

Enhancing the Hardness of Sintered SS 17-4PH Using Nitriding Process for Bracket Orthodontic Application

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Abstract. Brackets orthodontic create teeth movement by applying force from wire to bracket then transferred to teeth. However, emergence of friction between brackets and wires reduces load for teeth movement towards desired area. In order to overcome these problem, surface treatment like nitriding chosen as a process which could escalate efficiency of transferred force by improving material hardness since hard materials have low friction levels. This work investigated nitriding treatment to form nitride layer which affecting hardness of sintered SS 17-4PH. The nitride layers produced after nitriding process at various temperature i.e. 470°C, 500°C, 530°C with 8hr holding time under 50% NH₃ atmosphere. Optical metallography was conducted to compare microstructure of base and surface metal while the increasing of surface hardness then observed using vickers microhardness tester. Hardened surface layer was obtained after gaseous nitriding process because of nitride layer that contains Fe₄N, CrN and Fe-αN formed. Hardness layers can achieved value 1051 HV associated with varies thickness from 53 to 119 μm. The presence of a precipitation process occurring in conjunction with nitriding process can lead to a decrease in hardness due to nitrogen content diminishing in solid solution phase. This problem causes weakening of nitrogen expansion in martensite lattice.

1. Introduction

Orthodontic treatment performed to deal with malocclusion problem in human teeth. The principle of this instrument is based on provision of force on teeth through attachment bracket to teeth. Sliding method is commonly used as a way to create teeth movement by giving a force through arch wire which then proceed to the teeth with the use of orthodontic bracket [1]. This sliding method generate a frictional resistance between bracket and arch wire that lock bracket position and reduce destructed force to the teeth. Frictional resistance adopts up to 60% of provided forces which might cause the arch wire get caught and tilt the tooth [2, 3, 4].

Several factors have been involved in affecting the frictional resistance, such as bracket material [5], dimensions [6, 7] and arch wire material [8] have been investigated. Current research showed friction produced by sintered stainless steel has a friction rate of 40-45% less than cast brackets stainless steel since harder and smoother material has a low coefficient of friction [9, 10]. On behalf of this matter, the study was conducted to modifying material through increased hardness to reduce material friction.

In previous research, investment casting process used to manufacture bracket and the result shows rough surface that require further processing end [11]. It is necessary to study other manufacturing process for bracket manufacturing, namely metal injectin molding that produces sintered material.



Sintered stainless steel 17-4PH can achieve hardness up to 394.58 HV after sintering treatment at temperature of 1360 °C [12]. In the previous study, an aging treatment performed to enhance SS 17-4PH hardness with a 10% enhancement [13]. Therefore, this work tries to investigate an alternative technique to engineer the bracket material.

One of the most effective ways to increase hardness several times larger than initial hardness is nitriding treatment because SS 17-4 PH contains nitride former such as chromium. The most practical type of nitriding process to modify the bracket orthodontic surface is gas nitriding due to its complicated shape with many hard surface to reach [14]. Gas nitriding is also capable to overcome limitations of plasma nitriding since this treatment consists of gas that can easily penetrate into the pores of sintered material and capable to forming a nitride layer inside the pores [15]. Certain things that should be concerned during gas nitriding of precipitation hardened (PH) stainless steels summarized as two aspects: first is a surface passivation due to high contents of chromium (surface activation is necessary), second is presence of the precipitation processes proceeding in the matrix during thermo-chemical treatment [14].

2. Experimental

2.1. Material and Treatment

Cubical specimen (5x5x5mm) made of 17-4PH stainless steel feedstock for MIM provided by Ryer Inc. and contained approximately 7 wt.% of binder with particle distribution and size d10%: 2.8µm, d50%: 6.9 µm, d90%:18.6 µm. The feedstock composition is shown in Tabel 1.

Table 1. Chemical composition of SS 17-4PH manufactured by Ryer, Inc (wt.%).

