Correlation between microstructure and micro-hardness of 316L nitrided austenitic stainless steel

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Abstract. This paper presents the effect of duration of solution nitriding towards microstructure and microhardness of AISI 316L stainless steel. The AISI 316L stainless steel was exposed to high temperature gas nitriding process at 1200 °C by using 50% ammonia gas and 50% nitrogen gas for different durations of 8, 15 and 20 hours. The nitrided austenitic stainless steel then underwent several analyses and tests to find the effect of different durations of nitriding towards its microstructures and microhardness. From the experiments conducted to the nitried samples, it was found that the higher duration of nitriding resulted in the increase of microhardness of the samples due to the increase of nitrogen content in the stainless steel. However, there was no effect found on the microstructure of the nitrided samples. It was noted that the highest hardness was obtained from the nitrided sample of 20 hours that has 245.1 HV which is about 70% higher than the as-received sample.

1. Introduction
Stainless steel was developed in the early of 20th century and has become one of the most important materials in the world recently. The stainless steel has been applied in many types of industries such as medical equipment, textile, marine engineering, architecture, chemical engineering and other industries. Basically, any types of steels that contain more than 12 % chromium are considered as stainless steel. In order to increase the resistance towards localized corrosion, element like nickel is added into the stainless steel. Stainless steel has been classified into three groups according to its microstructure which are austenitic, martensitic and ferritic where each has a face-centered cubic, tetragonal crystal lattice and body-centered cubic structures. Compared to the other two groups, austenitic stainless steel has been widely used in the industry due to its strength, corrosion resistance, weldability and ductility. However, the only drawback for austenitic stainless steel is its low hardness. So, in this paper, austenitic stainless-steel type AISI 316L was exposed to solution nitriding process which is a gas nitriding done at high temperature between 1000 °C to 1200 °C where the material was exposed to nitrogenous environment in a vacuum condition. This heat treatment method increased the hardness of stainless steel due to the diffusion of nitrogen into the steel. Recent studies have been carried out on austenitic stainless steel which focused on the corrosion resistance, effect of coating to its strength and effective duration of nitriding process. Hence, this paper investigates the correlation between microstructure and microhardness of AISI 316L austenitic stainless steel when subjected to solution nitriding process at 1200 °C using 50% ammonia and 50% nitrogen gas at different durations of 8, 15 and 20 hours.
Normally, the classification of stainless steel is according to its microstructure. One of the elements in stainless steel is chromium which function is to prevent the oxidation of the steel by forming a protective film on the surface of the stainless steel. Recent study showed that the amount of chromium in stainless steel is at least 11% compared to other elements [1]. At temperature of about 1050 °C the solubility limit of Cr is about 13% in the γ phase. Thus, the steel itself is in the γ phase where the austenite will change to martensite due to the high temperature condition for the martensite start temperature [2]. Hence, the steel is in martensitic condition at room temperature. The increase in the content of chromium in stainless-steel transforms austenite to ferrite. Thus, the stainless steel is in ferrite phase at room temperature. To prevent this from happening, nickel is added into stainless steel to keep austenite condition at higher content of chromium due to the ability of nickel which is a powerful former of austenite structure. So, the insertion of at least 9 % of nickel was enough to keep the stainless steel in the austenite form even at a high content of chromium. As a result, the temperature of martensite-finish and martensite-start will decrease to zero [3]. Hence, the stainless steel is in the form of austenite when cooled to ambient temperature. Austenitic stainless steel usually composed of the elements of Fe, Cr and Ni that have a face-centered cubic (FCC) form due to the presence of some stabilizer elements for austenite like nitrogen, manganese and nickel [4]. Nitriding is a type of surface treatment which is thermo chemically conducted in order to increase the strength of the steel [5]. A perfect nitriding process results in the formation of nitrite in the steel structure. This can be proven by the formation of white layer comprising of Fe₅(N, C)₁₋ₓ and Fe₅N phases on the surface of the steel [6, 7]. The good properties like improvement in fatigue life, increased wear resistance, high surface hardness and anti-galling properties are achieved by the nitriding process which makes it suitable for case-hardening process of steel [8]. The low temperature used in the nitriding process had resulted in less deformation and distortion of the heat-treated parts. A low-temperature gas nitriding process is where the nitriding process is done at the temperatures ranging from 400 °C to 700 °C. In this process, the formation of nitrides occurred at the surface of the stainless steel due to the diffusion of nitrogen into the steel. As a result, the steel became hardened [9]. The drawback of this process is the decrease of the ability of the stainless steel against corrosion. The gas nitriding process that is done at the temperatures between 1000 °C to 1200 °C is called solution nitriding which is considered as the latest process to increase the strength of steel [10]. The solution nitriding process followed by quenching allows the nitrogen to diffuse interstitially into the steel which causes the increase of strength of stainless steel. This type of nitriding process is usually applied in the heat treatment process for austenitic, ferritic, martensitic and duplex stainless steels [11-13]. Recent studies had shown that high temperature gas nitriding causes the nitrogen to diffuse deeper into the stainless steel compared to low temperature gas nitriding. Another research had shown that the production of nitrides occurred at the surface of duplex stainless steel when it was subjected to high temperature gas nitriding at 1150 °C for 15 hours. Not only that, it was also found that the microstructure of austenitic stainless steel was not affected by high temperature gas nitriding [14]. For both steels, it was observed that the increase of pressure of nitrogen caused a higher absorption of nitrogen. Hence, the size of grain of steel increased along with the duration of high temperature gas nitriding when the steel had absorbed all the nitrogen.

