



Improvement of Erosion Resistance of Aluminum- Copper Alloy Type 2024 by Plasma Nitriding

Mohammed H. Maseekh^{*a}, Ali H. Ataiwi^b, Jamal J. Dawood^a

^a Materials Engineering Dept, University of Technology-Iraq, Alsina'a Street, 10066 Baghdad, Iraq.

^b Ashur University College, Baghdad, Iraq.

*Corresponding author Email: <mailto:mae.19.37@grad.uotechnology.edu.iq>

HIGHLIGHTS

- Samples from the aluminum-copper alloy 2024 were prepared to study the improvement of the erosion resistance of this alloy.
- A full thermal annealing treatment was performed.
- Plasma nitriding was performed as a surface treatment.
- Microstructure examinations (SEM, XRD), erosion, and hardness tests were carried out after each treatment, and comparing the results.

ABSTRACT

To increase the erosion resistance of 2024 Al alloys, plasma nitriding surface treatment was used. Nitrogen and argon gases are injected into an evacuated chamber until the pressure reaches 15 Pa. The process requirements for normal plasma nitriding were heating at 440°C for 8 hours, low voltage of 650 V, current of 25 mA, low gas consumption, and no air pollution. A continuous nitriding layer of AlN was formed. The microhardness reached a maximum value of 170 HV, about 3 times higher than that Al melts at, is transported upward through voids and capillaries in the AlN structures, and reacted with N plasma in the melt surface. The growth of the AlN structures promotes this transport of un-nitride alloy subjected to the same heat treatments. As a result, the erosion rate of the nitrided samples decreased by 10% when compared to the ones that are not nitrided.

ARTICLE INFO

Handling editor: Israa A. Aziz

Keywords:

Plasma nitriding; Aluminum alloy; Slurry erosion; Nitrided layer; Microhardness.

1. Introduction

Aluminum and its alloys have a wide range of applications, especially in the automotive and aerospace industries. Furthermore, compared to other metals, aluminum's reduced density and lightweight result in significant reductions in fuel consumption and cost-effectiveness [1]. Other desirable features of aluminum and its alloys include high specific strength, good machinability, high ductility, and strong resistance to some corrosives [2,3]. However, the low surface hardness, abrasion resistance, and heat and chemical stability of these alloys limit their commercial applicability [4]. As a result, improving the characteristics of aluminum alloys through surface treatment is critical for their use in the industry [5]. The formation of an aluminum nitride layer, known to improve the erosion wear resistance of alloy surfaces, is one way of surface hardening. Aluminum and its alloys are known to have poor tribological characteristics, which can be improved by nitriding [6]. However, even at high pressures, this is a difficult process because high aluminum-oxygen reactivity increases oxidation at the surface, restricting nitrogen diffusion [2-7]. Nitriding is a surface engineering technique for enhancing the surface qualities of metals that are widely utilized in various industries [8]. The traditional nitriding procedures can be carried out in a liquid medium, a gas medium (a combination of NH₃/H₂), or a plasma medium (low-pressure H₂/N₂) [9]. It is a way to add nascent (elemental) nitrogen to the surface of a metal part using the glow-discharge technique for eventual diffusion into the substance. A plasma is generated in a vacuum using high-voltage electrical energy, and nitrogen ions are driven toward the workpiece. The ion

bombardment heats the item while also cleaning the surface and supplying active nitrogen. Case chemistry is more controlled, case homogeneity is better, and part distortion is lower than with gas nitriding [10]. This research will employ the last medium to determine changes in hardness, erosion resistance, and microstructure. The main objective of this research is to gain high tribological surface characteristics to improve the hardness and erosion wear resistance of the 2024 alloy by plasma nitriding compared with full annealed alloy properties.

