

EFFECTS OF TEMPERATURE ON THE FORMATION OF NITRIDE SURFACE LAYER VIA THERMOCHEMICAL GASEOUS NITRIDING PROCESS

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Abstract. Thermochemical gaseous nitriding is a surface modification process used for specific applications especially wear resistance components. The work aims to develop a formation of a modified surface layer on duplex stainless steel (DSS) using a gaseous thermochemical nitriding process using a tube furnace. This study investigated the effects of the nitriding temperature on the hardness and microstructure of the modified surface layers obtained on duplex stainless steel. The thickness of the hard surface layer, microstructure, phase composition, top surface and hardness profile were evaluated. The results obtained demonstrated that different temperatures influence the hardness and structural characterization of the nitrided samples. The expanded austenite in nitrided layer DSS improved the hardness performance 1 to 3 times higher than the untreated DSS that has strong correspondence to the formation of microstructural features, intermetallic compound and hard layer thickness. It was found that the nitrided layer at a temperature of 550 °C produced the highest hardness at the top surface with 603.4 Hv. However, the formation of chromium nitride contributes to the reduction of the corrosion resistance of duplex stainless steel. Therefore, the nitriding temperature at 450 °C experienced a hardness increment with 428.8 Hv and the thickest hard surface layer without the formation of chromium nitride.

Keywords: Temperature, gaseous nitriding, duplex stainless steel, structural characterization

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Introduction

In the gaseous nitriding process, nitrogen gas is supplied to the furnace's treatment environment, usually ammonia gas (NH_3). It disassociates into nascent nitrogen and hydrogen when the material is heated with ammonia gas. Then, the nascent nitrogen diffuses into the material's surface, promoting the formation of a hard surface layer, namely the nitride layer. This process requires a suitable combination of temperature, time and gas composition. The surface modification using a low temperature of the thermochemical process is a successful method to solve the problem of energy costs and reduce the adverse effect on the environment. The traditional heat treatment process for steel usually requires high energy input to obtain the desired properties for surface modification. Example of conventional thermochemical heat treatments is carburizing, nitriding and carbo-nitriding which are generally used at a temperature between 800 °C and 1000 °C [1].

In this study, the low temperature thermochemical gas nitriding is one of the conventional thermochemical processes using the treatment temperature below 600 °C. The advantages of using this low-temperature thermochemical nitriding process are decreasing cycle times, reduce costs for electricity, increasing the manufacturing facility's production capacity, energy-saving, and reducing material distortion. Due to these reasons, this process is considered feasible technique to develop a hard surface layer with better surface properties in terms of hardness and wear resistance. It has become a substantial research interest for many years by many researchers [2-5]. The improvement of wear properties and hardness relies on developing of a hard layer and an underlying diffusion zone in the surface adjacent region of the sample [6,7]. Previous research by Balasubramanian et al., [8] has found that the plasma ion nitriding carried out at a temperature of 500 °C on titanium alloy has made it possible to produce nitrides in the surface layer. The result demonstrated excellent hardness, corrosion and wear resistance compared to the substrate material.

The study conducted by several researchers explored the opportunity to perform nitriding and carburizing techniques in the past. De Las Haras et al., [9] demonstrated that the austenitic stainless steel (316 L) nitrided using the plasma method is feasible to produce a hard surface layer due to the formation of expanded austenite and Fe_3N . The corrosion results showed an improvement in the corrosion resistance for the sample without the formation of chromium nitrides. Previously, Luo et al., [10] investigated the three different types of plasma processes: nitriding, carburizing nitrocarburizing. The treatment process was conducted on 316 L stainless steel. The findings reveal that the plasma nitriding and nitrocarburizing exhibited higher surface hardness, about 4.5 times better than the substrate material.

In contrast to the extensive study and exploration activities on austenitic stainless steel, much less investigation is given to duplex stainless steel thermochemical processing. But only a few research has been carried out so far on carburizing, plasma nitriding, and hybrid nitriding of duplex stainless steel. In this study, the duplex-2205 was gaseous nitrided at different temperatures of 400 °C, 450 °C, 500 °C and 550 °C by keeping all the other processing parameters the same to investigate the effect of temperature nitriding on the performance of duplex stainless steel (DSS).

