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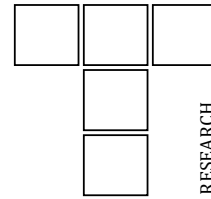
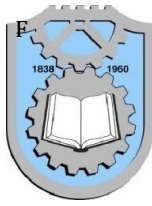
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The Role of Diffusion Media in Nitriding Process on Surface Layers Characteristics of AISI 4140 with and without Hard Chrome Coatings

K.A. Widi^{a,b}, I. Wardana^b, W. Suprpto^b, Y.S. Irawan^b

^aMechanical Engineering Department, National Institute of Technology National of Malang (ITN), Malang, East Java, Indonesia,

^bMechanical Engineering Department, Brawijaya University, Malang, East Java, Indonesia.

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Corresponding author:

Komang Astana Widi
Mechanical Engineering Department,
National Institute of Technology
National of Malang (ITN),
Malang, East Java,
Indonesia.
E-mail: aswidi@yahoo.com

ABSTRACT

The surface layer characteristics of the AISI 4140 tool steel treated by nitriding gas before and after hard chrome plating utilizing pure nitrogen diffusion media (fluidized bed reactor) and the without gas (muffle reactor) has been studied experimentally. The result shows that nitriding substrate with hard chrome layers has nitrogen atoms concentration almost twice greater than that without hard chrome layers. After being given a hard chrome plating, nitriding on AISI 4140 steel generally has a nitrogen concentration of up to 4 times more than the substrate without hard chrome coating. Almost the entire specimen showed the highest concentration of N atoms in the area below the surface (hardening depth of 200 to 450 μm). N atoms diffusion depth profile has a correlation with hardening depth profile, especially on the specimens layered with hard chromium. The substrate without hard chrome plating tends to have higher surface hardness than the sub-surface. The results show that the effectiveness and efficiency of the gas nitriding diffusion process can be produced without the use of gas in the muffle reactor but the specimen must be hard chromium coated first. This phenomenon can be explained by the role of the passive layer formation that works as a barrier to keep the spreading of N atoms concentrated in sub-surface areas.

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1. INTRODUCTION

Hard chrome is commonly used to improve components wear resistance. However, the thicker chrome layer causes cracks and increases layer porosity [1-3].^[10] Moreover, it required machining processes such as grinding, polishing and honing to improve surface

performance for better surface contact [4-5].^[10] A rough surface could reduce the wear resistance.^[10] This research aims to look for alternative solutions for improving the performance of hard chrome material, that is, to increase hardness and reduce the crack density on the surface by utilizing gas nitriding treatment.

The role of nitrogen atoms in the Fe-Cr alloy is to form precipitation with chrome elements producing hard nitrides and to form the excess nitrogen at the nitride / ferrite interface. The excess nitrogen atom cannot diffuse whereas the nitrogen atom that are interstices in the ferrite matrix can undergo diffusion process with excess nitrogen atom that movable [6].

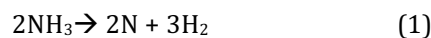
Various mechanisms about nitrogen atom diffusion into the substrate during nitriding process have been disclosed [7-9]. It is pointed out that the diffusion is determined by several factors, including the composition of materials, processing media, temperature and time [14-16]. However, until now the uniformity and stability of nitride layer formation is still not optimal. Of the four factors, the processing time is the most successful utilization in generating the depth and stability of the nitride layer. However the weakness of the nitriding process is that it is economically less profitable. Generally, nitriding treatment in industry requires a minimum of 72 hours [10]. The high cost compared to other thermo chemical process makes it less desirable. The high cost is due to the use of pure nitrogen gas in a long diffusion process. Only 30 % of the gas is effective while the remaining 70 % is escaped into the without gas. This ineffectiveness also results in extraordinary without gas pollution that can accelerate the process of global warming [11]. Therefore, in this study we discuss the effect of varying environment gas during nitriding process, that is, nitrogen and without gas on the characteristics of surface layer formation on the hard chrome coating AISI 4140.

2. METHODS

2.1 Material and Preparation

The specimen was made of AISI 4140 Steel with a diameter of 3 cm with chemical compositions as shown in Table 1. The specimen was coated with hard chrome. It was cut with a maximum size of 5 mm after nitriding treatment with cutting wire machine in extreme care to ensure that there is no change in microstructure and the layer formation on the surface. Figure 1 shows the nitriding process consisting of two-stage process. The boost process was conducted in a fluidized bed gas reactor by utilizing ammonia

(NH₃) and high purity (HP) N₂ gas (99.98 %). In this step, NH₃ dissociates into N and H₂ as equation 1.