Fe	C	Cu	Co	Cr	Mn	Mo	Nb
74.26	0.04	3.94	0.03	16.44	0.16	0.02	0.29
Ni	O	P	S	Si			
4.04	0.35	0.02	-	0.39			

Feedstock was compacted through injection molding machine at 200°C with 89m/min injection speed and 5.2 kN/m² injection force. Green part samples debounded by submerging the components into the hexane solutions while heated at 50 °C with agitation to remove primary binder. The remain binder then thermally debound at 510°C using heat rate of 1 deg/min for 60 minutes in the Barkeley furnace [16]. Before sintering, purging treatment with argon gas is needed to remove oxygen inside the tube furnace. Sintering process performed by heating the specimen up to 1360°C with a rate 5 deg/min in vacuum condition for 1.5 hour and slowly cooled until room temperature under vacuum [12]. After sintering, samples grounded using #400 SiC sandpaper and shot blasting to remove the oxide layer from material surface. The nitriding process was conducted at vacuum furnace with atmosphere condition which consisted 75m³/h N₂, 75m³/h NH₃, and 5 m³/h CO₂ and submitted to cooling down under N₂ atmospheric condition inside the treatment chamber. Samples were nitrided at 470, 500 and 530 °C, for a constant treatment time of 8 hours.

2.2. Characterization

Conventional metallographic procedure was applied for microstructural analysis. After nitriding process samples were cross-sectioned, mechanically polished and then they were slightly etched with Nital 2% with composition 2 ml of nitric acid and 98 ml of methanol. Microstucture was characterized using Zeiss Microscope to identify the white/compound zone and the diffusion zone. Thickness of the formed layers also measure with Labscope application under Zeiss Microscope.

For the surface hardness number, microhardness tester equipped with a vickers indenter was conducted with 0.01 kg load and 10 seconds dwell times. The result was the average value of three microhardness values at different positions of the treated layer.

X-ray diffraction analysis used to analyze formed phase on the nitride layer. The nitrided sample surfaces were exposed to x-ray without any mechanical surface preparation. This sample was characterized with a type PAN-Analytical using Cu Ka radiation. The scanning angle (2θ) comprises the range of $20-110^\circ$.

3. Results and Discussion

3.1. Effect of Gas Nitriding Process on Surface Microstructure of SS 17-4PH

Observation by optical microscopy in Figure 1 revealed cross-section microstructure of nitride layer in the surface of specimen. Nitride layers were produced at all nitriding temperature and indicates a boundary with the substrate. According to the different concentration of nitrogen content, microstructure can be distinguished into two zone which are compound/white layer and diffusion layer [17].

