International Review of Mechanical Engineering (I.RE.M.E.), Vol. 11, N. 8
ISSN 1970 - 8734 August 2017

White Layer Control on AISI 316L Using Temperature and Gas Nitriding Diffusion Stage Process

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Abstract – *The aim of the study was to compare the hardness properties resulting after the nitriding fluidized bed thermochemical treatments in different media and the diffuse temperature process, to evaluate the efficiency of the white layer formation on stainless steel substrats. The White layer is a layer with a high nitrogen atom concentration between the surface and the layer underneath. This concentration causes the layer to be hard and brittle. The use of diffusion stage after the boost stage (550 ^{0}C) in a fluidized bed reactor aims at reducing the formation of the white layer. The results show that a reduction in white layer is followed by the increase of brittleness in the form of crack formation in the layer underneath. The imbalance reaction due to the exothermic reaction is the primary reason. An increase in the atmosphere temperature without nitrogen gas during the diffusion stage increases the supersaturated reaction. The optimal process is fixed diffusion at boost temperature of 550 ^{0}C in the gas diffusion media without nitrogen. The use of atmosphere without nitrogen gas during diffusion increases the depth of diffusion of the nitrogen atom and reduces the white layer, thereby reducing brittleness. In addition, micro-cracks have been formed under white layers at the higher diffusion temperature of 650 ^{0}C.*

***Keywords**: Stainless Steel, White Layers, Higher Diffusion Temperature, Brittle, Exothermic*

I. Introduction

The gas nitriding process for stainless steel is often followed by the formation of white layers (consisting of iron nitrides Fe_4N - γ´ and/or $Fe_{2,3}N$ – ε). The diffusion layer is located bellow the white layer. The latter reduces the performance of stainless steel especially hardness and corrosion resistance. For most steels, temperature is one of the main influencing factors on phase composition and on the properties of the nitrided layer. A study by Yetim et al. [1] shows that the corrosion resistance of the nitrided layer decreases when the nitriding temperature is higher than 500 ^{0}C due to the formation of chrome nitride.

Stainless steel [1]-[19] has an excellent corrosion resistance due to the high content of Cr [2]. However, a high concentration of Cr is very difficult to be heat-treated to improve performance. Thus, it can be ascertained that stainless steel is rarely used for engineering purposes especially those requiring a wear resistance surface.

Equipments such as hydraulic and pneumatic components often use tool steel coated with hard chrome.

These are due to the influence of impurities such as nitrogen, oxygen and carbon that could react with the chromium. Gas nitriding process is a thermochemical surface hardening process that is widely used by the manufacturing industry because of its specialty, i.e., the resulting distortion is very low and is very suitable to be applied to small-sized components with high accuracy.

Stainless steel is not easy to be heat treated, especially at high temperatures due to the sensitization formation mechanism, where the material properties of stainless steel become brittle with low corrosion resistance. The phenomenon of corrosion formation could also occur in other materials, caused by reasons including the micro structure composition and morphology of the surface layer [2]. High temperature nitriding process on stainless steel also produces the S phase [3]. Other results [4], [5] suggest that, when nitriding temperature ranges from 500 ^{0}C to 650 ^{0}C, CrN emerges in the nitrided layer and increases the hardness and wear resistance of the modified layer.

The aim of this research is to observe the formation of the white layer on stainless steel at various temperature and media. The white layer is reduced by reducing the excess of nitrogen concentration on the surface of stainless steel specimens. The concentration of nitrogen atoms on the stainless steel surface was reduced by increasing the process temperature and reducing nitrogen gas and ammonia gas during boost process. In one of the authors' previous studies, utilizing chrome coating steel with a tool steel AISI 4140 type as substrate, the nitriding treatment without nitrogen gas medium during the boost process minimized the white layer [6].

Other occurring impacts are also discussed in this study such as the formation of cracks on the surface of the specimen. The elevated nitriding temperature has a positive effect on corrosion resistance [7].

 https://doi.org/10.15866/ireme.v11i8.11095

II. Methods

The stainless steel samples were surrounded by alumina powders in fluidised bed reactor. The samples were placed in the container maintaining a distance of about 10 cm between them and the edges of the container.

The process in fluidized bed reactor was the boost step using ammonia and nitrogen gas. The following step was the diffusion process that was carried out in muffle furnace (without nitrogen gas) and fluidized bed reactor (just used nitrogen gas).

The chemical composition of the stainless steel observed in this study is shown in Fig. 1(a) (spectrometry test).

The diffusion of N atom into the material during boost step changes the chemical composition and affects the white layer formation mechanism.