N atoms diffuse into specimen surface while H₂ escapes to the atmosphere.

Table 1. Chemical composition of tool steel AISI type 4140.

Chemical composition [%]						
Fe	Cr	Ni	Mn	Cu	Ca	Si
94,2	0,7	0,8	1,0	0,21	0,21	0,3

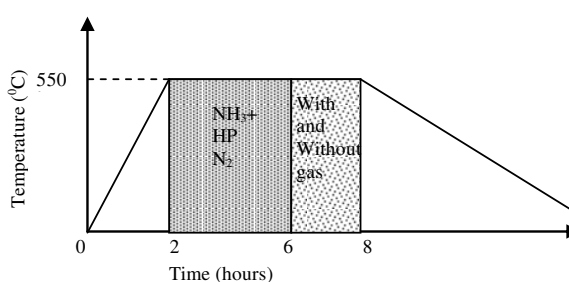


Fig. 1. Stages of the boost and diffusion in the nitriding process.

Boost process was done at temperature of 550 °C in 4 hours. The gas mixture was composed of 80 % NH₃ and 20 % N₂ and the total gas flow rate is 0.7 m³/h. The total gas flow rate in the fluidized bed reactor was based on process temperature as shown in Fig. 2. The subsequent process is a diffusion process, utilizing the processing time of 2 hours and the processing temperature of 550 °C with pure nitrogen gas in the fluidized bed reactor and without gas in the muffle reactor.

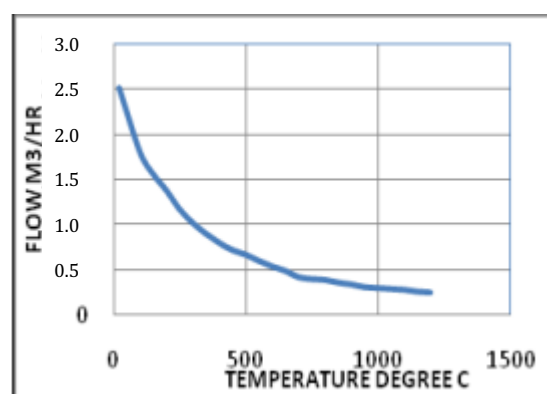


Fig. 2. Flowrate vs temperature thermochemical process in fluidized bed reactor tipe FH12M [12].

Materials characterization was performed after the nitriding diffusion process. Microstructure and phase on and under the surface layer was observed with SEM / EDAX by cutting the test specimens in transverse direction. The test provides information regarding the thickness and concentration of N atoms in each layer. The uniformity of nitrogen atoms diffusion into the substrate was evaluated by using XRD test equipment together with mikrovickers hardness tester at some depthwise distance.

3. RESULTS AND DISCUSSION

3.1. SEM Analysis

Nitride layer morphology formed on 4140 tool steels is shown in Fig. 3.^[42] The layers formed in the muffle reactor showed porosity defects that crept to the surface while that formed in the HP nitrogen media in fluidized bed reactor does not indicate porosity defects.^[42] This shows that the diffusion of HP nitrogen media is more effective in the formation of surface layer of nitride steel AISI 4140. But for applications that require damping capability and lubrication, the without gas media in muffle reactor would be more appropriate to be applied in producing spreading porosity.

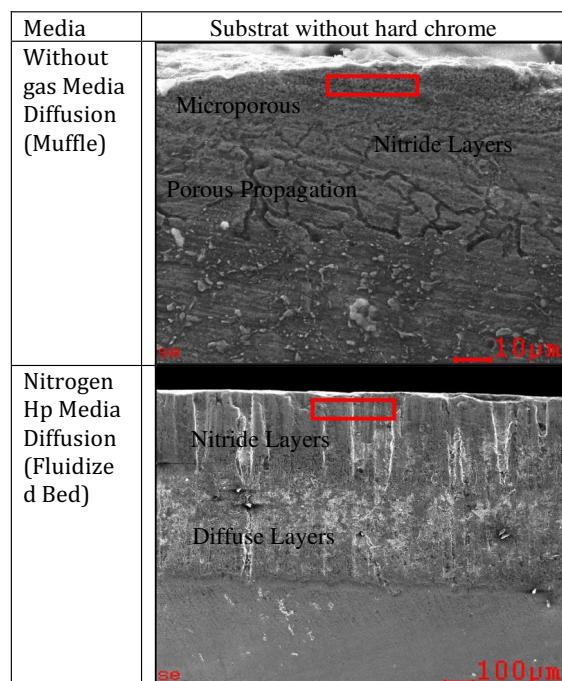


Fig. 3. Microstructure and measurement of nitride layers on tool steel substrate before hard chrome coating.

