Effect of N and C on surface formation of jagged – nodular and nitride-carbide structure on hard chrome steel during thermochemical treatment

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Abstract: The morphology of surface structure was changed from jagged to nodular structure. Martensite structure is formed from hard chrome plating after the oxidised diffusion of nitriding process. The investigation was conducted using SEM, EDAX, AFM and spectroscopy. This phenomenon belongs to an unusual structure. The morphology of crack density that disappears depends on the diffusion media of nitriding process. Such phenomena also happened under hard chrome plating forming carbide and bainite structure. With the changed structure of layers plating, friction and wear characteristic of hard chrome plating became better. Hard chrome coated tool steel substrate of AISI 4140 type was nitridised (550ºC, 4 hours of boost phase and 2 hours of diffusion phase) without gas diffusion media. The analysis of AFM shows the roughness value of the surface was increase after the treatment of nitriding. The nodular structure would provide width of oil storage as greater self lubricant. The structure formed can be illustrated like an area of farm. The structure could also omit the jagged area. The mechanism of nitrogen atom deposition that is interesting and relatively new was observed in this research as well.

Keywords: nodular; carbide; crack density; AFM; roughness; nitriding; hard chrome; morphology, self lubricant; SEM; EDAX.

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1 Introduction

Advanced environment-friendly materials and platings are the target of this study. The application of this material is for automobile parts and tools with the characteristic of low friction and wear resistance. Micro crack or crack density formed on the material surface functions to produce those characteristics. One of them is hard chrome plated steel material with jagged surface structure. The advantage of this structure is its good self-lubricant characteristic. But, the formation of crack density on surface structure oftentimes becomes the early cause of product failures. The change of surface structure under the hard chrome layer can be done by utilising the method of diffusion process of gas nitriding on any media or atmospheres. Not only would it upgrade the quality of hard chrome plating, this new method of treatment would change the crack density on surface structure that is initially jagged into nodular. Thus, such failures can be minimised and its ability as self-lubricant would stay the same or, even be better.

Figure 1 The illustration of jagged structure of chrome surface layer

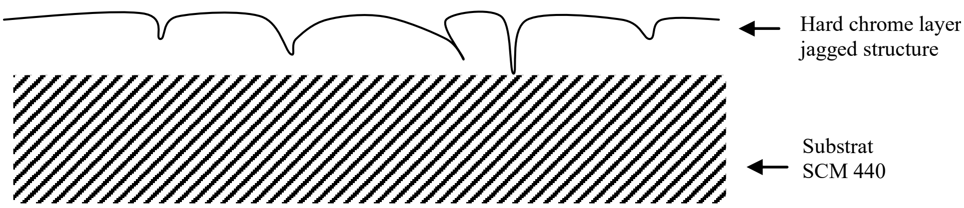
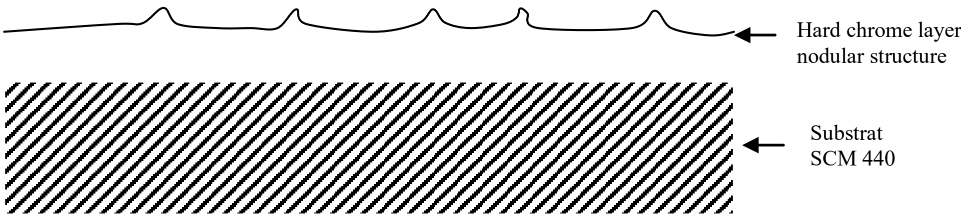


Figure 2 The picture of nodular structure illustration of the chrome surface layer



Chromium plated steel is usually utilised as hydraulic component, like for arm bucket cylinder on excavator, shaft, screw, etc. Based on that application, it can be seen that the pressure applied is generally friction pressure. Thus, hard surface layer that is of wear resistance is required. Alongside solidity, to extend the time of usage of the material with friction pressure, certain characteristic such an ability to produce its own lubrication (self-lubricant) is needed. The characteristic of self-lubricant skill is produced by forming micro crack/crack density on hard chrome surface. It is to reduce the maintenance of cylinder material. Generally, materials plated by hard chrome have jagged surface structure as shown in Figure 1. A structure with jagged surface is commonly susceptible to failures because of its sharpness and depth of notch that is high. It is also the beginning of crack fracture.

To anticipate this issue, then the better surface structure would be by forming nodular micro crack (Pauling Foothill Ranch, 2016) as shown in Figure 2. Markedly, nodular structure can only be produced on thin dense chrome plating and applied only for decoration. This structure can improve the fatigue and corrosion resistance characteristics but the character of self-lubricant will decrease. A good structure for friction application is by forming an optimal height of nodular structure. Wear resistance properties of the material is determined by the stability of the surface layer (Xue et al., 2015).

2 Research method

The specimen tested in this experiment was hard chrome plated steel with the substrate of SCM 440. The original diameter of the specimen was 2 cm and the thickness was 2 cm. Furthermore, the specimen was cut for the material characterisation experiment. The cutting procedure was done proportionally to the standard of test specimen of SEM, EDAX, and OES spectrometer utilising the cutting machine, wire cutting (Figure 3). The result of the chemical composition test of substrate specimen with OES method is shown in Table 1.

