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Correlations between Microstructure, Nitrogen Concentration and Micro Hardness of Nitrided Ferritic Stainless Steel

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***Abstract:*-- Gas Nitriding on Ferritic Stainless steels AISI 430 carried was out at 600 , for various period of nitriding process which were for 2 h, 8 h and 24 h. The effect of nitriding process period in term of microstructure, overall micro hardness, cross section hardness and nitrogen diffusion rate were investigated. The microstructures of the samples were carried out using Optical Microscope (OM) and Scanning Electron Microscope (SEM). The phase changes and Nitride precipitation formation were observed with respect to holding time of nitriding. Micro-analyses were also conducted on all samples using Energy Dispersive Spectroscope to investigate the effect of phase changes and it correlation toward the hardness of the materials. Unnitrided ferritic stainess steel was found having bigger grain size boundaries compare to nitride ferritic stainless steels. This is due to heat treatment during manufacturing process and concentration of nitrogen inside the steel. The size of grain boundaries reduces with nitriding time due to concertation of nitrogen inside the steels. The hardness value and concentration of nitrogen inside the steel reduce with the depth under the surface. The concentration of nitrogen in the steels increases with time of nitriding. Increasing in nitriding time increases the nitrogen composition inside the steel, thus reduce the grain size of the microstructure significantly and thus increase the hardness properties of the materials.**

Keyword: Ferritic Stainless steels; Gas nitriding; Hardness; nitrogen concentration

I. INTRODUCTION

Stainless steel is a type of steel which have sufficient corrosion resistant such as rust, easy for fabrication characteristic weld elements and also cast shapes. Generally stainless steel is a special alloy which contains iron, chromium, and any other elements with the intention of resist corrosion from many environments. [1] Stainless steel able to withstand corrosion due to the present of chromium elements inside the material, the chromium form a thin barrier around the grain boundaries to prevent oxidation happened. However chromium has high tendency to combine with carbon and oxygen. Oxidation also maybe happened if the manufacturer does not process it using special technique and process [1]. Intergranular corrosion is example of oxidation of chromium layer; happen due to the inadequate heat treatments, weldments and high-temperature service, which lead to formation of Carbide Precipitates around the grain boundaries [2]. Stainless steel can be classified into several types such as Ferritic Stainless steels, Austenitic Stainless Steels and Duplex Steels [3]. Ferritic stainless steels having Body-Center Cubic (BBC) microstructure, also having low carbon content around 0.19%, having 16% - 20% chromium content and few other materials such as silicon, molybdenum, vanadium, aluminum, niobium, titanium and tungsten have higher tendency to help the formation of ferrite [1]. Nitriding process uses either Ammonia or Nitrogen in high temperature environment, resulting monatomic nitrogen diffuse into the surface of the steel being treated [1]. The reaction of the nitrogen with steel causes the formation of very hard iron and alloy nitrogen compound which sometimes even harder than any other tools and carburized steels. The advantages of this process is the hardness process can be achieved without other heat treating process such as air quenching, water quenching and many more. This process also can prevent scaling and discoloration on the surface as the hardening process is accomplished in a nitrogen atmosphere [1].

II. LITERATURE REVIEW

A. AISI 430 Ferritic Stainless Steels

AISI 430 Ferritic Stainless steels are known as Stainless steel type 1.4016 in UK. This type of stainless steel has great properties such as good corrosion resistance, good formability and ductility. It also in pure form which is non-harden able, and come with excellent finish quality. Having excellent resistance to nitric acid make it suit to be use for chemical applications. Non-hardenable make it easier to deform eventually make it popular in domestic appliances and decorative trim. [4] Aside from corrosion resistance, AISI 430 Ferritic Stainless steel also having good heat resistance in term of oxidation, easily machined and weldability. Ferritic stainless steel can be ready welded by any fusion methods, however preheating to 150 to 200 is needed. The welded 430 FSS need to be annealing at 790 to 815 to reduce embrittlement of welded zone. [4]

Table 2 1: Chemical composition of AISI Ferritic Stainless Steels Grade 430 [5] [4]

Composition	Weight Percentage
Carbon, C	0.062
Chromium, Cr	15.72
Manganese, Mn	0.31
Molybdenum, Mo	0.13
Nickel, Ni	0.12
Sulphur, S	0.003
Phosphorus, P	0.03
Titanium, Ti	0.02
Silicon, Si	0.23
Iron, Fe	Balance

