DESIGN AND FABRICATION OF UREA-BASED NITRIDING DEVICE FOR PURE TITANIUM GRADE 1

Aria Wira Yuda[1)]
Doctoral Program, Faculty of Engineering, Sriwijaya University, Bukit Besar, South Sumatera, Indonesia
ariawy1@gmail.com

Amir Arifin[2)]
Department of Mechanical Engineering, Sriwijaya University, Bukit Besar, South Sumatera, Indonesia
amir@unsri.ac.id

Irsyadi Yani[3)]
Department of Mechanical Engineering, Sriwijaya University, Bukit Besar, South Sumatera, Indonesia
irsyadiyani@unsri.ac.id

Barlin Oemar[4)]
Department of Mechanical Engineering, Sriwijaya University, Bukit Besar, South Sumatera, Indonesia
barlin@unsri.ac.id

Rakhman[5)]
PT Pusri Palembang, Palembang, South Sumatera, Indonesia
rakhman@pusri.co.id

Abstract

The industrial use of pure titanium has been extensive, but, its products have been plagued by inadequate wear and erosion resistance. The technique of pack nitriding was chosen to increase the hardness of pure titanium products. However, achieving high hardness often necessitated high temperature processing. The nitriding carried out using urea as an alternative source of nitrogen, which will diffuse with the metal surface and form titanium nitride. In this study, an attempt is made to design and fabrication a nitriding device in the workshop. The device is made using stainless steel pipe 4" Sch. 160, 400mm long, which is closed with 4" SO #900 blind flange. To measure pressure in the nitriding chamber, a Pressure Gauge is installed at the top of the top flange. Heat supply from Jemix brand heat treatment machine. The nitriding pipe is covered with a heating coil and temperature control of the heating machine. Urea in granular form is put into the nitriding chamber and then the specimen is also placed in it. Nitriding process was performed at temperature of 475°C. Thermocouple with measurement range and reliability of up to 1200°C was utilised to gauge the temperature of the nitriding chamber and provide input to the temperature controller. The test findings indicate that the temperature control equipment performs effectively within a temperature stability range of between 1°C to 2°C. The Pure Titanium Gr. 1 plate after nitriding show a hardness improvement as compared to the non-treated plate. The test showed that Titanium surface hardness after nitridation for 2 hours, rose from 55.5 HRC to 70.5 HRC. It is anticipated that it can address industrial technical problems related to the premature degradation of Pure Titanium Gr. 1 plate.

Keywords: Titanium, Nitriding Device, Hardness, Urea Nitriding

1. INTRODUCTION

Titanium is sturdy and light material, with excellent mechanical qualities like high durability and resistance to corrosion. It is employed in medicine, petrochemical, and other industries [1-5]. Nevertheless, substandard wear properties frequently results in initial failure of titanium components [6], This study examines the devices to improve titanium mechanical properties, as well as the unavoidable wearing that occurs between the titanium and other metal. Thus, actions need to be done to improve the wear characteristics of titanium.

Significant efforts have been focused on improving the durability of titanium [9-13]. This way of adding TiN to the titanium plate's surface is often used to make them more resistant to wear [14,15]. Several techniques have been documented for the fabrication of TiN coatings, including vapor deposition [16,17], plasma nitriding [19], chemical deposition [18], as well as laser nitriding [20-21]. Because of its advantages, such as a brief nitriding duration and a robust metallurgical connection between the resulting nitriding layer and the underlying material [22,23], the technology of gas nitriding has garnered significant attention. In a nitrogen atmosphere, nitrogen moves into the surface area, where it cools and solidifies to form the TiNx phase.

