Jurnal Tribologi 45 (2025) 117-128

MYTRIBOS
Malaysian Tribology Society

Jurnal Tribologi
Website : jurnaltribologi.mytribos.org e-issn: 2289-7232

Jurnal Tribologi

Influence of thermochemical gas nitriding on morphology and dry wear of Duplex-S32205

Lailatul Hairina Paijan [1*], Md Abdul Maleque [2], Mohd Fadzli Bin Abdollah [3], Nor Ana Rosli [1]

[1] Faculty of Industrial & Manufacturing Technology & Engineering, Universiti Teknikal Malaysia Melaka, Hang Tuah Jaya, 76100 Durian Tunggal, Melaka, MALAYSIA.
[2] Department of Manufacturing and Materials Engineering, International Islamic University Malaysia, 53100 Kuala Lumpur, MALAYSIA.
[3] Faculty of Mechanical Technology and Engineering, Universiti Teknikal Malaysia Melaka, Hang Tuah Jaya, 76100 Durian Tunggal, Melaka, MALAYSIA.
[*]Corresponding author: lailatulharina@utem.edu.my

KEYWORDS

Thermochemical
Nitriding
Morphological
Hardness
Wear resistance

ABSTRACT

Surface modification is needed to improve the surface quality of Duplex-S32205 due to limitation of low hardness and wear properties of this material. The aim of this work is to evaluate the incorporation of nitrogen gas diffusion via low thermochemical gas nitriding process at temperature of 500 °C for duplex stainless steel S32205. The nitriding holding duration was varying for 4, 8 and 12 hours in the nitrogen environment of ammonia (NH_4) and nitrogen (N_2) gaseous. Microhardness and wear properties of the gas nitride layer were examined using microhardness tester, scanning electron microscopy and ball-on-disc tribotester. The nitride layer with holding duration of 12 hours produced the highest thickness layer and hardness of 88 μm and 603.4 HV, respectively. Meanwhile, the wear rate improved to 42 % and CoF to 30% compared to untreated material. It was demonstrated that nitriding process is capable to produce hard surface layer on S32205 with improved wear resistance properties.

Received 29 July 2024; received in revised form 7 September 2024; accepted 9 September 2024.
To cite this article: Paijan et al., (2025). Influence of thermochemical gas nitriding on morphology and dry wear of Duplex-S32205. Jurnal Tribologi 45, pp.117-128.

1.0 INTRODUCTION

One typical method for functionalizing the surface of stainless steels to enhance the wear properties is thermochemical treatment. The nitrogen enrichment results in the development of precipitates at temperatures above 500 °C or an interstitial solid solution below 450 °C, depending on the temperature-duration regime during the operation. The lattice parameters are decisively expanded upon supersaturation of the austenitic matrix. Expanded austenite, or S-phase, is the term for this phase state (Zhang et al. 2024, Nam et al. 2019, Paijan et. 2023).

Duplex stainless steels must undergo an initial surface activation process in order to remove the passive layer before they may undergo hardening process. To guarantee that there is no repassivation during the difusion enrichment, special equipment is needed. This usually results in high expenses and greatly increases the complexity of process management. On the other hand, the classical thermochemical treatments have evident economic advantages. The gas nitriding procedure, for example, has been widely used in industry due to its high degree of flexibility and relatively low processing costs (Prasanna et al. 2020, Maleque et al. 2019, Kutschmann et al. 2019).

In recent years, there has been a lot of interest in the problem of improving the characteristics of protective coatings by thermochemically treating the substrate. Physical vapour deposition (PVD) is one of the methods used by the industry to boost productivity, reduce wear, and extend tool life. Nitriding steel has been shown to significantly increase coating adhesion, which in turn improves tribological performance (Bhaskar et al. 2017, Sathish 2018). Therefore, by increasing the surface qualities of industrial equipment components, surface modification technology can extend their service life and minimize wear and corrosion-related damage and failure. Hence, it is essential to minimize the component wear & tear and increase the life. One of the techniques adopted by the industry to minimize wear and to improve is surface treatment and coating (Rezayat et al. 2023, Bekmurzayevaa et al. 2018, Paijan et al. 2022)

Divyasri et al. (2021) had demonstrated that the plasma nitriding treated at temperature of about 650°C can effectively improve the hardness and wear properties of AISI 301 LN austenitic stainless steel due to a formation of nitrogen solid solution and improved the grain size on the surface layer. The hardness increased two times higher than the untreated sample. Deepak et al. (2020) reported that the gas nitriding on AISI 310 stainless steel was an effective method in inreasing the hardness and wear behavior of the material. The gas nitrided specimen for 18 treatments has the highest hardness and wear resistance due to more formation of nitrides into the surface. Alphonsa et al. (2015) found that nitriding at 400°C using plasma techniques on DSS exhibited higher surface hardness without compromising the corrosion resistance. The increment is attributed to the high amount of nitrogen in the ferrite phase.

