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Nitride alloy layer formation of duplex stainless steel using nitriding process

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Abstract. Duplex stainless steel (DSS) shows a good corrosion resistance as well as the mechanical properties. However, DSS performance decrease as it works under aggressive environment and at high temperature. At the mentioned environment, the DSS become susceptible to wear failure. Surface modification is the favourable technique to widen the application of duplex stainless steel and improve the wear resistance and its hardness properties. Therefore, the main aim of this work is to nitride alloy layer on the surface of duplex stainless steel by the nitriding process temperature of 400°C and 450°C at different time and ammonia composition using a horizontal tube furnace. The scanning electron microscopy and x-ray diffraction analyzer are used to analyse the morphology, composition and the nitrided alloy layer for treated DSS. The micro hardnesss Vickers tester was used to measure hardness on cross-sectional area of nitrided DSS. After nitriding, it was observed that the hardness performance increased until 1100 Hv0.5kgf compared to substrate material of 250 Hv0.5kgf. The thickness layer of nitride alloy also increased from 5µm until 100µm due to diffusion of nitrogen on the surface of DSS. The x-ray diffraction results showed that the nitride layer consists of iron nitride, expanded austenite and chromium nitride. It can be concluded that nitride alloy layer can be produced via nitriding process using tube furnace with significant improvement of microstructural and hardness properties.

1. Introduction

Duplex stainless steel consists of approximately similar amounts of austenite and ferrite phases. DSS is widely used as a paper machinery and paper industry machinery, pressure vessels, pipes and heat exchangers as well as offshore applications and chemical tankers. It is because of the excellent performance with its high strength and stress corrosion resistance. However, duplex stainless steel expressed lower hardness and poor wear resistance during service. Therefore, a new development of surface modification could be a vital solution to produce hard protective layer or coating on duplex stainless steel. Surface modification can be categorized into several types which are melting process [1],[2], thermochemical nitriding [3], and laser cladding [4].

Thermochemical gas nitriding is categorized under surface hardening process, where nitrogen is diffused into the surface of steel using dissociated ammonia and nitrogen gas at a certain composition as the source. This process is mainly applied to steels and consists of enriching the surface of the material to be treated with certain metalloids. The gaseous compound containing the nitrogen element is supplied and deposited to the surface of material via diffusion mechanism. Steels that have undergone this treatment are characterized by good resistance to wear, abrasion and fatigue [5]. However, the process must be controlled and ensure the process temperature is not too high to avoid the reduction of corrosion resistance.

Subbiah et al. [6] demonstrated that low temperature nitrided process of AISI 316LN austenitic stainless steel have been successfully employed to increase the hardness and better wear resistance. The hardness of the untreated sample was found to be 330 Hv, while for treated sample achieved maximum surface hardness ~1269 Hv. The compound layer thickness increased by increasing the nitriding temperature. The formation of S-phase as the nitride layer contributed from the gas nitriding process at 500°C with the gaseous mixture of ammonia and hydrogen. Paijan et al. [7] observed that the thermochemical nitriding process on DSS using tube furnace has produced increment of hardness from 250Hv to 666.3 Hv. This is due to nitride layer formation at temperature treatment of 450°C for 6 hours with 50% of ammonia composition. This nitride layer is the result of the quantity of nitrogen supplied to the surface and its diffusion into the structure surface. However, at temperature 500°C, the dark phases in the nitride layer is associated with chromium nitride has developed and reduce the corrosion resistance of material. In this study, the mixtures of nitrogen and ammonia gas were used for low temperature nitriding techniques and the temperature is restricted at 400°C and 450°C.The purpose of this investigation is to analyse the characteristics of nitride alloy layer which was formed on DSS after nitriding using tube furnace.

2. Experimental procedures

The material used for this study was duplex stainless steel with the grade specification of AISI 2205. The chemical composition of the AISI 2205 duplex stainless steel is 22% chromium, 5.7% nickel, 3.1 moleybdenum, 0.17% nitrogen and 0.02 % carbon. The duplex stainless steel sample was cut into a small size of 12.5 mm x 33 mm x 10 mm. The surface of the duplex stainless steel sample was ground using 250, 350, 500, 800, and 1200 grades of emery paper. Then polished using alumina paste in order to remove the scratch marks or contamination during grinding.