The nitrogen atom was provided to materials at a temperature of 550 ^{0}C (for 4 hours) with NH_3 and N_2 gas atmosphere media.

The subsequent stage is the diffusion stage that is the penetration of nitrogen that was present on the surface of materials at a temperature of 550 ^{0}C and 650 ^{0}C with or without nitrogen gas stream. The flow rate of gas depends on the temperature of nitriding process with 80% NH_3 and 20% N_2 with a total gas flow rate of 0.7 m^3 / h (Figure 1(b)).

Temperature depends on the gas flow in fluidized bed furnace [8].

The cross section and surface morphology of nitrided layers was observed through a scanning electron microscopy (SEM). The phase composition of the nitrided layer was determined by an X-ray diffractometer (XRD). Vickers hardness was measured under a load of 5 kgf.

Fe	C	Si	Mn	Mo	Cr
80.0	0.0712	1.85	0.330	0.194	14.9

Ni	Cu	Nb	Ti	V	Pb
0.411	0.324	0.04	0.0061	0.140	0.124

Fig. 1(a). Chemical composition of AISI 316L samples (%)

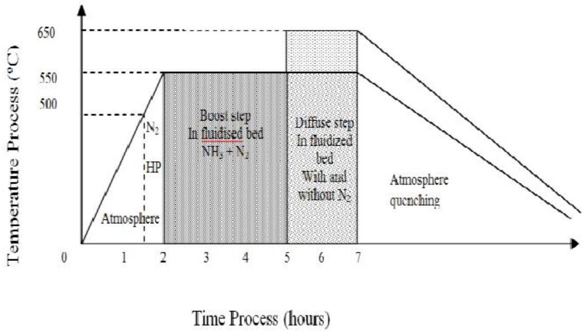


Fig. 1(b). Nitriding process by using two stage with different temperature and media in diffuse stage

III. Result and Discussion

Figures 2 show the nitride layer resulting from the diffusion process at various temperatures. Too high temperature during diffusion process in the muffle furnace (650 ^{0}C) creates a crack in the grain boundary under the white layer as shown in Figs. 2(c) and 2(d).

Consequently, surface peeling occurs on the white layers formed on the surface. The grain boundary cracks occur deeper during the diffusion stage with the increasing of temperature up to 650 ^{0}C compounded by the absence of nitrogen gas in the diffusion atmosphere.

This indicates that nitrogen gas has an important role in reducing brittleness of stainless steel by preventing the formation of grain boundary cracks at high temperatures.

This is due to the fact that high gas temperature in the nitriding process is reduced by flowing nitrogen gas which serves to lower the eutectoid temperature.

Figure 2(d) shows that the release of the white layer is due to the brittle phenomenon. Prominent differences also occurred in the structure beneath the lining compound, where brittleness is coupled with the formation of grain boundary cracks on the specimens that did not utilize nitrogen gas as a diffusion medium. In line with the increase in temperature, the grain boundary cracks formation also increases.

The use of nitrogen gas as a medium for diffusion at high temperatures reduces the stress between the grains and makes nitrogen atoms move through the grain boundaries. The release of nitrogen atoms is shown in EDAX analysis (Figures 3 and 4), in which the percentage of nitrogen decreased at 650 ^{0}C. The use of nitrogen gas atmosphere at 650 ^{0}C causes the nitrogen atom to be concentrated only on the top layer with a thickness of 5 μm.

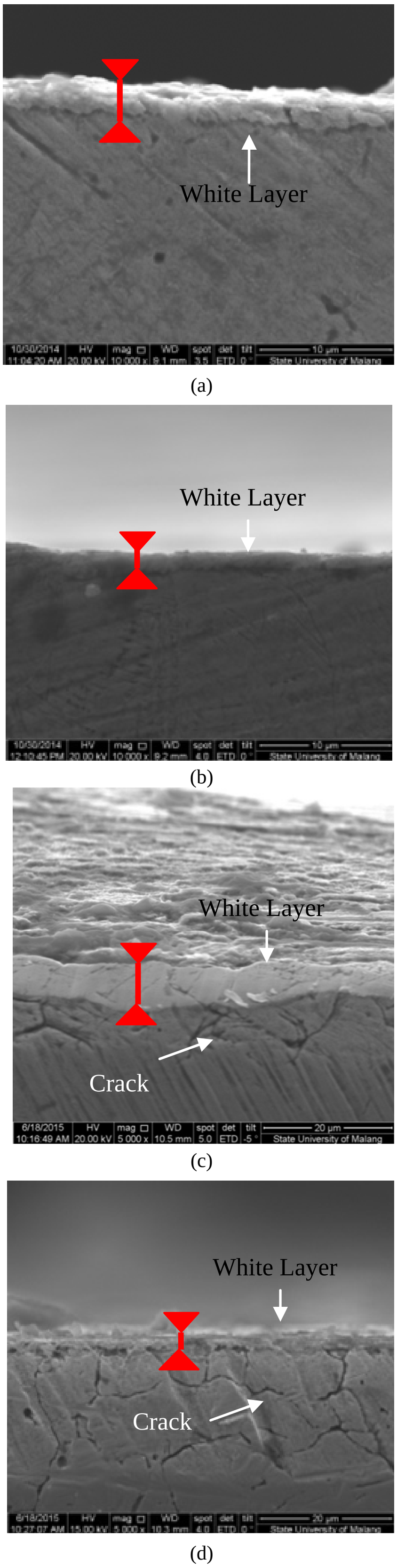
The specimen with diffusion media without nitrogen gas has shown that the nitrogen concentration is not detected either in the upper layer or in the lower layer.