In the open literature, study on thermochemical gas nitriding on Duplex-S32205 still limited. The focus of the present research is to increase the hardness and wear resistance of Duplex-S32205 by the diffusion of ammonia gaseous into the surface material at low temperature of 500°C under various treatment holding durations. The effectiveness of hard surface layer was evaluated in terms of characterization analysis and the wear performance.

2.0 EXPERIMENTAL PROCEDURE

2.1 Materials

The experimental substrate used in this work was duplex stainless steel, grade S32205. Table 1 provides this material's chemical composition. Using an EDM wire cut, the specimen size was sectioned to 50 mm × 33 mm and 10 mm. Emery paper with grades ranging from 240 to 1200 were used to grind the samples. After that, the samples were soaked in 2M hydrochloric acid for 15 minutes to remove native oxide layer on the surface material. This technique is important to increase the efficiency of nitrogen diffusion during the nitriding process. Following that, the samples were immediately placed onto a quartz boat in a vertical position and inserted into the tube furnace. To guarantee that the sample receives the ideal heating zone, it is positioned in the center of the tube furnace.

Table 1: Chemical composition of duplex stainless steel (S32205).

Steel grade	**Chemical Composition %**						
	C	Cr	Si	Mo	Mn	S	Fe
S32205	0.026	22.06	0.69	2.58	1.74	0.008	Balance

2.2 Low Thermochemical Gaseous Nitriding Process

The thermochemical low temperature gaseous nitriding method was carried out using a horizontal tube furnace system. The schematic cross-section of tube furnace used in the nitriding process and the schematic layout of the nitriding experimental setup are depicted in Figures 1 and 2, respectively. In the meantime, Figure 3 illustrates a nitriding heat cycle treatment at 500 °C for 4 hours. Nitrogen gas was used to purge the system for around 30 minutes in order to eliminate any impurities from the furnace environment. Next, the gas pipe flow valve was opened to create the ammonia gas supply. Once ammonia gas (NH_3) was added, the system started to reach the necessary temperature. The ammonia gaseous broke down into nascent nitrogen during the heating process and diffuses to the surface sample. For this experiment, the nitriding temperature was maintained at 500°C for varying holding durations of 4, 8, and 12 hours. The system was continuously fed with 0.5 NH_3/N_2 at a constant gas flow rate.

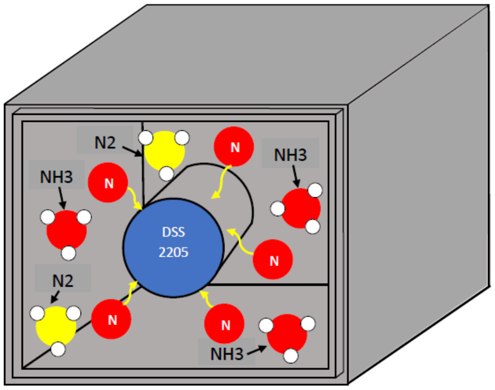


Figure 1: Schematic cross-section of tube furnace during nitriding process.

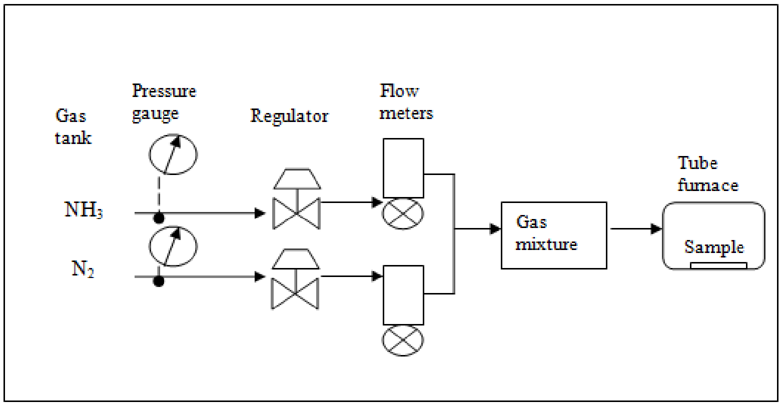


Figure 2: Schematic Diagram of the nitriding process experimental setup.

