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Investigation of Microstructure and Corrosion Propagation Behaviour of Nitrided Martensitic Stainless Steel Plates

Kamal Ariff Zainal Abidin[1, a], Elya Atikah Ismail[1], Azman Zainuddin[1], Patthi Hussain[1]

[1]Mechanical Engineering Department, Universiti Teknologi PETRONAS, Bandar Seri Iskandar, 31750, Tronoh, Perak, Malaysia

Abstract. Martensitic stainless steels are commonly used for fabricating components. For many applications, an increase in surface hardness and wear resistance can be beneficial to improve performance and extend service life. However, the improvement in hardness of martensitic steels is usually accompanied by a reduction in corrosion strength. The objective of this study is to investigate the effects of nitriding on AISI 420 martensitic stainless steel, in terms of microstructure and corrosion propagation behavior. The results indicate that the microstructure and phase composition as well as corrosion resistance were influenced by nitriding temperatures.

1 Introduction

Nitriding is an effective technique applied for many years to improve the surface hardness and wear resistance of low carbon and tool steels [3]. Nitriding allows diffusion of nitrogen into the surface of a metal to create a case hardened surface. However, the improvement in hardness in martensitic steels is accompanied by a reduction in corrosion strength due to the formation of chromium nitride and the depletion of free chromium in the steel matrix [4]. R. Karadas et al. [5] investigated the microstructures, phase compositions, hardness, wear and corrosion behaviour of the original and martensitic stainless steels that had undergone low temperature nitriding in a fluidized bed reactor. The results showed the surface hardness of the AISI 420 grade martensitic stainless steel increased about 6 times compared to the original state. The corrosion resistance was also enhanced. D.H. Mesa et al [6] tested high-nitrogen martensitic stainless steels under corrosion-erosion conditions in slurry compose and observe optimum temperature of the martensitic steel where the corrosion-erosion resistance is highest. As recent studies have shown serious limitations in highly corrosive environments. The objectives of this study are to observe and investigate the effects of nitriding on martensitic stainless steels, in terms of their microstructures and corrosion propagation behavior.

2 Experimental setup

The experimental setup for this study could be categorized into 3 parts, metallography preparation for grains observation, nitriding of the samples, and experimental analysis of the nitrided samples. The samples were cut into 5mm X 5mm plates using an abrasive cutter. Then the samples were mounted using a hot mounted press to ease the process of grinding and polishing of the samples. The sample surfaces were wet ground with SiC paper from 240 down to 1200 grit to produce a fine surface finish.

After grinding, the surfaces were polished with a fine grade Al2O3 paste. The main purpose of polishing is to produce a scratch-free surface with a mirror like finish. To reveal the microstructure of the sample under a microscope, the samples then undergo etching. This process involved a chemical reaction between the etchant and the sample. The etchant chosen to be used for AISI 420 in this study was 5% Nital. The microstructure of the as received sample was then investigated by using Optical Microscope (OM) with magnification of 500X. The nitrided samples also undergo this process so that a comparison of unnitrided and nitrided microstructures can be compared. For nitriding, the samples were placed on the alumina boat in the horizontal Carbolite Tube Furnace (CTF). Firstly, the temperature was set to 1100°C. Then, nitrogen gas was made to flow through the tube. The holding time was set to 10 hours. This process was repeated for 500°C also for 10 hours. All of the samples were cooled down gradually. After nitriding, the samples are observed under a microscope and a clearer and larger view is obtained using a scanning electron microscope. The chemical composition of the samples were determined by using Energy-Dispersive X-ray (EDX) Spectroscopy that is attached together with the Scanning Electron Microscope (SEM). Finally, a corrosion test was conducted. For this study the immersion test was chosen. Before immersing the samples, the sample weights were recorded. This experiment used 200 ml of 99% water + 1% HCl and conducted at room temperature for up to 140 hours. During the immersion test, samples were removed from the solution at a certain time interval, cleaned with deionized water, dried with warm air, and weighed with a balance to an accuracy of 0.1 mg.