B. Introduction of Nitriding

Nitriding is a hardening technique to strengthen steels by diffusing nitrogen into surface of steels and iron. The solubility of Nitrogen depends on few factors such as Furnace Temperature, Process control, Time, Gas flow, Gas activity control and Process chamber maintenance. [5] Nitrogen diffusion produced hard surface of the iron and significantly improve it corrosion resistance properties. [5] There is few Nitriding process available, such as The Floe Process, Salt Bath Nitriding, The ion, plasma nitriding and Gas Nitriding. [5] However in this project, only limited to Gas Nitriding process. Gas Nitriding is a simple technique which does not require any special equipment, this process involve nitriding at high temperature and nitriding at low temperature. High Temperature Gas Nitriding (HTGN) usually involves exposing the sample in nitrogen atmosphere in High temperature around 1000 -1200 . Meanwhile, Low Temperature Gas Niriding (LTGN) involve exposing the sample in nitrogen environment at Low temperature around 500-600 . [6] During the heating process, iron particle receive energy and then vibrate even further each other, the vibration of the particle create spaces between the particle which eventually give space for nitrogen to enter and fill up the space between the particles. This nitrogen finally acts as dislocation barrier which will significantly increase the strength of the steels. [7] After Nitriding Process, Compound zone or white layer created along the surface steels. [8] After the Compound zone, there are few more zone available such as Diffusion zone, transition zone and core material. [5]

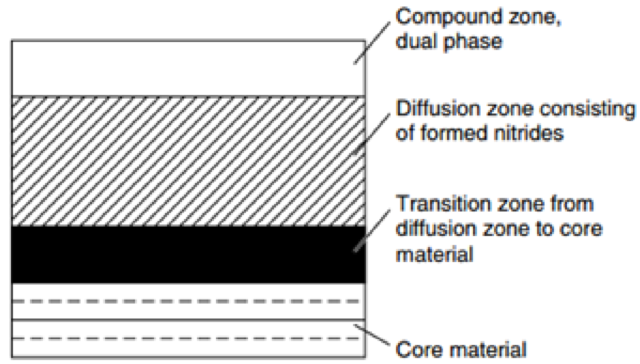

Figure 2 1: Schematic of a typical nitride case structure [6]

Strong attraction between Nitrogen ion and metal during Gas Nitriding, leads to formation of metal compounds such as Chromium Nitride and Ferrite Nitride. Refer to previous research, Precipitation of Metal-N nitrides usually occur in Low Temperature Gas Nitriding, while -N were precipitated at High Temperature Gas Nitriding. [6] Formation of Chromium compound will reduce the corrosion resistance of metal due to depletion of Cr particle in the solid solution. [9] The amount of nitrogen dissolve in the steel will influenced the microstructure of nitride steel. The microstructure probably

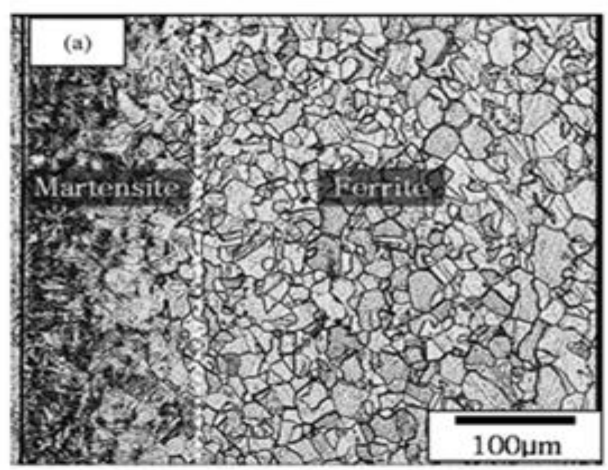

Figure 2 2: Optical micrograph of AISI 430 FSS after the HTGN treatment at 1100 in 15 min [11]

transforms either to austenite or martensite depends on the amount of nitrogen diffused [10]. Phase changes of microstructure during nitriding caused by formation of nitride [11]. Figure 2.2 (a) shows that the area near the surface was transform to martensite, while the interior area still remains