Okumiya et al. Combined barrel nitriding and plasma nitriding, a bilayer aluminum nitride on aluminum can be produced [11]. Khan et al. studied nitriding of aluminum alloy in nitrogen and nitrogen-helium mixture using a 100 Hz-pulsed DC glow discharge. Vickers micro hardness testing results show increases in surface hardness with processing duration and the addition of helium in nitrogen plasmas [12]. Visuttipitukul et al. investigated the influence of plasma nitriding by pre-sputtering, aluminum nitride nucleation, and nitrided layer growth processes N₂+pre-sputtering is used to effectively eliminate the preexisting oxide films of Al₂O₃ [13]. Dalke et al. calculated the wear behavior of nitrided spray-formed AlSi alloys. Using an N₂-Ar gas mixture at a nitriding temperature of 743 ± 10 K. The AlN layer exhibit an increased wear resistance compared to the non-nitrided condition for all applied test loads [14]. Li et al. investigated the effect of the thermal plasma nitriding method on 1060 and 6082 substrates. The AlN strengthening layer can be prepared on substrates, and the hardness and wear resistance increase as the N₂ flow rate increases from 1 L/min to 7.5 L/min. The average hardness of the nitrided layer is nearly 7 times that of the substrate. In addition, the wear resistance is increased to 2 times that of the substrate [15]. In this study, plasma nitriding was used at a temperature of 440° C for 8 hours to produce a nitride layer that increased the hardness 3 times and the slurry erosion rate by 10% compared to the untreated alloy. This research aims to gain high tribological surface characteristics to improve the hardness and erosion wear resistance of the 2024 alloy. Furthermore, it aims to study the effect of full annealing and surface treatment (plasma nitriding) on the microstructure, mechanical, and erosion properties.

2. Experimental Work

2.1 Materials

The materials used in the present work are aluminum-copper alloy type 2024, according to the American Society for Testing and Materials (ASTM). It is supplied from a local market. The sample's chemical composition, which is investigated by utilizing (AMETEK, SPECTRO MAXx), is shown in Table 1.

2.2 Sample Preparation

Samples for each test were prepared by machining. The first sample has been cut to the following dimensions for the erosion wear test: (20*30*4) mm, as depicted in Figure 1a. The second sample was cut to the following dimensions for scanning electron microscope examination (SEM): (8Ø*3 mm), as illustrated in Figure 1b. Finally, the third is machined to (10Ø*10mm) cylindrical shape for X-ray diffraction tests (XRD) shown in Figure 1c.

2.3 Annealing

All samples are annealed in an electric furnace at a temperature of 41°C. Heating is continued to rise at a rate of 7.65°C/min until the temperature reaches 400°C. Then, they were soaked for one hour at this temperature. The furnace is subsequently switched off, and the samples are allowed to cool naturally until room temperature is reached.

2.4 Plasma Nitriding

A locally manufactured plasma nitriding device was used to perform the nitriding. The plasma nitriding process is depicted schematically in Figure 2. On the cathodic sample stage, an extra screen and samples were inserted. As a result, plasma developed on both the sample and the auxiliary cathode screen. This supplemental screen reduces the edge effect by boosting the availability of active species. An enlarged mesh of AISI316L austenitic stainless steel (ASS) with 38 percent open area, a diameter of 200 mm, and a height of 70 mm served as the supplementary screen material. The distance between the sample and the screen is about 20 millimeters. To keep the oxygen partial pressure and moisture as low as possible, the plasma nitriding chamber is evacuated using rotary and mechanical booster pumps until 0.1 Pa of gas pressure is reached. Nitrogen and argon gases are injected into the chamber until the pressure reaches 15 Pa. The processing requirements for normal plasma nitriding are low energy (650 V and 25 mA), low gas consumption, no air pollution, and long nitriding time. As a result, the AlN layer is formed (at a temperature of 440 °C and more than (8 h).

2.5 The Slurry Erosion Test

This test is performed according to (ASTM G76) at room temperature. The slurry erosion wears the testing device supplied from the local market. A plastic (Perspex) tank is used as a chamber. This tank has dimensions of (300) x (200) x (200) mm. The pump joints and valves connected to the chamber are made from PVC. Silica sand with an average diameter of 400-800 µm was employed as erodent particles. The slurry is made up of 10% wt. sand, and the rest is tap water. At the erosion test machine, the specimen (20×30×3) mm is mounted into the test stage across the nozzle with a horizontal distance of 100 mm from the nozzle's end to the test surface. The impingement angle is 45° for times 2, 4, and 6 hours. All erosion tests are carried out at room temperature. In addition, the specimens are weighted every two hours on an electronic balance to determine the extent of weight loss.