This porosity formation is a supersaturated effect of N atoms reaction [14].^[7] The large number of movable N atom is the results of the boost process in fluidized bed reactor and the hydrogen element from the without gas as the heating process in the muffle reactor cause the gas molecules move to the specimen surface.^[31] The absence of barrier on the specimen surface in restraining the entry of gas from the atmosphere is a major factor in the movement of this porosity.^[7] Utilization of HP nitrogen gas as an inert gas in the diffusion nitriding process serves as deterrence entry of gas from the atmosphere.^[31]

The porosity defects reduce hardness up to 2 times as much.^[8] This may lower the mechanical properties.^[8] The nitrogen composition data shows that despite the increase of porosity the concentration of N atoms in the without gas diffusion media is higher.^[7] This indicates that the nitrogen atoms do not form nitride compound layer, but reside in the ferrite grain.^[12] Unlike the case in which the concentration of nitrogen atoms diffusion media are lower due largely N atom has formed nitride compound.

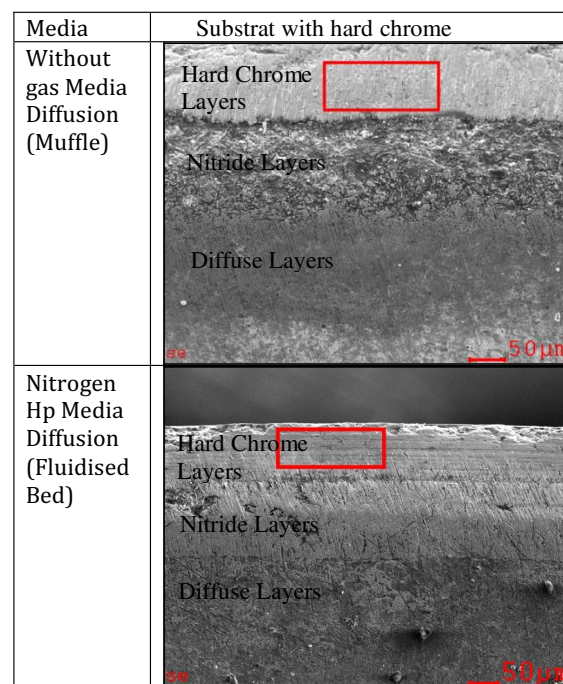


Fig. 4. Microstructure and measurement of nitride layer on the substrate after the coated hard chroming.

The data in Fig. 4 at a depth of up to 82 microns shows that the concentration of chromium alloy is very high. This indicates that the surface layer

is a hard chrome layer. The layer below the hard chrome layer to a depth of 185 microns on a specimen that treated in muffle reactor showed a nitride layer with a low chromium content. However, the diffusion of HP nitrogen media at this depth still show a layer of hard chrome indicating that concentrations of chromium is still high. At the depth more than 185 microns, the nitride layer has low chrome composition. The bottom layer is a diffusion layer because the nitrogen diffusion layer can still be detected in this layer as shown in Fig. 5 whereas the chromium element is not present at the EDAX test results.

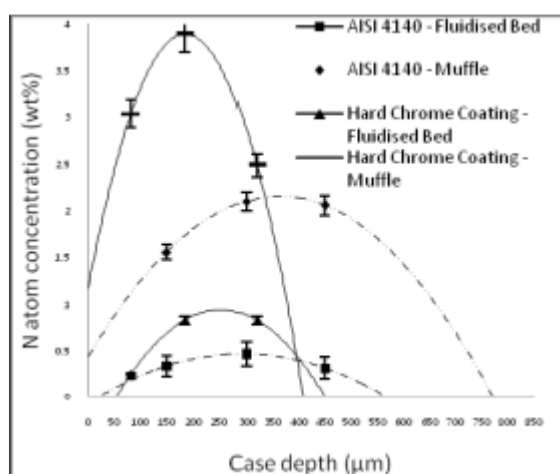


Fig. 5. N atomic concentration of atmospheric diffusion of AISI 4140 before and after hard chrome coated layer in nitriding process formed on each layers.^[8]