Prior to nitriding process, the samples were immersed in concentrated hydrochloric acid (2M) for 15 minutes with the purpose to remove native oxide film on the surface. This oxide layer is believed to act as a barrier for diffusional nitrogen transport. After immersion, the samples were removed from the beaker. Then, the samples were placed at the alumina specimen holder and put in tube furnace immediately. Prior to heat treatment, the furnace was purged by nitrogen for 30 minutes to remove air containing oxygen whilst heating up to the desired temperature. The nitriding thermal cycle is showed in figure 1.

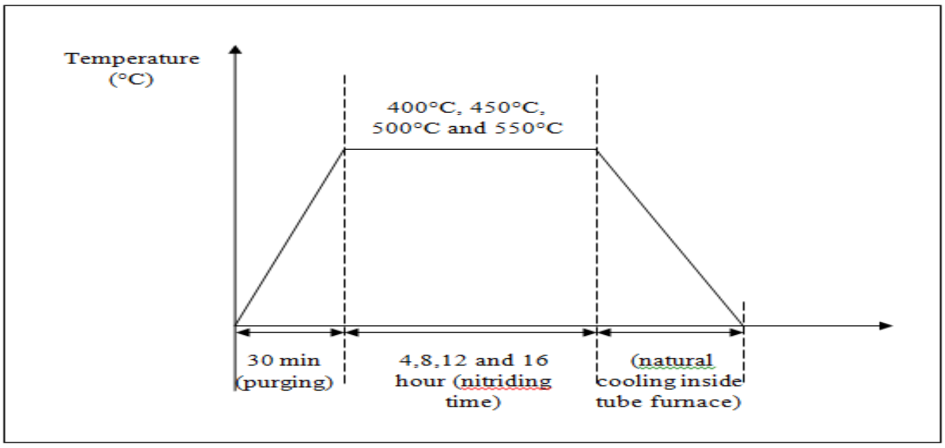

Figure 1. Nitriding thermal cycle for DSS.

The nitrided alloy layer was analysed for their hardness property using Vickers hardness tester on the cross sectional area. The test used load of 500 gm and dwelling time of 10 seconds. The phase analysis was done using x-ray diffraction whereas thickness layer measurement and micrograph using scanning electron microscopy. Table 1 showed the parameters for the experiments.

Table 1. Parameters for the experiment.

No. of run	Temperature (°C)	Time (hrs)	*Composition of ammonia(%)
1	400	4	20
2	400	8	30
3	400	12	40
4	400	16	50
5	450	4	30
6	450	8	20
7	450	12	50
8	450	16	40

*Balance is nitrogen gas

3. Results and discussion

3.1. Thickness layer and microstructure analysis

The nitride thickness layer of the nitrided duplex stainless was measured using scanning electron microscopy. Table 2 has showed the thickness layer of the nitrogen diffused with the respective parameters. Referring to figure 2 and 3, white layer is visibly which was formed on all nitrided samples. The white layer is also known as compound zone is made up of a nitride which is either involving of iron nitride or others complex nitride layer. It is not desirable because of the white layer is very brittle however, it has an extremely hard behavior. Therefore, it is necessary to remove the white layer after nitriding process to maintain the performance of nitrided samples. Besides that, an alloy nitride layer could be seen in all of the nitrided duplex stainless steel except for the samples treated at 400°C for 4, 8 and 12 hours and sample 450°C at 4 hours. However, the mentioned samples exhibited the existance of the diffusion zone as well as the white layer.

The largest thickness layer was produced at 450°C temperature for16 hours of nitriding time with 40% ammonia composition. The longer time and higher temperature of nitriding process has developed high amount of nitrogen element diffused in the nitride alloy layer of DSS [7]. According to the previous research, the thickness layer is dependable on the nitriding temperature [8]. The lowest thickness layer was developed at 400°C for 4 hours with 20% ammonia composition. This is due to insufficient temperature and time for nitrogen to diffuse in the surface layer. However, after 12 and 16 hours of nitriding, the nitrogen was reacted with chromium to form cromium nitride precipitate with dark phases which led to the depletion of chromium in the solid solution phase of the nitrided alloy layer as can be seen in figure 2 (c and d) and figure 3 (c and d). The formation of chromium nitride precipitates leads to the deterioration in corrosion resistance of DSS.

