrided specimen.

In addition to changes in the surface morphology, the nitriding process using a hollow cathode device also causes a phase transformation of $\alpha$-Ti to the metastable phase of $\omega$-Ti accompanied by the formation of the TiN compound shown in the XRD spectroscopy results in Figure 6.

Figure 6. Left panel: Comparison of X-ray diffraction patterns of the nitrided specimen after subjecting for 4 hours to plasma nitriding by using a DC bias voltage of -600 V for different gas pressure at 75 Pa, 50 Pa, and 30 Pa. Right panel: Comparison of X-ray diffraction patterns of the nitrided specimen after subjecting to plasma nitriding by using a DC bias voltage of -600 V at a gas pressure of 30 Pa for different time processing of 4 hours and 8 hours.

In the nitrided specimen, there were 3 phases identified, i.e. $\alpha$-Ti, $\omega$-Ti, and TiN, respectively. The calculation results of lattice parameters for each phase of pure titanium and nitrided samples are summarized in Table 1. The c/a ratio of $\alpha$-Ti phase around 1.58 and the c/a ratio of $\omega$-Ti around 0.61 are obtained from the nitrided specimens. The phase transformation occurs because a high concentration of nitrogen was deposited in the interstitial lattice of pure titanium.

In the process of using lower pressure, there is an increasing formation of $\omega$-Ti and TiN with the calculation of the interphase concentration of nitrided specimens were summarized in Table 2. Based on Table 2 it appears that the gas pressure reduction even triggers a phase transformation from $\alpha$-Ti to $\omega$-Ti, while the increasing concentration of $\omega$-Ti also intensify the formation of TiN. In the long
process of 8 hours, the interphase concentration of TiN increased significantly while the interphase concentration α-Ti decreased. It can suggest that the formation of TiN as a compound layer which occurs more effectively after the saturation condition in the diffusion process. In this study, the saturation condition occurs faster in use of low gas pressure combined with high voltage DC bias.

Table 1. Lattice parameter of α-phase, ω-phase and TiN in the untreated pure Titanium and seven plasma nitrided specimens

| Sample Condition                      | α-Ti phase | ω-Ti phase | TiN  |
|--------------------------------------|------------|------------|------|
|                                      | a = b      | c          | c/a  | a = b | c          | c/a  | a = b = c |
| Untreated pure Titanium              | 2.9531     | 4.6826     | 1.5857 |      |            |      |           |
| Nitrided at 75 Pa, -500 V DC bias, 4 h | 2.9780     | 4.7150     | 1.5834 4.632 | 2.8300 | 0.6110     | 4.1582 |
| Nitrided at 50 Pa, -500 V DC bias, 4 h | 2.9510     | 4.6650     | 1.5808 4.657 | 2.8754 | 0.6174     | 4.3535 |
| Nitrided at 30 Pa, -500 V DC bias, 4 h | 2.9450     | 4.6650     | 1.5840 4.610 | 2.8100 | 0.6095     | 4.2520 |
| Nitrided at 75 Pa, -600 V DC bias, 4 h | 2.9527     | 4.6830     | 1.5860 4.651 | 2.8643 | 0.6158     | 4.3950 |
| Nitrided at 50 Pa, -600 V DC bias, 4 h | 2.9520     | 4.6680     | 1.5813 4.649 | 2.8580 | 0.6146     | 4.2870 |
| Nitrided at 30 Pa, -600 V DC bias, 4 h | 2.9450     | 4.6610     | 1.5827 4.632 | 2.8370 | 0.6125     | 4.2590 |
| Nitrided at 30 Pa, -600 V DC bias, 8 h | 2.9450     | 4.6560     | 1.5810 4.657 | 2.9179 | 0.6265     | 4.2460 |

Table 2. Phase concentration of α-phase, ω-phase and TiN in seven plasma nitrided specimens

| Sample Condition                      | Phase concentration (at.%) |
|--------------------------------------|---------------------------|
|                                      | α-Ti                  | ω-Ti                  | TiN       |
| Nitrided at 75 Pa, -500 V DC bias, 4 h | 66.45                 | 33.46                 | 0.46      |
| Nitrided at 50 Pa, -500 V DC bias, 4 h | 64.16                 | 33.98                 | 1.87      |
| Nitrided at 30 Pa, -500 V DC bias, 4 h | 53.18                 | 40.73                 | 6.09      |
| Nitrided at 75 Pa, -600 V DC bias, 4 h | 89.65                 | 8.64                  | 1.71      |
| Nitrided at 50 Pa, -600 V DC bias, 4 h | 62.49                 | 30.38                 | 7.13      |
| Nitrided at 30 Pa, -600 V DC bias, 4 h | 34.04                 | 57.25                 | 8.71      |
| Nitrided at 30 Pa, -600 V DC bias, 8 h | 24.79                 | 37.11                 | 38.1      |

One of the factors that can explain why the addition of hollow cathode can improve the efficiency of nitriding process is the high-density of the plasma inside the hollow pipe. In observation with the naked eye, the high-density plasma is characterized by higher emitted light intensities inside hollow tube compared to a planar cathode glow discharge as shown in Figure 2c because there was a high field current on the cathode surface [7]. The effect of the hollow cathode geometry is an increase in the density of plasma because of the electrostatic trapping of electrons between hollow cathode gaps. The trapping electrons oscillate inside the cavity, expanding all their energy for excitation and ionization of atoms [8]. These electrons cause a significant increase in the various collision processes between the plasma species (ions, electrons, atoms and neutral molecules), intensifying the ionization reactions and excitations [9]. As a result, there is also an increase in the quantity of the species (comprised basically of positive ions and neutral species) that impinge on the cathode surface (with a sample placed inside the cathode) that it is connected to the negative power source. Moreover, the
result of this interaction is the bombardment of nitrided surface specimens by the plasma species which tend to activate surface diffusion of the nitrogen atoms that are deposited on the sample to achieve the formation of the TiN compound layer [10].