The detached nitrogen atom has an impact on fragility indicated by a decrease in hardness that dropped significantly by up to 280 HV on the surface. Meanwhile, the highest hardness values occur in specimens processed at 550 ^{0}C with nitrogen gas as diffusion medium, as shown in Figure 5. However, micro-cracks started to form under the white layer, which caused the hardness value to precipitously decline.

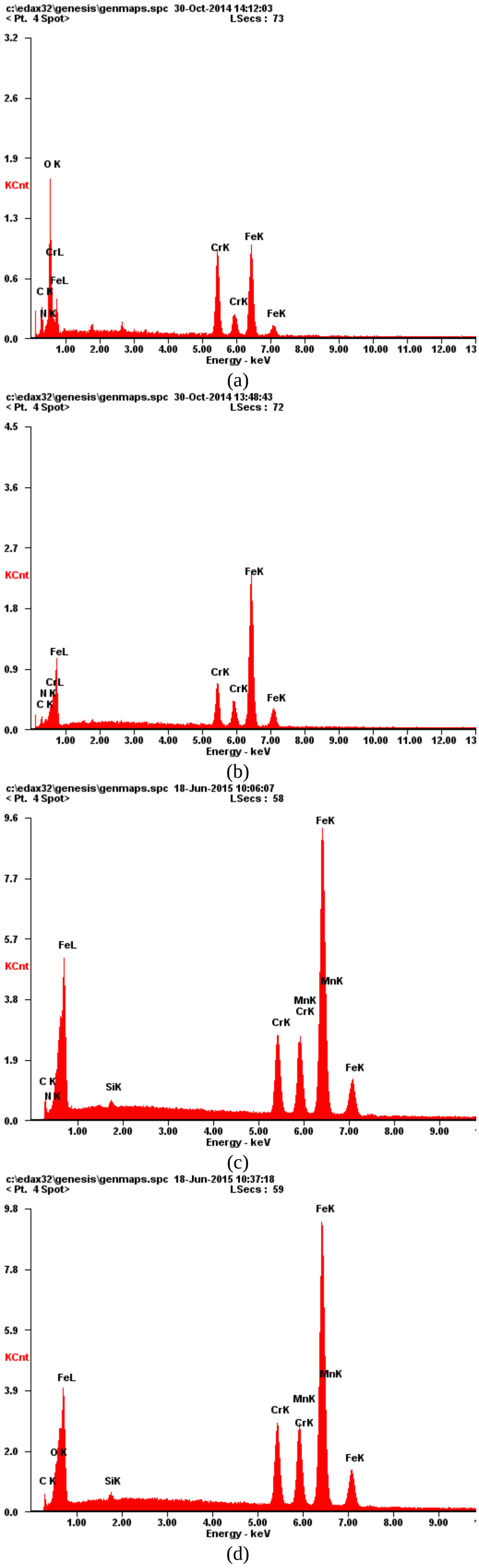
The SEM image and EDAX data indicate that, at high temperature diffusion, the nitrogen atoms release in the atmosphere the so-called supersaturated reactions. This supersaturated reaction reduces the formation of white layers but it is followed by the formation of micro-cracks beneath the white layers. The micro-cracks formation phenomenon can be considered as an unbalanced reaction.

The increase in temperature at the diffusion stage is less effective without the use of nitrogen as a medium.

This ineffectiveness is in terms of energy required and bad quality of the nitriding result. Excessive temperature process could increase the rate of reaction.



