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Research article

Enhancing Corrosion Resistance of AISI 1045 Steels Using Melamine Based Nitriding

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ABSTRACT

Nitriding of AISI 1045 steel using melamine derived from urea significantly enhances its corrosion resistance characteristics. The nitriding process forms a compound layer on the steel surface with a thickness ranging from 5 µm to 20 µm, which contributes to the material's improved performance. Cyclic voltammetry and microscopic analysis demonstrate that the melamine-nitrided AISI 1045 steel exhibits superior corrosion resistance property than the untreated steels. The layer acts as a barrier, reducing the steels' susceptibility to corrosive media. The results indicate that melamine-based nitriding not only improves corrosion resistance but also enhances the mechanical properties of the steel, such as wear and friction resistance. Nitriding of AISI 1045 using melamine derived from urea, offering a promising approach for surface modification in industrial applications where durability and wear resistance are critical. The study highlights the potential of using urea-derived melamine as an effective nitriding agent for improving the surface integrity of AISI 1045 steel, thereby extending its operational lifespan in aggressive environments.

1. INTRODUCTION

Thermochemical heat treatment process of surface treatment of metal objects through diffusion of carbon, nitrogen, boron or combination of each atoms. The most widely used types of thermochemical heat treatments are: nitriding, carburizing, boriding, nitrocarburizing and carbonitriding [1, 2].

Nitrding is the diffusion of nitrogen to the surface of metals at the temperature between 500 °C-590 °C [3, 4]. At the time of nitriding, the diffusion of nitrogen forms two layers: compound layer and diffusion zone. The compound layer include [ε –$Fe_{2-3}N$), γ' -Fe_4N or mixture of (ε+γ') [5, 6]. The compound layer having a thickness between 5 µm to 20 µm, has a good wear, friction and corrosion resistance characteristics [7, 8]. In the diffusion zone, nitrogen diffuses interstitially and forms metallic precipitates with high fatigue resistance property. The diffusion zone is a layer next compound layer having a thickness of 100s μm [5, 9].

Urea is a nitrogenous fertilizer having 40-45 % of nitrogen and decomposes to ammonia and isocyanic acid at 350 °C and subsequently to melamine at 400 °C. The decomposed ammonia reacts with the surface of the metal and release nitrogen. Isocyanic acid decompose to ammonia and carbon dioxide at 600 °C [10]. Carbon dioxide reacts with hydrogen that was released from ammonia and yields carbon monoxide. Melamine on heating liberates only nitrogen. Finally active nitrogen adsorbed to the surface of the metal [11].

Corrosion is a deterioration of materials results by chemical or electrochemical reaction of a metal with the environment. Corrosion is the most serious problem in the modern time results losses every year hundreds of billion dollars [12, 13]. Corrosion results failure in transportation, electric power generating plants, chemical process and manufacturing plants, constructions and household materials. Airline accidents, bridge collapse, failure of welded liquid gasoline pipeline, ship sinking and structure collapse are the usual failures due to corrosion [14, 15].

Studies shows that each nation invests approximately 1 to 5 % of its GDP for corrosion costs. The global cost of corrosion estimates US$2.5 trillion [16]. This is direct economic cost of corrosion. The indirect costs causing from actual corrosion are more challenging to estimate, but they are possibly even greater. The indirect sources of corrosion costs include: plant downtime cost, loss of product, loss of efficiency, contamination and overdesign [17].

The corrosion rate of metals can be calculated using the following formula [18, 19].

$$CR=KW/(\rho At)$$

Where, CR is the corrosion rate in mmpy (millimeter per year), K is corrosion constant having a value 87.6, W is weight loss of the sample due to corrosion, ρ is the density in g/cm^3, A is the area of the sample in cm^2 exposed to 5 % of sodium chloride solution and t is exposure time in hours.