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Vol 3, Issue 4, April 2018

as ferrite phase. Figure 2.3(b) shows the depth of martensite phase increase further compare to Figure 2.2 (a). This show that by increasing the nitriding time will also increasing the penetration of nitrogen into steel [10]. The penetration of nitrogen depends on carbon content inside the steel. From previous research, that nitrogen did not permeate through the 0.13C-13 Cr

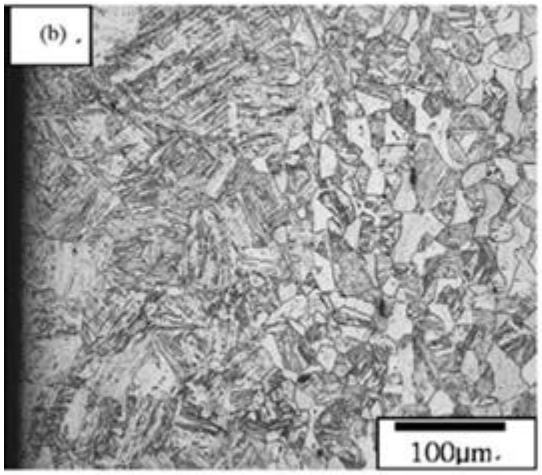

Figure 2 3 Optical micrograph of AISI 430 FSS after the HTGN treatment at 1100 in 10 hours [11]

martensitic stainless steel due to the effect of carbon [10]. However, differ with Low Temperature Gas Nitriding (LTGN) process which running at 500-600 , lower than crystallizations temperature. The amount of nitrogen dissolve in the steel probably will little bit influence the microstructure of nitride steel. Nevertheless, the more amount of nitrogen diffuse will enhance the strength of the steel due to increasing number of dislocation barrier available.

C. Hardness Properties

Hardness Properties of the material can be done using Vickers pyramidal hardness test, this is an effective tool for characterizing the microstructure of materials according to ASTM E384-10 specification. Vickers Hardness value is measured by the ratio of Force F required to produce an indent with a given surface area A. [12] Previous researches have been done toward HTGN, the corrosion resistance and hardness properties of the surface layer increase. However, there also some disadvantage of nitriding, aside increasing the surface hardness, it also increase the brittleness of the materials. [10] [6] The steel become harder due to increasing slip dislocation barrier; at the same time reduce the ductility of the metal since there limited dislocation spaces available, make it become brittle. [7] Earlier research have been done state that, gas Nitriding process will enhance the hardness value at the surface, however the hardness value will drop to the centre of the samples due to the high nitrogen concentration at the surface area. However, due to limitation of diffusion and diffusion barrier, the concentration of nitrogen drops towards the centre of the samples. [13]

III. METHODOLOGY

The sample of the experiment need to be mounted, grinding and polished to 1 micron in order to reduce the surface roughness of each sample. Nitriding of each samples conducted at 600 for 2 hours, 8 hours and 24 hours nitriding times. The flow rate and pressure of nitriding is at 50 – 100 mmHg with gas composition 500 and 500 . The sample need to be etching in Viella's Etching solution before observing the microstructure via Optical Microscope. Scanning Electron Microscope-Energy Dispersive Spectroscopy (SEM-EDX) is used to investigate the nitrogen composition diffuse into the steels all of the samples. Investigating Micro hardness of surface and cross section hardness of Ferritic Stainless Steels, Vickers Hardness LECO LM247 AT is being used following ASTM E384 standard.

IV. RESULT AND DISCUSSIONS

A. Optical Microscope

Figure 4.2 and Figure 4.3 shows the microstructure of Unnitrided FSS at 100x Magnification and 500x Magnification respectively. Figure 4.1 and Figure 4.4 shows the microstructure of Nitrided FSS in Ammonia environment for 2 Hours at 600 at 100x Magnification and 500 x magnifications correspondingly. 100x and 500x magnifications in Figure 4.5 and Figure 4.6 are of microstructure of Nitrided FSS in Ammonia environment for 8 Hours at 600 . Meanwhile, Figure 4.7 and Figure 4.8 show the microstructure of Nitrided FSS in Ammonia environment for 24 Hours at 600 at magnification of 100x and 500x accordingly. All samples are under slow cooling process. Figure 4.3 shows that the sizes of grain boundaries are bigger compare to the rest of the sample, this due to the slow cooling process during heat treatment and manufacturing process at high temperature (1000 to 1200) which higher than crystalline temperature. Throughout the cooling process, the small grain will merge each other resulting bigger size of grain formed. Figure 4.4, Figure 4.5 and Figure 4.8 shows that the number of grain boundaries increases with nitriding time, the size of grain boundaries decreases with nitriding