Table 2. Thickness layer and surface hardness of nitride alloy layer with respective parameters.

No. of Run	Temperature (°C)	Time (hrs)	Percentage of Ammonia	Thickness layer (μm)	Maximum surface hardness

					$(Hv_{0.5kgf})$
1	400	4	20	5.00	305.0
2	400	8	30	37.78	450.8
3	400	12	40	55.35	417.4
4	400	16	50	95.52	1000
5	450	4	30	15.6	353.0
6	450	8	20	45.00	513.3
7	450	12	50	88.00	428.8
8	450	16	40	100.00	1100.0

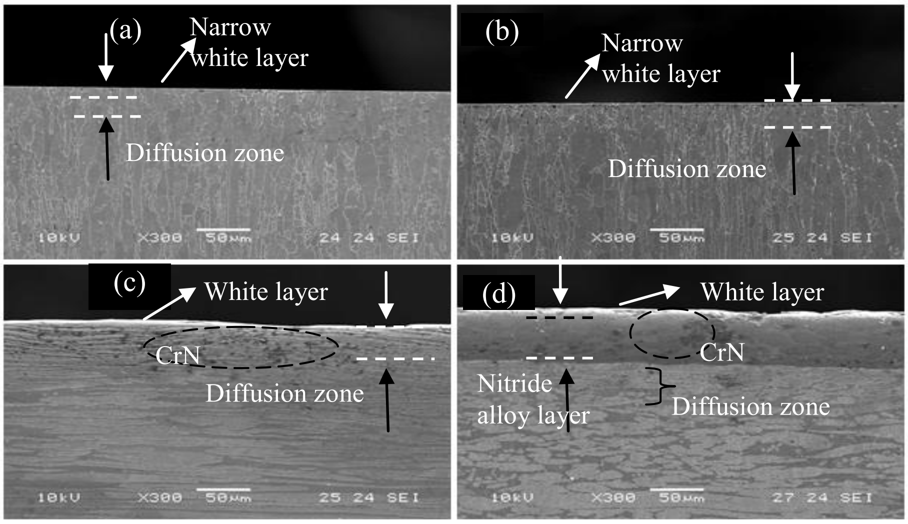

Figure 2. SEM micrographs of cross-sectional area at 400 ºC of nitrided alloy layer: (a) 4 hour, (b) 8 hour (c) 12 hour and (d) 16 hour.

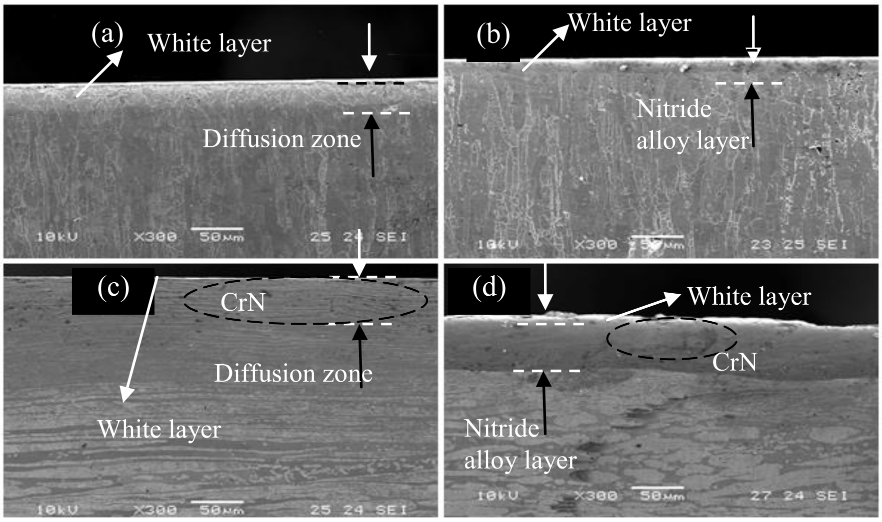

Figure 3. SEM micrographs of cross-sectional area at 450 ºC of nitrided alloy layer: (a) 4 hour, (b) 8 hour (c) 12 hour and (d) 16 hour.