The most popular way to get ready for surface laser nitriding is with a continuous wave or pulsed laser. When a continuous wave laser makes a nitride layer, it is generally thick (tens microns) and has a rough surface (>2 microns) with a substrate that is susceptible to deformation [24,25]. In comparison, the pulsed laser nitriding technology has demonstrated distinct advantages such as rapid treatment, minimal heat-affected zone, prevention of undesired substrate heating, extensive and sideways treatment, specific surface treatment, and adaptability to materials with intricate surface shapes [26]. Based on relevant reports [26,27], Thin nitride layers can be directly formed on titanium alloy surfaces by irradiating them with pulsed laser light in the presence of nitrogen. A study has shown that the use of pulsed laser nitriding resulted in a considerable reduces micro-motion wear and raises surface hardness at both high and normal temperatures [28,29]. An investigation has verified that the duration of pulsed laser nitriding directly affects the thickness of nitrided surface. Furthermore, we have seen substantial enhancements in the hardness, and wear properties of the nitrided surface [21]. Moreover, many empirical investigations have demonstrated that specific process variables [30-35], the application of nitriding technique can influence the mechanical properties of layers generated on metal surfaces.

In this research, a nitrogen source was used from urea fertilizer. Urea fertilizer is synthesized through chemical processes and has a relatively high concentration of nitrogen. Most urea fertilizers available in the market consist of the nutrient element nitrogen (N) at a level of 46%. Each 100 kilos of urea fertilizer contains 46 kilograms of nitrogen. In general, urea fertilizer has a fairly rough texture. Urea fertilizer is in the form of white crystal-like granules with chemical formula NH_2CONH_2.

Due to the nitrogen content in urea fertilizer, research on the nitriding process on steel surfaces was carried out using urea as a nitrogen source. At a temperature of 460-600^oC the nitrogen content in urea decomposes into N atoms which compound on the surface of the test sample.

This paper discusses the process of design, manufacture and testing of temperature control equipment that has been used in material hardening operations using nitriding at PT Pusri Palembang. To make this tool, local components are used which are easily available on the market. For the component assembly process, mechanical and electrical workshop facilities are used within PT Pusri Palembang, which is located in Palembang. Equipment testing and operation was carried out in the laboratories of PT Pusri Palembang and Sriwijaya University.

2. MATERIAL AND METHOD

2.1 Titanium Grade 1 Specimen

Pure Titanium Grade 1 is renowned for being among the most malleable and pliable grades, showcasing an exceptional ability to be welded into various forms. This pure titanium possesses exceptional qualities of being resistant to corrosion and being easily weldable, thus making it suitable for a wide variety of uses [36]. The compositions of Titanium plates that were treated in this study are provided in Table 1.

Table 1 Composition of Titanium Grade 1 (%.wt)

Name	Value		Name	Value
Ti	99.5		Fe	Max 0.2
H	Max. 0.015		N	Max. 0.03
O	Max. 0.18		C	Max. 0.1

2.2 Urea

With the highest Nitrogen content, urea stands as the predominant nitrogenous fertilizer in the market (as described in Table 2). This research used urea in granule form produced by PT. Pusri Palembang, South Sumatera, Indonesia as a fertilizer plant since 1959.

Table 2 Properties of Urea

Shape	Nitrogen content	Biuret	Moisture	Size	Specific Gravity
Granule	Min. 46.9 %. weight	Max. 1.0 %. weight	Max 0.5 %. weight	2-4 mm	0.74 gr/cc

2.3 Nitriding Device

The next preparation is to make a nitriding shell made of steel pipe with adjusted dimensions as a container for placing urea and test samples when undergoing the nitriding process in the heating furnace.

According to its use, the design of the temperature control equipment must comply with the operating requirements and design concept of the nitriding system. In general, the design and operation concept of nitriding for hardening industrial component materials can be described based on the sketch in Figure 1.