Austenitic stainless steels possess high corrosion resistance; however, it has poor mechanical properties such as low hardness. Thus, high hardness is necessary so that it can be used in the high wear condition. The objective of this study is to improve the hardness of the austenitic stainless steel by nitriding technique. Nitriding was carried out at the elevated temperature.

2. Materials and methods

Stainless steel AISI 316L was used in this work. This type of stainless steel has a better corrosion resistance compared to type 304 stainless steel. The austenitic stainless steel is divided into three samples for different durations of solution nitriding which are 8, 15 and 20 hours. The stainless steel was ground and polished. The three samples of the AISI 316L then were then exposed to solution nitriding using 50% ammonia gas and 50% nitrogen gas for different durations of nitriding for 8, 15
and 20 hours for each sample, respectively. The nitrided samples were let to cool naturally. After that, all the nitrided samples were mounted, ground and polished. For metallography purpose, the nitrided samples were etched using Viella’s Etchant. Then, the microstructure of the nitrided samples were observed under optical microscope. The chemical composition of the nitrided samples were analysed using EDS embedded with SEM machine to obtain the nitrogen content in the steel. Lastly, the as-received and nitrided samples were subjected to microhardness testing machine in order to acquire the hardness value for each sample along the cross-sectional area.

The data obtained through all the experiments and tests were analysed to investigate the correlation between the microstructure and microhardness of the nitrided austenitic stainless steel.

3. Results and discussion

3.1. Microstructure

Figure 1 shows the optical micrograph of as-received sample of AISI 316L conducted in this study. The image of this as-received sample was taken using optical microscope with the use of Marble’s Etchant. Figure 1 also shows that the as-received sample had undergone cold working due to the rolling effect on its surface. The microstructure of the as received sample contains some recrystallization of twins and has a small grain size.

![Optical Micrograph of as-received AISI 316L.](image)

All the three samples of AISI 316L were undergone the solution nitriding for different durations of 8, 15 and 20 hours All the samples were let to cool naturally by means of air cooling. The nitrided samples were then ground, polished and etched with Viella’s Etchant to increase the visibility of its microstructures to be observed by LECA Optical Microscope. Figures 2, 3 and 4 show the micrographs of the nitrided samples for 8, 15 and 20 hours, respectively, with the presence of twins on the microstructures. The presence of twins is considered normal for low stacking fault energy metals that have face-centered-cubic structures like austenitic stainless steel. It is observed that the formations of twins in this paper consist of two types which are trans granular twin and suspended twin. These two types of twins are clearly shown in figures 2, 3 and 4 below. The trans granular twins are made up from four parts whereby two sides are in coherent twin planes and both ends are the grain boundary. For the suspended twins, they also have four parts, where the incoherent twin plane is at the head, the coherent twin planes are at both sides and the grain boundary is at the end.
Moreover, it was also observed that the grain size of austenite in the samples increased with the increase of duration of solution nitriding because of slow cooling process. If the samples were quenched after nitriding process, the grain sizes became smaller and the toughness was higher. However, the duration of solution nitriding did not affect the single-phase structure of austenite. Thus, the diffusion of nitrogen into the steel is totally in solid solution austenite leaving no trace of nitrides behind. All the nitrided samples had experienced slow cooling process from temperatures of about 1200 °C. Next, the samples were exposed to the sensitization temperature of austenitic stainless steel which is in the range of 450 °C to 870 °C. At these temperatures, a normal austenitic stainless steel experienced the formation of chromium carbide precipitation on its grain boundaries. However, for all
the nitrided samples, it was observed that there was no formation of chromium carbide precipitation on its grain boundaries due to the low carbon content in the AISI 316L.

