

# S-Phase Layer Development on 316 LVM Using Low Temperature Hybrid Thermochemical Treatment Process

Mohd Shahrman Adenan, Siti Umrah Zainal, Esa Haruman

**Abstract:** This investigation focuses on the improvement of surface properties of medical grade austenitic stainless steel (AISI 316LVM). The aim is to develop a homogenous supersaturated hard layer of expanded austenite (s-phase) at the surface of AISI 316LVM using low temperature hybrid thermochemical heat treatment process. The s-phase layer produced by this process is able to improve the surface properties of AISI 316LVM, overcoming its drawback of low surface hardness and wear resistance, without impairing the corrosion resistance of the steel. During the heat treatment process, ammonia (NH<sub>3</sub>) and methane (CH<sub>4</sub>) gasses were introduced into the furnace with temperatures of 425°C and 475°C, at 6 and 12 hours with gas composition of 75% of NH<sub>3</sub>, 10% of CH<sub>4</sub>, and 15% of Nitrogen (N<sub>2</sub>). Characterization on the microstructure showed the formation of the S-phase layer with variation of thickness according to parameters used. The S-phase formation was confirmed with phase analysis using XRD. Besides, the surface hardness also significantly increased from 210.9 HV to 1170.0 HV. In conclusion, low temperature hybrid heat treatment process is able to produce a homogenous hard s-phase layer.

**Keywords :** 316 LVM, Hybrid surface treatment, Ammonia, Methane, S-phase layer, Surface hardness.

## I. INTRODUCTION

The demand of Austenitic stainless steels are largely used in various application nowadays because its characteristic to withstand corrosion is well known due to high content of chromium elements up to 16%-18% [1] [2] [3]. Moreover, Austenitic stainless steel is very good in biological biocompatibility as well thus it makes this material capable to use as biomedical implant. As of that, on the usage of medical grade austenitic stainless steel (AISI 316LVM) as biomedical implant material is increasing due to pricey cost of superior implant material such as titanium and chromium cobalt. However, drawback of AISI316LVM in low surface hardness and wear resistance limits this material for only certain applications such as bone screws, bone plates, wires and etc. To overcome this drawback, surface engineering is the most suitable method that can be applied; however, the process is limited to thermochemical process, either using plasma or conventional gas method. In order to reduce of the cost of the process but may remain the result, the conventional method in tube furnace is tested respect to thermochemical parameter such as temperature as and holding time.

Revised Manuscript Received on 20 October, 2019.

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In these processes, the layer of the stainless steel can be improvised by forming a supersaturated layer containing nitrogen (N) and/or carbon (C) which is known as austenite expanded phase or s-phase. Theoretically, the superior layer will be improved the surface hardness. Previous researchers reported that the hardness values are lower than 1700 HV [1].

## II. PROCEDURE FOR HYBRID THERMOCHEMICAL TREATMENT

### A. Preparation of specimen

The material used for specimen was austenite stainless steel grade AISI 316LVM with chemical composition of 17.67% Cr, 14.76% Ni, 0.002% Ti, 1.86% Mn, 0.017% C and the balance of Fe. The material was machined into thickness of 8 mm with 25mm diameter. The specimen was grounded and polished in series using silica carbide sand paper from grit 230, 320, 400, 600 and 1200 and continued with polishing process from 9.5, 5, 3 and 1 micron using alumina polishing powder until mirror finished. Specimens were then cleaned in ethanol solution for 20 minutes using ultrasonic cleaning to remove grease and dirt.

### B. Procedure of hybrid thermochemical treatment

Prior to heat treatment process, the specimens were soaked into hydrochloride acid, HCl (2M) solution for 30 seconds to remove native oxide film on the surface. The specimens were then placed on the sample holder then inserted into a tube furnace with Kholer D001-Inline Static Mixer for mixing of gasses. The setup of the experiment is shown in Fig 1 and parameter used is shown in Table 1. Nitrogen (N<sub>2</sub>) was purged into the furnace, with heating rate of 5°C per minute, until the heat increased up to 425°C and 475 °C prior to the experiment. Then NH<sub>3</sub> and CH<sub>4</sub> were fed into the mixing chamber for 6 hours and 12 hours subjected to the experiment. The pressure and flow rate were kept maintained at 50 kPa and 0.72 m<sup>3</sup> per hour. The gas composition for experiments was 75% of NH<sub>3</sub>, 10% of CH<sub>4</sub> and 15% of N<sub>2</sub>.