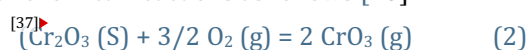
In this study, there are two stages in the mechanism of infiltrating nitrogen atoms into the surface of the specimen, that is, the boost phase and the diffusion stage (spreading the nitrogen atom). Boost phase is utilizing NH_3 and HP N_2 gas.^[7] HP N_2 gas acts to dismantle the oxide layer that has been already formed on the specimen before the treatment.^[7] Demolition reaction of the passive layer by HP N_2 gas creates cracks or pores in the passive layer that provide pathway for nitrogen gas from NH_3 to diffuse into the surface.^[8] This is the reason of the use of HP N_2 gas during the temperature of the boost process between 500 °C and 550 °C. The ammonia gas was utilized when nitriding temperature reaches 550 °C.^[10]

A phenomenon that occurs at the stage of diffusion shown in Fig. 4 can be explained as the

following mechanism.^[8] Crack or pores created by HP N_2 also provide a pathway for oxygen to contact with the specimen surface and reacts with Cr to produce Cr_2O_3 and with nitrogen atom to produce N_2O_5 .^[8] Hence the chromium oxide becomes greater in specimens that utilizing HP nitrogen compared to that without gas. When the chromium element is oxidized, nitrogen atoms react with Fe to form nitriding and oxidation reactions run simultaneously within a short time in 2 hours.^[16] It can be concluded that within the 2 hours diffusion nitriding period the chromium nitride has not been formed yet.^[7] Instead, the nitride steel and oxide chrome are formed as shown by XRD.^[16]

This shows that the affinity of oxygen is more easily formed with chrome elements, while the affinity of nitrogen is more easily formed with the iron element.^[7] Nitrogen also has a good affinity with the oxygen that is formed on the interface oxide trapped during the process of formation of the oxide layer.^[8]

The utilization of the without gas atmosphere in the form of oxygen at temperature of 550 °C help the diffusion mechanism of nitrogen atoms into the material.^[34] The mechanism of diffusion by using atmospheric without gas (which contains nitrogen and oxygen) result in the depletion layer of chromium oxide (Cr_2O_3) that have been formed during the boost phase. This mechanism occurs due to the presence of the oxygen element in the without gas that would cause the evaporation of the reaction of the oxide layer with chemical reactions as follows [13]:



The positive effects from this reaction is the nitrogen atom diffusion into the material becomes more rapidly penetrate the oxide layer at chromium grain boundaries.^[28] This phenomenon is in accordance with the test data: the lower the concentration of oxides chromium, the greater the concentration of nitrogen atoms.^[18] The thinning oxide layer on the surface by a 2 hours process has not shown any supersaturated reaction where the nitrogen atoms escape into the atmosphere.^[37] Even the depth test data of the composition of the nitrogen atom (Fig. 5) showed a stable composition to a depth of 320 microns. But different things appear in the diffusion process that use nitrogen atmosphere. The high chrome

oxide layer gives low effect to nitrogen diffusivity. The XRD observation also shows that the Fe_2N phase formation is very low. This is consistent with the theory of evaporation in which the use of a nitrogen atmosphere will thicken the oxide layer at the grain boundaries so that the movement of diffusion between the grains is very difficult to form. The thickness of the chrome oxide layer is provided by the EDAX test results in Fig. 5 that show Cr_2O_3 form until the second layer, while the without gas atmosphere media only shows Cr_2O_3 on the uppermost layer. Low nitrogen atom on each nitrogen diffusion layer in the atmosphere is the result of the supersaturated reaction. The atmospheric nitrogen solves this oxide layer to create a cracks and pores. The nitrogen atoms that have been formed during boost stage become easier to move out towards the specimen surface through cracks and pores to become nitrogen gas [3,4].

The phenomenon of thickening and thinning of the oxide layer is similar to the mechanism of oxidation model shown by Tedmon. At first, when the diffusion passes through this thin layer rapidly, Cr_2O_3 evaporation is not significant. But in a thick layer, the evaporation rate becomes comparable to the growth rate of diffusion.