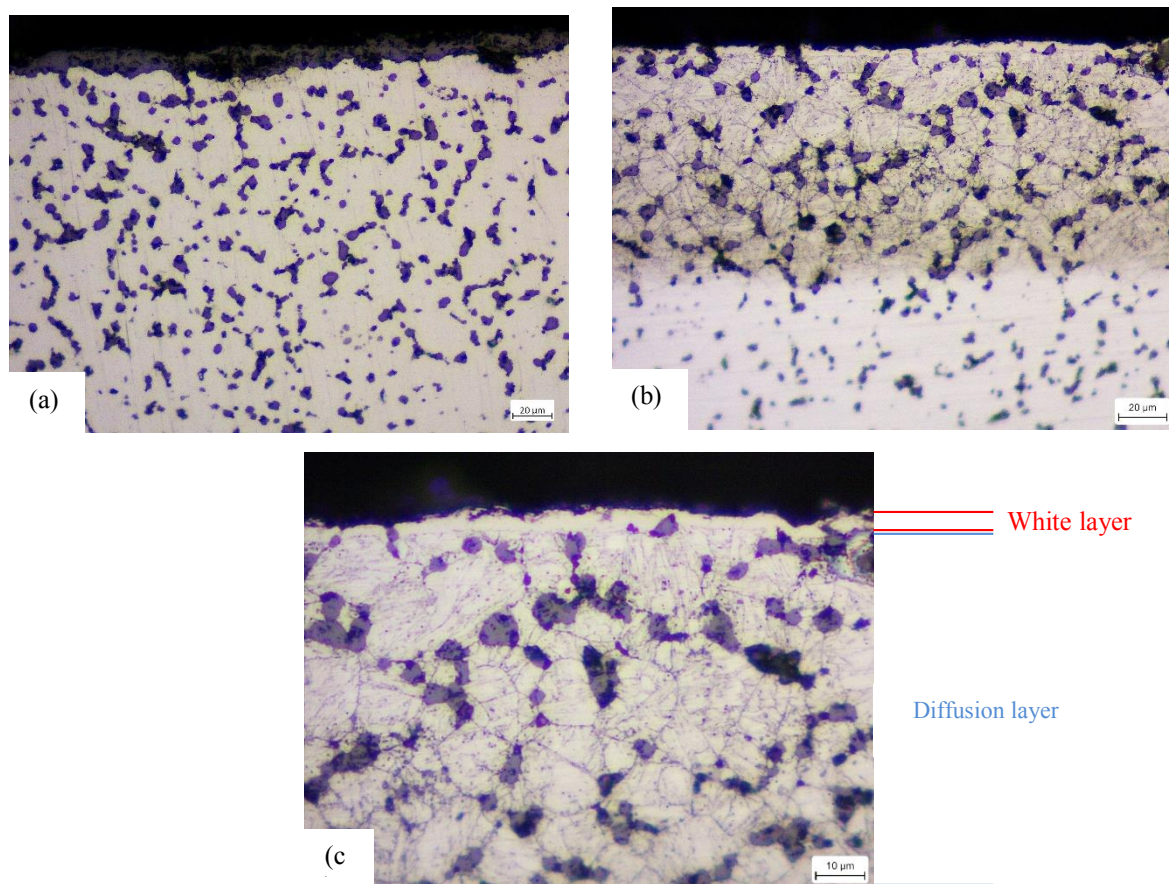


Figure 1. Microstructure of 17-4 PH stainless steel (a) untreated specimen (b) nitrided specimen at 530°C at 500X magnification (c) nitrided specimen at 530°C at 1000X magnification.

Compound layer is white nitride colour that comprises high concentration of nitrogen and configures a ceramic layer made of iron nitrides $\text{Fe}_4\text{N}-\gamma'$. As a metastable compound, ammonia was dissociated into active nitrogen-hydrogen gas mixture and brings up nitrogen potential or activity of nitrogen dissolved in iron. In conjunction with increasing active nitrogen-hydrogen gas mixture nitrogen, the solubility also increases until the nitrogen potential is high enough to reach the equilibrium of nitrogen in $\text{Fe}_4\text{N}-\gamma'$ [18]. Formation of this ceramic layer then makes the hardness on the surface of the material increases since compound layer results in a tensile residual stress.

Another nitride layer formed is diffusion layer. This layer contains low concentration of nitrogen and defined as base microstructure hardened by interstitial atom in solid solution and/or by nitrides

precipitation. Due to high concentration of chromium in stainless steel 17-4 PH, type of precipitate which is formed is CrN. Increasing hardness on this layer is caused by interstitial nitrogen in iron and volume expansion of nitrides precipitation that fabricates a compressive residual stress field in the diffusion layer [17].

3.2. Effect of Nitriding Temperature on Nitride Layer Thickness

Gas nitriding process on SS 17-4 PH indicated formation of two type nitride layer such as compound/white layer and diffusion layer. Based on the results presented in the graph below, it can be conclude that the thickness of those two types of layer was convinced on temperature process. Layer thickness owned by compound/white layer varies between 2–5 μm under the temperature range of 470–530°C while diffusion layer thickness varies between 53–119 μm . Overall data exhibit an increasing thickness of nitride layer along with increased temperature. This result occur because of the increase in diffusivity of the interstitial elements into base metal as the temperature increases. Temperature enhancement can raise activation energy of nitrogen atom to diffuse and this behavior is intended for atomic diffusion that is controlled by thermally activated treatment [19].