Table 1: The chemical composition of the used Al-Cu alloy of type 2024

	Cu	Fe	Si	Mn	Mg	Cr	Zn	Ti	Al	Other alemensts
Actual composition	4.1%	0.44%	0.47%	0.61%	1.09%	0.82%	0.2%	0.11%	92.1%	0.06%

3. Results and Discussion

SEM image for the microstructure of the annealed sample is shown in Figure 3a. Second phase CuAl₂ particles (white spots) are distributed within the alpha matrix, which is common in Al-Cu alloys. The image of the eroded sample after the erosion test is shown in Figure 3b. Annealing is used to improve the alloy's ductility, reduce internal stresses, and improve the internal structure of the alloy by making it more homogeneous and improving its cold working ability. This, in turn, reduces the hardness of the alloy, as noted in the hardness test. The wear resistance is reduced. Thus, the annealed samples will have the lowest erosion resistance.

Figure 4a shows SEM micrographs of the dendritic regions of the AlN nitride layer adhered to the substrate. Surface coverage with AlN is a function of nitriding duration for such an AL Cu alloy. Figures 4c and d show the images of the eroded sample, which show a higher slurry erosion resistance than the annealed and not nitrided specimens due to the high hardness nitride layer. An excellent AlN coating produced on aluminum alloy can significantly improve erosion wear resistance. The erosion rate in the nitrided condition is dramatically reduced by roughly 10 % compared to the annealed condition, as shown by the erosion test results in Tables (2 and 3) and Figures (6 and 7). The lowest values of erosion rates appear and are represented by a semi- straight curve Figure 8, the weight loss becomes very small, indicating the unique properties resulting from these treatments. In nitriding, atomic nitrogen is formed at the surface of the aluminum and diffuses inwards, reacting with the solute atoms to form very fine nitride precipitates. The lattice strains associated with these precipitates are high enough to nucleate dislocations, which, together with the precipitates themselves, have a strong hardening effect.

Figure 5, Shows X-ray deflection (XRD): Case (a) represents the X-ray diffraction patterns of Al- Cu 2024 After annealing without nitriding. High-intensity peaks represent the Al- α phase and the Al₂ Cu (θ) second phase. The surface of the annealed and nitrided spacemen is shown in Figure 5b. The nitride surface of AlN 2024 is analyzed by XRD. The results show that these two different layers had very similar diffraction patterns and only two kinds of phases. AlN and Al substrate are revealed. Tables (2 and 3) show the results of erosion tests for the annealed and the nitrided samples, respectively. The impact angle of 45 degrees is adopted.

Table 2: The results of erosion wear for annealed samples

No. of Experiment	Time (h)	Angle	Total weight (Ws) (gm.)	Weight loss (Wl)	WS-WL (gm.)	Erosion rate Ws/Wl \times p
1	2	45 ⁰	6.5221	6.3520	0.1701	0.0725
2	4	45 ⁰	6.5221	5.847	0.675	0.228
3	6	45 ⁰	6.5221	5.8308	0.6913	0.2947

Table 3: The values of erosion wear after plasma nitriding

No. of Experiment	Time (h)	Angle	Total weight (Ws) gm.	Weight loss (Wl)	WS-WL gm.	Erosion rate Ws/Wl \times p
1	2	45 ⁰	6.5662	6.5231	0.0432	0.0183
2	4	45 ⁰	6.5662	6.5299	0.0363	0.0154
3	6	45 ⁰	6.5662	6.5324	0.0337	0.0143

