Effects of gaseous nitriding AISI4140 alloy steel on corrosion and hardness properties

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Abstract. Corrosion is one of the major problems in the industry especially on machinery since it weakens the structure of the machinery part and causes the mechanical failure. This will stop the production and increase the maintenance cost. In this study, the corrosion behaviour of gas nitriding on a screw press machine shaft made from AISI 4140 steel was investigated. Pitting corrosion was identified as a major cause of the shaft failure and this study was conducted to improve the corrosion resistance on the AISI 4140 alloy steel shaft by gas nitriding as a surface hardening treatment. Gas nitriding was performed with composition of 15% ammonia and 85% nitrogen at temperatures of 525 °C, 550 °C and 575 °C and with the soaking time of 30, 45 and 60 minutes, respectively. The samples were prepared as rectangular sized of 30mm x 12mm x 3mm for immersion testing. The results showed that corrosion rate of untreated samples was 77% higher compared to the nitrided samples. It was also found that hardness of the nitrided samples was higher than untreated sample. All in all, it can be concluded that gaseous nitriding can significantly improve the surface hardness and the corrosion resistance of the shaft made of AISI 4140 alloy steel, hence reduces the pitting that is the root cause of failure.

1. Introduction
Gas nitriding is a thermochemical case hardening process used to increase wear resistance [1], surface hardness [2] and fatigue life by dissolution of nitrogen and hard nitride precipitation [3]. This process involves the atomic nitrogen from dissociating ammonia gas diffusing into the steel surface in the temperatures range 450-590 °C [4]. Gas nitriding represents one of the factors in enhancing the service life of the shaft in a screw press machine. The present study has shown the existence of γ-Fe3N phases in all compound zones of the nitrided specimen surface.

This research is mainly carried out to investigate the frequent occurrences of shaft failure in a screw press machines in a Malaysia palm oil mill. It had been reported that the shaft was operating in a corrosive environment due the facts that the extracted palm oil contains high concentration of palmitic and oleic acids [6]. The chemical reaction between those acids and metal surface under high operating temperature leads to deterioration of the shaft, which eventually causing the metal shaft to experience corrosive wear and pits formation. Pitting is one of the mechanisms in triggering widespread fatigue crack initiation and reducing life of the shaft. The pitting corrosion was identified as the main root causes of the premature shaft failures [6]. The capability of surface heat treatment such as nitriding to
overcome the pitting corrosion has been reported and confirmed. The nitrided components have an increased resistance against atmospheric corrosion and corrosion in neutral aqueous media [7, 8]. The corrosion resistance of nitride layers increases in the order $\gamma'$-nitride, $\varepsilon$-nitride, $\varepsilon$-carbonitride, and can be improved by post-oxidation [7].

2. Experimental procedure

2.1. Gas nitriding

The screw press machine shaft made from AISI 4140 alloy steel was machined as rectangular sized 30 mm x 12 mm x 3 mm in length, width and thickness, respectively, by using a horizontal band saw and lathe machine. The gas nitriding treatment was applied in a tube furnace (as shown in Figure 1) at the temperatures of 525 °C, 550 °C and 575 °C, with soaking time of 30, 45 and 60 minutes, respectively, as in Figure 2. A gas mixture of 85% nitrogen and 15% ammonia flow was maintained throughout this process, which was controlled by a gas control panel. The nitrogen flow started from the beginning of this process while ammonia started to flow when the temperature of furnace reached about 300°C. The ramp time to reach the peak temperature, the soaking time and the cooling time were all set up before carrying out the process. In this study, the ramp time was set up to 2 hours with increments of 4°C per minute while the soaking time followed the parameters set in the machine. Normal cooling condition was carried out in the furnace until it reached the ambient temperature.