The increasing of plasma density inside the hollow cathode tube also depends on the pressure. In low pressure, the mean free path of electrons is large. Hence the electrons gain a lot of energy from applying an electric field to create more excitement and ionization through inelastic collisions with other plasma particles, and then the higher density of ion and electron was formed inside the hollow tube [5]. The effect of gas pressure on the hollow cathode discharge depends on the product gas pressure by the inter-cathode distance (p.d). Hence the decrease in p.d value by decreasing pressure for fixed inter-cathode distance in this study made the density of ions increases sharply. The other reason is it was connected with higher efficiency of ionization in the hollow cathode cavity, which is determined by the ratio of sheath width of gap lengths. The ionization efficiency is due to the ability of oscillating electrons to create secondary electrons in the sheath that caused an exponential increase of the discharge current when a substantial fraction of ionization events occur in the sheath [8, 11]. In this study, it was observed that the sheath width increased in the lower gas pressure, so the ratio of sheath width of gap lengths increased too. This condition shows that the higher ion density will be formed as the result of decreasing gas pressure in the nitriding process by using the hollow cathode device. The final result is expected on the increase of ion density is the possibility of the more effective diffusion process so that the surface hardening process can occur more optimally.

The increase of nitrogen concentration as interstitial elements leads to a drastic increase in surface hardness of nitrided specimen. In this study, the initial value of surface hardness of pure titanium increased from 300 HV to 624 HV after nitriding process by using DC bias of -600 V and gas pressure of 30 Pa for 4 hours, and then the hardness value increased again to 792 HV after 8 hours time processing. The trends of increasing hardness value against the lowering gas pressure after subjected to 4 hours plasma nitriding process are shown in Figure 7. It appeared that the hardness value increased in the process of using lower pressure, which is the higher hardness is found in the process by using DC bias of -600 V rather than -500 V with same gas pressure. It shows that the hardening process occurs more effectively in the nitriding process carried out at the lower gas pressure and the higher value of DC bias.

![Figure 7](image_url)  
*Figure 7. The correlation between increasing hardness value and lowering gas pressure.*

4. Conclusion

The high-density plasma generated by RF-DC plasma system was applied to low-temperature nitriding of the pure titanium at 450 °C. The use of hollow cathode device with lowers gap distance increasing ion density in plasma, and greatly affects the success of the titanium nitriding process as a process at
high temperature. The effective diffusion process of nitrogen atoms as a solid solution into a titanium matrix drives the increase of surface hardness. Variation of gas pressure and DC bias voltage as plasma nitriding parameters plays a major role in the hardening mechanism of pure titanium. The lower gas pressure combined with a high DC bias voltage can increase the surface hardness significantly because it causes the phase transformation of $\alpha$-titanium to $\omega$-titanium which drives a formation of fine TiN precipitates as the compound layer. The formation of $\omega$-titanium can be a trigger for the formation of the compound layer because it facilitates the higher possibility of diffusion processes in the nitrided specimen. The use of lower pressure combined with a higher DC bias voltage also accelerates the saturation condition in the diffusion process of nitrogen atoms into a titanium matrix and then it will increase the concentration of TiN on the top surface of nitrides specimen.

5. References

[1] Buijs K and Stainless V L 2008 Stainless World 1-4
[2] Holz M and Walker G P 2011 Ti Fact, International Titanium Association (USA: Northglenn CO) p. 1-24
[3] Zhecheva A, Wei Sha, Malinov S and Long A 2005 J. of Surface & Coating Technology 200 pp 2192-2207
[4] Koyuncu E, Kahraman F and Karadeniz O 2009 J. of Achievements in Material and Manufacturing Engineering 37 (2) pp 434-441
[5] Yunata E E, Aizawa T, Santjojo D J H D 2014 8th SEATUC Meeting and Symposium (Malaysia: Universiti Teknologi Malaysia) 6 (14) pp1-4
[6] Aizawa T, private communication
[7] Awsi S K 2013 American Journal of Modern Physics 2 (6) pp 276-281
[8] Kolobov V I and Tsendin L D 1995 Plasma Source Sci. Technol. 4 pp 551-560
[9] Brunatto S F, Kühn I and Muzart J L R 2001 J. Materials Research 4 (4) pp 245-250
[10] Alves C Jr, Guerra Neto C L B, Morais G H S, da Silva C F and Hajek V 2006 Surface & Coating Technology 200 pp 3657-3663
[11] Barankova H and Bardos L 2001 Surface and Coatings Technology 146–147 pp 486-490

Acknowledgements

The authors would like to thank Tatsuhiko Aizawa from Shibaura Institute of Technology, Japan for the research facilities provided as well as guidance for the implementation of the research in LLC Nanofilm & Coat Laboratory, Ota-ku, Tokyo. The authors are also thankful to ASMAT Research Collaboration, University of Brawijaya, which is funded through Program Hibah Kerjasama Luar Negeri JSPS Dikti with the contract number 033/SP2H/LT/DRPM/2/2016, so that this research can be accomplished.