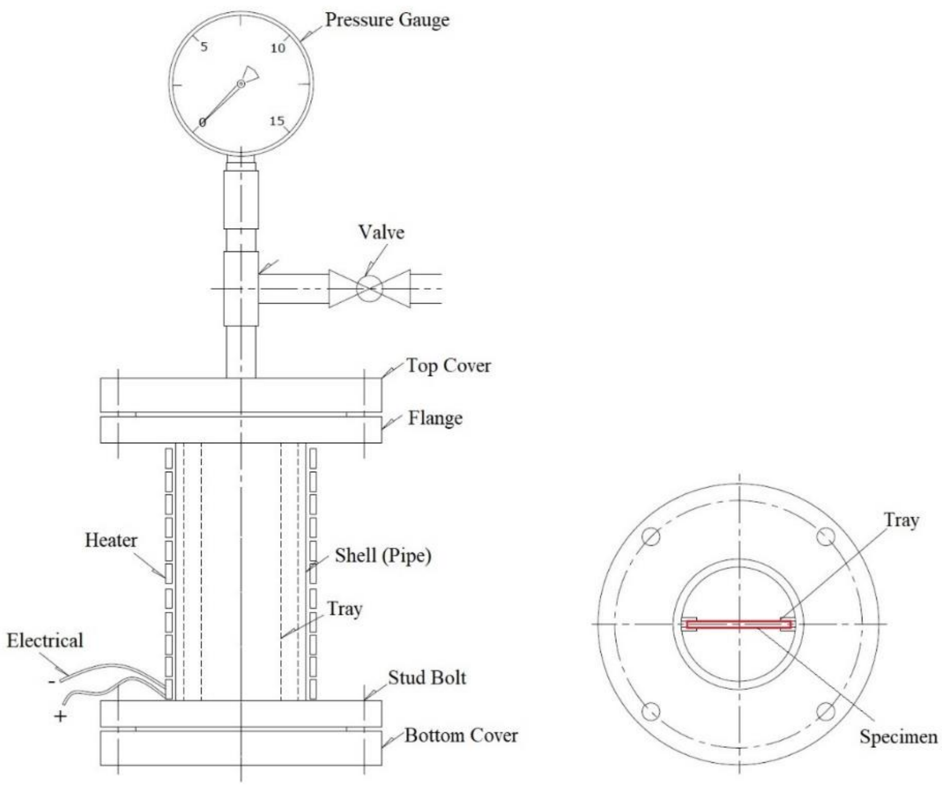
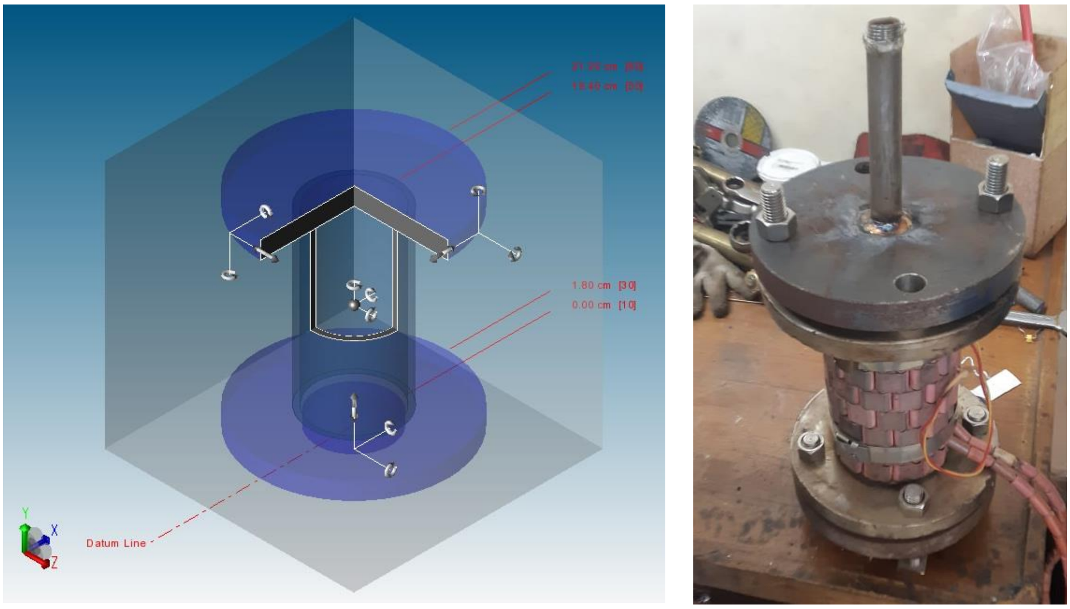