3.2. XRD Analysis

Figures 6 and 7 show that many phases of alloying elements, present on chromium coated steel indicating that nitriding diffusion reaction has been formed. This nitride forming reaction is shown by the presence of a phase element Fe_2N and $\text{FeN}_{0,0897}$. It can be observed that the Fe-Cr phase in the atmospheric without gas diffusion in muffle reactor shifts the peak position to the right. This indicates that a change in the structure of the lattice parameter is greater. This means that there is infiltration of nitrogen atoms in the cubic lattice parameters. This is supported by EDAX test results where the percentage of nitrogen atom is greater in the without gas atmosphere supported media with a higher hardness values as shown in Fig. 5.

The observations results indicate the oxidation process has taken place at a temperature of 550 °C which affect the blockage of chromium ion release into the atmosphere that is shown by the high content of Cr and chromium oxide (Cr_2O_3)

on the surface of the material. Chromium oxide on the surface of the diffusion of atmospheric nitrogen utilization is higher than atmospheric without gas diffusion, but is inversely proportional to the concentration of nitrogen and oxygen atoms on the surface more than on atmospheric without gas diffusion. Increased concentration of nitrogen atom is coupled with increased concentration of iron nitride.

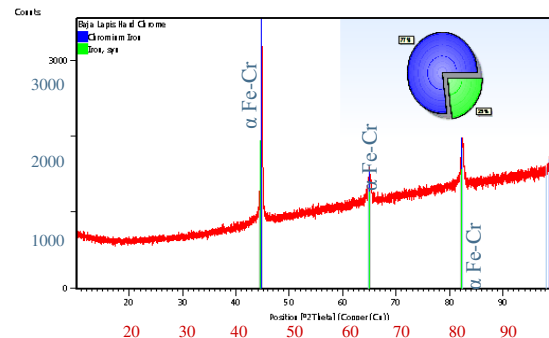


Fig. 6. XRD analysis graph of hard chromium coated steel specimens before nitriding treatment.

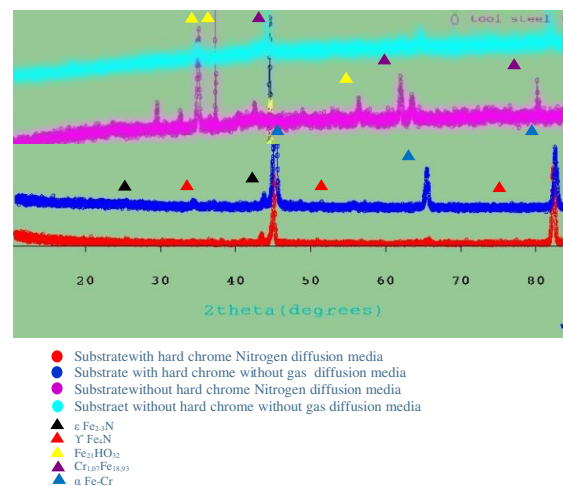


Fig. 7. Tool steel XRD analysis before and after hard chrome coating treated by nitridization with different diffusion media.

3.3. Case Depth Microhardness

Hardening depth analysis in this study will be linked with the influence of alloying elements and diffusivity content of nitrogen and oxygen atoms. By looking at the correlation of the test results as shown in Figure 8, the formation of hardening depth mechanism can be definitely known. The result shows that increased concentration of nitrogen does not necessarily

correlate with an increase in violence due to the hardness which is also influenced by the carbon. Excessive carbon may lead to brittleness and this occurred at a depth of hardening of 185 microns (under a layer of hard chromium - which is a AISI 4140 substrate material) coupled with a carbon concentration of up to 41.29 wt%. This brittleness phenomenon is formed by chrome bind with carbon to form hard and brittle carbide elements called sensitization. At a depth of 320 microns, the hardening level has increased significantly, reaching about 1100 HV in lower content of carbon element that is 16.28 wt%. Fragility mechanism that occurs under a layer of hard chromium can also be observed in the SEM structure test result.

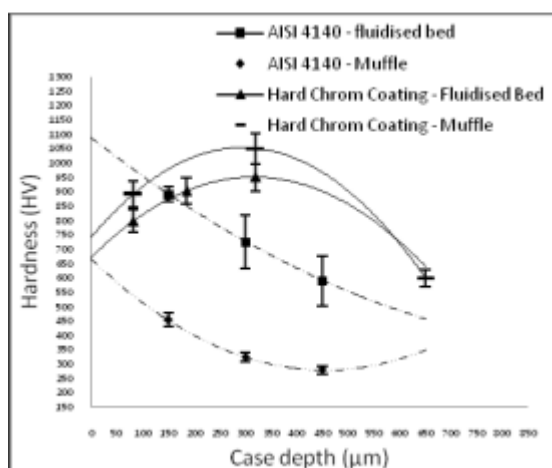


Fig. 8. Hardness case depth of atmospheric diffusion of AISI 4140.