2. METHODOLOGY

2.1. Material Collection

The AISI 1045 steel needed for pack nitriding thermochemical heat treatment was collected from Burka Gibe Metal Shop, Jimma, Ethiopia. The collected AISI 1045 steel rod was cut to the desired size. Samples are then cut to the desired size using cutting machine. The round metal bars (shafts) with a diameter of 26 mm are reduced to 10 mm using milling machine and then cut to height of 4 mm. After the samples are milled and grounded using silicon carbide emery papers from the coarsest 120, 240, 320, 400, 600, 800, and 900 to the finest 2400.

2.2. Experimental Design

The experimental design investigated the effect of nitriding on corrosion of AISI 1045 steel. It includes from the collecting of the steels until their characterization.

The prepared samples were pack nitride in a furnace (Nabertherm GmbH B180). Samples were buried with urea in silica crucibles inside a box made up of stainless steel and sealed by fire clay to prevent any entering of gases to the sample and to prevent escaping of gases from the system.

The samples having urea heated to the temperature of 400 °C at the rate of 10 °C/min and waiting for 1 hour to obtain melamine. After waiting time of 1 hour, the temperature rises to 550 °C at heating rate of 5 °C/min to decompose the melamine in to ammonia, then the ammonia to nascent nitrogen. At this temperature the sample also waited for specified period of time. The nascent nitrogen diffuses to the steel. The diffusion depth depends in time and the temperature used. Elevated temperature and long diffusion time allows the nitrogen to diffuse in more depth. At this research the samples were treated at 550 °C and at a duration of soaking time 3 and 4 hours.

Samples were removed from the furnace and cooled in air and other samples cooled inside the furnace and their difference was studied.
The chemical composition of AISI 1045 steel has given in the, Table 1.

Table 1. Chemical composition of AISI 1045 (wt. %).

Element	C	Mn	S	Cr	Al	Mo	V	P	Si	Ni	Fe
Percentage	0.45	0.75	0.008	0.017	0.048	0.002	0.02	0.011	0.257	0.13	Balance

2.3. Cyclic voltammetry

The cyclic voltammetry has used to study electrochemical reactions. It provides information about the location of oxidation and reduction potentials of chemical species.

2.4. Corrosion Rate Measurement Using Weight loss of Coupons

For accurate results and to work with coupons, the reliability and reproducibility depends in the proper preparation of the sample. Good results depends good sample preparation, in the immersion of the sample to the solution and removal and cleaning of the corrosion products.

2.4.1. Solution Preparation for the Immersion of Coupons

5 % of Sodium chloride solution was prepared to observe the effect of corrosion to the treated and untreated samples. During the soaking of the coupon samples to the NaCl solution, samples must be put in separate containers in order to prevent any electron flow between the different samples. The samples immersed to the solution of sodium chloride become corroded and further studies made to study the degree of corrosion.

2.4.2. Cleaning corrosion product cycles

The corrosion cleaning method used in this work was manual wire bristle cleaning.

After cleaning, it weighted in an electronic balance to see the weight difference before and after corrosion. The weight difference is the weight loss (W) due to corrosion. The corrosion rate of the AISI 1045 steel is calculating using the following formula.

$$\text{Corrosion rate} = KW/\,(\rho A t) \qquad (1)$$

The constant K value varies according to the unit of area, A and the unit of the corrosion rate measured. ρ is the density of the specimen in grams per cubic centimeter.

For area in inch^2 CR in mpy, k=5.34×10^5,
For area in cm^2 CR in mpy, k=3.45×10^6,
For area in cm^2 CR in mmpy, k=8.75×10^4

3. RESULT AND DISCUSSION

3.1. Microstructure

The microstructure of the specimens was studied using metallurgical optical microscope and scanning electron microscope.

The prepared sample etched with 2% Nital was put in the stage and observed through the objective lenses has a magnification of 200X. The samples were cross sectioned and the image of the compound layer, diffusion zone and base metal were displayed in the computer screen. The microstructure of the untreated and treated samples of AISI 1045 steels is given in Figure 1a and 1b respectively.

The microstructural structure of compound layer and diffusion zone is shown in Figure 1c. The upper layer is called the compound layer contains gamma prime and epsilon iron nitrides. The next layer is called the diffusion layer. Diffusion zone thicker than the compound layer. It contains precipitates of iron nitrides.