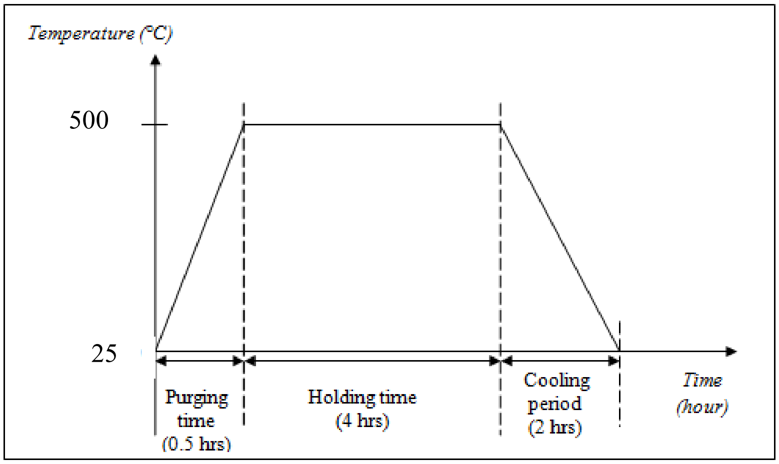


Figure 3: Nitriding Heat Cycle Treatments at 500 °C for 4 hours.

Table 1: Process parameter for various treatment durations of thermochemical nitriding process.

Sample	**Temp. (°C)**	**Ammonia composition. NH_3/N_2 (%)**	**Nitriding duration (mm/s)**
1	500	50	4
2			8
3			12

2.3 Microstructural Characterization and Micro-Hardness Profile

To assess the quality of the thermochemical gaseous nitriding process at various nitriding holding durations, the nitrided sample was sliced into cross-sections. The morphology of the nitride layer was exposed by manually grinding, polishing, and etching the cross-sectional sample. The etching reagent used for Duplex-S32205 is Kalling's reagent. Next, the sample was inspected, and the nitride layer thickness was measured using scanning electron microscopy (SEM). Next, the hardness profile was measured using the micro-vickers hardness method, which involved indenting the substrate material for 10 seconds with a pyramid diamond indenter and a 500-gf load. Vickers hardness tester (Brand: Innovatest, Model: Falcon 500G2), which is based on ASTM E384, was used to measure the hardness.

2.4 Reciprocating Wear Testing

Using an alumina ceramic ball, the reciprocating dry wear test was employed to evaluate the nitride layer's surface performance. This test procedure followed ASTM D6079. Considering alumina ceramic has a high hardness (2000 HV0.5), a 6 mm diameter ball was used as the counter-body. Alumina ceramic ball was fastened to a ball holder, and the nitrided sample (dimensions: 15 mm × 15 mm × 6 mm) was placed to the steel holder. The experiments were conducted with a fixed load of 30 N for ten minutes, a 5 Hertz movement frequency, a 10 mm stroke, and a 23 ± 2°C ambient temperature. The wear tests were conducted at least three times using the identical experimental settings to guarantee the accuracy of the results. After the wear test, the sample's weight loss was calculated using a weight balance to identify the sample's wear rate. The wear rate of sample is calculated using the following standard formula and expressed as mm^3/Nm:

$$\text{Wear rate} = \frac{(\text{Weight loss } (g)/\text{density } (\,g/mm^3\,)}{(\text{Normal load } (N) \times \text{reciprocating distance } (m))} \tag{1}$$

The results for coefficient and friction value were directly generated by the Winducom software from the reciprocating wear test apparatus. Furthermore, scanning electron microscopy was used to study the wear tracks' SEM micrographs.

3.0 RESULTS AND DISCUSSION

3.1 Morphological and Structural Aspects of The Nitride Layers

A thermochemical gas nitriding process at 500°C led to nitrogen enrichment in S32205. Figures 4 (a-c) illustrate the nitrided layers depending on the nitriding duration. The etched cross-sections layer in the Kalling's reagent reveals the nitride layer on the top surface of the sample. The formation of the nitrided layer was inhomogeneous along the coating thickness due to different diffusion rate on the surface layer. As the nitriding duration was increased to 4, 8 and 12 hours, the nitride layer thickness grew steadily from 21.97 µm, 61.7 µm and 88 µm, respectively. The increased nitride layer thickness during longer nitriding holding durations may be attributed to continuous nitrogen atom diffusion on the sample during the nitriding holding period and a greater nitrogen concentration on the substrate surface. The findings demonstrate that the thickness of the nitride layer is significantly influenced by the nitriding holding duration. The similar result also observed by Ibrahim et al. (2014) demonstrates the increment of nitride layer with longer treatment duration on AISI 420 martensitic stainless steel using high temperature gas nitriding process.

Figure 4(b-c) illustrates the generation of dark phases, that it was believed as chromium nitride (CrN) in the sample that underwent 8 hour and 12-hour nitriding process. This CrN formation's drawback is that it may result in a reduction in corrosion resistance. EDX spectra result in Figure 5 (a-b) confirms the association between the production of the dark phases and the precipitation of chromium nitrides in the nitride layer. The composition of CrN increase with the increment of nitriding durations. It can be seen and proved that the percentage of CrN at sample nitrided at 8 hour and 12 hours increased from 21.3% to 45%, respectively. Similar outcome was obtained by Mahmoud et. al (2014), who showed that extending the niriding treatment duration to 24 hours at 1200 °C causes a formation of CrN to form in the alloyed zone of AISI 316 stainless steel.