3.2. Chemical composition

The nitrided samples of AISI 316L were investigated using SEM with EDS to reveal the chemical composition of the nitrided austenitic stainless steel especially for the nitrogen content in the steel. The EDS analysis was done at random spots on the surface of the nitrided austenitic stainless steel. Table 1, table 2 and table 3 show the result captured from the EDS analysis by SEM at different durations of solution nitriding.

**Table 1.** EDS analysis by SEM of Nitrided AISI 316L for 8 hours.

| Element Name  | Weight Concentration (%) |
|---------------|--------------------------|
| Iron          | 63.0                     |
| Chromium      | 15.0                     |
| Oxygen        | 5.8                      |
| Nickel        | 9.1                      |
| Nitrogen      | 3.6                      |
| Molybdenum    | 2.9                      |
| Silicon       | 0.6                      |

**Table 2.** EDS analysis by SEM of Nitrided AISI 316L for 15 hours.

| Element Name  | Weight Concentration (%) |
|---------------|--------------------------|
| Iron          | 60.7                     |
| Chromium      | 14.9                     |
| Oxygen        | 5.2                      |
| Nickel        | 8.2                      |
| Nitrogen      | 7.2                      |
| Molybdenum    | 3.1                      |
| Silicon       | 0.6                      |

From the result of the EDS analysis in table 1, table 2 and table 3 above, it was clearly shown that the nitrogen content in the steel increases with the duration of solution nitriding even though the EDS analysis was executed at random spots on the surface of the steel not at the same spot. The lowest nitrogen content is 3.6 wt.% for 8 hours of solution nitriding whereas the highest nitrogen content is 8.5 wt.% for 20 hours of solution nitriding. Hence, the higher the duration of nitriding, the higher the diffusion of nitrogen into the steel is.

3.3. Microhardness test

The Vickers hardness test was completed by using the LECO Microhardness Tester LM247AT. The Vickers hardness test was conducted at the cross-sectional surface of the as-received sample and the nitrided austenitic stainless-steel samples. The result obtained from the test was plotted in the charts as shown in figure 5 and figure 6. The error bar in figure 5 was estimated to be ± 5 HV due to some human error in conducting the hardness test.

Based on the chart in figure 5, hardness of nitrided austenitic stainless-steel increases with the increase in the duration of solution nitriding. It was also observed that the hardness is high at the surface of the as-received austenitic stainless steel and starts to decrease when approaching the centre of the steel due to the cold working of the as-received austenitic stainless steel. For nitrided AISI
316L, the hardness also is high at the surface and slowly decreases as it approached the centre of the nitrided AISI 316L due to higher concentration of nitrogen on the surface and the diffusion of nitrogen into the steel was less diffused to the centre.

Table 3. EDS analysis by SEM of Nitrided AISI 316L for 20 hours.

| Element Name   | Weight Concentration (%) |
|----------------|--------------------------|
| Iron           | 62.8                     |
| Chromium       | 15.4                     |
| Nickel         | 9.1                      |
| Nitrogen       | 8.5                      |
| Molybdenum     | 3.5                      |
| Silicon        | 0.7                      |

Figure 5. Chart of Hardness VS Cross-Sectional Distance for untreated and nitrided AISI 316L samples.

Figure 6. Plot of Surface Hardness VS Duration of Nitriding for AISI 316L.
The chart in figure 6 shows the effect of duration of solution nitriding on surface hardness of the AISI 316L. The surface hardness is expected to increase with the increase of the duration of solution nitriding until 22 hours before the surface hardness becomes constant. The highest surface hardness was obtained from the nitrided samples for 20 hours that has 245.1 HV which is 70% higher than the hardness of the as-received samples that only has 168 HV. Hence, this proves that micro-hardness increases with the duration of solution nitriding.

4. Conclusion
The addition of nitrogen into steels was indicated by the improvement of hardness on the steel. The highest hardness was acquired from the sample that was nitrided for 20 hours that have 245.1 HV which is about 70% higher compared to the hardness value of as-received sample. Longer duration of solution nitriding caused higher diffusion of nitrogen into steel. As a result, the hardness of the nitrided AISI 316L was increased by 46 % when compared to untreated sample and the grain size remained the same as received. From this study, it was found that the microstructure for both the as-received and nitrided samples were almost similar where both have the presence of twins. In conclusion, the increase of duration of solution nitriding has led to the increase of the micro-hardness of austenitic stainless steel but had no effect on its microstructure.

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