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International Journal of Engineering Research in Mechanical and Civil Engineering (IJERMCE)

Vol 3, Issue 4, April 2018

time. The Metal- Nitride Precipitation concentration increases as shown in Figure 4.4, Figure 4.6 and Figure 4.7 respectively, this conclude that increasing in nitriding time will increase hardness of material at the same time also increase the Metal-Nitride concentration in the steels.

a. Unnitrided Ferritic Stainless Steel

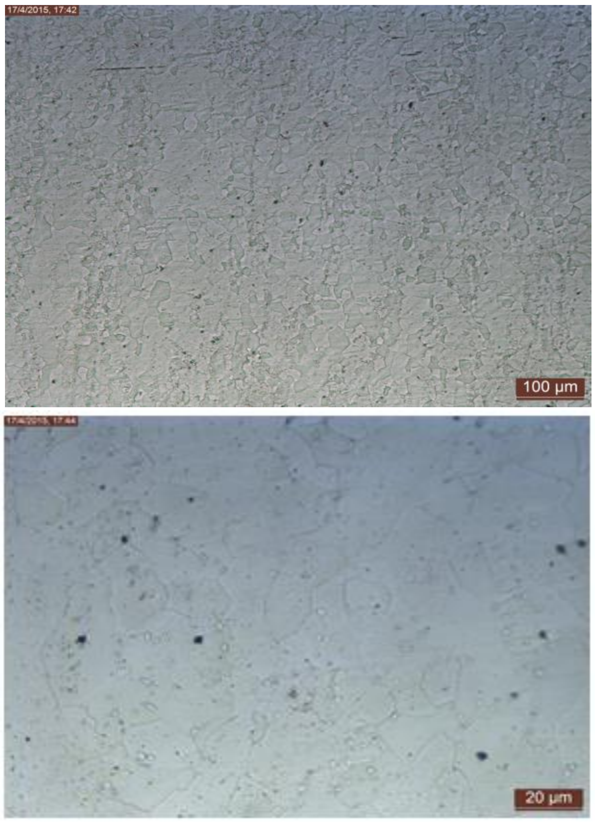

Figure 4 2: Optical Microscope of Unnitrided FSS (500x Magnification)

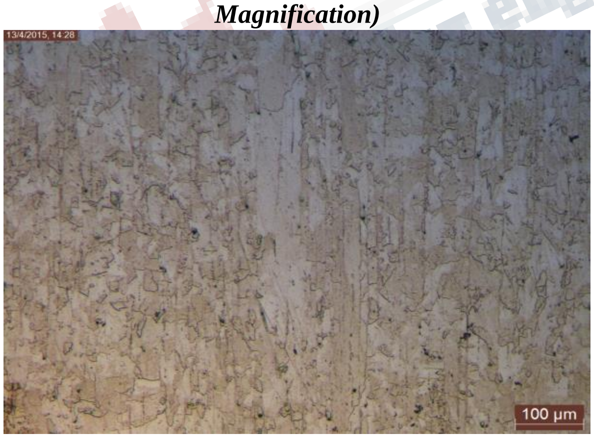

Figure 4 3: Optical Microscope of Nitrided FSS for 2 Hours in Ammonia Environment at 600 (100x Magnification)

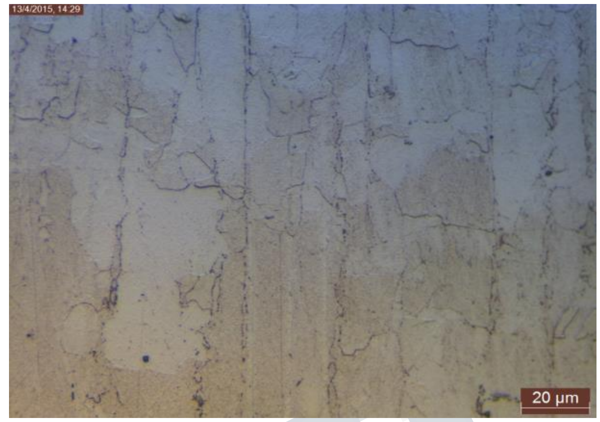

Figure 4 4: Optical Microscope of Nitrided FSS for 2 Hours in Ammonia Environment at 600 (500x Magnification)