Materials and Methods

The material used in this study is DSS with grade 2205, which was received in the form of a plate with a dimension of 100 mm x 50 mm x 10 mm. The chemical composition of this material consists of chromium of 24.2 %, nickel of 4.82 %, molybdenum of 4.14 %, manganese of 1.59 % and balance of Fe. The samples were ground, and mirror polished using 0.3 μm and 0.05 μm Al_2O_3 pastes. In order to elevate the effective diffusion of nascent nitrogen into the surface, the samples are soaked in concentrated hydrochloric acid (HCl) for 15 minutes to remove the native oxide film on the surface. Then, the samples were placed in a sample holder namely a quartz boat with a vertical position to maintain the position of the samples during the nitriding process in the tube furnace. The sample is placed in the middle of the furnace to ensure that it receives the optimum heating zone and effective diffusion. The schematic diagram of the nitriding process is shown in Figure 1.

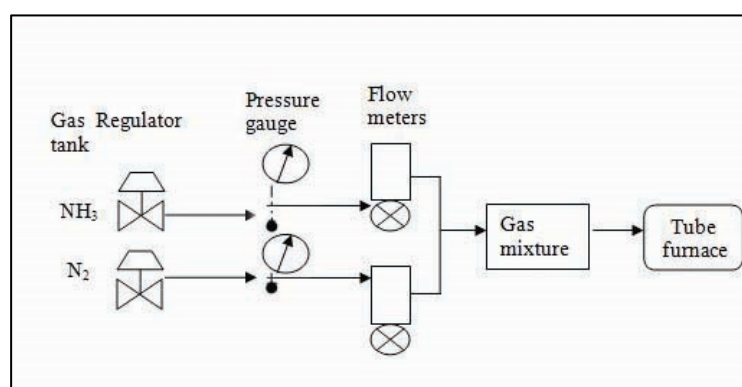


Figure 1: Schematic diagram of the Nitriding process experimental setup

The tube furnace of the thermochemical nitriding was subjected to a purging process using nitrogen gas for 30 minutes before the treatment. It keeps oxygen-containing air out of the furnace and any other leftover gaseous that could interfere with the nitriding process. When the temperature reached to the desired temperature, ammonia gas was introduced into the furnace to promote the diffusion of nascent nitrogen into the sample's surface. During the whole process, the gas flow rate for ammonia was kept at the same level at 0.3 % and nitrogen at 0.7 %. Meanwhile, the temperature varied between 400 °C and 550 °C. The sample ID is coded in Table 1 to classify the samples undergoing various treatment conditions.

Table 1: Sample ID for nitrided samples

Sample ID	Nitriding temperature (°C)	Nitriding time (hours)	Ammonia gas flow rate NH ₃ (%)
Untreated DSS	0	0	0
400-8-0.3	400	8	0.3
450-8-0.3	450	8	0.3
500-8-0.3	500	8	0.3
550-8-0.3	550	8	0.3

After the last cycle, the tube furnace was turned off and the sample was slowly cooled down inside the furnace. Then, the sample was cut into a cross-section layer to evaluate the

thickness layer, micro-hardness profile and microstructural observation. The samples were subjected to a standard metallographic preparation method including cutting, mounting, grinding, polishing and etching techniques. The surface of the samples was fine-ground using abrasive paper to a 1200-grit finish. After that, the samples are polished with 0.3 μm and finally with 0.05 μm alumina paste to remove very fine scratches and obtain a mirror-like surface. Then, the samples were etched using Kalling's reagent to reveal the microstructure and then dried using a hot dryer for one minute.

The top surface and hardness profile of the nitrided samples were measured using the Wilson-Welpert of Vickers micro-hardness tester. The hard surface layer of the sample is captured and measured to evaluate the thickness of the layer using a scanning electron microscopy machine, model JEOL JSM-5600. The intermetallic compound determination of the nitrided samples was performed using an XRD analyzer.