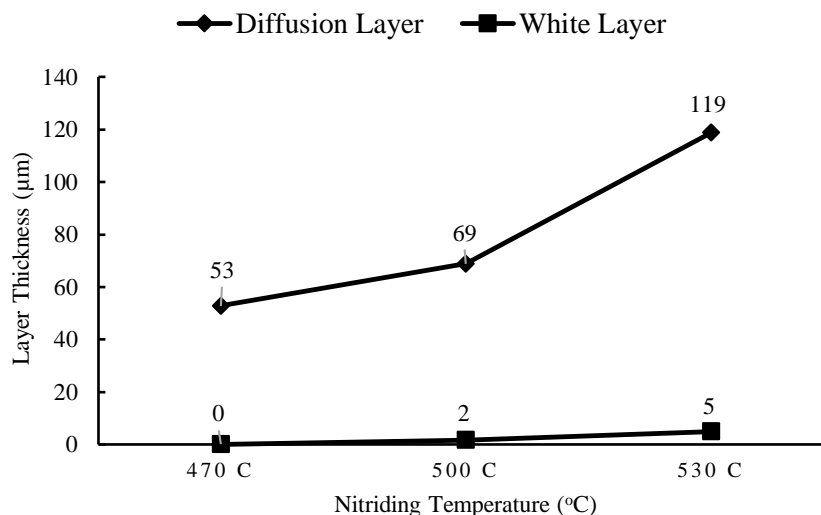


Figure 2. Effect of Nitriding Temperature on thickness of nitride layer.

On a research that was conducted by Cardoso [20], deployment of nitrogen during nitriding treatment ensued through volume (lattice) diffusion and through high diffusivity paths (e.g. grain boundaries and dislocations), which both of mechanism were performed depending on temperature process. Diffusion process that occurs through high diffusivity paths required low activation energy since this mechanism already has stored activation energy. Therefore, this mechanism remarkably takes place during low-temperature of nitriding treatment. On the other hand, nitriding treatment with high temperature process occurs through volume diffusion. It happens because of grain growth and defects annihilation due to temperature increment.

3.3. The Effect of Nitriding Temperature on Material Hardness

Graphic in Figure 3 showed microhardness number of nitride layer as a function of temperature. This figure indicated microhardness number between 1008 HV at temperature 470°C and 1051 HV at temperature 530°C. Material hardness was high on the surface and decreased along with the indentation of hardness towards the base metal since nitride layer only formed on the surface of material. The highest attainment for microhardness number was obtained while nitriding process was carried out at temperature 530 °C with 2.7 times greater than sintered SS 17-4 PH (395 HV). Therefore, interstitial

nitrogen atom inside iron lattice, nitride compound precipitation and ceramic layer formation on the surface of material affect hardness enhancement in material.

Hardness enhancement was expected to reduce friction value on bracket surface as the result of study about relationship between hardness and friction on comparison of bracket SS 17-4 (investment casting) in contrast to Synergy® (RMO, USA) and Gemini® (3M, USA) from commercial bracket. Bracket Synergy® (RMO, USA) that had a hardness value of 265 HV conducts 1.37 friction coefficient, while SS 17-4PH (investment casting) with 295 HV generated 1.17 friction coefficient and Gemini® (3M, USA) with 312 HV produced 0.67 friction value [21]. Therefore, the enhancement of hardness up to 1051 HV is expected to reduce friction coefficient less than the friction values above.