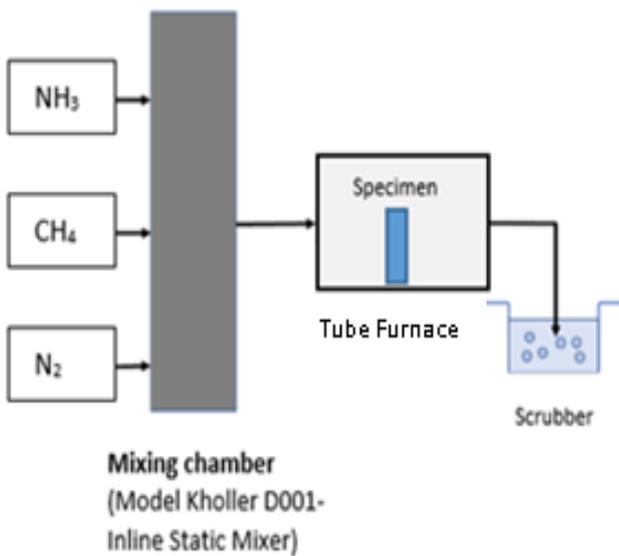
### C. Procedure of evaluation

After treatment, the specimen was etched with Kalling No2 solution for one minute. The layer enriched with carbon and nitrogen is capable to resist reaction with the etchant in order to reveal microstructure. After the treatment, the microstructure of the specimens was analysed using Optical Microscopic, model Olympus BV41M and Scanning Electron Microscopic (SEM), Hitachi model SU3500. Elementary profile was characterized by line scan model, Hitachi EDX Quantax70 at the cross sectional area of the specimen. The surface hardness was also observed using Micro Vickers Hardness model MVK-H,

Mitutoyo with 50 gf of indentation load. X-ray diffraction (XRD) analysis was investigated by using Rigaku with Cu-Ka radiation in range 30° to 120° and parameter 0.05° of sampling step, 2°/min of speed, 40 kV, 40 mA and 1.544 Å.

**Table- I: Hybrid treatment parameter**

No	Specimens	Temperature (°C)	Holding time, (h)
1	425HP6H	425	6
2	425HP12H		12
3	475HP6H	475	6
4	475HP12H		12