Figure 1: Scheme of nitriding equipment

This system functions to regulate the temperature in the nitriding chamber so that a constant operating temperature is obtained. The temperature of the nitriding equipment is designed to provide room and sample material temperatures of up to 700ºC. As a heating source, Jemix Heat Treatment machine is used. Part of the equipment consists of: a temperature measuring system, control instrumentation for temperature setting and a relay system. For sensors and temperature measurements, a thermocouple is used. The thermocouple measurement results are received by temperature control, then from this temperature control the signal is carried by the thermocouple and the temperature setting previously set is adjusted according to requirements. If the temperature has reached the desired degree according to the temperature setting, the temperature control will give a signal to stop the voltage given to the relay.

The device is made using stainless steel pipe 4" Sch. 160, 400mm long, which is closed with 4" SO #900 blind flange. Maximum Allowable Working Pressure (MAWP) for shell of nitriding device calculation perform in accordance with ASME Section VIII Division 1 using Software PV Elite 2020. From calculation, obtain MAWP of 45 kg/cm2 in temperature 700ºC.



(a) (b)

Figure 2: (a). Geometry Design; (b) Nitriding shell assembly

The design of temperature control equipment contains design concepts on a prototype scale which are prepared based on data and specifications of temperature control system components. Component determination and material selection are carried out by referring to temperature control equipment design data and reference studies. To reduce equipment manufacturing costs, components are designed to be made by assembling basic element materials available on the local market. To increase efficiency, the design of this equipment is designed with the following considerations:

1. Casing is made according to space requirements or size of temperature control components.
2. Ease of operation and maintenance which requires a compact design, and easy to dismantle and assemble.
3. A good control, measurement and regulation system ensures the safety of equipment and operators from electrical hazards.

The nitriding equipment manufacturing process involves preparing tools, selecting materials and fabricating work. Preparation of fabrication equipment is carried out by preparing machines, tooling and testing equipment. Selection of materials taking into account oil-free dirt, especially for making equipment casings, and in welding work. Carrying out fabrication by paying attention to size, dimensions in workmanship according to the dimensions contained in the drawing, carrying out work such as cutting, drilling and welding.

3. RESULTS AND DISCUSSION

The temperature control equipment that has been assembled is then used and connected to the nitriding equipment. A picture of the temperature control installation is shown in Figure 2. The operation and workings of the temperature control device are described as follows:

The electrical power supply is obtained from PT Pusri's electrical grid via a socket and the MCB (mini circuit breaker) is turned ON. The temperature setting on the temperature control is selected according to the operating temperature and the heating system is operated with the heating switch in the ON position. During the ongoing nitriding operation, the temperature of the nitriding chamber is indicated by the display on the temperature control system according to the selected value. ON and OFF conditions indicate the accuracy of the tool. If the operation is complete, set the temperature control setting to room temperature and once room temperature is reached the switch for the heater can be turned off (OFF) and then the MCB is also turned off, then turn off the electric power supply.
The temperature control system consists of several components, namely:

- temperature controller of the Jemix Heat Treatment machine
- relay: Solid-State-Relay (SSR).
- thermocouple
- Heat sinks and cable terminals

Type K thermocouple is a temperature measuring instrument that has a measuring range of up to 1200ºC. From the data obtained it can be said that the heating system is stable at temperatures of 200ºC, 400ºC and 500ºC for 2 hours with different indications at temperature differences in the range of 1ºC to 2ºC from the specified temperature.

3.1 Hardness Test

The Handy Hardness Tester, SONOHARD SH-21A, which had measuring range of Rockwell hardness from 10.0～70.0 HRC. Measuring indenter is diamond indenter for Micro-Vickers (facing-to-surface angle of 136˚) was employed to determine the hardness level by tiny indentation (approx.0.1mm). The portable ultrasonic hardness tester, SONOHARD SH-21A, with direct reading of hardness values in HRC as shown in Figure 3. The applied load according to JIS B 7731. The hardness values that are mentioned are the average results obtained from taking 5 readings for each individual specimen.

(a) (b)

Figure 3: (a). Measuring indenter; (b) Digital display

Table 3 Samples are produced using process parameters.