Figure 3 The specimen after cutting process

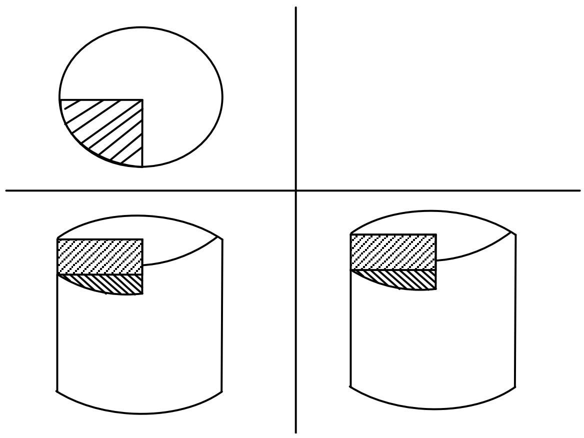
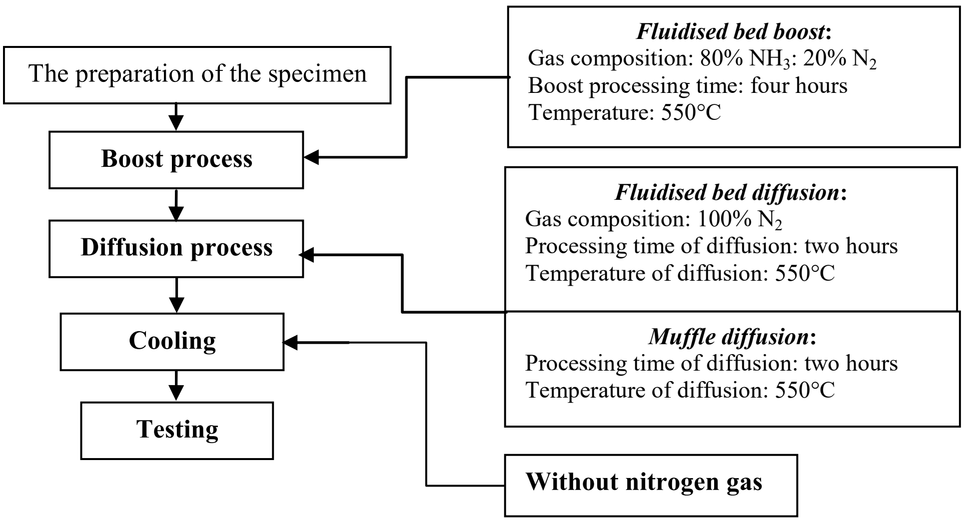


Table 1 The result of chemical composition test on tool steel of OES spectrometry specimen with the type of SCM 440

Specimen	*Fe*	*Cr*	*Mn*	*Mo*	*C*	*V*
AISI 4140 steel	97.4	0.140	0.790	0.0038	0.307	0.0083

Nitriding process consists of two stages those are boost process (the process of taking N atom from the disentangled NH_3 gas) and diffusion process (the spreading process of N atom within substrate). Diffusion process would be the focus of this research to produce an optimal spreading process of nitride layer. Boost process was carried out at 550°C with four hours of processing time within fluidised bed reactor utilising ammonia gas and HP nitrogen (high purity 99.98%) with the composition gas ratio of 80 NH_3: 20 N_2 and the total gas flow rate of 0.7 m^3/hour (according to the fluidised instrument of standardisation with FH12M) measured using the measuring instrument of gas emission that was placed on the fluidised bed reactor. Meanwhile, the next process was observation of diffusion process that took two hours of processing time and the temperature of 550°C by only channelling the gas media with high purity nitrogen (using fluidised bed reactor) or without nitrogen gas (using muffle reactor). The scheme of flow diagram is shown in Figure 4.