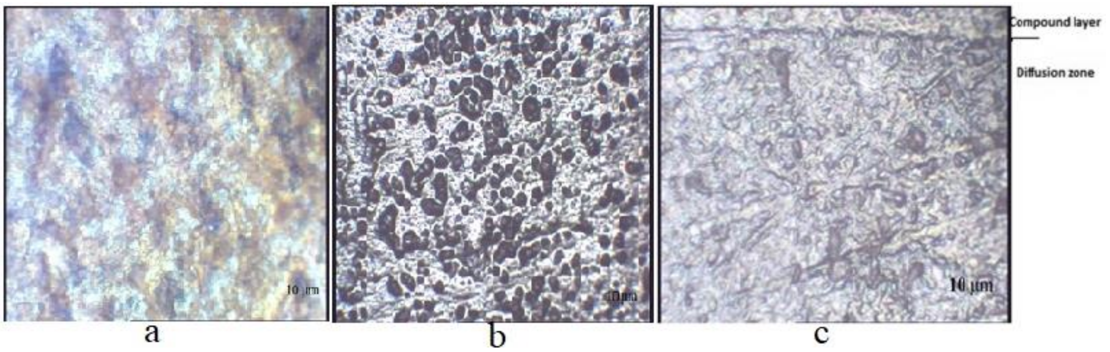
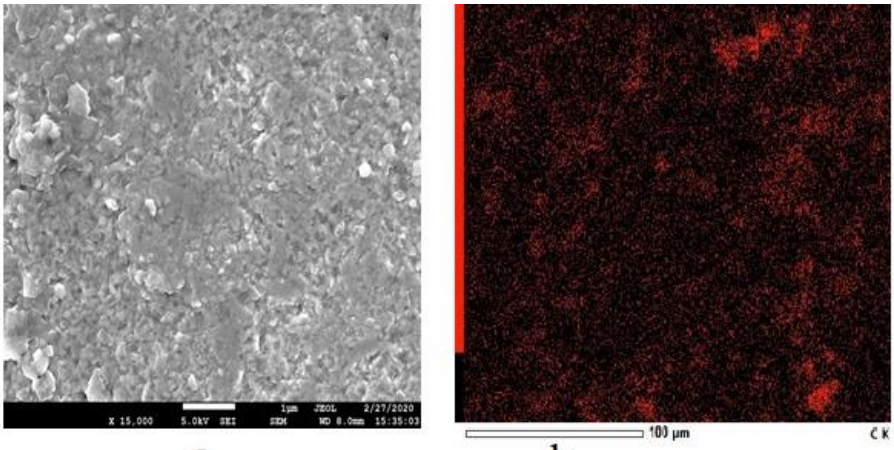


Fig. 1. Microstructure of (a) Untreated AISI 1045 steel in 5 % NaCl solution at 200X, (b) Nitrided AISI 1045 medium carbon steel at 200X, (c) Compound layer and diffusion zone of AISI 1045 steel at 200X.

The surface composition and microstructure of the specimens were investigated using the electron microscope.

The microstructural result of electron microscope is shown below. Elemental analysis at the surface of the medium carbon steels studied using SEM. In the Figure 2b, elemental carbon shows as black, the clustered red color is nitrogen and the dotted white color is iron. Due to scarcity of funds, we could record only one SEM micrograph of the samples.



a b

Fig. 2. (a) Microstructure of AISI 1045 carbon steel using SEM, (b) Atomic elements at the surface of AISI 1045 carbon steels after nitriding using SEM.

3.2. Phase Identification

The phase of the specimens were studied using X-ray diffractometer (XRD 7000) using CuKa operating at 25KV and 25 mA at the step size of 0.01 installed with JADE5 software. The recorded 2θ (degrees) angle was from 20°-90°.

Sharp and high intensity additional peaks were observed in the nitrided steels. These are iron nitride and iron nitride ($Fe_{2\text{-}3}N$, Fe_8N and Fe_4N) peaks.