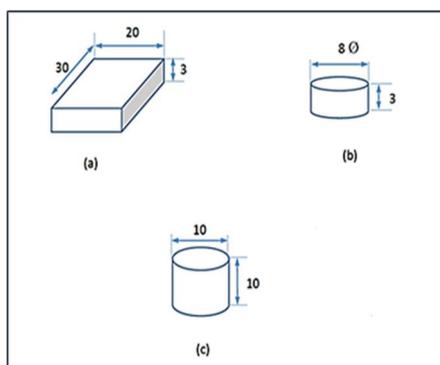


Figure 1: Dimensions of samples for (a) erosive wear and hardness test, (b) scanning electron microscope (SEM), and (c) X-ray diffraction (XRD), optical microscope: All dimensions in mm

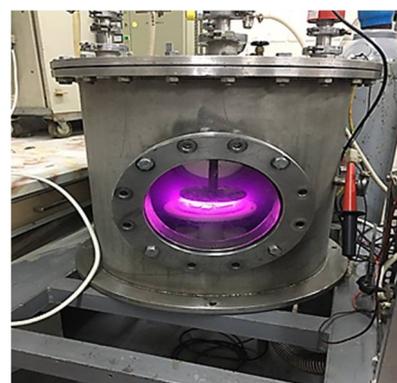


Figure 2: Plasma nitriding device

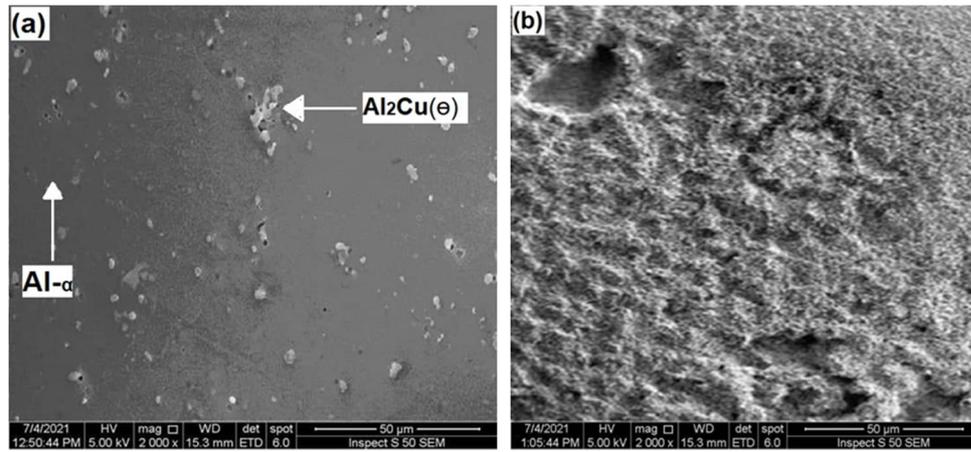


Figure 3: The SEM image of the annealed sample: (a) Before the erosion test, (b) After the erosion test