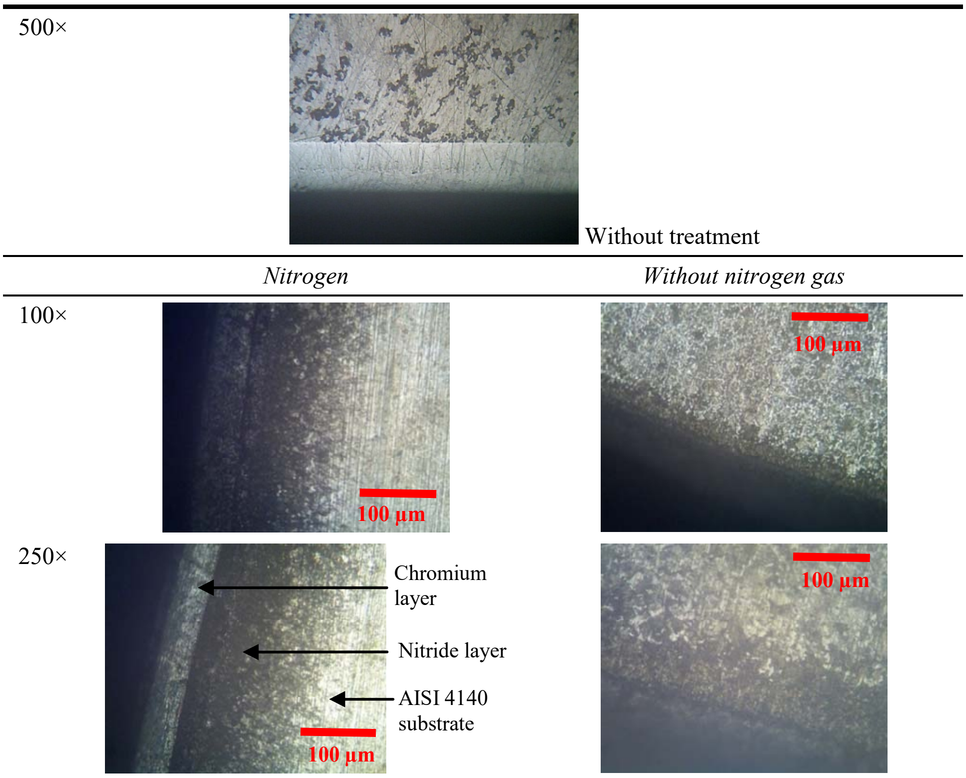
Figure 4 The flow of research diagram



3 Result and discussion

Micro crack on surface often plays a great role on material failures since the crack has great concentration of tension. The existence of pressures, especially fatigue pressure, on micro crack surface could be the early cause of the fracture. Somehow, the most important role for the application of friction pressure is self-lubricant characteristic. The characteristic of this material is usually in the form of pores or micro crack on the surface. The self-lubricant does not only increase the efficiency of the friction but also affects the corrosion resistance to be better. According to the result of micro structure analysis on the cross-section of hard chrome plated steel (Figure 5), it shows that there were three layers formed. Those are hard chromium layer (white), nitride-carbide layer (black), and diffusion layer (the combination of black and white).

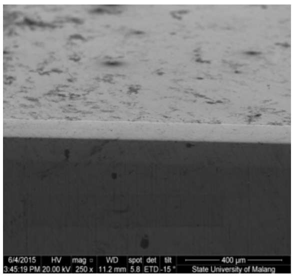
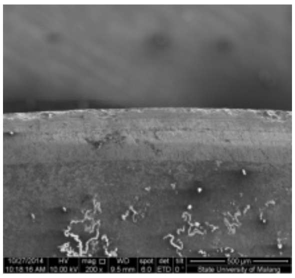
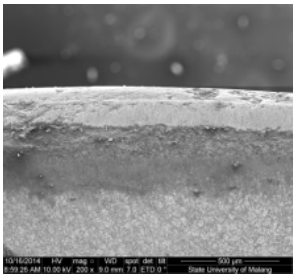
Figure 5 The cross-section picture of chromium plated steel's micro structure (see online version for colours)



Note: With magnification of 100×.

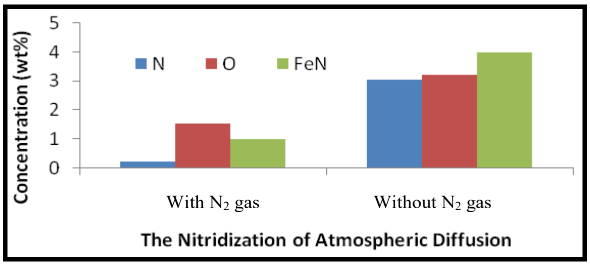
Based on the observation on cross-section of the hard chrome layer structure, the specimen utilising atmospheric diffusion without nitrogen gas (Figure 6) shows that the chromium layer is thinner and the structure difference of morphological characteristic between chromium layer and the layer under it is very obvious. On the other hand, specimen utilising the treatment of atmospheric diffusion with nitrogen gas does not show any micro crack but even pointed out macro crack on the surface (Figure 7). It is due to the role of excessive nitrogen gas on the demolition mechanism of chromium oxide layer whereas it made gap/crack not only on the oxide layer but also on the chromium layer. Yet, the crack formed on the surface is only few microns and does not break through all chromium layer (based on the observation on cross-section there is no gap/crack found all over the chromium layer). This excessive nitrogen would be responsible for the formation of gap/crack on micro crack structure that caused macro crack formation on the surface. It is denoted by the increase of nitrogen atom release (formed during the boost process) through gap/crack flaws. Besides, the nitrogen gas that is inert and cold would have a function to increase the reaction of pull and push tension of core part (substrate) and outer part (chromium layer) to be greater so that there is macro crack on the surface. The reaction is also supported by the usage of alumina powder as fluid media within fluidised bed reactor that caused the crash between alumina powder and specimen surface. The formation of shallow surface crack could be easily omitted through machining process such as grinding, polishing, and honing to upgrade the performance of chromium layer during the surface contact since the finer surface would give better value of wear resistance. However, for the friction application, it would be less effective since the self-lubricant characteristic has decreased.

Figure 6 The result of SEM test on chromium plated steel

Early specimen	*Atmosphere with nitrogen*	*Atmosphere without nitrogen*
		

Note: With magnification of 100×.

Figure 7 The relation of atmospheric diffusion concentration of FeN vs. O vs. N coated steels (see online version for colours)



The nitriding of atmospheric diffusion without nitrogen gas media within muffle reactor is more effective in producing concentration of nitrogen atom diffusion rather than in utilising the nitrogen atmosphere within fluidised bed. It is because the atmosphere without nitrogen gas increases the formation of passive surface layer during the occurrence of diffusion process so that the nitrogen atom trapped inside the material during the boost process would not be released to the atmosphere easily since there is hindrance from passive layer formation that is better on the atmospheric diffusion without nitrogen gas. Besides, the heat energy produced would be more stable because of that passive layer and a higher temperature would be produced to jar the atoms so that nitrogen atom would be more easily to diffuse into the material.