3.2 Vickers micro-hardness

The hardness of nitride alloy layer at the surface of DSS was tabulated in Table 2. It can be observed that all nitride alloy layer has improved the hardness compared to untreated hardness of 250Hv. This improvement associated from the formation of expanded austenite and be confirmed from the XRD result in figure 4. The hardening effect is significant due to diffusion of nitrogen into the surface of nitrided specimen to form expanded austenite or S phase layer. This result has a good agreement with previous researcher by Subbiah et al. [6]. The highest hardness produced at 450°C of temperature and 16 hours of time with 40% ammonia composition while the lowest thickness layer was developed at 400°C for 4 hours with 20% ammonia composition. This result depending on the amount of the nitrogen diffusion in the layer at different time and temperature. The trend of hardness is increasing as the temperature and time for nitriding process increase. In addition, the formation of CrN in the nitride layer at a specific range of temperature an time could lead to increasing of hardness.

3.3. Phase analysis of XRD

The phase analysis was conducted on the surface of the untreated and nitride alloy layer duplex stainless steel. In figure 4, the untreated DSS consists of α and γ phases at angle of 35º to 90º. For all treated DSS in figure 4 and 5, both peaks still exist but the peak was slightly shifted to lower angle due to formation of expanded austenite, $\gamma_{N.}$ This is the result of the quantity of nitrogen supplied to the surface and its diffusion into the structure. However, after the nitriding time increased to 12 and 16 hours, the chromium nitride precipitate is formed in the nitride alloy layer. The formation of this phase is similar to those observed in plasma nitrided and fluidized bed nitrided samples of austenitic stainless steels, and can be attributed to the decomposition of the expanded austenite and formation of chromium nitrides [3]. The formation of CrN on the nitride layer makes the nitrided duplex stainless steel become harder which increases the hardness properties, but the previous researcher found that it also led to weakening the corrosion resistance [8].