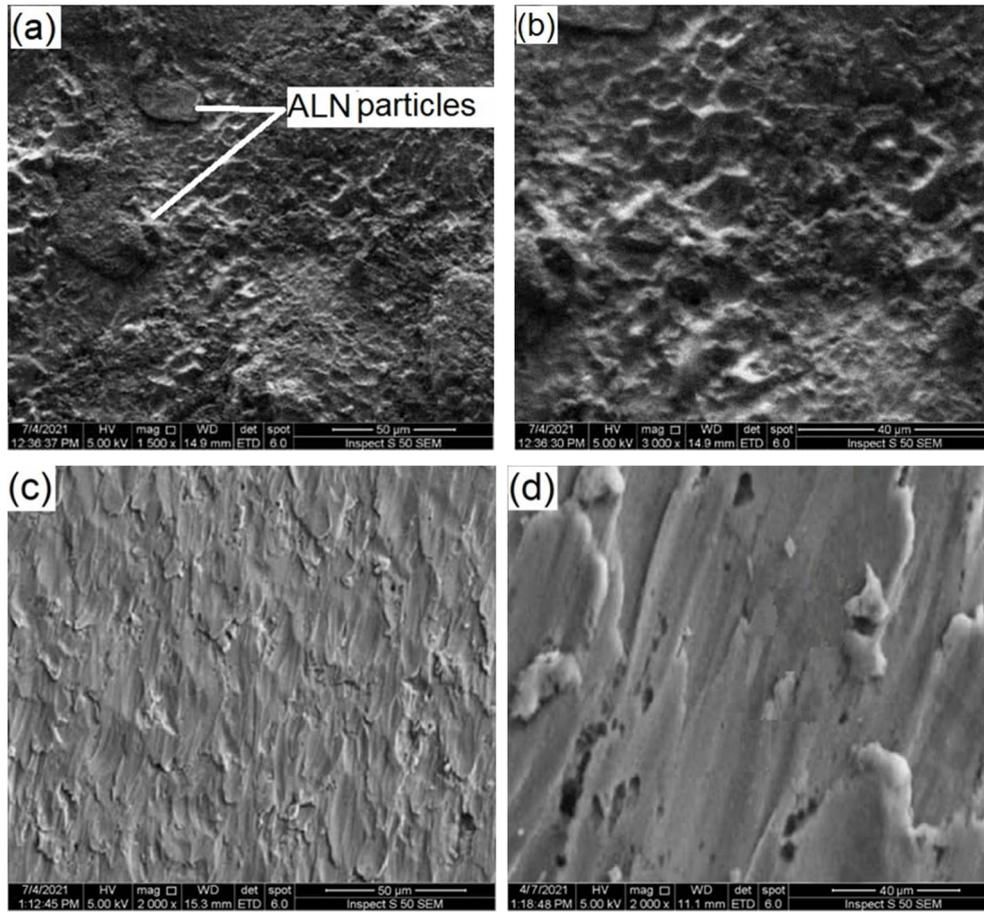


Figure 4: SEM micrographs of the dendritic regions of AlN nitride layer (a)magnification X320 (b) Increased magnification micrograph in (a) X475 (c) eroded nitride samples X360 (d) Increased magnification micrograph in (c) X400

Table 4: The hardness value of treated samples compared with the annealed sample

Specimen condition	Average Vickers hardness (HV)
Annealing	56
Plasma nitriding	105

By referring to Table 2., which represents the erosion rate against the time of annealed samples, the erosion rate at an impact angle of 45o increases with increasing exposure time. The reason is due to the weak properties of the annealed alloy in general, especially the hardness, as shown in Figure 6. Vickers hardness results after the annealing and plasma nitriding processes are presented in Table 4. The lowest hardness value appeared after the annealing process. On the other hand, the surface microhardness increases significantly after the plasma nitriding possesses higher surface hardness values than the untreated, as shown in Figure 8.