The concentration of oxygen element is much greater on process parameter by using nitrogen gasless atmosphere than by utilising the atmosphere with nitrogen during the nitriding of diffusion process in which it is with the ratio of 1.56 wt %: 3.22 wt % (almost twice of the process parameter of nitrogen atmosphere) (Figure 7). The concentration of oxygen element is not determined from the thickness of chromium layer. It is shown that the thickness of chromium layer of steel utilising nitrogen gasless atmosphere is only 82.2 µm while, on the nitrogen atmosphere, the thickness of chromium layer is up to twice the size of it. It means the thickness of chromium layer does not influence the depth of nitrogen atom diffusion but it is more depends on the stability of oxide layer.

The chromium layer on nitrogen atmospheric diffusion indicates high level of density and hardness where the surface cutting area is more followed by the brittleness on the surface area (detached material). It is not shown on the specimen using no nitrogen gas as the media for diffusion. The percentage of nitrogen atom in the inner part (nitride-carbide layer) is higher compared to on the surface part. It indicates that nitrogen atom diffusion is better on steel with nitrogen gasless atmospheric diffusion media with an increase of 0.85 wt % while, on the specimen with nitrogen media, it increased up to 0.58 wt%.

Crack density/micro crack existing on the initial surface of chromium steel is still depicted on the steel which used nitrogen gasless atmospheric media during the diffusion process. However, the condition of the crack is hidden. Meanwhile, on the specimen with nitrogen for diffusion media, there is surface crack and the crack density is not visible either it is seen using tools like optic microscope, electron microscope, or AFM. Layers formed on chromium plated steel could be observed based on the colour differentiation on each layer consisting of three layers with different percentage of chemical composition, which are chromium layer, nitride-carbide layer, and diffusion layer.

According to Atomic Force Microscopy (AFM) observation, there is morphological difference of the specimen surface on hard chrome plated steel after the nitriding treatment using nitrogen atmospheric media and nitrogen gasless atmospheric media (Figure 8). Based on the data result of AFM test on specimen surface of chromium plated steel getting nitriding treatment with nitrogen gas atmosphere, it shows that the roughness of the surface is better which is of approximately 88.23 nm for the average. On the other hand, an average roughness of approximately 71.36 nm is shown during the diffusion process of the specimen treated with nitrogen gasless atmosphere. The profile of nitride layer surface is observed using nanometer scale. The topographic result of the comparison between the two specimens indicates that the grain structure formed on surface is influenced by the atmosphere of nitriding process during the diffusion phase. The nitrogen gas atmospheric media has a lower surface gradient profile (more homogenous) compared to the treatment done with nitrogen gasless atmospheric diffusion. The homogeneity could be explained as a cause of the nitride layer formation on the specimen surface initiated by nucleation formation of phase ϒ′ and then followed by phase ε formation (Figure 11). The phase formation would start on the grain boundaries (the area of valley) since there is high concentration of tension. The media of atmospheric diffusion would cause many nitrogen atoms trapped within the valley which later formed nitride layer. Besides, nitrogen atom diffusing to the surface specimen would be absorbed more easily and deposited through grain boundaries.

The surface topography of AFM test result is in line with the analysis result of micro photograph of SEM surface. On nitrogen gasless atmospheric media, it shows that the convex and concave peak of the gradient is sharper but the average roughness is lower. The lower surface roughness is correlated with the result of EDAX composition analysis where it shows higher concentration of nitrogen atom content. It is congruent with the phenomenon that has been stated previously which is the phase formation of nitride layer would deposit more easily on sharper valley area at grain boundaries. With greater concentration of nitrogen, a greater nucleation formation of nitride layer would be depicted along with lower value of surface roughness.

Figure 8 The result of AFM test on the specimen of chromium plated steel before and after the nitriding treatment on the diffusion media with and without nitrogen gas (see online version for colours)

Hard chrome specimen without treatment	*Hard chrome specimen after the nitriding of nitrogen atmospheric media*	*Hard chrome specimen after the nitriding of nitrogen gasless atmospheric media*