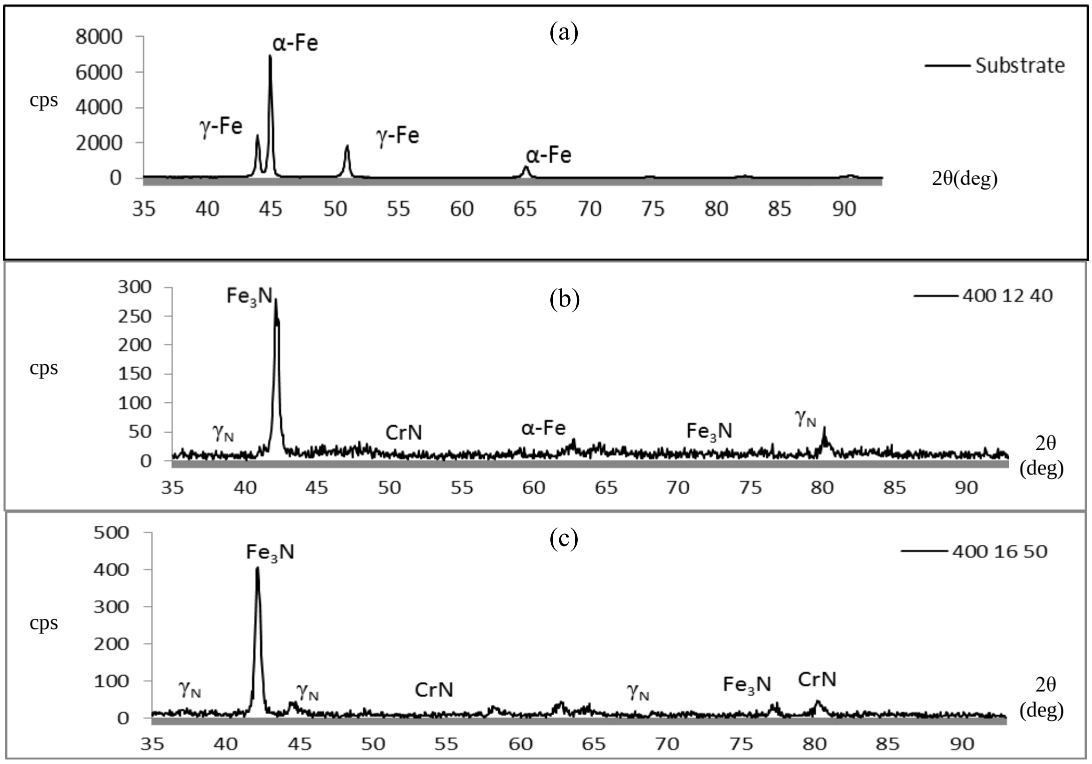

Figure 4. XRD patterns for DSS (a) substrate material (b) nitriding at 400°C + 12 hours + 40%NH_3 (c) nitriding at 400°C + 16 hours + 50%NH_3.

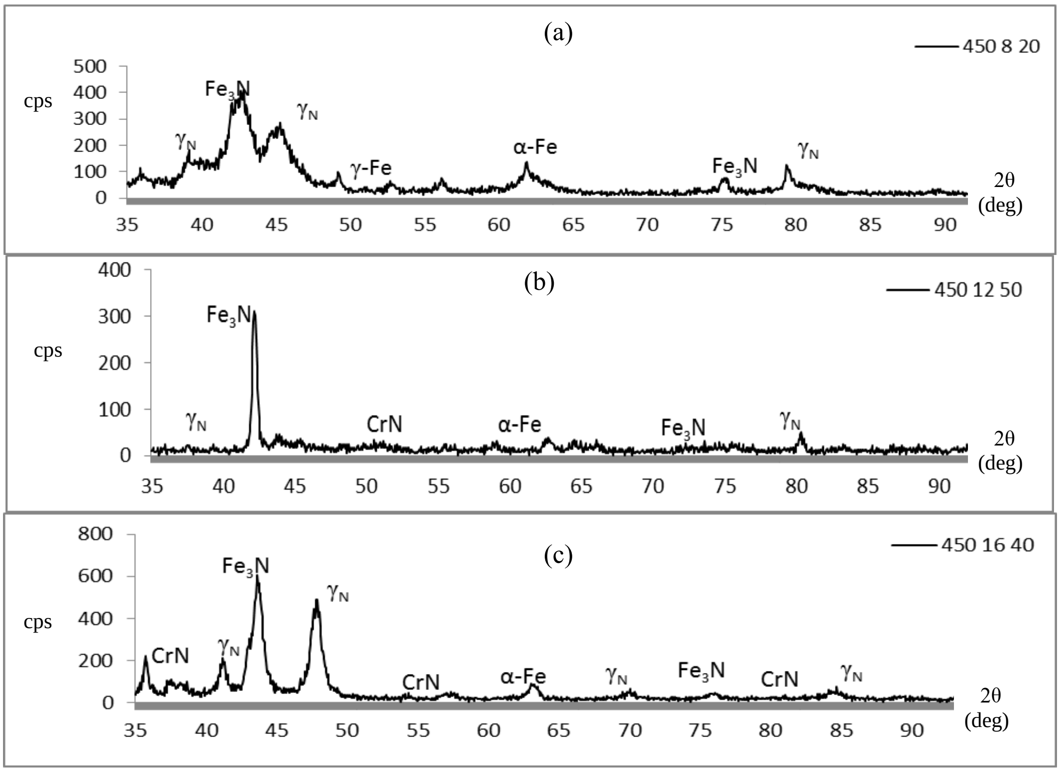

Figure 5. XRD patterns for nitriding DSS at 450°C (a) 8 hours + 20%NH_3 (b) 12 hours + 50%NH_3 (c)16 hours + 50%NH_3.

4. Conclusion

From the results, it can be concluded that the nitriding process is a feasible technique to produce hard nitride alloy layer on DSS. At temperature 400ºC and 450ºC, the formation of expanded austenite can be developed; however, increased treatment time such as 12 and 16 hours significantly contributes to the formation of chromium nitride which in turn can reduce the corrosion resistance. Therefore, the possible formation of chromium nitride temperature and time range should be avoided.

Acknowledgement

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