Sample	Urea Mass (in grams)	Temperature (Celsius deg.)	Holding time (hours)	Heating Rate (ºC/hour)
1	100	475	2	300
2	150	475	2	300
3	200	475	2	300
4	250	475	2	300
5	300	475	2	300
6	350	475	2	300

The nitriding experiment was performed in nitriding pipe (Figure 2). Titanium plate was placed in stainless steel pipe on a sample tray of the same material. The pipe is covered by top cover and bottom cover and warm up using an electric induction component. At the top cover, a pressure gauge to monitor internal pressure and a valve to release the gas.

Data from nitriding research on the Titanium surface are listed in Figure 4.

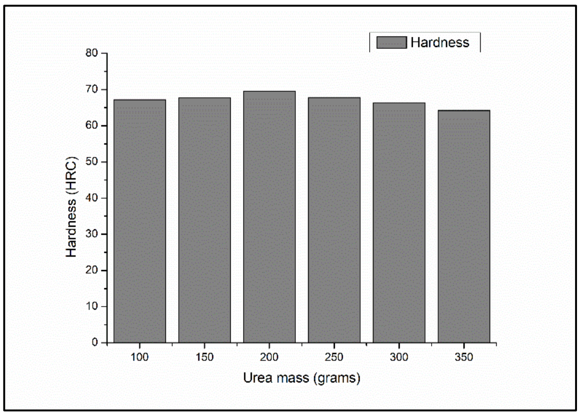


Figure 4: Hardness test measurement on the 6 samples

The results of measuring the level of surface hardness obtained using SONOHARD SH-21A in the form of the average value of the level of hardness from the 5 positions measured.

Among the several parameters used for nitriding in this study, it appears that urea mass plays an important role for the increase in surface hardness. This is because increasing gas pressure in the process will increase the opportunity for nitrogen atoms to diffuse into the titanium crystal lattice.

Because the nitriding process in this study was carried out at a temperature of 475°C, where this temperature is still very far below the transition temperature for the formation of beta titanium (n-Ti), namely 883°C, it can be said that it is impossible for the n-Ti phase to form at this research. The formation of the n-Ti phase in the nitriding process will increase the diffusion coefficient of nitrogen, so that the nitrogen concentration contained in the crystal will be greater as a result of the interstitial diffusion process. Several previous research results stated that TiN usually only forms at nitriding process temperatures above 800°C [25], because TiN will only form if the concentration of nitrogen contained in the crystal lattice is large enough.

4. CONCLUSION

We have demonstrated the possibility of nitriding of titanium in an urea chamber by heating from a heat treatment machine. The design and assembly of temperature control equipment for nitriding system has been successfully carried out. From the results of the nitriding test as Titanium treatment using urea as a nitrogen source, it can be concluded as follows:

1. There is an improvement in hardness compared to untreated specimens (non-nitriding).
2. Nitriding can effectively enhance the hardness of Titanium (Ti) Gr. 1 under non-vacuum condition. In the case of the nitriding temperature 475°C for 2 h, Titanium (Ti) Gr. 1 nitrided at urea mass of 200 grams exhibits the most excellent hardness.
3. As urea mass rises from 100 to 350 grams, the hardness of nitrided titanium shows an upward trend, which results from the increase of nitrogen ion released.

The obtained results demonstrate the possibility of using the urea chamber sources for nitriding of Titanium Gr. 1.

5. ACKNOWLEDGMENTS

The authors appreciates the kind assistance and collaboration of PT. Pusri Palembang in South Sumatera, Indonesia, for allowing the use of the workshop.

REFERENCES

[1] A. Gao, R. Hang, L Bai, B. Tang, P.K. Chu, Electrochemical surface engineering of titanium-based alloys for biomedical application, Electrochim. Acta 271 (2018) 699-718.

[2] A.X.Y. Guo, L Cheng, S. Zhan, S. Zhang, W. Xiong, Z. Wang, G. Wang, S.C. Cao, Biomedical applications of the powder-based 3D printed titanium alloys: A review, J. Mater. Sci. Technol. 125 (2022) 252-264.