Results and Discussion

Hardness Analysis

The micro-hardness depth profile across the nitrided layer was conducted to measure the attainment of hardness value from the gaseous nitriding process. The hardness depth profile for the untreated DSS and nitrided sample at various temperatures is shown in Figure 2. It is noticeable that the nitrided layer DSS experienced went through an abrupt decrease in the hardness as it moved from the top surface into the downwards direction close to the substrate layer. This demonstrates that the hard surface layer was developed due to expanded austenite formed within a few microns, as observed by Sun and Haruman [11] and Maleque et al. [12].

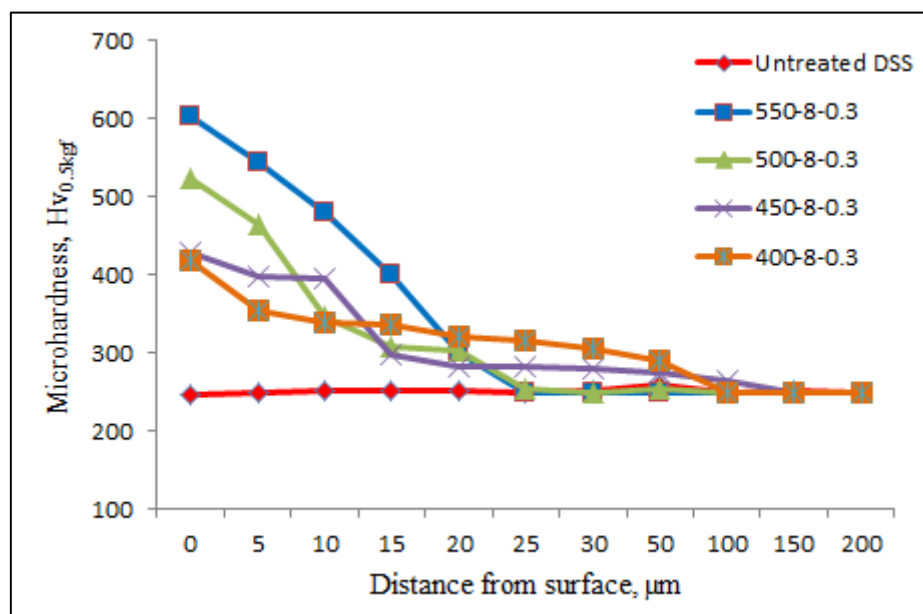


Figure 2: Hardness profile of the nitrided layer DSS cross-section at different temperatures of the nitriding process

It was discovered that the curve followed a similar trend with the gradual drop of the hardness from the outermost surface region of the nitrided layer to a position near the substrate interface, where it decreased rapidly. It could be attributed to the formation of expanded austenite from the influence of the nascent nitrogen that successfully diffused on the surface of DSS during the low-temperature thermochemical nitriding process. The findings in this study are in line with other researchers who also found that the lower temperature technique is feasible for producing expanded austenite in the diffusion layer [13,14].

The maximum surface hardness on the top surface is shown in Table 2. It can be seen that the hardness values for samples nitrided at 400 °C for eight hours are 417.4 Hv. The hardness values consistently increased for sample nitrided at 450 °C, 500 °C and 550 °C with hardness values of 428.8 Hv, 523.1 Hv and 603.4 Hv, respectively. The expanded austenite in nitrided layer DSS has produced hardness one to three times greater than the untreated DSS that has strong correspondence to the formation of expanded austenite microstructure. It proves that the temperature had a significant effect on producing higher hardness of the sample. The variation of surface hardness as a function of the nitriding temperature depends on the growth of the nitriding temperature relative to the surface hardness, which increases simultaneously.