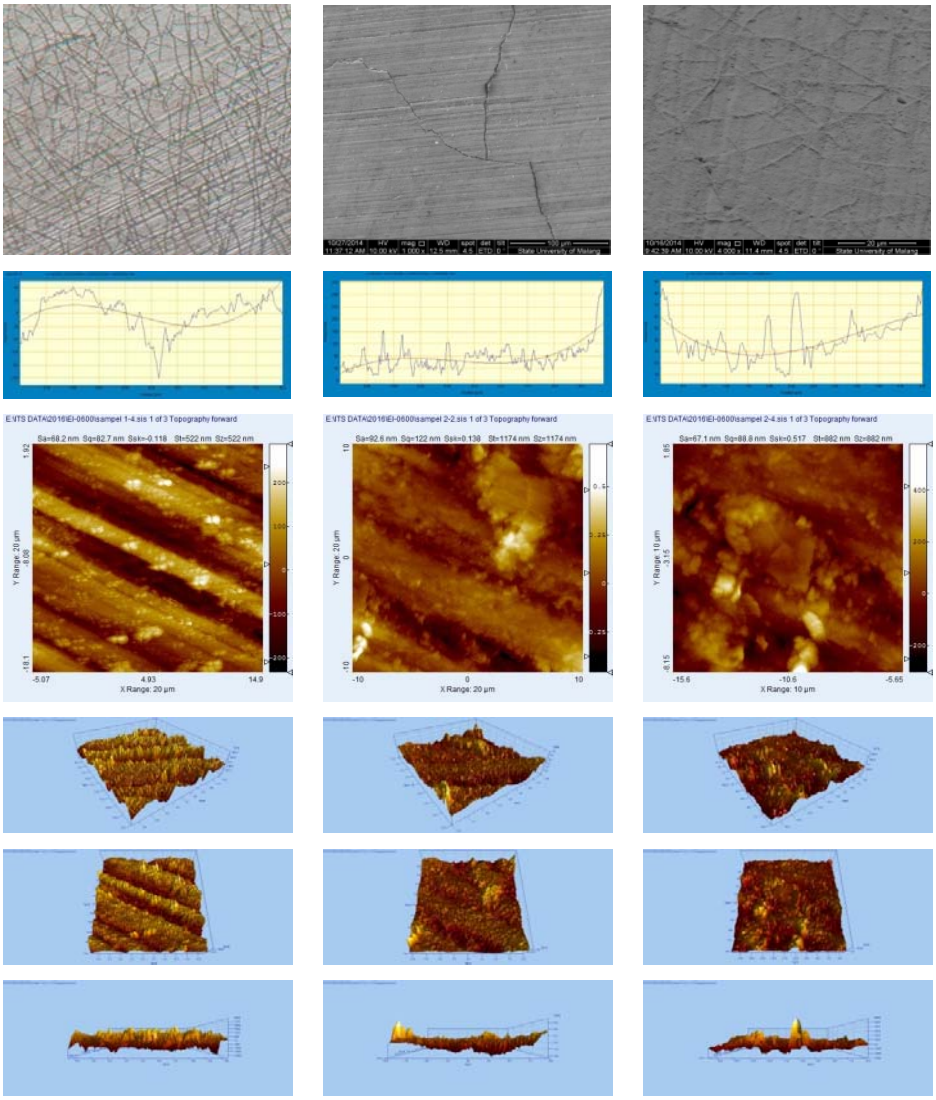
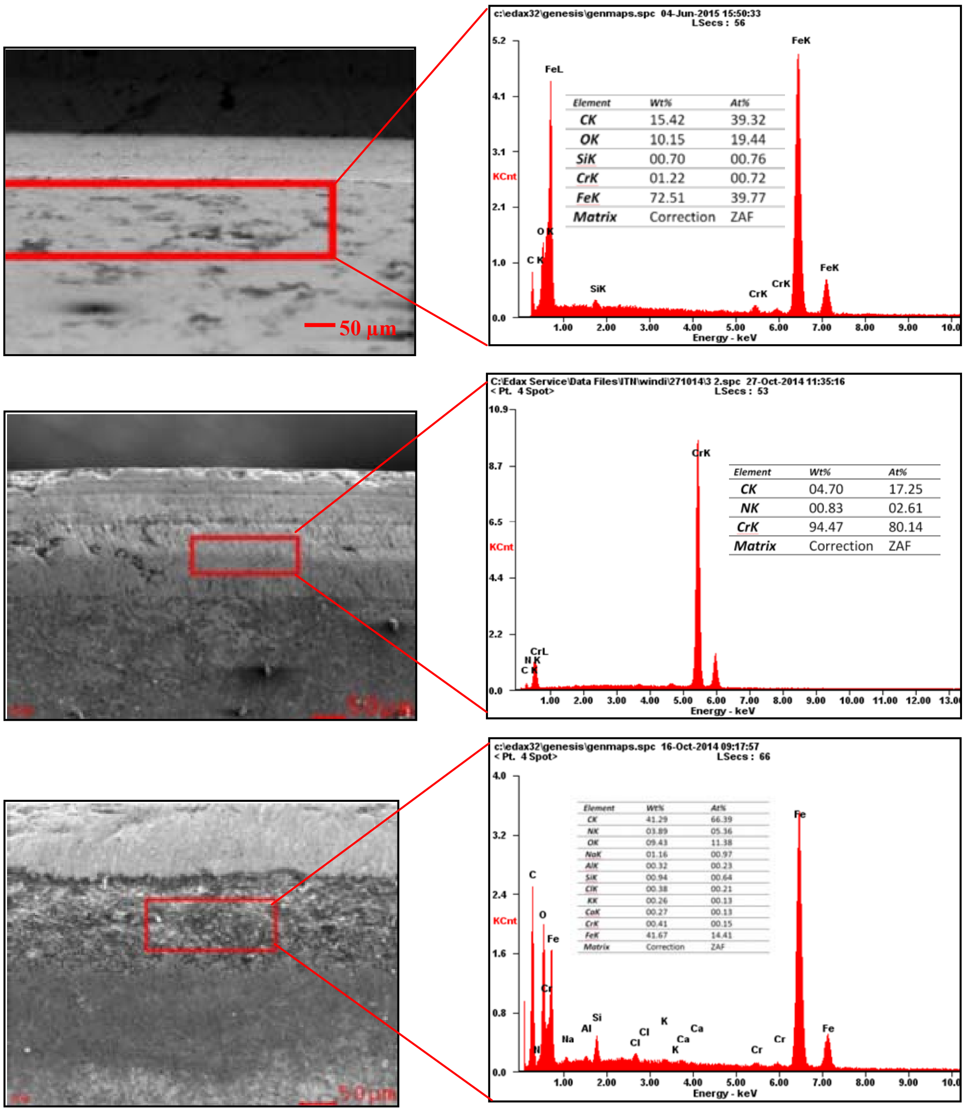