This mechanism occurs in specimens that are subjected to atmospheric without gas as diffusion media. This is the impact of the phenomenon of evaporation of the Cr_2O_3 layer. This depletion of the Cr_2O_3 layer results in higher heat input. As a result, sensitization and frailty is more easily to occur. The layer below hard chrome layer that is the AISI 4140 substrate material has quite large carbon content and this result in the depletion layer of carbon ions to be more easily move to the surface. The amount of these carbon ions, the chromium element in hard chromium coating and excess heat will facilitate this sensitization reaction. The XRD test result shows the formation of carbide phase Cr_{23}C_6 large enough. The phenomenon of sensitization is a defect that is easily formed in the steel with a high chromium content which is usually formed at temperatures of 400-850 °C. With the formation of carbides at

the grain boundaries which cause depletion of chromium content at grain boundaries, causing the loss of ability to resist corrosion rate and lead to brittleness and fragility at grain boundaries. This is evidenced by the depletion of chromium content on the test results at 185 microns depth of atmospheric without gas diffusion that is only 41.67 wt% while the nitrogen atmosphere at the same depth contain up to 94.47 wt% chromium. This phenomenon can be easily formed in the absence of an alloying element that has a greater affinity than chromium to bound carbon such as niobium and titanium elements. By utilizing these alloying elements the availability of carbon to bond with carbon reduces [14].

3.4. Surface Morphology of SEM

Based on the microstructure analysis of the cross section of the surface and cross section coated steel hard chrome (Fig. 9), it is shown that there are three layers formed, namely a layer of hard chrome (white), a layer of nitride (black) and the diffusion layer (a combination of black and white).

	AISI 4140 steel	
	nitrogen atmosphere	Without gas atmosphere
Surface section		
Cross section of nitride layer, diffusion layer, substrate		

Fig. 9. SEM of AISI 4140 without hard chrome plating.

Tracking the results of the testing also showed that the depth of hardening is different in each layer. The micro tracking photo showed that below hard chromium layer has a very small diameter with significant hardness up to 1204 HV.

Figures 9 and 10 show the persistence of the micro cracks on the surface of the steel, especially in specimens utilizing diffusion of atmospheric without gas.

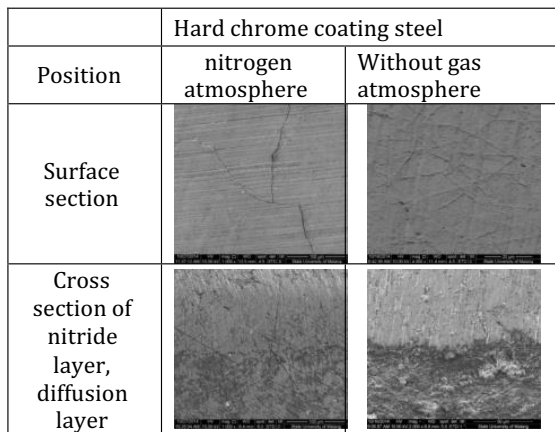


Fig. 10. SEM of AISI 4140 with hard chromium coating.

Based on the theory of micro crack mechanism formation, the higher the layer thickness of the hard chromium the more cracks are formed as shown in Fig. 10. The mechanism is still shown in nitriding process which utilizes atmospheric without gas diffusion. On the contrary the atmosphere of nitrogen gas diffusion media showed no micro cracks but there are formations of macro cracks.^[6] This occurs as a result of the excess layer thickness even by reference states that hard chrome coating thickness addition can formed porosity.^[12]

Observations on the cross-sectional structure of the layer of hard chromium specimens utilizing diffusion atmospheric without gas (Fig. 10) shows that the hard chromium layer is thinner and morphological characteristics of the structural differences between the hard chromium layer and the layer below was distinctive.^[14] While on specimens treatment utilize atmospheric nitrogen gas diffusion showed no micro cracks but has shown a macro cracks on the surface.^[31] This is a result of excess nitrogen gas role in dismantling mechanism of chromium oxide layer which not only create a gap or crack on the oxide layer but also create crack on the hard chrome layer.^[14] However, cracks formed on the surface is only a few microns and do not penetrate all layers of hard chromium.^[9] This is supported by the data that no crack along the hard chrome layer is found on cross-sectional observations.^[9] Excess nitrogen is responsible for the cracks formation in the micro cracks structure, resulted in the formation of macro cracks on the surface of which is marked by increased release of nitrogen atom which had been formed during the boost process through this crack defect.