Additionally, Table 2 demonstrated that sample 400-8-0.3 experienced the lowest hardness value of 417.4 Hv compared to other samples. It might be due to a low temperature of 400 °C promoting the high amount of nitrogen atoms to diffuse onto DSS surface. Even though the holding time in this sample was similar to other samples, it was not enough for the nitrogen atom to diffuse uniformly on the surface of DSS. The highest hardness was observed at sample 550-8-0.3 due to the higher nitriding temperature of 550 °C, which promotes the higher nitrogen concentration to diffuse on the surface of the nitrided sample.

Table 2: Thickness of hard surface layer and top surface hardness values for untreated and nitrided samples

Sample ID	Thickness of hard surface layer (μm)	Microhardness ($\text{Hv}_{0.5\text{kgf}}$) top surface
Untreated DSS	0	250
400-8-0.3	60.30	417.4
450-8-0.3	61.70	428.8
500-8-0.3	55.35	523.1
550-8-0.3	52.10	603.4

Structural Characterization of Nitrided Layers

Figure 3 shows the SEM cross-sectional view of the hard surface layer at different temperatures of the nitriding process. The SEM images show the formation of two different layer: nitride layer at the top of the surface and substrate layer at the bottom of the layer. The microstructure of the nitride or hard surface layer is in a form of bright appearance and resist to the etching reagent. The hard layer is known as expanded austenite in the upper layer samples due to the nitrogen diffusion on the DSS surface.

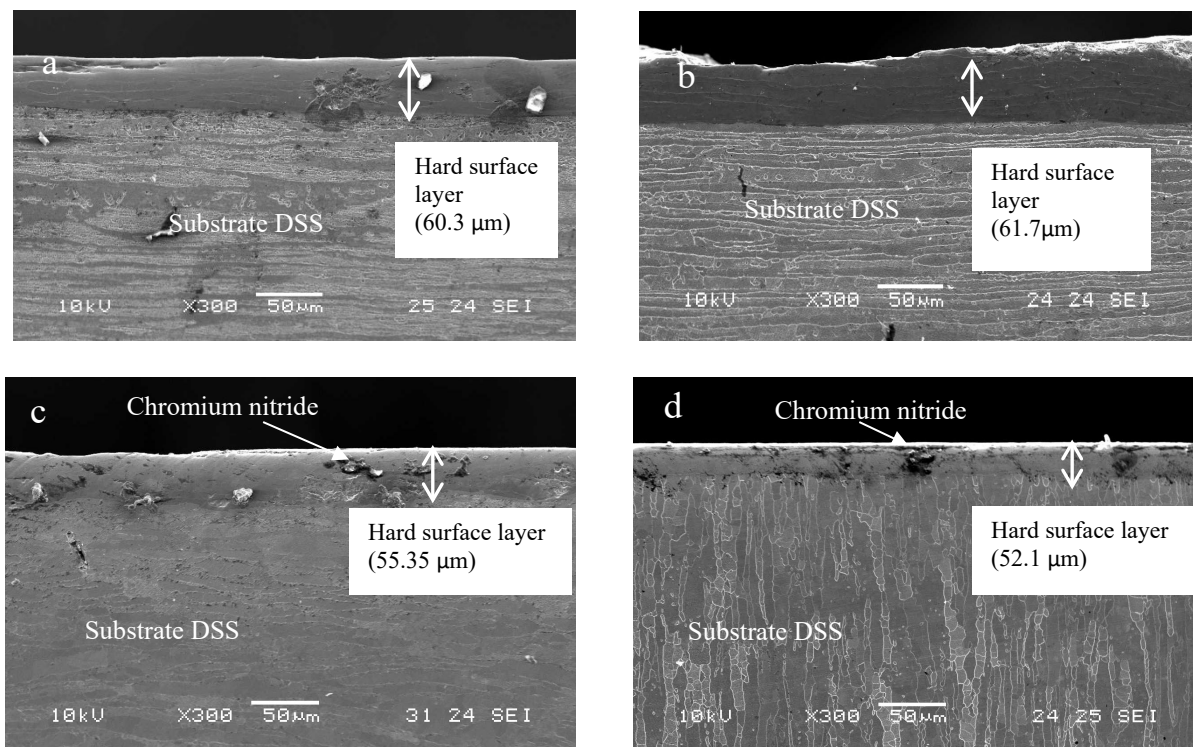


Figure 3: SEM cross-sectional view of nitrided layer at different temperature for samples; (a) 400-8-0.3, (b) 450-8-0.3, (c) 500-8-0.3 and (d) 550-8-0.3