3 Results and discussion

3.1 Metallography

Figure 1 shows the microstructure of as received AISI 420 at a magnification of 500X. The microstructure shows a fine distribution of ferrite and martensite over the whole cross section. Grain boundaries can be seen clearly. Figures 2 and 3 below are the microscope image of samples MSS 500 which was nitrided at 500°C and MSS 1100 which was nitrided at 1100°C.

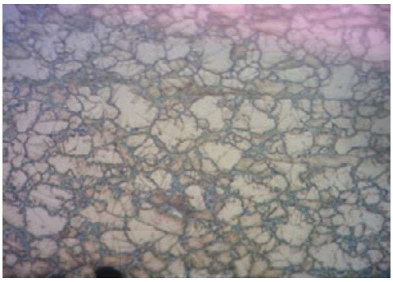


Figure 1. 500X of as received sample (MSS 0)

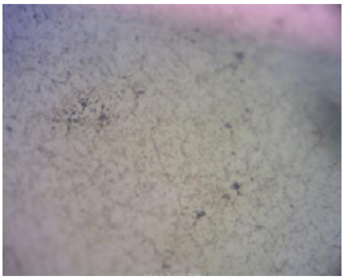


Figure 2. 500X of MSS 500

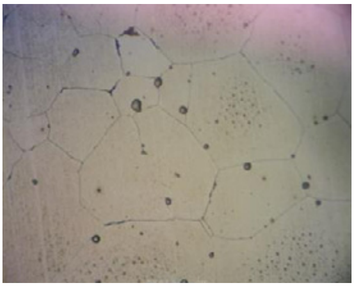


Figure 3. MSS 1100 at 500X (centre)

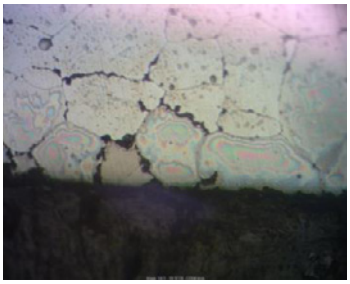


Figure 3. MSS 1100 at 500X (edge)

From the figures above, the nitrided samples showed that the martensite has expanded in size. In the nitrided samples, there were some black region alongside the grain boundaries indicating intergranular corrosion where the boundaries of crystallites of the material are more susceptible to corrosion than their insides. In martensitic stainless steel where chromium is added, precipitation of chromium carbide at the grain boundaries, result in the formation of chromium-depleted zones adjacent to the grain boundaries (this process is called sensitization) causing the steel or alloy to be susceptible to intergranular corrosion or intergranular stress corrosion cracking [7]. In this case, carbide precipitation occurs due to nitriding at a temperature above 500°C. Comparing the micrographs of samples nitrided at 500°C and 1100°C it can be seen from Figure 2, there seems to be no sensitization effect on the grain boundaries but in figure 3 and 4, the sensitization effect is very obvious, especially at the edge (surface) of the samples.