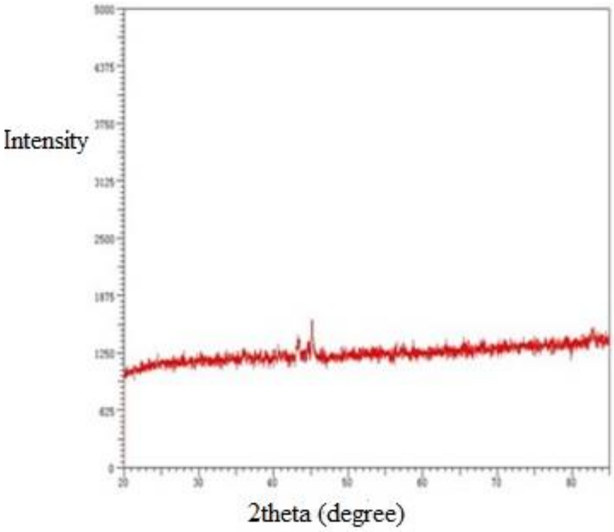


Fig. 3. XRD of nitrided AISI 1045 medium carbon steel.

The most undesirable among iron nitrides is γ'-Fe_4N. Its most intense peak is observed at 2θ=45 degree (Figure 3). It is nearly absent (very weak) in the case of nitrided mild steel and medium carbon steel suggesting that our quality of surface engineering is good present but its intensity is not high enough. Other noticeable peak due to γ'-Fe_4N were observed at 2θ= 43 degree.

3.3.Electrochemical Reaction Measurements Using Cyclic Voltammetry

Cyclic voltammetry measurements were made using potentiostat (BASi EPSILON). The machine was connected with a computer having Epsilon software to draw the voltagrams and record data from the Basi Epsilon machine. The initial and final potential set was -150 mV and scan rate (rate change of potential with time) of 100 mV/s. The Basi Epsilon machine contains 3 electrode leads and 1 grounded lead.

To characterize the samples using CV, 5% of NaCl solution was taken as a corrosive environment. The set up contains Ag/AgCl reference electrode, platinum wire as auxiliary electrode and the sample to characterize as a working electrode. Cyclic voltammetry experiment was made for the 3 samples without using NaCl solution to understand the effect of the NaCl solution to the samples. All the samples were soaked in the 5% of NaCl solution for 48 hours and CV experiments was made.

In potentiostatic, the potential changes linearly as a function of time. As the potential changes, the current response was measured. The current response was obtained due to electron transfer between the energy levels of the working electrode and molecular energy level of the system under investigation. In case of untreated steel (Figure 4a) corrosion appears at -0.1V but in case of nitride steel oxidation/ reduction takes place at higher voltage i.e -1.20V according to Figure 4b and 4c. This proves that corrosion in nitride steel requires higher voltage or in other words more resistant to corrosion.