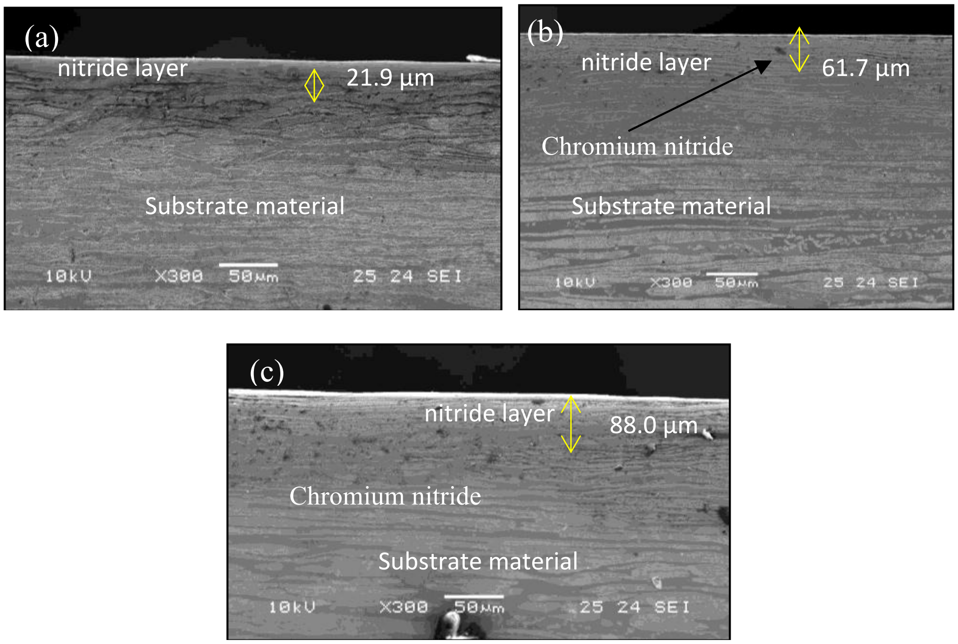
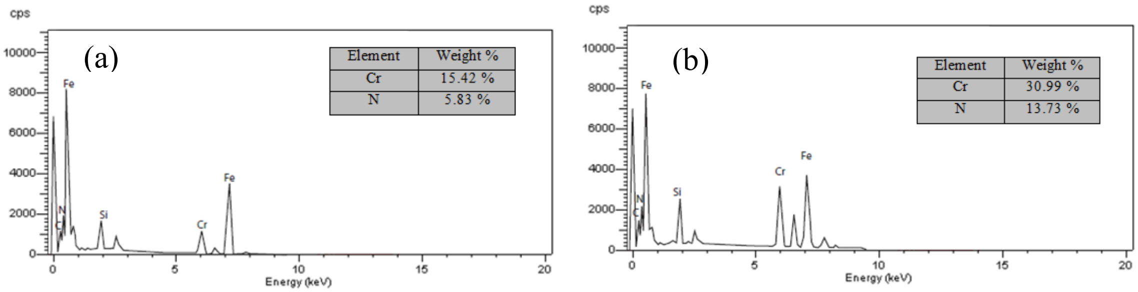


Figure 4: SEM images for surface nitride layer treated at 500 °C for (a) 4 hours (b) 8 hours and (c) 12 hours.



Element	Weight %
Cr	15.42 %
N	5.83 %

Element	Weight %
Cr	30.99 %
N	13.73 %

Figure 5: EDX spectra for nitride layer showing the formation of chromium nitride treated at 500 °C for (a) 8 hours and (b) 12 hours.

3.2 Vickers Micro-Hardness Profile of Surface Coated Duplex-S32205

To measure the hardness value attained from the low temperature gaseous nitriding process, a micro-hardness depth profile was carried out over the nitride layer. Figure 6 displays the hardness depth profile for the nitriding process at various nitriding holding durations. It was evidently showing that all nitride layer Duplex-S32205 micro-hardness depth profiles resulted in a gradual decrease as it approaches the core material. This demonstrates the nitride layer forms a hard layer due to nitrogen diffusion from the thermochemical nitriding process.