Samples nitrided at a temperature of 400 °C and 450 °C showed a thickness layer of nitrogen-enriched with 60.3 μm and 61.7 μm , as presented in Figures 3(a) and (b) respectively. Meanwhile, the sample nitrided at temperature of 500 °C and 550 °C showed a hard surface layer with a thickness of 55.35 μm and 52.1 μm as can be seen in Figures 3(c) and (d) respectively. It can be seen that the sample exposed at 450 °C produced the largest thickness of the hard surface layer. It demonstrated the effective nitrogen diffusion into the surface of DSS at the temperature of 450 °C with the incorporation of a gas mixture ratio of 0.3 NH_3/N_2 for eight hours. The lowest thickness layer was observed at 550 °C with a hard surface layer of 52.1 μm . However, the hardness value for this sample is the highest compared to other samples. It might be contributed by the formation of chromium nitride in this sample as found by other researchers [15]. These structural features existed in the near surface region appeared in the form of dark phases for the sample treated above 500 °C in samples 500-8-0.3 and 550-8-0.3 as shown in Figures 3(c) and (d). This dark phase has been confirmed as a chromium nitride by XRD result, as shown in Figures 4(d) and (e).

The results obtained from dark phases have been agreed with previous work carried out by other researchers [2,3,11,16]. These phases have been claimed as chromium nitride, which can decrease the corrosion resistance of the DSS. This can be explained by the reaction of the chromium with nitrogen during the thermochemical nitriding process to incorporate each other to become chromium nitride. This phenomenon contributes to the reduction of chromium in the nitrided layer. The presence of chromium nitride initiates mainly at the upper part of the nitride surface. This is due to higher nitrogen accumulation on the surface compared to the sub-surface layer. However, this nitriding temperature can be considered acceptable for interior components applications.

XRD Analysis

The XRD spectra of the untreated and nitrided layer DSS at different temperature is shown in Figure 4. It can be observed that the DSS without treatment consists of α (ferrite) and γ (austenite) structures at 37.5° to 75° . For all nitrided layer samples in Figure 4 (b) to (e), it can be seen that both peaks for austenite at 43.94° and ferrite at 44.95° still remain but the peak slightly moved to lower angles. This could be explained due to the formation of γ_N (expanded austenite) and other intermetallic compounds. It was found that the diffusion of nitrogen to the surface layer contributes to the lattice movement and extension in the nitrided layer [16]. It also can be observed that a new intermetallic compound of Fe_3N (iron nitride) was developed in all nitrided samples.

In Figure 4, the samples nitrided at a temperature of $400^\circ C$ and $450^\circ C$ for eight hours exhibited the formation of expanded austenite without the presence of chromium nitride (CrN). These results suggest that the optimum hard surface layer can be obtained at this nitriding temperature without impairing the corrosion resistance of the DSS. However, samples nitrided at $500^\circ C$ and $550^\circ C$ were found to form chromium nitride precipitation in the nitrided layer. This agrees with the results reported by other researchers [9,14] on the formation of chromium nitride in austenitic stainless steel when nitrided by plasma and fluidized bed nitriding process. Moreover, the formation of CrN resulted in the increment of hardness value at the nitride layer [17].