C. Nitrided Ferritic Stainless Steel at 8 hours

Figure 4 5: Optical Microscope of Nitrided FSS for 8 Hours in Ammonia Environment at 600 (100x Magnification)

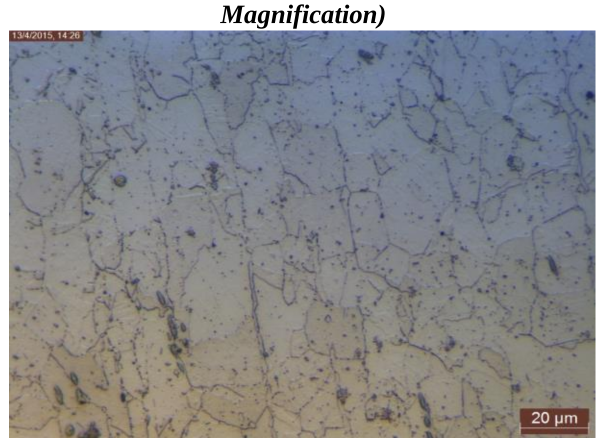

Figure 4 6: Optical Microscope of Nitrided FSS for 8 Hours in Ammonia Environment at 600 (500x Magnification)

ISSN (Online) 2456-1290

International Journal of Engineering Research in Mechanical and Civil Engineering (IJERMCE)
Vol 3, Issue 4, April 2018

D. Nitrided Ferritic Stainless Steel at 24 hours

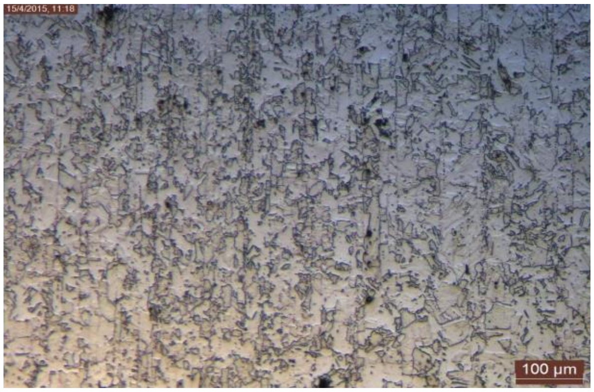

Figure 4 7: Optical Microscope of Nitrided FSS for 24 Hours in Ammonia Environment at 600 (100x Magnification)

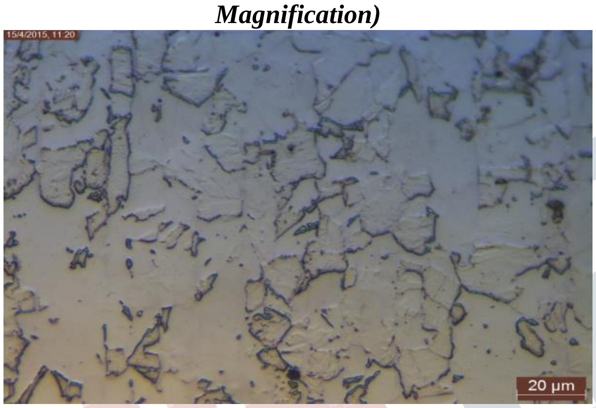

Figure 4 8: Optical Microscope of Nitrided FSS for 24 Hours in Ammonia Environment at 600 (500x Magnification)

***B.* Micro Hardness Properties**

a. Overall Micro Hardness Properties

Vickers Hardness testing conducted to investigate hardness at random area of the samples. The indentation locations have been shown in Figure 3.4 above, with spacing around 20 between and Zip-Z pattern of indentation. The Vickers Hardness testing conducted using 100gf load, equivalent to 100 Hv. The Result of Vickers Hardness of overall area as shown in Table 4.1 and Figure 4.9 below. Table 4.1 and Figure 4.9 shows that the comparison Vickers hardness for Unnitrided FSS, Nitrided FSS in Ammonia environment for 2 hours, 8 hours and 24 hours. From the result shows that the hardness of FSS increases with Time Nitriding, Unnitrided FSS have lowest hardness due to High Temperature heat treatment (1000-1200) which above crystalline temperature follows by slow cooling, lead to merging of grains, forming bigger size grain, reducing the number of grain boundaries available, thus reducing strength of material.