Figure 9 The result of EDAX sensitation composition test on chromium plated steel, (a) without treatment (b) nitriding treatment of nitrogen diffusion media (c) nitriding treatment of nitrogen gasless nitrogen media (see online version for colours)



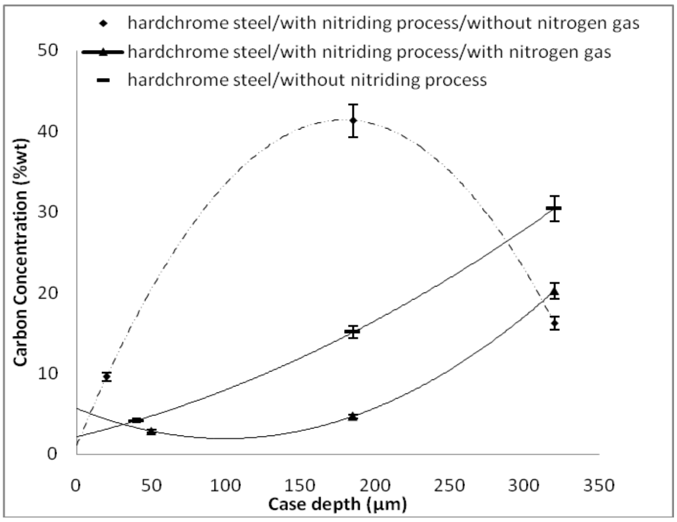
The phenomena of nitrogen atom diffusion within the material during nitride phase formation at diffusion stage is influenced by the concentration of iron and chrome element that plays an important role in helping the formation of nitride iron phase. It is where the nitrogen atmospheric diffusion shows so much nitrogen concentration within the material that disappeared and is released to the atmosphere since the inert characteristic of nitrogen would reduce the formation of passive surface layer. It is supported by the testing data which indicates that nitride phase formed on nitrogen atmospheric diffusion is fewer than on the usage of nitrogen gasless atmosphere. Nitrogen atom which does not form hard nitride phase would be created in free nitrogen.

It is where the phenomenon of free nitrogen formation is highly influenced by the chromium element which helped the diffusion process of N atom by forming oxide layer (based on EDAX observation).

On chromium plated steel (SCM 440 substrate), the media of nitrogen gasless atmospheric diffusion indicated the nitrogen atom concentration on the surface is about 12 times more than the media of nitrogen atmosphere only four times of it formed nitride phase of Fe_2N so that the rest of it certainly formed free nitrogen atom. It is influenced by the high concentration of chrome.

The nitriding and oxidation reaction underwent together within a short period of time that is of two hours. In conclusion, the test result shows that within the nitriding diffusion time of two hours, the chromium nitride has not been formed yet but there is only nitride iron and chromium oxide. It shows that the oxygen affinity is easily formed of chromium element but the nitrogen affinity is easily formed of iron element (Widi et al., 2016). Nitrogen also has good affinity with the oxygen formed on trapped oxide interface during the process of oxide layer formation. The mechanism can be analysed by considering that if the nitriding reaction happened earlier than the oxidation reaction, there would be chrome nitride phase (Cr_2N) formed and the next reaction is the chromium oxide formation (Cr_2O_3).

Figure 10 The relation of hardening depth towards the nitrogen and carbon atom diffusion



The early specimen layer of hard chrome plated steel has 15 wt % composition of chrome as EDAX test result while the layer under the chrome shows the composition of SCM 440 steel [Figure 9(a)]. After getting nitriding treatment with nitrogen diffusion media, the specimen of hard chrome plated steel shows chemical composition change which is of the presence of nitrogen atom on the material surface [Figure 9(b)]. Carbon atom is also detected on the layer under the hard chrome layer. The same thing is shown on the specimen with nitrogen gasless diffusion media but the concentration of carbon atom has been very high. It can even be displayed that the carbon concentration has exceeded the nitrogen atom concentration [Figure 9(c)]. The profile of carbon atom diffusion depth on every level is shown in Figure 10.