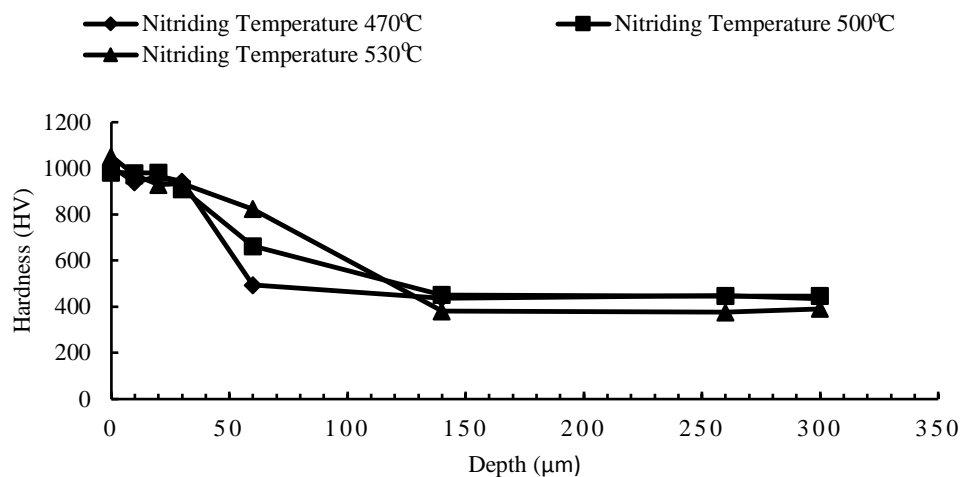


Figure 3. Microhardness profile of SS 17-4 PH from surface to base material.

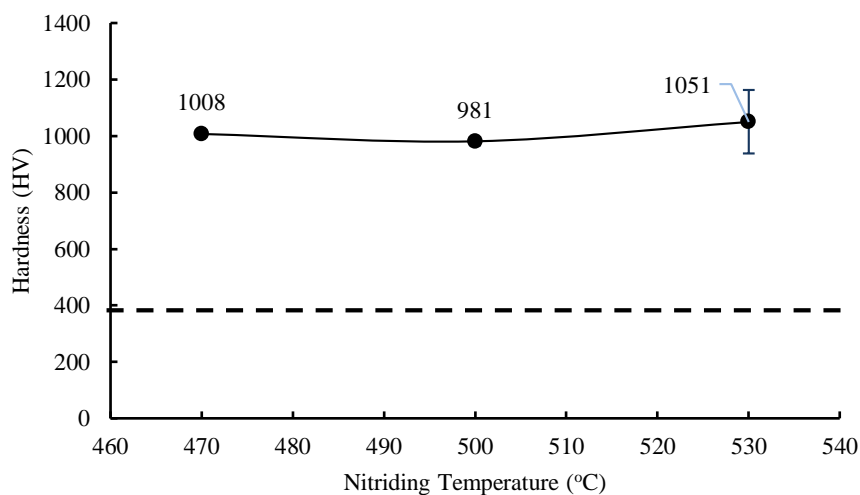


Figure 4. Effect of Nitriding Temperature on microhardness at the surface of SS 17-4PH

Based on Figure 4, hardness at the surface of material influenced by temperature process. This figure explained the decreasing hardness of material at temperature 500 °C. Hardness reduction on material occurred in relation to precipitation of chromium nitride, which reduces nitrogen content in solid solution phase. Therefore, nitrogen expansion in the martensite lattice has weakened. As illustrated by Wang [22], equilibrium solubility limit of nitrogen within martensite structure has been exceeded at temperature more than 450 °C and at the same temperature, mobility chromium also increases. Therefore, formation of CrN or Cr₂N is more desirable. The presence of precipitation process which happened in the matrix during nitriding treatment caused distinction on the nitriding kinetics and structure characteristic [23].