[3] Z.b. Cai, Z.y. Li, M.g. Yin, M.h. Zhu, Z.r. Thou, A review of fretting study on nuclear power equipment, Tribal. Int. 144 (2020).

[4] Z.Y. Huang, H.Q. Liu, H.M. Wang, D. Wagner, M.K. Than, Q.Y. Wang, Effect of stress ratio on VHCF behavior for a compressor blade titanium alloy, Int. J. Fatigue 93 (2016) 232-237.

[5] S. Luo, D. Thu, L. Hua, D. Qian, S. Yan, Numerical analysis of die wear characteristics in hot forging of titanium alloy turbine blade, Int. J. Mech. Sci. 123 (2017) 260-270.

[6] K.G. Budinski, Tribological properties of titanium alloys, Wear 151 (2) (1991) 203-217.

[9] Y. Yu, J. Gong, X. Fang, L Zhou, W. He, L Zhou, Z. Cai, Comparison of surface integrity of GH4169 superalloy after high-energy, low-energy, and femtosecond laser shock peening, Vacuum 208 (2023), 111740.

[10] Y. Yu, L Zhou, Z. Cai, S. Luo, X. Pan, J. Zhou, W. He, Research on the mechanism of DD6 single crystal superalloy wear resistance improvement by femtosecond laser modification, Appl. Surf. Sci. 577 (2022), 151691.

[11] Z. Zhang, S. Pan, N. Yin, B. Shen, J. Song, Multiscale analysis of friction behavior at fretting interfaces, Friction 9 (1) (2021) 119-131.

[12] Z. Zhang, N. Yin, S. Chen, C. Liu, Tribo-informatics: Concept, architecture, and case study, Friction 9 (2020) 642-655.

[13] Y. Yu, L Zhou, M. Li, Z. Cai, S. Luo, W. He, X. Fang, Research on fretting regime transition of DD6 single-crystal superalloy via femtosecond laser-induced asperity and hardened layer, Appl. Surf. Sci. 610 (2023), 155392.

[14] M. Lepicka, M. Gradzka-Dahlke, D. Pieniak, K. Pasierbiewicz, K. Kryfiska, A. Niewczas, Tribological performance of titanium nitride coatings: A comparative study on TiN-coated stainless steel and titanium alloy, Wear 422 (2019) 68-80.