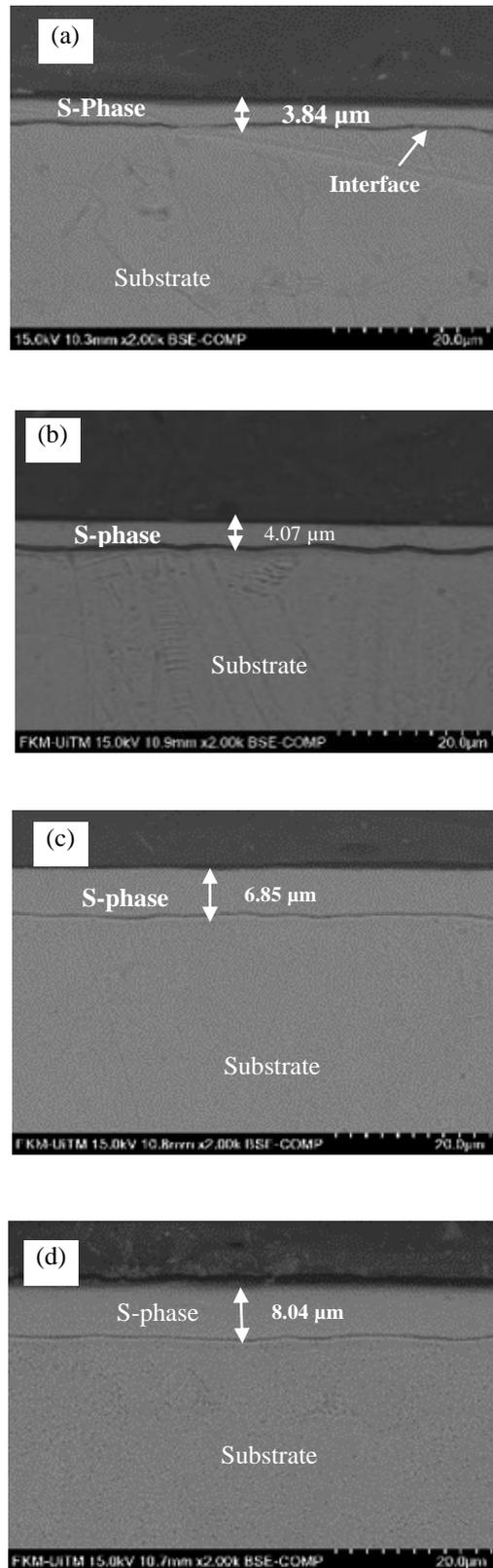


**Fig. 1: Schematic of the horizontal tube furnace gas disappear**

**III. RESULT AND DISCUSSION**

**A. Morphology of S-phase layer**

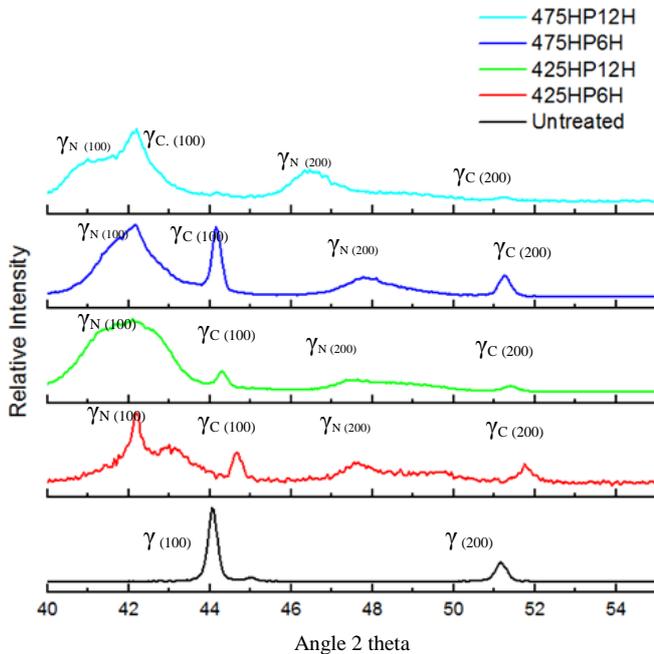
Typical layer morphology of s-phase layer influenced by hybrid treatment is shown in Fig 2. The layer appeared as “bright” under optical microscopic. The whitish appearance was uniform and homogenous which appeared on the surface of substrate. This indicated that the layer occurred at surface was good for corrosion resistance in the chemical [1]. The thickness of layer was measured and shown in Table II. According to the thickness influenced by parameters, generally the thicker layer liaises at temperature 475°C in both holding times in 6 hours and 12 hours. This can be seen in Fig 2 which presented the layer thickness of (c) and (d) are thicker than (a) and (b). In fact, previous researcher has mentioned that the result in plasma could produce a uniform thicker s-phase than conventional method treatment process because the native oxide film is removed mostly by bombardment of positive charged particles and different mass transfer mechanism unlike the conventional method process [2].



**Fig.2: The layer morphology result on respective parameter upon completed hybrid thermochemical process in conventional gas using tube furnace, (a) Specimen 425HP6H, (b) Specimen 425HP12H, (c) Specimen 475HP6H, and (d) Specimen 475HP12H**

**B. XRD result**

The result of XRD of specimens was plotted in separate layer. Fig 3 illustrates the stack line graph of the different peaks of specimens. The treated specimens indicated that the austenite highest peak slightly shifted to the lower Bragg angle and it became broader compared to the untreated specimen. The peak of Sample 475HP12H shifted into the lowest angle at 41° and was broader against untreated.