3.4. Effect of Nitriding Temperature on Phase Formation inside Nitride Layer

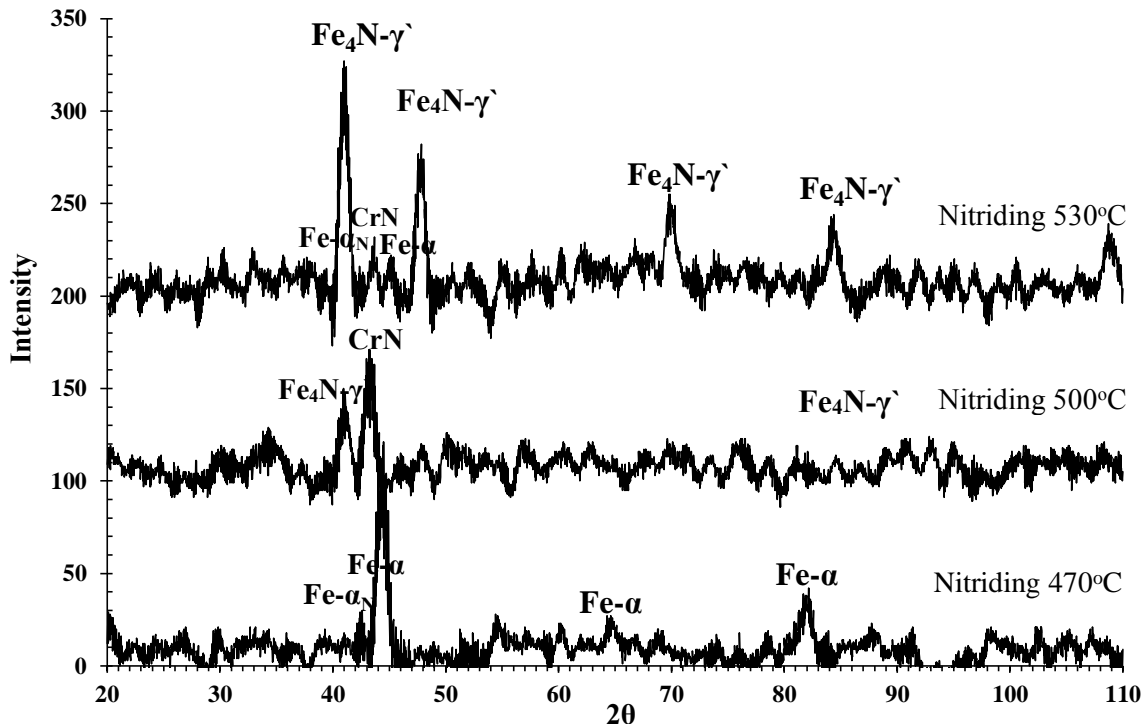


Figure. 5 Effect of Nitriding Temperature on Phase Formation inside Nitride Layer.

The X-ray diffraction results of stainless steel 17-4PH with three different nitriding temperatures were shown in Figure 5. The main phase that appears during nitriding temperature at 530 °C is $\text{Fe}_4\text{N}-\gamma'$ with some CrN precipitates. The presence of these phases is appropriate with the OM micrograph shown in Figure 1. $\text{Fe}_4\text{N}-\gamma'$ phase was established as white nitride layer that indicated a high nitrogen concentration area. High intensity of $\text{Fe}_4\text{N}-\gamma'$ peak on this parameter specified the thickness of the white layer formed on this surface. Otherwise, this figure also showed decreasing intensity of $\text{Fe}_4\text{N}-\gamma'$ peak at temperatures below 530 °C even disappearing at nitriding temperature 470 °C parallel to compound layer thinning. At nitriding temperature 470 °C nitrogen potential was not high enough to reach the equilibrium of nitrogen in $\text{Fe}_4\text{N}-\gamma'$. Therefore, compound layer was not formed on the surface. Figure 5 also showed the high peak of CrN formed at 500 °C nitriding temperature so that the hardness of the material at this temperature decreased as shown in Figure 4. The high peak of CrN showed that the amount of CrN precipitates formed at this temperature were more plentiful than other parameters.

4. Conclusion

From the study above, it can be concluded that the experimental results reveal that gas nitriding significantly improve the hardness of 17-4 PH up to 1051 HV which is 2,7 times greater than ordinary bracket (395 HV). A white layer made of iron nitrides ($\text{Fe}_4\text{N}-\gamma'$) makes the hardness on material surface increase because it generates a tensile residual stress while diffusion layer strengthens material by interstitial atom in solid solution ($\text{Fe}-\alpha_N$) and/or by the precipitates of chromium nitrides (CrN) which fabricate a compressive residual stress field in the diffusion layer. The surface hardness increases as an increasing of nitriding temperature and formed nitride layer up to 119 μm width at 530 °C. Numerous CrN precipitates which are formed at temperature 500 °C reduce material hardness because nitrogen

content in solid solution phase disappear. Thus, the optimum parameter with the maximum hardness value and the thickest nitride layer is achieved at nitriding temperature 530°C.

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