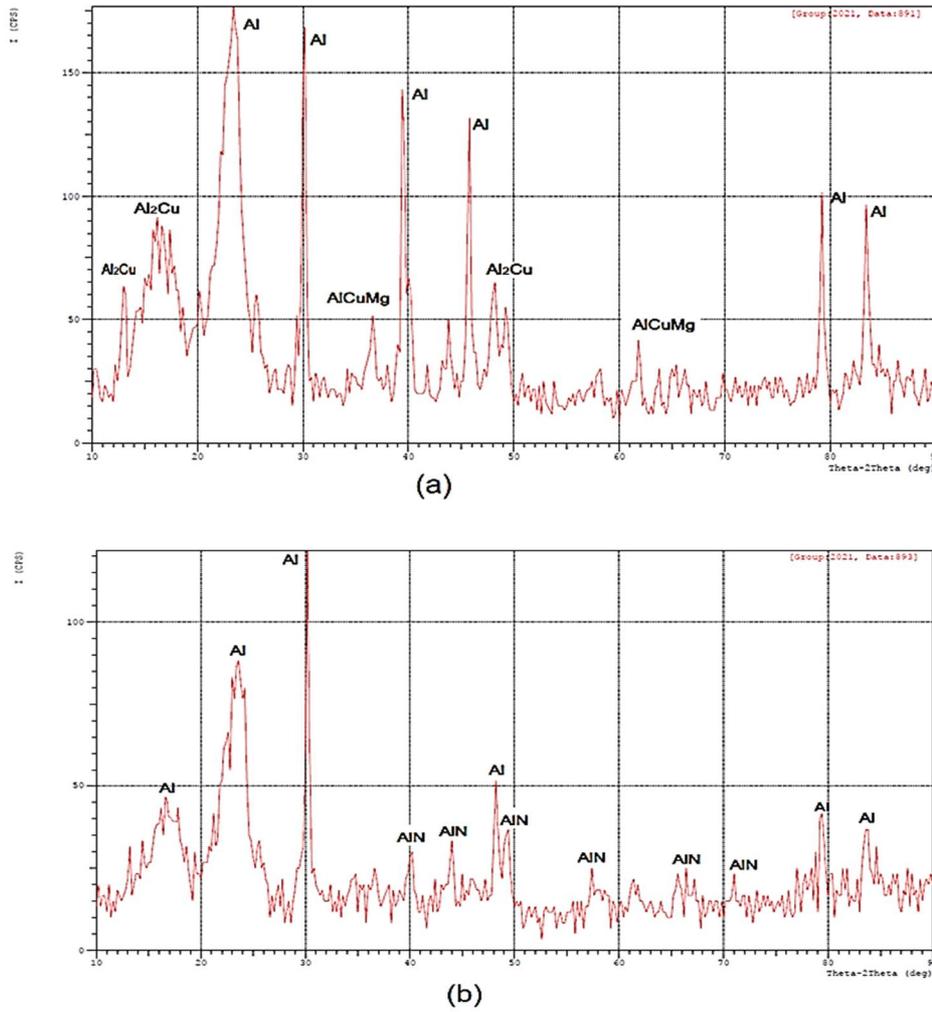


Figure 5: XRD Patterns: (a) Al-Cu 2024 after annealing, (b) After plasma nitriding