Figure 6 shows that, in comparison to other samples, the sample that was nitrided at 4 hours had the lowest hardness value (523.1 HV). This could be the result of not keeping the high concentration of nitrogen atoms strong enough to allow them to permeate into the Duplex-S32205 surface. In addition, samples nitrided for longer holding durations for 8 and 12 hours have developed the highest hardness values with 551.6HV and 603.4 HV, respectively. Hardness in the nitride layer Duplex-S32205 was twice as high as that of the untreated material (250 HV), which is strongly correlated with the formation of nitride layer as described in the morphological and structural characteristics of the layers. This reveals that a temperature of 500°C and a longer holding durations are important factors in producing a higher hardness. By extending the nitriding duration, more nitrogen was incorporated into the Duplex-S32205, increasing its hardness. The presence of CrN, which causes an increase in hardness, also contributed to the maximum hardness attained after 12-hour nitriding durations. From this outcome, it can be seen that the nitriding duration has a direct impact to the improvement of hardness and the formation of CrN, in which this is in a good agreement with previous studies (Maleque et al. 2018)

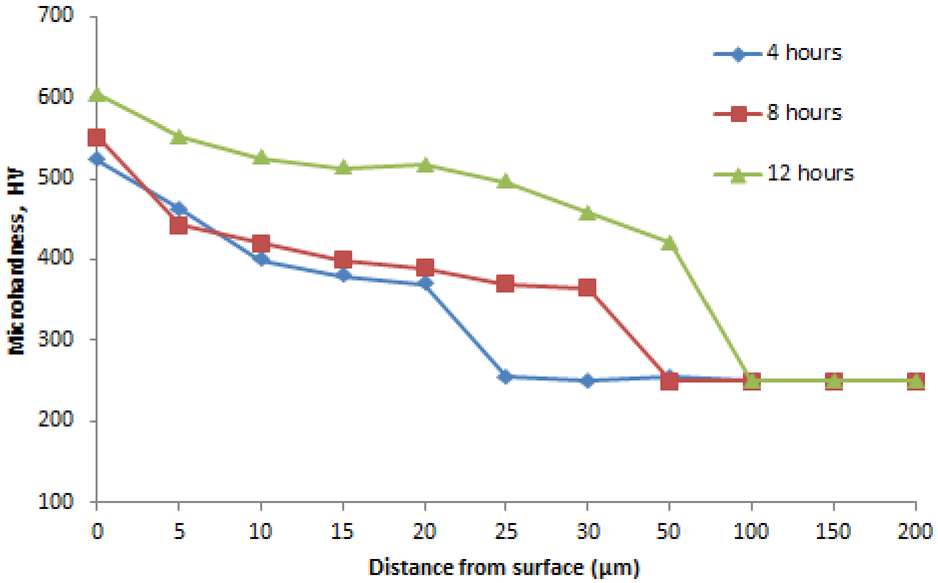


Figure 6: Hardness profile of the nitride layer Duplex-S32205 cross section for nitriding temperature of 500 °C for holding duration of 4, 8 and 12 hours.

3.3 Liner Motion of Reciprocating Wear

The wear rate and CoF of nitrided surface Duplex-S32005 were compared in this work at various nitriding process holding durations. Figures 7 and 8 display the wear behavior results of the nitrided sample for wear rate and CoF, respectively, when evaluated against an alumina ceramic ball. It was found that when wear rate and CoF are reduced, the nitride layer improves wear characteristics. Table 2 presents a percentage value comparison between the wear performance value of the nitrided samples and the untreated Duplex-S32205.

The sample with the lowest wear rates and friction (Figures 7 and 8) displayed values of 4.13 x 10^{-4} mm^3/Nm and 0.51, respectively, at a holding duration of 12 hours. The wear rate and CoF characteristics have improved by roughly 42 % and 27.1%, respectively, in comparison to the untreated Duplex-S32205. After 8 hours of holding, the sample exhibits the second-lowest wear rate and friction with value of 4.25 x 10^{-4} mm^3/Nm and 0.59, respectively. About 40.3 % of the wear properties increased for wear rate, and 15.7 % for CoF. The increased hardness of the sample, with 603.4 HV and 551.6 HV at the surface, which can sustain the applied stress during wear testing, may account for this behavior. This observation aligns with earlier findings about the formation of expanded austenite, which contributes to the hardness increment that are covered in sections 3.1 and 3.2.

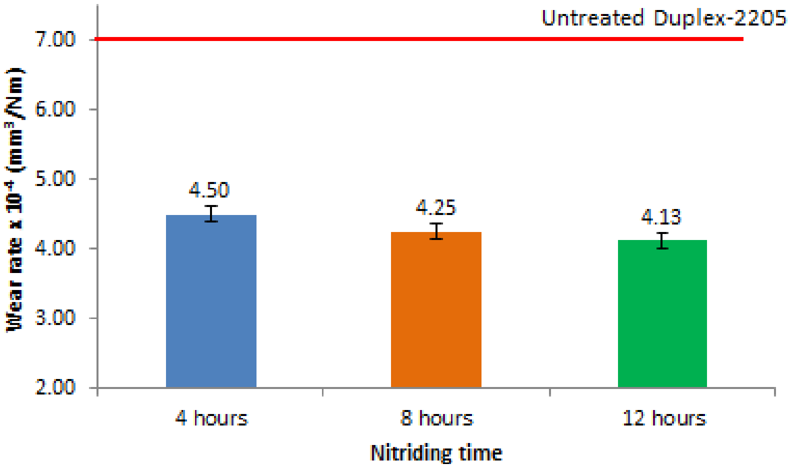


Figure 7: Wear rate of the nitride layer for nitriding temperature of 500 °C for holding duration of 4, 8 and 12 hours.