3.2 Microstructure and Morphology

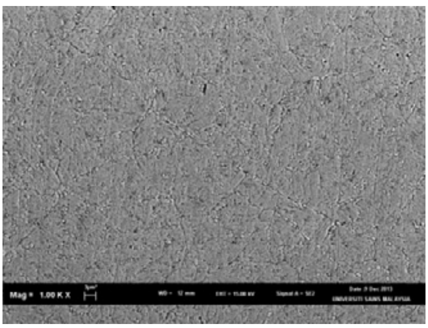


Figure 4. SEM micrograph of MSS 500 at 1000X

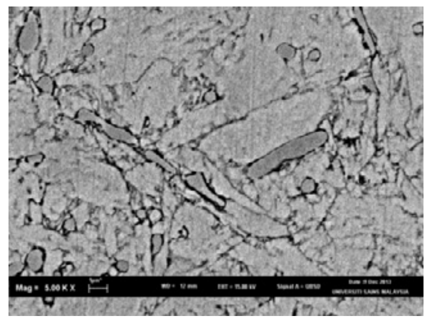


Figure 5. SEM micrograph of MSS 500 at 500**0X**

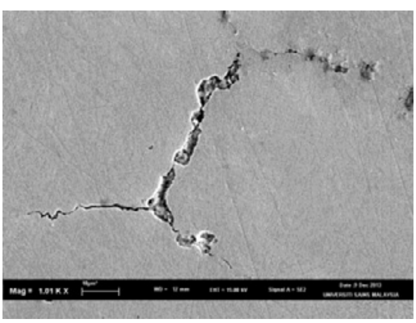


Figure 6. SEM micrograph of MSS 1100 at 1000X

Figure 5 is a micrograph of MSS 500 at 1000X taken by SEM while figure 6 is at 5000X. Some white rounded structures can be observed here; which correspond to carbides formed during the heat treatment [8]. This is proven in EDX analysis later in the report. Figure 7 above is 1000X magnification view of MSS 1100 particularly at its grain boundary. In this figure, the intergranular corrosion can be seen clearly. Elemental analysis by EDX of the corrosion will confirm if it is carbide precipitation.

3.3 Elemental Analysis of Nitrided Layer

The EDX microanalyses of the nitrided layer of the sample MSS 500 and MSS 1100 are shown in Figure 8 to 11. EDX is very important in this study to confirm the presence of carbide precipitation in the grain boundaries of the samples. The spot analysis performed by the EDX provides a precise weight percentage of the elements in the particular spot.

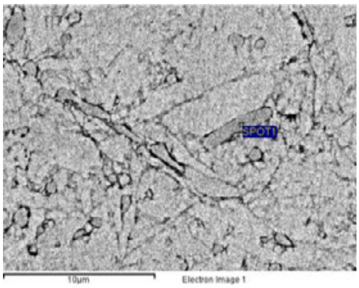


Figure 7. Spot analysis of MSS 500 at 500X

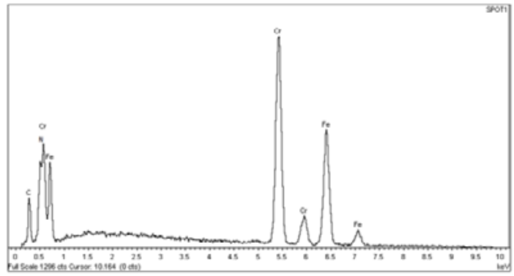


Figure 8. EDX analysis of MSS 500

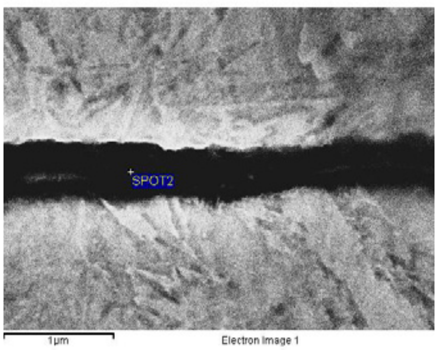


Figure 9. EDX spot analysis of MSS 1100

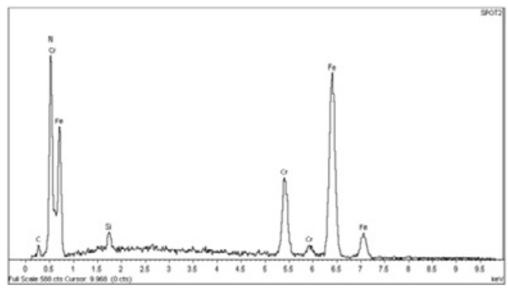


Figure 10. EDX analysis of MSS 500

Based on the EDX results and the elemental analysis of MSS 500 and MSS 1100 in the figures above, it can be observed that MSS 1100 have higher chromium nitride content than MSS 500.