[15] L Zhang, M. Shao, Z. Wang, Z. Zhang, Y. He, J. Yan, J. Lu, J. Qiu, Y. Li, Comparison of tribological properties of nitrided Ti-N modified layer and deposited TiN coatings on TA2 pure titanium, Tribol. Int. 174 (2022), 107712.
[16] Y.H. Wang, Z.B. Yang, S.Y. Hu, Y.H. Zhao, H. Ren, F. Gong, Z.W. Xie, Tailoring growth structure, wear and corrosion properties of TiN coatings via gradient bias and arc enhanced glow discharge, Surf. Coat. Technol. 450 (2022), 129015.
[17] Y.H. Wang, F. Guo, H. Ren, S.Y. Hu, Y.J. Chen, Y.H. Zhao, F. Gong, Z.W. Xie, Enhancing wear resistance of TiN coating by gradient bias voltage and arc-enhanced glow discharge, Ceram. Int. 48 (6) (2022) 8746-8750.
[18] R Sitek, J. Kaminski, J. Borysiuk, H. Matysiak, K. Kubiak, K. Kurzydlowski, Microstructure and properties of titanium aluminides on Ti-6A1-4V titanium alloy produced by chemical vapor deposition method, Intermetallics 36 (2013) 36-44.
[19] K. Szymlciewicz, J. Morgiel, L. Maj, M. Pomorska, M. Tamowski, T. Wierzchon, TEM investigations of active screen plasma nitrided Ti-6A1-4V and Ti-6A1-7Nb alloys, Surf. Coat. Technol. 383 (2020), 125268.
[20] C.L. Donaghy, R. McFadden, S. Kelaini, L Carson, A. Margariti, C.-W. Chan, Creating an antibacterial surface on beta TNZT alloys for hip implant applications by laser nitriding, Opt. Laser Technol. 121 (2020), 105793.
[21] X. Zong, H. Wang, Z. Li, J. Li, X. Cheng, Y. Zhu, X. Tian, H. Tang, Laser nitridation on Ti-6.5A1-3.5Mo-1.57.r-0.3Si titanium alloy, Surf. Coat. Technol. 386 (2020), 125425.
[22] X. Zong, H. Wang, J. Li, X.u. Cheng, Z. Li, H. Tang, Microstructure characterization and evolution mechanism of titanium during laser surface nitriding, Mater. Charact. 190 (2022) 112029.
[23] A. Zhecheva, W. Sha, S. Malinov, A. Long, Enhancing the microstructure and properties of titanium alloys through nitriding and other surface engineering methods, Surf. Coat. Technol. 200 (7) (2005) 2192-2207.
[24] A.M. Kamat, S.M. Copley, J.A. Todd, Effect of processing parameters on microstructure during laser-sustained plasma (LSP) nitriding of commercially-pure titanium, Acta Mater. 107 (2016) 72-82.
[25] A.M. Kamat, S.M. Copley, J.A. Todd, A two-step laser-sustained plasma nitriding process for deep-case hardening of commercially pure titanium, Surf. Coat. Technol. 313 (2017) 82-95.
[26] Y. Huang, Y. Zhu, Y. Zhao, L. Wu, L Zhang, Y. Zhang, J. Wu, F. Tan, Experimental investigation for pulsed laser nitriding of metals, Opt. Laser. Technol. 157 (2023), 108661.
[27] D. Htiche, P. Schaaf, Laser nitriding: investigations on the model system TiN. A review, Heat Mass. Transfer. 47 (5) (2011) 519-540.
[28] A.R. Kulkarni, M. Manikandan, A.K. Shukla, S. Subramaniam, V. Balaji, I. Palani, M. Jayapralcash, Influence of laser-nitriding on mechanical and elevated temperature fretting wear behavior of A356-alloy, Surf. Coat. Technol. 413 (2021), 127072.
[29] A.R. Kulkami, A.K. Shukla, S.M. Prabu, S. Subramaniam, V. Balaji, I. Palani, M. Jayaprakash, Investigations on enhancing the surface mechanical and tribological properties of A356 Al alloy using pulsed laser-assisted nitriding, Appl. Surf. Sci. 540 (2021), 148361.
[30] E. Carpene, P. Schaaf, Laser nitriding of iron and aluminum, Appl. Surf. Sci. 186 (1¬4) (2002) 100-104.
[31] M. Han, K.-P. Lieb, E. Carpene, P. Schaaf, Laser-plume dynamics during excimer laser nitriding of iron, J. Appl. Phys. 93 (2003) 5742-5749.
[32] E. Gyorgy, A. Perez del Pino, P. Serra, J.L. Morenza, Surface nitridation of titanium by pulsed Nd: YAG laser irradiation, Appl. Surf. Sci. 186 (1-4) (2002) 130-134.
[33] P. Schaaf, Laser nitriding of metals, Prog. Mater. Sci. 47 (1) (2002) 1-161.

[34] N. Ohtsu, K. Kodama, K. Kitagawa, K. Wagatsuma, Comparison of surface films formed on titanium by pulsed Nd: YAG laser irradiation at different powers and wavelengths in nitrogen atmosphere, Appl. Surf. Sci. 256 (2010) 4522-4526.
[35] A.H. Farha, O.M. Ozkendir, U. Koroglu, Y. Ufuktepe, H.E. Elsayed-Ali, Nitridation of Nb surface by nanosecond and femtosecond laser pulses, J. Alloy Compd. 618 (2015) 685-693.
[36] Welsch G, Boyer R, Collings EW. Materials properties handbook: titanium alloys. ASM international; 1994.

Biodata:
Aria Wira Yuda is a doctoral Program, Faculty of Engineering, Sriwijaya University, Bukit Besar, South Sumatera, Indonesia. His Email is ariawy1@gmail.com.