Figs. 2. SEM analysis on the nitride layer, (a) with nitrogen diffusion media at 550 ^{0}C, (b) with a gas diffusion media without nitrogen at 550°C, (c) with nitrogen gas diffusion media at 650 ^{0}C, (d) without nitrogen diffusion media at 650 ^{0}C



Figs. 3. EDAX analysis of the white layer, (a) with nitrogen diffusion media at 550 ^{0}C, (b) with a gas diffusion media without nitrogen at 550 ^{0}C, (c) with nitrogen gas diffusion media at 650 ^{0}C, (d) without nitrogen diffusion media at 650 ^{0}C

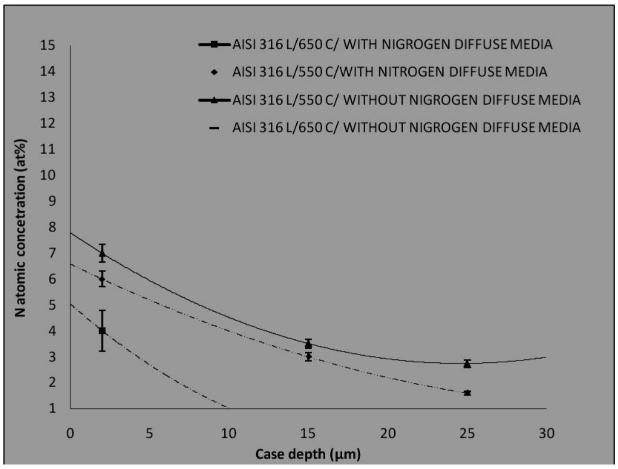


Fig. 4. The depth of nitrogen atoms concentration influenced by the temperature and diffusion media in AISI 316 L nitriding process

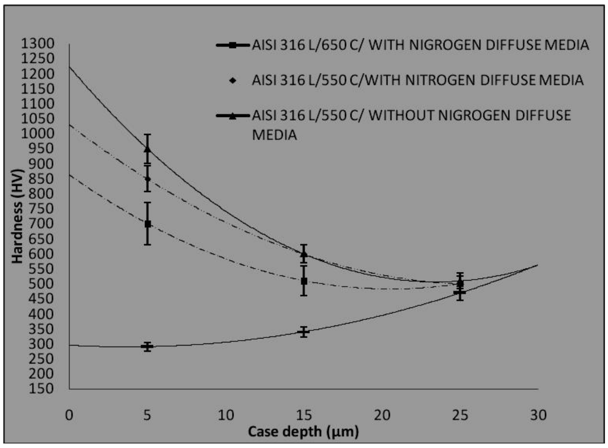


Fig. 5. The relationship of hardening depth to the temperature and diffusion media in AISI 316 L nitriding process

However, the reaction equilibrium constant (*Kc*) could be reduced due to the exothermic reaction.

The concentration of nitrogen atoms is very low in the area below the white layer (high concentration gradient difference), where the supersaturated reaction is followed by sensitization reactions.

These reactions occur due to excessive diffusion time at a high temperature (650 ^{0}C) which causes many nitrogen atoms to be released into the air. In the absence of a nitrogen atom, the carbon atom interacts with chromium to form chromium carbide. The formation of chromium carbides results in the formation of micro-cracks below the white layers.

Therefore, it is very important to understand this phenomenon in order to control the formation of white layers and the brittleness below the white layers.

By Nitriding on stainless steel, it is not possible to produce a single layer of Fe_4N - γ´ or $Fe_{2,3}N$ - ε without the formation of the white layers.

The Nitriding process is important to avoid the presence of oxygen and other contaminants on the surface acting as a barrier to nitrogen diffusion into the substrate [9].

The compound layer formed on the entire specimen has a high concentration of nitrogen. The low hardness value in the specimen, especially at higher diffusion temperatures up to 650 ^{0}C, without diffusion media indicates a supersaturated reaction that takes place at the grain boundaries.

It can be concluded that the high nitrogen concentrations are mostly found in the grain boundaries which produce cracks along them. This reaction is called the denitriding phenomenon. The nitrogen atom formed at the grain boundaries does not produce a nitride bond with other elements such as chromium and iron, but it stands on its own, called as nitrogen excess [5]. The nitrogen excess occurs due to an excessive number of nitrogen atoms and the inability to bond with other elements, as the atmospheric pressure around the specimen during the diffusion process is lacking. In addition, the higher temperature reduces the pressure, which has a lower ability to force nitrogen atoms to bind with chromium and iron. Consequently the nitrogen excess escapes to the outside atmosphere.

The diffusion rate of nitrogen is very high on the surface area. The diffusion rate decreases with the increase of diffusion depth. In other words, in order to increase the diffusion rate, NH_3 gas is indispensable in generating nitrogen atoms to urge the nitrogen atoms that already exist at the grain boundary to diffuse into the lattice structure of chromium and iron elements.