Figure 11 The relation of the depth of hardening towards hardness

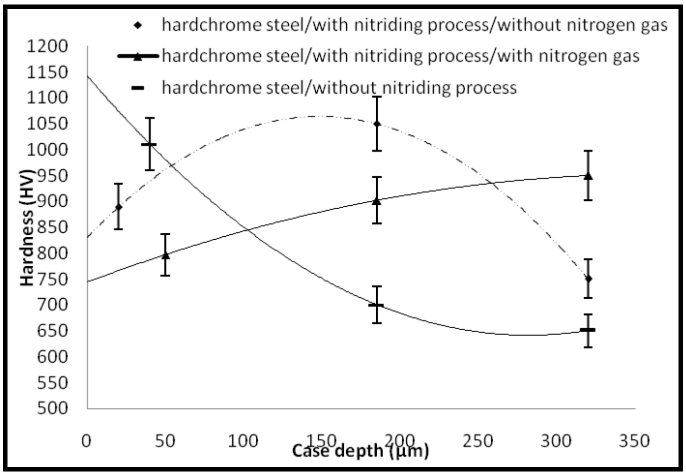
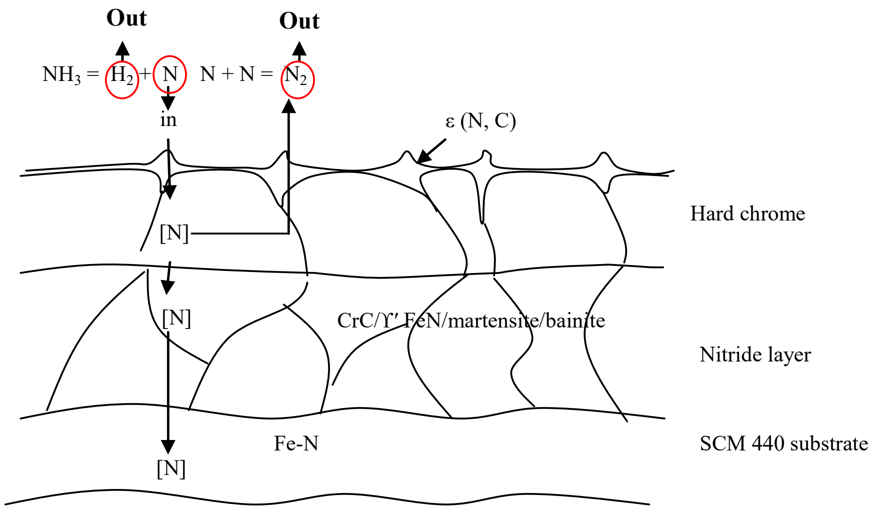
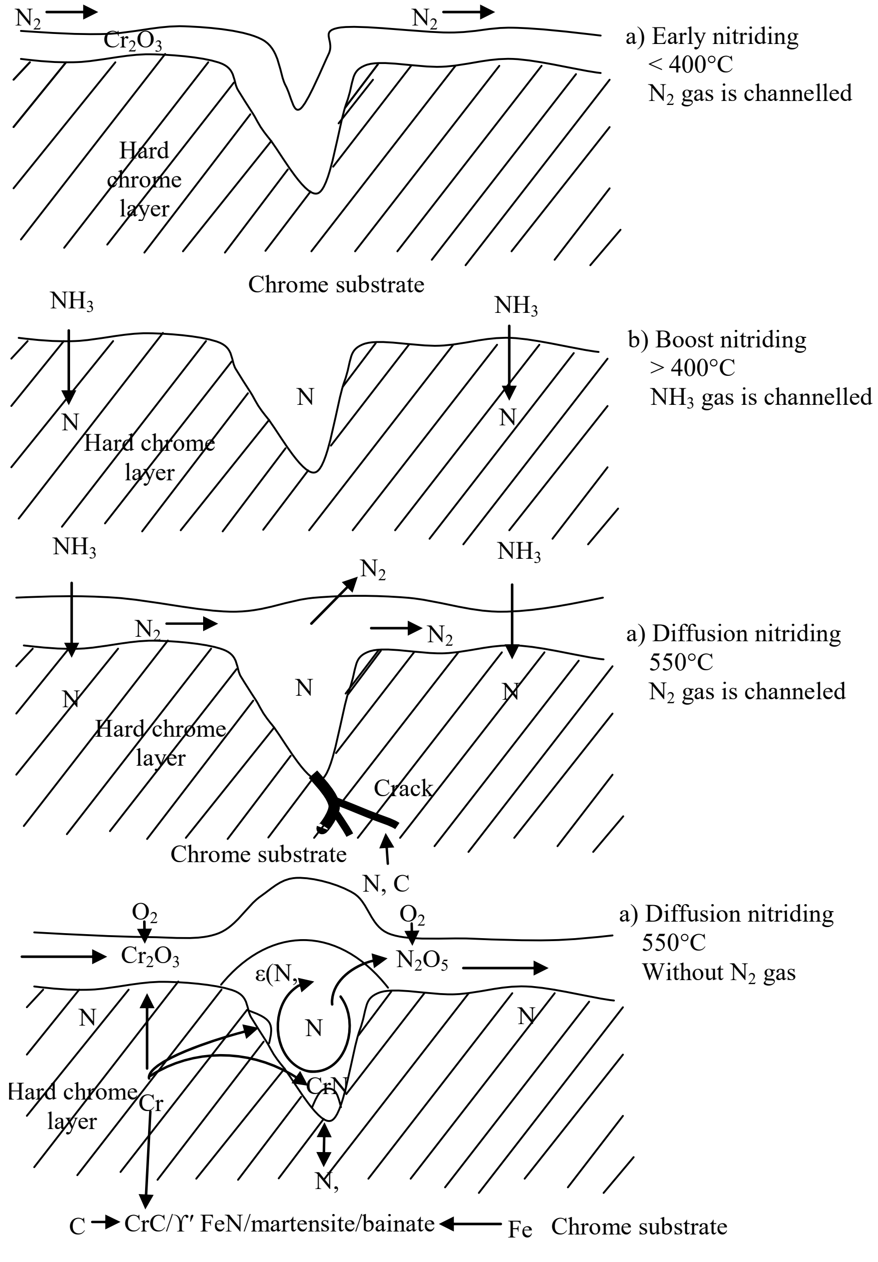