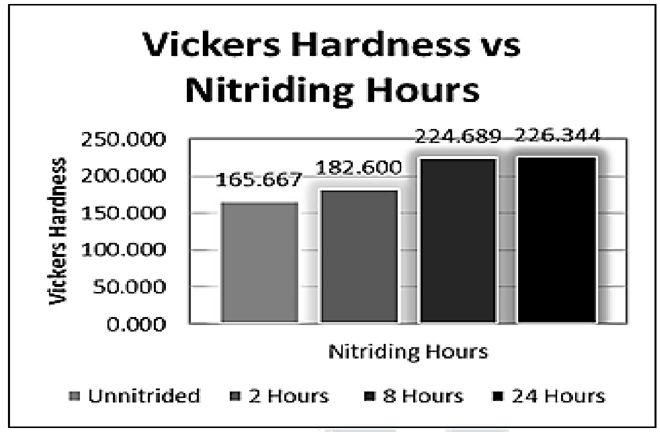

Figure 4 9: Vickers Hardness value for overall cross section FSS

b. Cross-Section Micro Hardness Properties

Figure 4.10 shows the Vickers Hardness value with the depth under the surface for Unnitrided and Nitrided Ferritic Stainless steel, Unnitrided FSS, Nitrided in Ammonia environment for 2 hours, 8 hours and 24 hours. For Unnitrided FSS, the hardness value changes randomly with the depth under the surfaces. Meanwhile, for Nitrided FSS in Ammonia environment, the hardness value decreases with increases of depth under the surface, proportional to the nitrogen content diffuse under the surface of Nitrided FSS for 2 hours, 8 hours and 24 hours. The surface having high hardness value due to the high concentration of nitrogen available compare to Inner area due to diffusion barrier and diffusion limitation to the centre of the materials. Vickers hardness of unnitrided FSS change randomly with cross section distance due to unbalance cooling of the material and different concentration of inert particle inside the material. Outer layer will cool faster than inner layer resulting formation of bigger size of grains in the inner area**.**

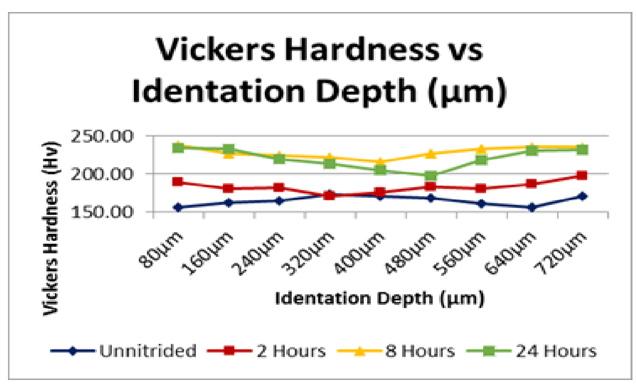

Figure 4 10: Cross-section hardness of Nitrided Ferritic Stainless Steels

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International Journal of Engineering Research in Mechanical and Civil Engineering (IJERMCE)
Vol 3, Issue 4, April 2018

C. Scanning Electron Microscope EDX

Figure 4.11 shows SEM-EDX of Unitrided Ferritic stainless steel, the reading is pointed at random location to investigate particle concentration inside the steel. Meanwhile, Figure 4.12, Figure 4.13 and Figure 4.14 shows SEM-EDAX of nitride FSS at different period of time. The reading is taken every 80µm, to investigate the nitrogen particle diffusion rate inside the steel. From Figure 4.15, we can conclude that the nitrogen diffusion rate decreases with cross-section depth under the surface. Figure 4.16 shows average particle concentration of nitrided Ferritic stainless steels at 2 hours, 8 hours and 24 hours. From the figure we can clearly see that overall nitrogen particle concentration increases with nitriding time. Increasing in composition of nitrogen will increase the dislocation barrier, fill up the space available, finally will increase the overall hardness of the material, as shown in Figure 4.17 below.