Therefore, the compound layer thickness can be improved [6]. In stainless steel, sensitization reactions also affect the hardness value. Carbides formation improves compound layers hardness and diffusion layers.

However, this study shows that a high carbon concentration does not cause brittleness, as shown by the low hardness and more brittle micro structure layer [11].

It is also the result of the decarburization reaction.

This brittleness is due to an excessive temperature diffusion. Unstable nitride and carbide phase formation is the reason of the very low hardness.

The result shows that the depth of nitrogen atoms concentration distribution is correlated to hardening depth. With the increase of nitrogen atoms concentration, hardness also increases. In this study, the highest concentration of nitrogen atoms is in the diffusion process without nitrogen gas atmosphere at 550 ^{0}C. This shows that oxygen plays a role in assisting the increase in the spread diffusion of nitrogen atoms in the stainless steel. Based on the illustration in Figure 6, it can be seen that the role of the passive layer on stainless steel nitriding process is very useful in improving the process efficiency. The use of nitrogen gas during the diffusion phase reduces the thickness of the passive layer surface of the specimen. The thinner passive layer has an impact on the formation of the initial crack on the surface of the specimen. This is due to the formation of thermal stress in the form of collisions alumina powder on the surface of the specimen. The passive layer facilitates low nitrogen molecules into the material during the diffusion process (Figure 6).

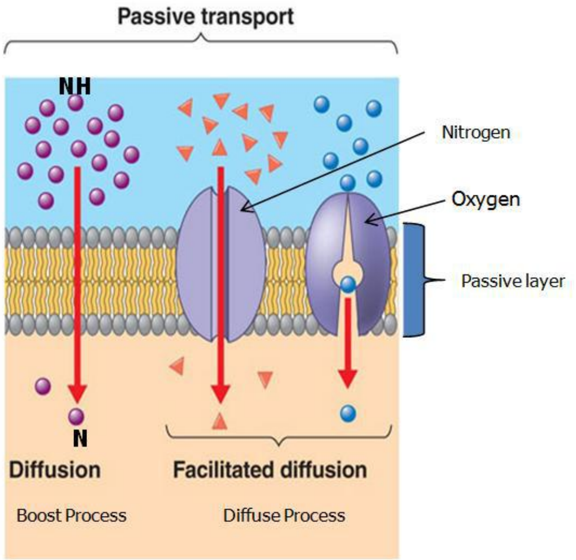


Fig. 6. Ilustration of passive layers effect on AISI 316 L nitriding process

Ammonia gas produces a nitrogen atom as a nitride - forming element. Ammonia gas served to increase the concentration of nitrogen atoms on the surface during the boost process. The role of nitrogen gas during the boost process is to facilitate the entry of nitrogen atoms into the specimens by dismantling the passive layer surface. And, at the same time, nitrogen gas hampers the entry of oxygen during the boost process. It is because nitrogen gas is an inert gas. The role of the atmosphere in the reactor muffle during the diffusion process is reshaping the passive layer that has been lost during the boost process. Oxide layer formation on the surface of the specimen withstands the loss of nitrogen atoms during the boost process.

Nitrogen atoms diffuse more deeply so that the depth of hardening improves. The role of alloying chromium element is to form a passive layer with oxygen [12].

The illustration shown in Figure 6 is in accordance with the test results and by reference to previous studies that include [13] that is: "formation of Y phase in the 7-30 minutes nitriding process required further stage of the process that is more effective to dissolve the white layer, so that the solubility of the atom can be more uniformed'.

At too high temperature, nitrogen reacts with Fe to produce FeN which is very hard and brittle [14].

The low alloy steel provides a deeper depth case but a lower overall hardness [15]. The use of air circulation can increase the dissociation of ammonia and nitrogen [6]. The presence of oxygen could lower the activation energy in the formation of the oxide layer [16].

IV. Conclusion

White layers can be minimized with the use of the phase diffusion method after the phase boost treatment by utilizing higher temperature in less than 2 hours processing time in a nitrogen atmosphere media. 316L Stainless steel shows that the depth of nitrogen atomic diffusion significantly increases (about 6 µm depth from 6,04 wt % to 1,19 wt % without nitrogen diffusion medium and about 5,11 wt % to 0,83 wt % atomic nitrogen in nitrogen diffusion media). Thermochemical fluidized bed nitriding gas process on stainless steel can be used to minimize the formation of white layers on the surface but the crack will appear.

Acknowledgements

This work was supported by the Research fund of RISTEKDIKTI Indonesia Government and by the Materials Laboratory, Mechanical Engineering Department at ITN Malang.

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