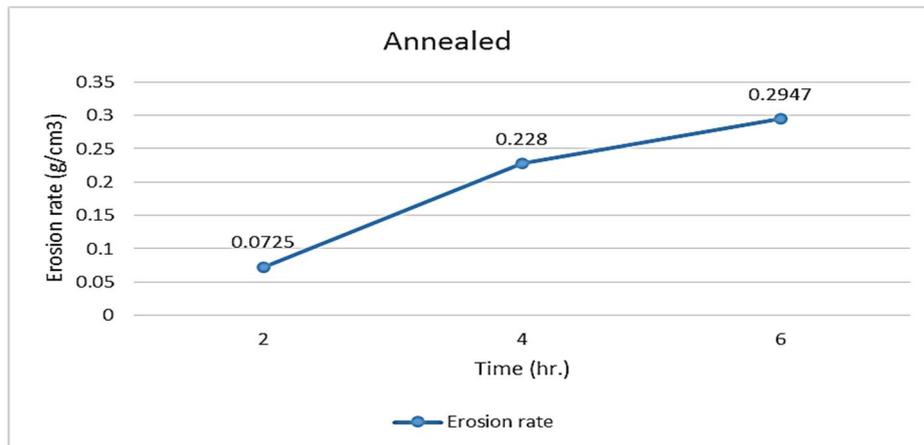


Figure 6: The erosion wear rate of annealed samples at 45° impact angle

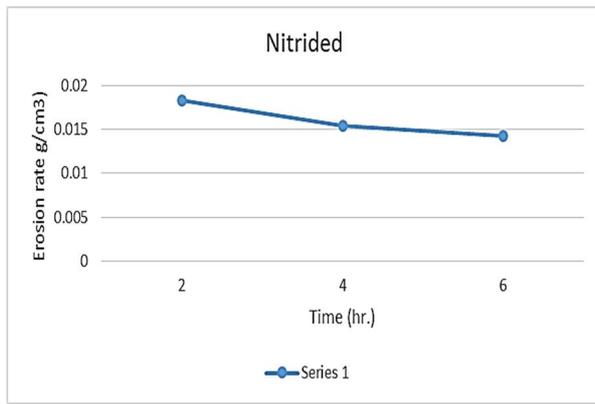


Figure 7: The erosion wear rate of nitrided samples

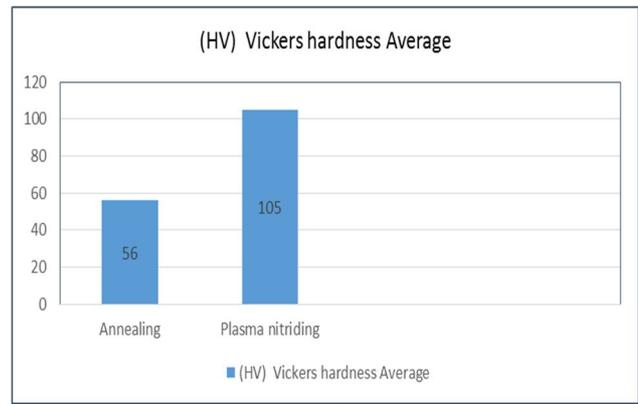


Figure 8: The difference in hardness according to treatment

Furthermore, the hardness of AlN is thought to be higher than that of Al [16-18]. As a result, the AlN coating is superb. Therefore, in addition to the high hardness and good tribological properties given by nitride surfaces, nitriding also produces compressive residual stress, enhancing wear properties.

4. Conclusion

Throughout the current study, it has been concluded that:

1. It is shown that plasma nitriding is used to create a unique coating on the surface of a 2024 Al alloy.
2. The surface hardness of the 2024 Al alloy is significantly improved by using the plasma nitriding process as a result of obtaining a multilayer structure and increasing the nitriding temperature to a maximum of 105 HV.
3. With increasing nitriding temperature, the slurry erosion wear rate of 2024 Al alloy is reduced to the lowest value compared to the erosion rate value of annealed alloy.

Acknowledgment

I am greatly indebted to my supervisors, Dr. Ali Hussein Ataiwi and Dr. Jamal Jalal Dawood, for their valuable efforts, help, and encouragement throughout this project.

Author contribution

All authors contributed equally to this work.

Funding

This research received no specific grant from any funding agency in the public, commercial, or not-for-profit sectors.

Data availability statement

The data that support the findings of this study are available on request from the corresponding author.

Conflicts of interest

The authors declare that there is no conflict of interest.

References

- [1] F. Zhang, M. Yan, J. He, F. Yin, Microstructure evolution and wear resistance of nitride/aluminide coatings on the surface of Ti-coated 2024 Al alloy during plasma nitriding, *Ceram. Int.*, 43 (2017) 10832-10839. <https://doi.org/10.1016/j.ceramint.2017.05.109>
- [2] M. Moradshahi, T. Tavakoli, S. Amiri, S. Shayeganmehr, Plasma nitriding of Al alloys by DC glow discharge, *Surf. Coat. Technol.*, 201 (2006) 567-574. <https://doi.org/10.1016/j.surfcoat.2005.12.002>
- [3] B.M. Girish, H.R. Vitala, B.M. Satish, Effect of nitriding on wear behavior of graphite reinforced aluminium alloy composites, *J. Surf. Eng. Mater. Adv. Technol.*, 1 (2011)73-79. <https://doi.org/10.4236/jsemat.2011.12011>
- [4] V. I. Dimitrov, A model of AlN layer formation during ion nitriding of Al, *Appl. Phys. A*, 79 (2004) 1829-1832. <https://doi.org/10.1007/s00339-003-2253-y>
- [5] M. F. Yan, Y. D. Zhu, Y. X. Zhang, M. L. Zhang. Combining thermo-diffusing titanium and plasma nitriding to modify C61900 Cu–Al alloy, *Vacuum*, 126 (2016) 41-44. <https://doi.org/10.1016/j.vacuum.2016.01.015>