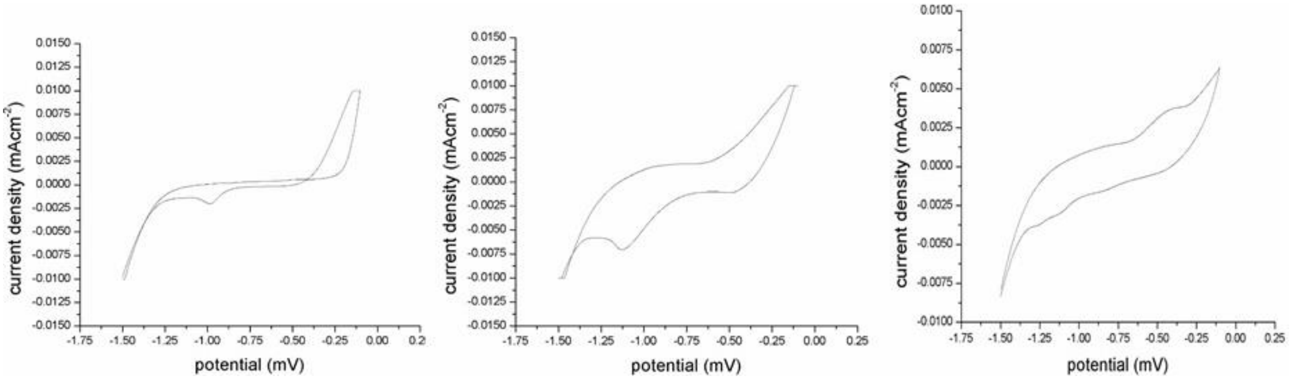


Fig. 4. CV analysis for oxidation/reduction measurement (a) Untreated AISI 1045 medium carbon steel soaking for 48 hours, (b) Nitrided AISI 1045 medium carbon steel treated at 550 ^{o}C for 3 hours, (c) Nitrided AISI 1045 medium carbon steel treated at 550 ^{o}C for 2 hours.

3.4. Weight Loss Measurement

Untreated and treated samples were immersed to 5% of NaCl solution for 1 day, 3 days, 5 days and 7 days to see the effect of duration of time for corrosion rate and weight loss of the samples.

The table below shows the measurement of weight loss before immersion to 5% NaCl solution and after the immersion in 5% of NaCl solution for 48 hours.

Table 2. Weight loss measurement.

Sample Type	Before immersion (g)	W1 (g)	W2 (g)	W3 (g)	W4 (g)	(W1+W2+W3+W4)/4 (g)	Weight loss (g)
Untreated samples	2.4965	2.4923	2.4917	2.4915	2.4914	2.4918	0.0047
Nitrided for 2 hours at a T of 550^{o}C	2.6063	2.6059	2.6054	2.6052	2.6052	2.6054	0.0009
Nitrided for 3 hours at T of 550^{o}C	2.7206	2.7201	2.7198	2.7197	2.7195	2.719775	0.000825

The weight loss was small in the nitrided samples. It is due to a low corrosion in the nitrided samples. It forms thin layer called compound zone. This layer prevents losing of materials due to corrosion and preserves from weight loss.

The weight loss, W and corrosion rate, CR of the samples is given in Table 3.

Table 3. Corrosion penetration measurement

		1 day		3 days		5 days		7 days	
Sample Type	W_o (g)	W (g)	CR (mmpy)	W (g)	CR (mmpy)	W (g)	CR (mmpy)	W (g)	CR (mmpy)
Untreated samples	2.4965	0.0047	7.96	0.0051	0.96	0.0058	0.40	0.0065	0.23
Samples nitrided for 2 hours at a temperature of 550 ^{o}C	2.6063	0.0009	1.53	0.0013	0.25	0.0017	0.12	0.0024	0.083
Samples nitrided for 3 hours at a temperature of 550 ^{o}C	2.7206	0.000825	1.40	0.0016	0.30	0.002	0.14	0.0029	0.10

W_0 is the initial weight of the sample before immersed to the solution. W_1, W_2, W_3 and W_4 are weight measurements after the sample removed from the NaCl solution.

Weight loss and corrosion rate was higher in the untreated samples due to the absence of protective layer (the compound layer).

4. CONCLUSION

Nitriding using melamine derived from urea improves the corrosion resistance of AISI 1045 steels. The compound layer having a thickness between 5 μm to 20 μm, has a good wear, friction and corrosion resistance characteristics. The cyclic voltammetric and the microscopic results shows that, the melamine nitrided AISI 1045 steels have more corrosion resistance than the untreated steels. The corrosion resistivity come due to the formation of the compound layer.

REFERENCES

[1] F. Czerwinski, *Thermochemical Treatment of Metals. Heat Treatment-Conventional and Novel Applications*, vol. 5, Norderstedt, Germany: Books on Demand, 2012, pp. 73–112.

[2] J. R. Davis, *Surface Hardening of Steels: Understanding the Basics*, Materials Park, OH, USA: ASM International, 2002.

[3] M. A. J. Somers, "Nitriding and nitrocarburizing; current status and future challenges," in *Proc. Heat Treat. Surf. Eng. Conf. Expo.*, Chennai, India, 2013.