3.3 Corrosion analysis

Corrosion resistance of the steel was reduced after nitriding due to the formation of chromium nitride and the depletion of free chromium in the steel matrix.[9]. The corrosion test conducted was by immersing the samples in 1% HCl solution. The weight loss is taken at time intervals and the corrosion rate can be obtained. The formula used for calculating the corrosion rate is

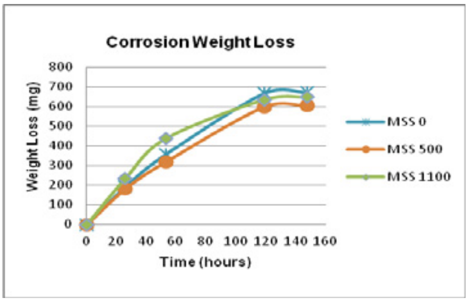
$$R_{corr} = \frac{m}{S \times t}$$

Where m = weight loss (g), S = surface area (m^2), t = time immersed (h), Unit = $g\ m^{-2} h^{-1}$. Table 1 below shows the weight loss taken at time intervals for up to 140 hours where the samples are taken out of the solution and weighed so the weight loss can be calculated. The weight was taken at a value of 0.1 mg to ensure precision.

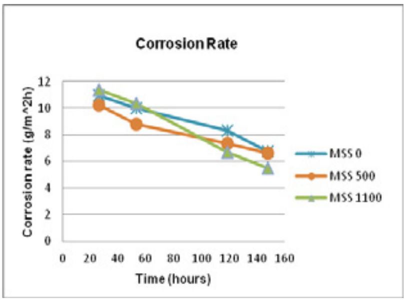
Table 1. Weight loss at time intervals

	26 H	**53 H**	**119 H**	**148 H**
MSS 0	0.1923 g	0.3568 g	0.6670 g	0.6727 g
MSS 500	0.1827 g	0.3189 g	0.5987 g	0.6050 g
MSS 1100	0.2344 g	0.4360 g	0.6329 g	0.6467 g

Graph 1 and 2 shows the corrosion weight loss plotted against the time of immersion. It can be seen that MSS 1100 suffers high corrosion rate in the beginning but lower at the end. On the other hand, MSS 0 which is the as received sample, started with a very low corrosion weight loss but gradually increase to experience the most weight loss. MSS 500 suffers the least corrosion rate compared to the untreated AISI 420 and MSS 1100. However, MSS 1100 still has a lower corrosion rate than the as received samples.



Graph 1. Weight loss



Graph 2. Corrosion rate

4 Conclusions

The micrographs obtained for the samples showed how the samples were nitrided and the results are further enhanced with the use of SEM and EDX. Elemental analyses were also done to calculate the weight percentage of each element in the specific spots on the samples. The corrosion test conducted was an immersion test where the samples were immersed in 1% HCl solution for up to 140 hours and the weight loss due to corrosion is taken at several time intervals.Based on the results, it can be concluded that samples nitrided at a high temperature would cause carbide precipitation on the grain boundaries and hence reduce their corrosion resistance. Hence, the best nitriding temperature would be at a low temperature so as to achieve the highest corrosion resistance. It was also shown that untreated samples suffers the worst corrosion weight loss and corrosion rate. These results shows that nitriding AISI 420 does enhances the corrosion resistance of the material.

References

1. F.L. Laque and H.R. Copson, *"Corrosion resistance of metals and alloys",* Second Edition, Reinhold Publishing Corporation. (1963)
2. R.M. Davison, "*Corrosion of stainless steels", ASM International, Metals Handbook*, Ninth Edition, Corrosion, **13**, 547-565 (1987)
3. Xi, Y.-t., et al., Surface and Coatings Technology **202(12),** 2577-2583 (2008)
4. T. Bell, Y. Sun, Heat Treatment of Metals **29**, 57-64 (2002)
5. R. Karadas, O. Celik, H. Cimenoglu, Defect and Diffusion Forum, 312-315 (994-999) (2001)
6. D.H. Mesa, A. Toro, A. Sinatora et al. Wear **255**, 139-145 (2003)
7. http://www.corrosionclinic.com/types_of_corrosion/intergranular_corrosion_cracking.htm
8. P. B. Sonia, C. Raul, S. Silvia et al., Surface and Coatings Technology **204,** 3280-3286 (2010)
9. T. Bell, Y. Sun., Heat Treatment of Metals **29**, 57-64 (2002).