Additionally, the sample nitrided for 4 hours of holding duration showed the maximum wear rate and coefficient of friction (CoF), with values of 4.50 x 10^{-4} mm^3/Nm, and 0.64, respectively. When compared to Duplex-S32205 that has not been treated, this data demonstrates improvements of roughly 36.8% for wear rate and 18.6% for CoF. This is well connected with a lower hardness value, which can be attributed to the sample's poor nitrogen diffusion. A lower hardness sample will exhibit more plastic deformation at the contact area with the alumina ceramic ball during reciprocating movement for a given weight. This shows that for samples with a lower hardness, the deformation makes it easier for the oxide coating to break, increasing the oxide-free surface area and friction. Because of its diminished hardness, the sample is more likely to sustain adhesive wear from the rubbing friction of the counter-face alumina ceramic ball.

It is evident that the COF result and wear rate result follow a similar trend, with the COF decreasing with longer nitriding holding durations of 8 and 12 hours for the gaseous nitriding method. The observed outcome may be explained by the increased hardness of the samples, which varied between 551.6 HV and 603.4 HV. The higher hardness value and higher concentration of nitrogen element in the nitride layer, which smoothen the surface after the nitriding process, are related to the lower CoF produced. This is in agreement with the earlier discovery by Wetwet and Mahboubi (2024) that the hardness and wear resistance of the material was enhanced by the plasma nitriding technique used to AISI 4140 steel, where the coating surface reduced the CoF.

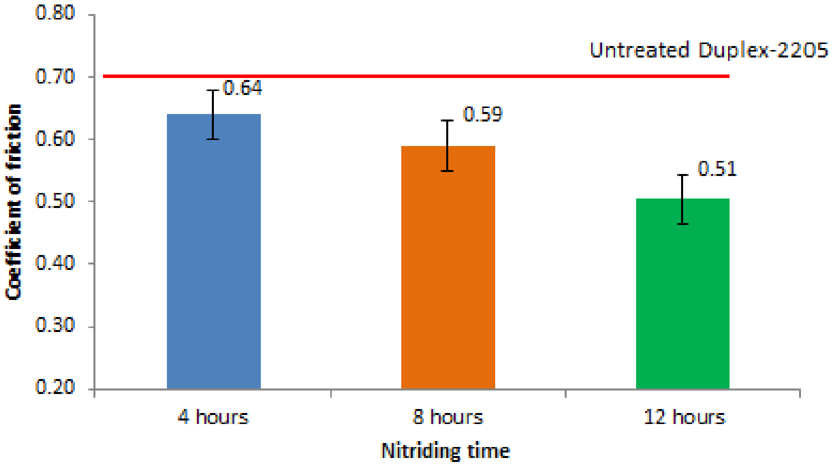


Figure 8: Coefficient of friction of the nitride layer Duplex-S32205 cross section for nitriding temperature of 500 °C for treatment duration of 4, 8 and 12 hours.

Table 2: Wear rate and CoF value of the nitrided samples and compared with that of untreated Duplex-S32205 in percentage.

Nitriding holding duration	**Wear rate x 10^{-4} (mm^3/Nm)**	**CoF**	**Compared with that of untreated Duplex-S32205 in percentage**	
			Wear rate (%)	**CoF(%)**
Untreated Duplex-S32205	7.12	0.7	-	-
4 hours	4.50	0.64	36.8	8.6
8 hours	4.25	0.59	40.3	15.7
12 hours	4.13	0.51	42.0	27.1

3.4 Worn Surface Analysis

Figure 9 displays SEM pictures of the SEM micrographs of the wear track for the treated and untreated Duplex-S32205 samples. The worn surface characteristics show that the samples that were not treated and those that were nitrided exhibit distinct wear behaviors. The untreated sample exhibits extensive wear with ploughing and grooves, as seen in Figure 9a. Conversely, Figure 9(b-d) illustrates how the worn surfaces of the nitrided samples have a smooth oxidized surface and a largely smooth appearance with mild abrasive wear. On the surface of nitrided samples, an adhering oxide layer forms. This layer functions as a lubricant, minimizing adhesive wear and limiting metal-to-alumina contact, therefore lowering the wear mechanism.