[4] M. Drouet and E. Le Bourhis, "Low temperature nitriding of metal alloys for surface mechanical performance," *Materials*, vol. 16, no. 13, p. 4704, 2023, doi: 10.3390/ma16134704.

[5] E. T. Fisha, "Improving surface hardness of AISI 1045 steels using melamine derived from urea," *Heat Treatment and Surface Engineering*, vol. 6, no. 1, p. 2301248, 2023, doi: 10.1080/25787616.2023.2301248.

[6] J. Ratajski, "Relation between phase composition of compound zone and growth kinetics of diffusion zone during nitriding of steel," *Surf. Coat. Technol.*, vol. 203, no. 16, pp. 2300–2306, 2009, doi: 10.1016/j.surfcoat.2009.02.021.

[7] S. R. Hosseini, F. Ashrafizadeh, and A. Kermanpur, "Calculation and experimentation of the compound layer thickness in gas and plasma nitriding of iron," *Surf. Coat. Technol.*, vol. 204, pp. 553–566, 2010.

[8] H. J. Spies, "Corrosion behaviour of nitrided, nitrocarburised and carburised steels," in *Thermochemical Surface Engineering of Steels*, Elsevier, 2015, pp. 267–309, doi: 10.1533/9780857096524.2.267.

[9] R. S. Mikheev, I. E. Kalashnikov, and P. A. Bykov, "Investigation of the diffusion zone formation mechanisms during the production of functional steel-aluminium compositions by arc processes," *Mater. Sci. Forum*, vol. 1052, pp. 14–20, 2022, doi: 10.4028/p-1k2d4m.

[10] A. M. Bernhard et al., "Hydrolysis and thermolysis of urea and its decomposition byproducts biuret, cyanuric acid and melamine over anatase TiO2," *Appl. Catal. B: Environ.*, vol. 115, pp. 129–137, 2012, doi: 10.1016/j.apcatb.2011.12.013.

[11] M. Ortiz-Domínguez et al., "Analysis of nitride layers on ARMCO pure iron: The powder-pack nitriding process," *Microsc. Microanal.*, vol. 24, no. S1, pp. 1076–1077, 2018, doi: 10.1017/S143192761800586X.

[12] J. R. Davis, *Surface Engineering for Corrosion and Wear Resistance*, Materials Park, OH, USA: ASM International, 2001.

[13] G. Koch, "Cost of corrosion," in *Trends in Oil and Gas Corrosion Research and Technologies*, Elsevier, 2017, pp. 3–30.

[14] Y. Yang et al., "Corrosion induced failure analysis of subsea pipelines," *Rel. Eng. Syst. Saf.*, vol. 159, pp. 214–222, 2017, doi: 10.1016/j.ress.2016.11.014.

[15] D. Messina and E. Proverbio, "Effect of prestressing corrosion on failure in bridges," *Struct. Concrete*, vol. 24, no. 1, pp. 227–238, 2023, doi: 10.1002/suco.202200360.

[16] A. R. Prasad, A. Kunyankandy, and A. Joseph, "Corrosion inhibition in oil and gas industry: Economic considerations," in *Corrosion Inhibitors in the Oil and Gas Industry*, 2020, pp. 135–150, doi: 10.1002/9783527822140.ch5.

[17] M. V. Biezma and J. R. San Cristobal, "Methodology to study cost of corrosion," *Corros. Eng. Sci. Technol.*, vol. 40, no. 4, pp. 344–352, 2005, doi: 10.1179/174327805X75821.

[18] F. Malaret and X. S. Yang, "Exact calculation of corrosion rates by the weight-loss method," *Exp. Results*, vol. 3, p. e13, 2022, doi: 10.1017/exp.2022.5.

[19] K. M. Shwetha, B. M. Praveen, and B. K. Devendra, "A review on corrosion inhibitors: Types, mechanisms, electrochemical analysis, corrosion rate and efficiency of corrosion inhibitors on mild steel in an acidic environment," *Results Surfaces Interfaces*, p. 100258, 2024, doi: 10.1016/j.rsurfi.2024.100258.