A. Unnitrided Ferritic Stainless Steel

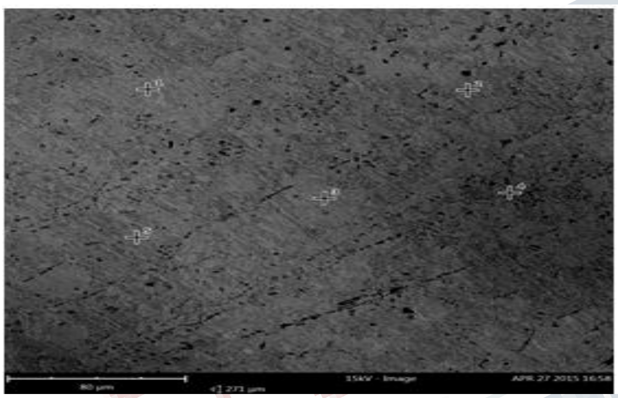

Figure 4 11: SEM- EDX of Unnitrided FSS

B. 2 Hours Nitrided Ferritic stainless steel

Figure 4 12: SEM-EDX of Nitrided FSS in Ammonia environment for 2 hours at 600 follows by slow cooling.

C. 8 Hours Nitrided Ferritic stainless steel

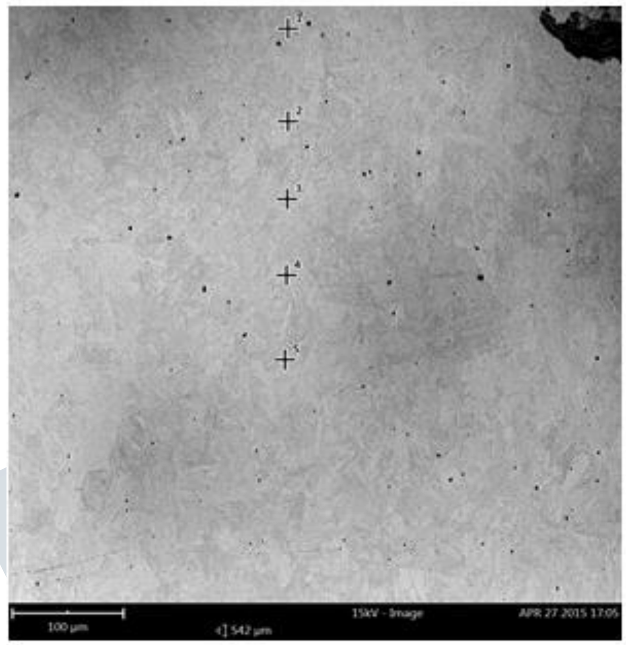

Figure 4 13: SEM-EDX of Nitrided FSS in Ammonia environment for 8 hours at 600 follows by slow cooling.

d. 24 Hours Nitrided Ferritic stainless steel

Figure 4 14: Figure 4 8: SEM-EDX OF Nitrided FSS in Ammonia environment for 24 hours at 600 follows by slow cooling.

ISSN (Online) 2456-1290

International Journal of Engineering Research in Mechanical and Civil Engineering
(IJERMCE)
Vol 3, Issue 4, April 2018

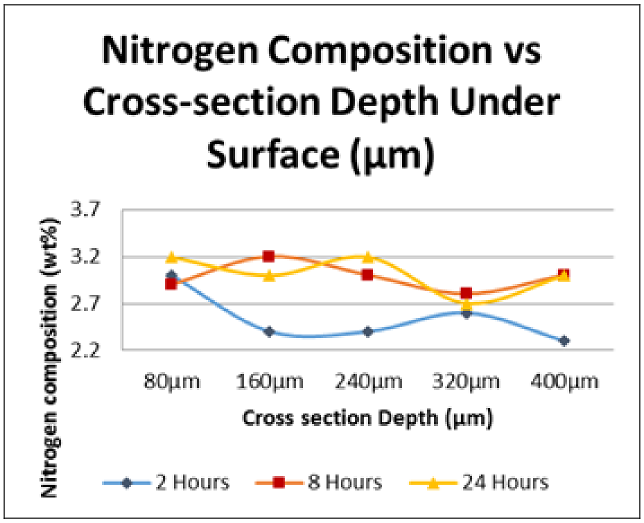

Figure 4 15: Cross Section Particle Concentration of nitride Ferritic Stainless Steel

Table 4 1: Average Nitrogen composition of nitride FSS in Ammonia environment for 2 hours, 8 hours and 24 hours