^[12] In addition, the nitrogen gas that is inert and cold increases the tensile and compression stress, reactions of the core, substrate and outer hard chromium layer thus causing the macro cracks on the surface.^[16] This reaction is also supported by the utilization of alumina powder as a fluid medium in the fluidized bed reactor which resulted in a collision between alumina powder and the surface of the specimen.^[28] Micro cracks formed on the specimen that utilizes atmospheric diffusion of without gas does not create a gap (concave) but these micro cracks arise out (convex) which change the structure of the layer of hard chrome from jagged to nodular.^[9] Nodular structure generally can only be produced in a thin layer of chrome for decoration application called thin dense chrome plating.^[6] But nitriding process utilizing diffusion of atmospheric without gas inside the muffle reactor can generate a thick layer structure of chromium for engineering applications called hard chromium.^[26] The formation of a superficial surface cracks can be removed easily through machining processes such as grinding, polishing and honing to improve the performance of the hard chrome layer when the contact surface occurs as a smoother surface will give better wear resistance.^[7]

At atmospheric diffusion nitriding of the without gas inside the muffle reactor the media is more effective in producing concentrations of nitrogen atom diffusion than utilizing a nitrogen atmosphere in the fluidized bed reactor.^[14] This is because the atmospheric without gas as diffusion processes increase the formation of the passive layer surface.^[9] Consequently, the nitrogen atom that already resides in the materials during the boost process cannot be easily released into the atmosphere due to obstruction of the formation of a passive layer.^[17] In addition, the heat energy produced becomes more stable because of passive film roles in which a higher temperature is generated to vibrate the atoms so that nitrogen atom is easier to diffuse.^[19]

The concentration of the oxygen is much higher in the process which utilizes the without gas atmosphere compared to that utilizing a nitrogen atmosphere during the process of diffusion nitriding, i.e., 7.09 wt% compared to 4.44 wt% which is almost 2-fold.^[27] The concentration of oxygen is not determined by the thickness of the hard chromium layer which

is only 82.2^[12] microns at the process that utilize without gas atmosphere, while the nitrogen atmosphere has a hard chrome coating thickness of up to 2 times as much. This means that the size of the hard chrome layer thickness has no effect on the nitrogen atom diffusion depth but more on the stability of the oxide layer.

Figures 9 and 10 also show that in general the nitriding of steel coated with hard chrome formed multiple layers that show the diffusion process occurs very well. And the utilization of the without gas atmosphere show the inter-layer boundaries are clearer than those utilizing nitrogen diffusion process.

Utilization of nitrogen as a medium for diffusion in the hard chromium steel does not result in micro cracks yet macro cracks are formed on the surface. Utilizing the without gas as the atmospheric diffusion result in surface morphology of micro crack arising. For the materials without nitriding, the micro-cracks are sunken inward.

Hard chromium layer in a nitrogen atmosphere shows a high density and hardness which is shown by a more uniform surface area followed by fragility (loose material) area like a sanding end surface. It is not appears in the specimen which utilizes the without gas as a medium for diffusion.

Layer formation under hard chromium layer shows that the use of atmospheric without gas has a more brittle morphology which is fibrous and granular form which is indicated by the number of particles uprooted on the surface. But under the lining, the violence shows better profile in which the fault has not shown. It indicates that the diffusion of nitrogen in this area have better concentration than the layer above it.

3.5. Macro Structure Analysis

Figure 11 shows macro structure of the hard chrome coated steel specimens.^[9] In general, specimens treated at muffle reactor, that is atmospheric diffusion without gas show bluish color, while specimens treated with the atmospheric diffusion of nitrogen at fluidized bed reactor get darker or black, where it shows lower surface oxygen concentration and that the

nitrogen atom out to the atmosphere is more. Discoloration on the surface of the specimen after nitriding process by utilizing atmospheric without gas diffusion becomes lighter while utilizing nitrogen media get darker. The darker color occurs because of oxidation reaction as a result of higher oxide layer (up to 93.36 wt%). Meanwhile in atmospheric without gas only 75, 87 wt% Cr₂O₃. As the previous research, iron oxide also effected of the darker surface formed on the specimens [15].