- [6] C.Tan, T.Kuang, K. Zhou, H. Zhu, Y.Deng, X. Li, P. Cai, Z. Liu. Fabrication and characterization of in-situ duplex plasma-treated nanocrystalline Ti/AlTiN coatings, *Ceram. Int.*, 42 (2016) 10793-10800. <https://doi.org/10.1016/j.ceramint.2016.03.207>
- [7] A. Yazdani, M. Soltanieh, H. Aghajani. Active screen plasma nitriding of Al using an iron cage: Characterization and evaluation, *Vacuum*, 122 (2015) 127-134. <https://doi.org/10.1016/j.vacuum.2015.09.018>
- [8] A. Nishimoto, K. Nagatsuka, R. Narita, H. Nii, K. Akamatsu. Effect of the distance between screen and sample on active screen plasma nitriding properties, *Surf. Coat. Technol.*, 205 (2010) S365-S368. <https://doi.org/10.1016/j.surfcoat.2010.08.034>
- [9] P. Hubbard, J. G. Partridge, E. D. Doyle, D. G. McCulloch, M. B. Taylor, S. J. Dowey. Investigation of nitrogen mass transfer within an industrial plasma nitriding system I: The role of surface deposits, *Surf. Coat. Technol.*, 204(2010) 1145-1150. <https://doi.org/10.1016/j.surfcoat.2009.08.029>
- [10] P. Visuttipitukul, T. Aizawa, H. Kuwahara, Advanced plasma nitriding for aluminum and aluminum alloys, *Mater. Trans.*, 44 (2003) 2695-2700. <https://doi.org/10.2320/matertrans.44.2695>
- [11] M. Okumiya, M. Yoshida, R. Ichiki, C. Tekmen, W. Khalifa, Y. Tsunekawa, K. Tanaka. Surface modification of aluminum using a combined technique of barrel nitriding and plasma nitriding, *Plasma Processes Polym.*, 6 (2009): S287-S290. <https://doi.org/10.1002/ppap.200930705>
- [12] N. Khan, M. S. Shah, R. Ahmad. Nitriding of Aluminium Alloy in Nitrogen and Nitrogen-Helium Mixture Using 100 Hz-Pulsed DC Glow Discharge, *Plasma Sci. Technol.*, 12 (2010) 452. <https://doi.org/10.1088/1009-0630/12/4/14>
- [13] P. Visuttipitukul, T. Aizawa. Plasma nitriding design for aluminium and aluminium alloys, *Surf. Eng.*, 22 (2006) 187-195. <https://doi.org/10.1179/174329406X108898>
- [14] A. Dalke, Anke, Effect of nitride layer thickness on reciprocating sliding wear behavior of AlN layers on spray-formed Al alloys, *Tribol. Lett.*, 67 (2019). <https://doi.org/10.1007/s11249-018-1122-y>
- [15] X. Li, Microstructural Characterization and Formation Mechanism of Nitrided Layers on Aluminum Substrates by Thermal Plasma Nitriding, *Metals*, 9 (2019) 523. <https://doi.org/10.3390/met9050523>
- [16] S. Gredelj, A. R. Gerson, S. Kumar, G.P. Cavallaro, Characterization of aluminium surfaces with and without plasma nitriding by X-ray photoelectron spectroscopy. *Appl. Surf. Sci.*, 174 (2001) 240-250. [https://doi.org/10.1016/S0169-4332\(01\)00169-6](https://doi.org/10.1016/S0169-4332(01)00169-6)
- [17] K. Nomoto, S. Nishijima, K. Katagiri, M. Nunogaki, T. Nishiura, T. 9 Okada, Effects of ion implantation and plasma treatment on 10 tribological properties of aluminium and Al-Mg alloy, *Surf. Coat. Technol.*, 57 (1992) 157-161. [https://doi.org/10.1016/0257-8972\(92\)90231-X](https://doi.org/10.1016/0257-8972(92)90231-X)
- [18] C. C. Samant, A. D. Rupji, S. V. Gogawale, D. C. Kothari, V. H. Kulkarni, Study of surface hardness of Al-6063 under plasma nitridation, *Surf. Coat. Technol.*, 158 (2002) 658-663. [https://doi.org/10.1016/S0257-8972\(02\)00236-0](https://doi.org/10.1016/S0257-8972(02)00236-0)