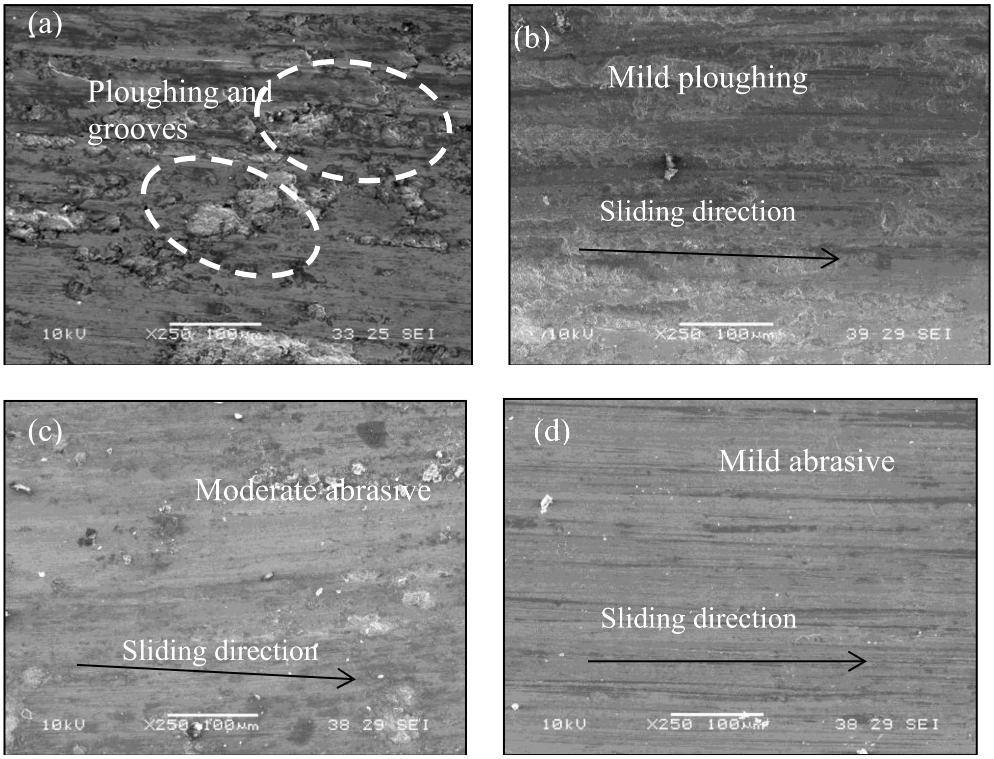


Figure 9: SEM micrographs of the wear track for (a) untreated Duplex-S32205, nitride layer treated at temperature of 500 °C for (b) 4 hours (c) 8 hours and (d) 12 hours.

The nitrided layer that formed during the sample's 4-hour holding period caused mild plowing, which enhanced the sample's abrasive wear and suggested that the surface had a strong bond throughout the wear test, as seen in Figure 9b. As shown in Figure 9c, there is a noticeable improvement in the abrasive wear in the sample with moderate striation after 8 hours of wear, indicating a greater interaction between the nitride layer and counterpart material. Additionally, as observed in Figures 9d, when the nitriding holding duration is increased to 12 hours with light striation, the worn surface in the sliding direction is continuously improved. Increasing the concentration of nitrogen diffusion to a longer holding duration improves the wear resistance qualities by decreasing the contact between the coated surface and the ceramic ball due to the harder surface. The coating's wear rate corresponds with the lack of noticeable spalling. This is due to the sample's greater homogenous distribution of expanded austenite, higher micro-hardness values, and maximum load-bearing capacity. Furthermore, some researchers have indicated that the longer nitriding duration can account for the observed increase in hardness and wear resistance (Deepak et al., 2020 and Divyasri et al., 2021).

CONCLUSIONS

In summary, the impact of low temperature thermochemical gaseous nitriding on the morphology, hardness, and wear-reciprocating resistance of duplex stainless steel was investigated in this work. The following conclusions and remarks are derived from the research outcomes stated in the work:

(a) A nitride layer that ranges in thickness from 21.9 µm to 88 µm is successfully formed to create a hard nitride layer.

(b) Samples free of chromium nitride and nitrided for 4 hours produced a hardness value of 523.1 HV without compromising their corrosion-resistance.

(c) The sample for 12 hours nitride holding period produced the best wear rate value of 4.13 x 10^{-4} mm^3/Nm, and its friction of 0.51. These results indicate that a 12-hour nitriding holding period yields outstanding wear performance with 42% better compared to untreated samples.

(d) The hardness and wear performance increased with increasing nitride duration. However, nitride duration for 12 hours leading to chromium nitride formation on the nitride layer.

(e) Low temperature gaseous nitriding is an efficient technique for improving the wear qualities of duplex stainless steel and offers an exciting potential application for the high load and long lifespan wear sector.