![Figure 1. Tube furnace and specimen holder](image1)

![Figure 2. Selected temperature and soaking time for gas nitriding](image2)

2.2. Corrosion testing

Corrosion tests were carried out under static or stagnant position on untreated and nitrided samples in aqueous solution containing dirty crude palm oil, which was adapted from ASTM G-31. All specimens were immersed in the dirty crude palm oil at 80 °C for 720 hours or 30 days and they are shown in Figure 3. The temperature of 80°C was selected because the shaft may be operating at that particular temperature in the screw press machine. A hole was made on the sample and a string was attached to it. Before testing was carried out, the initial weight of the samples was measured using microbalance. After the immersion process, the corroded samples were removed and cleaned using ultrasonic cleaner. Following the cleaning stage, samples were immersed in nitric acid (HNO$_3$) for 2-3 minutes to remove the corroded part. The specimens were rinsed by distilled water and weighed to obtain final weight as shown in Figure 4. The weight loss is converted to corrosion rate as calculated using Equation 1 [9].

$$ CR = \frac{\text{weight loss (g)} \times K}{\text{Density (g/cm}^3) \times \text{Exposed Area (A)} \times \text{Exposure Time (hr)}} $$

(1)

where $CR$ is corrosion rate (mm/year), $K$ is constant factor, $8.76 \times 10^4$ and $A$ is exposed area (cm$^2$).
2.3. Microhardness testing

After undergoing the nitriding process, the specimens from each different parameters of heat treatment were sectioned at the middle to a cross-section with thickness of 3 mm and mounted with the phenolic powder. Then, the surfaces were ground with grit paper size 240. The specimens were later polished with alumina powder size of 1 µm to make sure the surfaces were smooth and flat prior to performing the hardness test. The hardness testing was carried out using Mitutoyo Vickers microhardness tester machine Model AVK-1C with indenter load of 30 kgf value. The indentations were uniformly spaced through from the nitrided layer towards to the core with an interval of 0.8 mm as shown in Figure 5. Three indentations were produced at each point and the average was recorded.

3. Results and discussion

Corrosion rate is the speed at which any metal in a specific environment deteriorates [10]. Table 1 shows the corrosion weight loss of the untreated and the gaseous nitrided AISI 4140 alloy steel after immersion in dirty crude palm oil solution for 720 hours. An accurate assessment and/or prediction of corrosion is required if the damage prediction models are to be reliably used to predict both the rate and severity of damage [11]. Corrosion rate, in unit of millimeter per year (mm/year), was calculated using Equation 1 as tabulated in Table 1.
Table 1. Result for immersion testing using dirty crude palm oil as the solution

| Sample No. | Description       | Area (mm²) | Initial Weight (gram) | After Immersion Weight (gram) | Weight loss(gram) | Corrosion Rate (mm/yr) | % of Reduction |
|------------|-------------------|------------|-----------------------|-------------------------------|-------------------|------------------------|----------------|
| 1          | Untreated         | 821.11     | 8.53                  | 8.48                          | 0.05              | 8.87                   | 0              |
| 2          | 525°C 30min       | 834.72     | 8.55                  | 8.51                          | 0.03              | 5.95                   | 33             |
| 3          | 525°C 45min       | 830.17     | 8.69                  | 8.66                          | 0.03              | 5.60                   | 37             |
| 4          | 525°C 60min       | 827.90     | 8.97                  | 8.95                          | 0.02              | 4.12                   | 54             |
| 5          | 550°C 30min       | 889.34     | 9.33                  | 9.30                          | 0.03              | 5.75                   | 35             |
| 6          | 550°C 45min       | 851.32     | 9.51                  | 9.49                          | 0.02              | 4.53                   | 49             |
| 7          | 550°C 60min       | 876.81     | 9.07                  | 9.06                          | 0.02              | 3.18                   | 64             |
| 8          | 575°C 30min       | 826.78     | 8.83                  | 8.80                          | 0.03              | 5.25                   | 41             |
| 9          | 575°C 45min       | 821.08     | 9.26                  | 9.23                          | 0.02              | 4.37                   | 51             |
| 10         | 575°C 60min       | 847.69     | 9.21                  | 9.20                          | 0.01              | 2.01                   | 77             |