Nitriding Hours	Unitrided	2 Hours	8 Hours	24 Hours
80µm	0.0	3	2.9	3.2
160µm	0.0	2.4	3.2	3
240µm	0.0	2.4	3	3.2
320µm	0.0	2.6	2.8	2.7
400µm	0.0	2.3	3	3
Average Nitrogen Composition	0.0	2.540	2.980	3.020

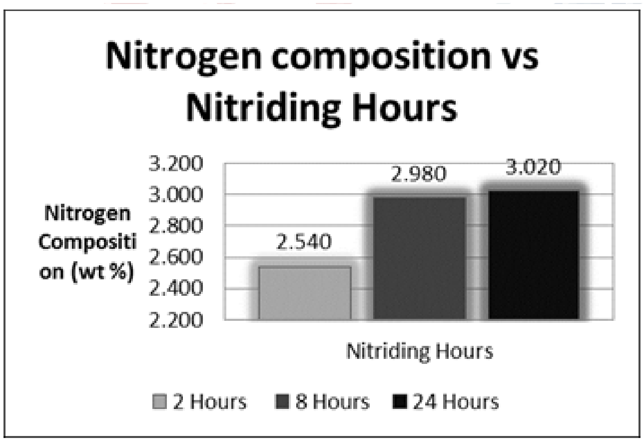

Figure 4 16: Nitrogen compositions at different nitriding time

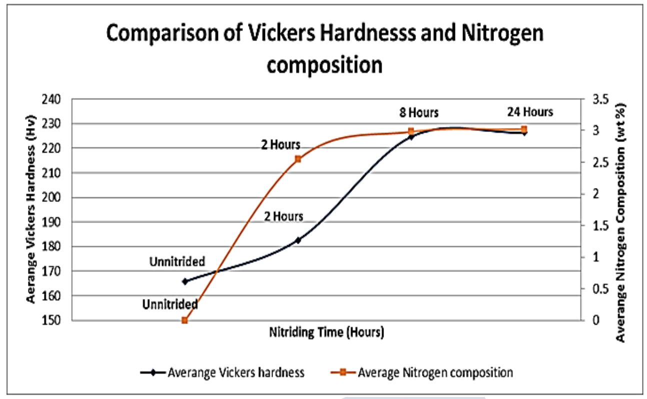

Figure 4 17: Comparison of Vickers hardness and Nitrogen composition with Nitriding time

IV. CONCLUSION AND RECOMMENDATIONS

A. Conclusion

Unitrided Ferritic Stainless steel grade 430L have bigger sizes of grain compare to Nitrided Ferritic Stainless Steel, this is due to heat treatment during manufacturing process. Heating at higher than crystalline temperature, small grain merges each other forming bigger size of grain. The number of grain boundaries increasing with time of nitriding respectively, thus increase the hardness value of Nitrided FSS. The hardness value for untrided, 2 h nitride, 8 h and 24 h were 165.67 Hv, 182.6 Hv, 224.69 Hv and 226.34 Hv, respectively. Thus the highest hardness was determined for sample nitride at 24 h. The hardness increase by 30 % compares to untrided sample. The hardness increases at decreasing rate, due to high concentration of nitrogen inside the steel. Micro hardness of materials decreases with depth under the surface, the weakest point is located at the centre of the material which is the deepest depth diffusion rate can diffuse. This due to the concentration of metal particle increases along the diffusion path, reducing the space for diffusion rate to occur. The concentration of Nitrogen inside the metal reduces with the depth under the surface. Nitrided Ferritic stainless steels at 24 hours have the highest nitrogen content compare to Nitrided Ferritic stainless steel at 8 hours and 2 hours. Unnitrided Ferritic stainless steels have the lowest nitrogen content. The nitrogen composition of nitrided FSS increases at decreasing rate with respect to nitriding time. The micro hardness of FSS depends with microstructure of the material. The smaller the grain size, the harder the materials. The strength of material increases proportionally with increasing of composition of nitrogen in the steel. Therefore, the objectives of the research have been achieved.

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Vol 3, Issue 4, April 2018

B. Recommendation

Some improvements need to be done in order to obtain more detail and more precise result. Recommendation for the result improvement is effect of nitriding towards corrosion rate of the steel, and comparison effects of nitriding in argon environment, nitriding in nitrogen environment and also nitriding in high temperature gas nitriding.

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