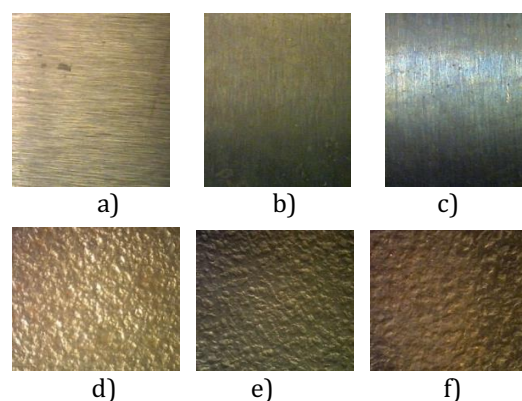


Fig. 11. Photo of macro specimen surface a) layers of hard chromium early specimens, b) layers of hard chrome on specimen with nitriding by atmospheric nitrogen diffusion treatment, c) layer of hard chromium on specimens with nitriding by atmospheric diffusion without gas, d) AISI 4140 initial specimens, e) AISI 4140 specimens with nitriding by atmospheric nitrogen diffusion treatment, f) AISI 4140 specimens with atmospheric diffusion without gas nitriding.

This surface oxidation formed due to the excess nitrogen released to the atmosphere, hence there are spaces for oxygen from outer atmosphere to infiltrates the specimen's surface. This infiltration causes the specimen easily oxidized and more oxygen element was detected after the treatment. Chrome role in the bound formation with nitrogen atoms decrease as this passive layer during diffusion process is influenced by oxidation reaction on the surface. Low corrosion resistance because of the chromium element's role is reduced due to the release of nitrogen atom also affects material hardness. Therefore, the phenomenon of chromium nitride forming reaction that influence the value of high hardness and corrosion resistance resulting in low corrosion resistance cannot be formed here, because the specimens utilizing hydrogen atmosphere has a

higher hardness at the surface. However, these phenomena are possible below the layer with increasing hardness.

Chromium is the most effective corrosion resistance, but in fact it often oxidized at room temperature. The oxide layer that formed at high temperature have green, black, blue, and yellow (as shown in the macro image of hard chrome steel surface) depending on the thickness and the compounds formed in the oxide layer. This is influenced by the temperature and oxygen content that are binding on chrome-iron.^[9] Solid oxide layer tends to be followed by the effectiveness of oxygen bond to the metal underneath.^[9] This is shown in the specimen with hard chrome without gas atmosphere in which the higher oxygen content forms a denser oxide layer.^[14] Consequently, the nitrogen would not be easy to escape into the atmosphere that is shown by a greater nitrogen atom concentration. When the oxide layer is intact then the oxidation process get slower.

4. CONCLUSION

It can be concluded in general that atmospheric diffusion during nitriding process and alloying element composition (mainly chrome and iron) have important role in producing oxide layer. In which nitriding diffusion process shows phenomenon of passive layer evaporation (Cr_2O_3) that affect the rate of diffusion nitrogen atom into the material and supersaturated reaction. Supporting evidences can be shown as follow:

1. The relation of chrome and iron alloying elements to the depth of nitrogen atom diffusivity shows that the higher chromium element the higher the rate of nitrogen atom diffusion into the material. And by utilizing atmospheric without gas diffusion shows that nitrogen atom concentration is higher in all layers than by utilizing nitrogen atom diffusion.
2. The relation of atom diffusion to phase formed at atmospheric nitrogen diffusion reveals that the use of atmospheric without gas diffusion has iron nitride content for about twice or four times compared to the use of atmospheric nitrogen.
3. The relation of oxide element to diffusion atmosphere shows atmospheric without gas diffusion inside the muffle reactor has lower oxide layer compared with utilizing nitrogen atmosphere.

Mechanism of the increasing of nitrogen atom diffusion that formed in this research consists of some stages, (i) stage of the surface oxide layer dismantling by pure nitrogen gas (stress and strain process at oxide layer), (ii) stage of inserting atom N through dissociation NH_3 (atom N concentration that is significant at the area near the surface) reaction, (iii) stage of the formation of surface passive element during the diffusion process by diffusion media (mainly by nitrogen atmosphere and chrome element).

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