Nitriding the sample at temperature of 575°C for 60 minutes gave a huge impact on the reduction of the corrosion rate by a value of 77%. As depicted in Figure 6, higher nitriding temperature resulted in lower corrosion weight loss, which in turns led to lower corrosion rate when compared to the untreated sample. During the test, gas bulbs were continuously emitted from the surface of untreated AISI 4140 alloy steel sample. Upon completion of the test, the sample surface possessed a rough morphology and was covered with appreciable dark-coloured corrosion products. All these evidences suggested that the sample AISI4140 alloy steel had deteriorated corrosion resistance in the diluted dirty crude palm oil at temperature of 80°C (working temperature of shaft) but with a variation in the rate of reactivity. The increase in corrosion potential with increasing nitriding time could possibly be attributed to increasing amount of nitrides, which were formed at high nitriding temperature. Nitriding improves the corrosion resistance due to the formation of the compact nitride compound layer[12]. The compound layer at the surface consists of iron nitrides, whilst the diffusion layer beneath the compound layer consists of an interstitial solution of nitrogen in the $\alpha$-Fe lattice. A thicker and denser nitried layer would enhance the corrosion resistance [13, 14]. Results of the immersion tests that were applied to the liquid nitried samples also pointed out that the presence of white layer was another important factor affecting the characteristics of pit formation [15]. This could be due to the fact that the white layer containing the maximum concentration of nitrogen aids to prevent formation of pits at the surface of the immersed sample. In other words, pit formation is very rare at the surface of samples that contain white layer after the application of simple immersion tests, which can again be tied up to the maximum nitrogen concentration reached in white layer.

The degree of corrosion resistance in the immersion test is related to the amount of iron dissolved in a defined time by the test solution. The corrosion resistance of the layer increases with formation of $\gamma$-nitride. This is valid for resistance against pitting corrosion, as well as for uniform corrosion, that is characterized by the free corrosion potential and the immersion test [7]. This is also supported by the findings of Ebrahimi et al. [12], who mentioned that pitting was formed in both untreated and nitried samples, however the pits in untreated samples were finer and higher in number [12]. In addition, the corrosion potential of the nitried samples was shifted to the noble direction with the increment of the nitriding time[16]. Increase in nitriding temperature and soaking time had resulted in an increase of nitrogen diffusivity, leading to the formation of a thicker compound layer. Thick oxide layer can seal the pores in the compound layer more effectively, and positively affect the corrosion resistance of the AISI 4140 alloy steel. As a result, corrosion resistance of the shaft was significantly improved by gas nitriding process. It is important to emphasize the fact that the compound layer is very beneficial in the case of the shaft with regards to wear and corrosion resistance if the porosity in the nitride layer is under control.

The hardness profile of nitried samples with nitriding temperature and soaking time ranging from 525°C to 575°C and 30 minutes to 60 minutes, respectively, is presented in Figure 7. Surface hardness of the samples had increased with increment of nitriding temperature and soaking time, while the core
possessed hardness in the range of 250–300 VHN. The highest thickness of nitride layer with a value of 438.6µm was recorded when the sample was nitrided at 550 °C temperature for 60 minutes of the soaking time. The sample possessed surface hardness of 340.8 HV whilst the untreated sample without the presence of the nitride layer recorded a surface hardness of 263.5 HV. Previous work has also reported that hardness value of the compound and diffusion layer is greatly influenced by the nitride layer formed at different temperatures of the nitriding process[15]. Higher surface hardness has been found to lead to higher corrosion resistance. Apart from an increasing surface hardness, the compound layer has been reported to be responsible for excellent wear and corrosion resistance of the nitrided parts [16].

Figure 6. The graph of corrosion rate versus nitriding time

Figure 7. Hardness value of nitride and untreated sample

4. Conclusion
The immersion test showed that gas nitriding had significantly improved the corrosion resistance of AISI 4140 alloy steel by 77% as opposed to the untreated sample. This is due to the formation of the nitride layer that protects the surface from harsh environment when the shaft is working in a corrosive environment and exposed to the dirty crude palm oil, which have contamination of free fatty acid. Diffusion of nitrogen into steel formed a nitrided layer that enhanced the surface hardness. Optimum corrosion resistance and hardness were achieved at a nitriding temperature of 575°C at 60 minutes.

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