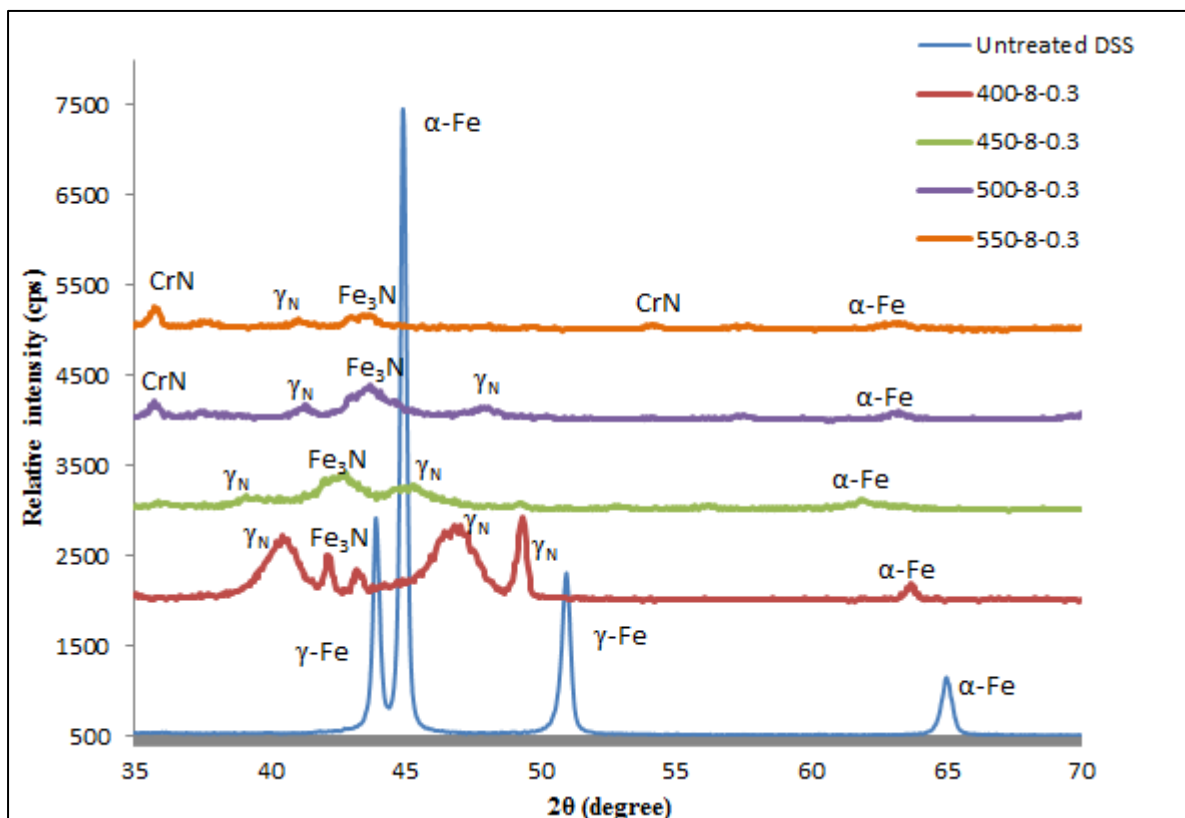


Figure 4: XRD Spectra of untreated DSS and nitrided layer at different temperature

Conclusions

The research aims to study the effects of temperature on the development of the nitride layer via the low temperature thermochemical gaseous nitriding. Based on the experimental results and discussions, the following conclusions can be summarized from this work:

- 1) The hard surface of nitrided layer DSS was successfully developed using a gaseous nitriding process incorporating NH_3 and N_2 gaseous via nitriding process at a different temperature from 400 °C to 550 °C.
- 2) The hardness values of the nitrided layer increased about one to three times higher than untreated DSS.
- 3) The structural characterization demonstrated the presence of a continuous and homogenous layer of expanded austenite in the nitrided layer. However, a higher temperature of 500 °C and a holding time of eight hours produced chromium nitride on the surface.
- 3) XRD spectra analysis shows the intermetallic compound on the top surface such as γN , Fe_3N and CrN at the nitrided layer.
- 4) The hardness increment correlates well to the formation of the hard surface layer, microstructural features, and intermetallic compounds.

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Author Contributions

All authors contributed toward data analysis, drafting and critically revising the paper and agree to be accountable for all aspects of the work.

Disclosure of Conflict of Interest

The authors have no disclosures to declare

Compliance with Ethical Standards

The work is compliant with ethical standards

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