Figure 12 The mechanism illustration of layer ε and ϒ′ area formation at diffusion stage in muffle reactor (see online version for colours)



As the process temperature increases, the ability of atom diffusion into the material increases which result in an increase of the hardness (Khosravi et al., 2015). The observation result shows that an increase of nitrogen concentration does not always have correlation with an increase of hardness because the hardness is also influenced by the carbon element (Figure 11). The excessive carbon element would cause hardening and it happened on the hardening depth of 185 microns (under the hard chrome layer which is the material of SCM 440 substrate) along with the increase of carbon concentration up to 41.29%. This hardening phenomenon is formed because the iron element bonded with carbon element formed hard carbide. In the hardening depth of 320 microns, the level of hardness increased significantly that is up to 1,204 HV whereas the content of carbon element is lower which is of 16.28 wt %. The mechanism happened on the specimen getting gasless atmosphere as the diffusion media. The phenomenon created is nitriding oxidation.

Figure 13 The sensitation phenomena on hard chrome plated steel during the nitriding process



The phenomenon of chrome and carbon bond release is shown from diminish of chromium content on the result of nitride later depth test on air atmospheric diffusion that is just of 41.67 %. While on nitrogen atmosphere with the same level of depth, the chromium content is up to 94.47 wt %. This phenomenon can be easily formed because there is no alloy element having greater affinity than chrome to bond the carbon as the niobium and titanium element.

Svenson (2006) shows that there are three types of surface geometric model that can be produced from the result of metal plating in groove filling or stracth made after the finishing process, those are negative micro throw, geometric levelling, true levelling. To change the surface structure, the process of grinding, polishing and buffing are commonly done. To create the characteristic of being decorative (to make it glossy), the surface structure is made smoother. The type of true levelling is usually glossier and commonly made by plating nickel. The model of nitrogen atom deposition towards the formation of geometric surface layer found in this research has not been observed. Thus, the mechanism of nitrogen atom deposition on any diffusion media in this research can be generally pointed out in Figure 12. Figure 13 shows the more detailed mechanism in the formation of structure layer and the role of passive layer.

The mechanism shown in Figure 13 can be explained as the stages of layer formation on the surface and under hard chrome at any condition of the nitriding of diffusion media either it is with nitrogen or without nitrogen gas. It is explained as followings:

1 In the early nitriding process (before the temperature reached 400°C), the gas channelled is only nitrogen gas having inert characteristic. It would cause the passive layer of chromium oxide formed on the hard chrome plated steel to disappear. The utilisation of nitrogen gas before boost process also functions to restrain the other elements entering the atmosphere to reach the specimen. Therefore, during boost process, nitrogen atom would deposit to the specimen surface more easily.

2 During the boost process (above the temperature of 400°C), the gases channelled are nitrogen and ammonia while most nitrogen atoms are still trapped inside the crater/groove and not optimally diffused into the material yet.

3 The utilisation of nitrogen gas as the atmospheric diffusion would cause many N atoms go to the outer part of the atmosphere to create crack on the surface.

4 The existence of atmosphere/air would cause nitrogen atom are trapped inside the crater. With temperature, the chromium atom does not only create chromium oxide on surface but also bonded with nitrogen atom trapped inside the crater to create chromium nitride.

5 Nitrogen atom that has entered the material also moves towards the surface through the gaps of grain boundaries to the crater surface so that the chromium nitride layer formed become more convex.

6 Many chromium ions moved to the surface causing carbon atom to move into the deeper layer to reach the substrate.

7 Carbon atom existing on grain boundaries would bond the alloy element of iron and chrome on substrate to form chromium carbide and iron carbide in the form of bainite and sementite.

8 Nitrogen atom functioned to create iron nitride and chromium nitride.

9 The function of nitrogen is also as the austenite stabiliser so that the formation of bainite and sementite structure can be made under the hard chrome layer at lower temperature that is of 550°C.

4 Conclusions

In conclusion, formation of jagged – nodular and nitride-carbide structure on hard chrome steel during thermochemical treatment has a strong effect on surface roughness resulted in atmospheric diffusion media. When jagged structure is performed deeper on surface, the effect of roughness is smaller because N atom is easier to be deposition and nodular structure increases. The result of the surface topographic observation shows that the crack density of hard chrome plated steel material that is at first concave having crater (jagged structure) after nitriding of diffusion process with nitrogen became convex (nodular structure). In this research, it can be generally concluded that the atmospheric diffusion during the nitriding process together with the composition of alloy elements (especially chrome and iron) plays a role in producing oxide layer where at nitriding of diffusion process there is a phenomenon of passive layer evaporation (Cr_2O_3) that would influence the rate movement of nitrogen atom diffusion within the material and supersaturated reaction. On chromium plated steel, it is shown that the diffusion depth of homogenous N atom is up to 320 µm that is between 2.49 and 3.29 wt % with the Cr concentration of 84.15. On chromium layer, it is up to 0.41 wt % for nitrogen gasless diffusion media and 0.25 up to 0.83 wt % of N atom with Cr concentration of 95.31 wt % on chromium layer with nitrogen diffusion media.

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