ACKNOWLEDGEMENTS

The financial support for this research was provided by FRGS/1/2023/TK10/UTEM/02/1 and FRGS/1/2023/FTKIP/F00554. Authors also are grateful to Universiti Teknikal Malaysia Melaka for the support that made this study possible.

REFERENCES

Alphonsa, J., Raja, V.S., Mukherjee, S. (2015). Study of plasma nitriding and nitrocarburizing for higher corrosion resistance and hardness of 2205 duplex stainless steel, Corrosion Science 100, 121–132.

Bekmurzayevaa, A., Duncanson, W.J., Azevedoc, H.S., Kanayeva, D. (2018). Surface modification of stainless steel for biomedical applications: Revisiting a century-old material, Materials Science & Engineering C, 93, 1073–1089

Bhaskar, S.V. and Kudal, H.N. (2017). Tribology of nitrided-coated steel-a review. Tribology of nitrided-coated steel-a review, Arch. Mech. Tech. Mater. Vol. 37, 50-57.

Deepak, T.L, Ananda Mithra, G., Lokesh, K., Sai Chandra, B. and Subbiah, R. (2020). Stability of expanded austenite by gas nitriding process on austenitic stainless steel material under low temperature conditions, Materials Today: Proceedings, 27, 1681–1684.

Divyasri, B., Krishna, P.R., Jayappa, P., Reddy, G.K., Kumar, V., Shankarachary, B., Surya, B. and Subbiah, R. (2021). Assessment of Wear Properties Under Sliding Conditions on AISI 301LN Austenitic Stainless Steel by Plasma Nitriding Process. MATEC Web of Conferences, 309, 01182.

Ibrahim, N.N.M, Hussain, P. and Awang, M. (2014). Microstructure and Hardness of High Temperature Gas Nitrided AISI 420 Martensitic Stainless Steel, MATEC Web of Conferences 13, 04017.

Kutschmann, P., Lindner, T., Börner, K., Reese, U. and Lampke, T. (2019). Effect of Adjusted Gas Nitriding Parameters on Microstructure and Wear Resistance of HVOF-Sprayed AISI 316L Coatings, Materials, MDPI, 12, 1760.

Mahmoud, H.R.S, Yusoff, S.A., Zainuddin, A. , Hussain, P., Ismail, M. and Abidin, K. (2014), Effective Duration of Gas Nitriding Process on AISI 316L for the Formation of a Desired Thickness of Surface Nitrided Layer, MATEC Web of Conferences 13, 04021.

Maleque, M.A., Lailatul, P.H., Fathaen, A.A., Norinsan, K. and Haider, J. (2018) Nitride alloy layer formation of duplex stainless steel using nitriding process, IOP Conf. Series: Materials Science and Engineering, 290, 012015.

Maleque, M.A., Lailatul, H., Norinsan, K. and Rahman, M.M. (2019). Optimization of Gaseous Nitriding Process Parameters for Hard Surface Layer of Duplex Stainless Steel. International Journal Materials Engineering Innovation, Vol. 10, No. 3, 165 – 185.

Nam, N.D., Xuan, N.A., Bach, N.V., Nhung, L.T., Chieu, L.T. (2019). Control Gas Nitriding Process: A Review. Journal of Mechanical Engineering Research & Developments, 42(1), 17-25.

Paijan, L.H., Maleque, M.A., Mamat, M.F. and Abu Bakar, M.H. (2022). Effects of Temperature on the Formation of Nitride Surface Layer via Thermochemical Gaseous Nitriding Process, Malaysian Journal of Microscopy Vol. 18 (2), 122-131.

Paijan, L.H. and Maleque, M.A. (2023). Morphological and wear behavior of low temperature thermochemical gaseous nitriding process. Jurnal Tribologi 36, 57-69.

Prasanna, G.L., Tanya, B., Subbiah , R., Kumar, V.V. (2020). Effect of nitriding on duplex stainless steel – A review. Materials Today: Proceedings 26, 950–955.

Rezayat, M., Karamimoghadam, M., Moradi, M., Casalino, G., Roa Rovira, J.J. and Mateo, A. (2023). Overview of Surface Modification Strategies for Improving the Properties of Metastable Austenitic Stainless Steels. Metals, 13, 1268.

Sathish, T. (2018), BONN Technique: Tribological Properties Predictor for Plasma Nitrided 316L Stainless Steel, Materials Today: Proceedings 5, 14545–14552

Wetwet, Z., Mahboubi, F. (2024). The Effect of Plasma Nitriding Time on the Tribological and Mechanical Properties of Electroless Nickel–Boron-Reduced Graphene Oxide (Ni–B-rGO) Nano-Composite Coatings. Trans Indian Inst Met.

Zhang, Z., Wang, D.; Liu, G., Qian, Y., Xu, Y., Xiang, D. (2024). Surface Modification of 42CrMo Steels: A Review, Wear and Corrosion Resistance. Coatings 14, 337.