**Fig. 3: Phase analysis by XRD**

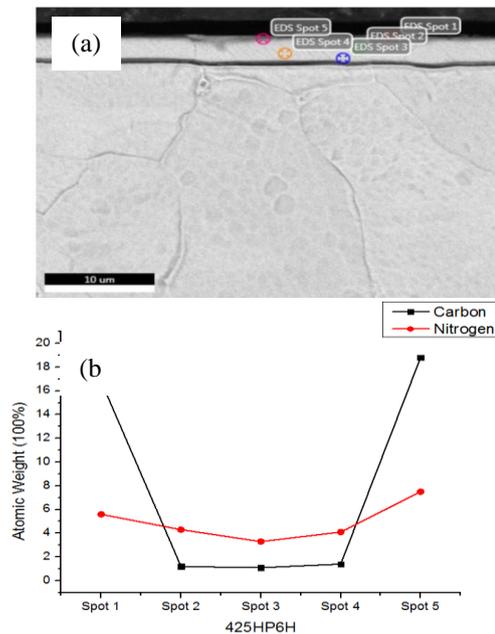
The specimens of 425HP6H, 425HP12H and 475HP6H were liaised at angle 42° respectively and the peaks were broader as well. At higher temperature and longer holding time, a wide peak appeared consisting of both  $\gamma_N$  (100) and  $\gamma_C$  (100) at lower 2 $\theta$  angle. The following peak represented  $\gamma_N$  (200). Thus,  $\gamma_C$  (200) slightly disappeared from the graph. Then, when the holding time was decreased, it showed that  $\gamma_N$  (100) peak was higher as the following peak,  $\gamma_C$  (100). Meanwhile, when both next peaks were decreased in height,  $\gamma_N$  (200) was broader than  $\gamma_C$  (200). Hence, when the temperature decreased to 425C with long holding time, the pattern was slightly similar to 475HP12H, but  $\gamma_N$  (100) and  $\gamma_C$  (100) were not combined in a peak. The  $\gamma_C$  (100) had low peak and slightly disappeared followed by  $\gamma_N$  (200) and  $\gamma_C$  (200). The differences between peak profile of treated and untreated specimen are subjected to incorporation diffusion of nitrogen and carbon atoms into face centered cubic (FCC) structure of austenite phase in order to influence lattice expansion and distortion [2] [3]. Thus, the new phase consisting of nitrogen enriched expanded austenite,  $\gamma_N$  and carbon enriched expanded austenite,  $\gamma_C$  was formed. S-phase layer occurred when carbon atom had diffused during dissolving at lower part of nitride layer by nitrogen atom [4][5]. The atomic weight of carbon atoms had influenced it to diffuse further and nitrogen front still continued to diffuse into the substrate, leading to the gradual leveling of carbon concentration and thus reducing carburizing layer [6].

**Table- II: The layer thickness of samples**

No	1	2	3	4
Specimens	425HP6 H	425HP 12H	475HP6 H	475HP1 2H
Layer Thickness, $\mu\text{m}$	3.84	4.07	6.85	8.04

**C. Elementary of s-phase**

In order to confirm elementary of layer, the specimen was examined using EDS [7]. The results are represented in Fig 4, 5,6 and 7. The specimen 425HP6H showed that carbon and nitrogen decreased at spots 1 and 2. For spots 3 and 4, the weight of carbon did not change but at point 5, the carbon increased drastically. Meanwhile, the weight of nitrogen was seen to decrease at spot 3 and then increased at point 4 and point 5 as it went up to the bottom. The specimen 425HP12H indicated that the weight of carbon was higher than nitrogen at spot 1 to 5; however, at spot 3, it can be seen that it dropped slightly but started to increase at point 4 and 5. The carbon of weight percentage gradually decreased towards the substrate but the nitrogen weight percentage slightly retained from the top to the bottom layer. However, 475HP12H had different weight percentage than 425HP6H, 425HP12H and 475HP6H. At spot 2, the interchange of carbon and nitrogen occurred. The percentages of atomic weight of nitrogen further increased when travel distance to substrate unlike carbon which decreased gradually. According to Fig 4, the weight percentage of carbon was greater than carbon at nitrogen at the top of s-phase layer and declined towards substrate. The carbon element gave a higher diffusivity to diffuse further to substrate than nitrogen; thus, the speedy arrival diffused carbon atoms into interstitial sites sooner than nitrogen [8][9][10].



**Fig. 4: The s-phase spots of elementary profiling of carbon and nitrogen atomic weight on 425HP6H. (a) Spots of evaluation (b) Graph of atomic weight between C and N respects to the spots.**

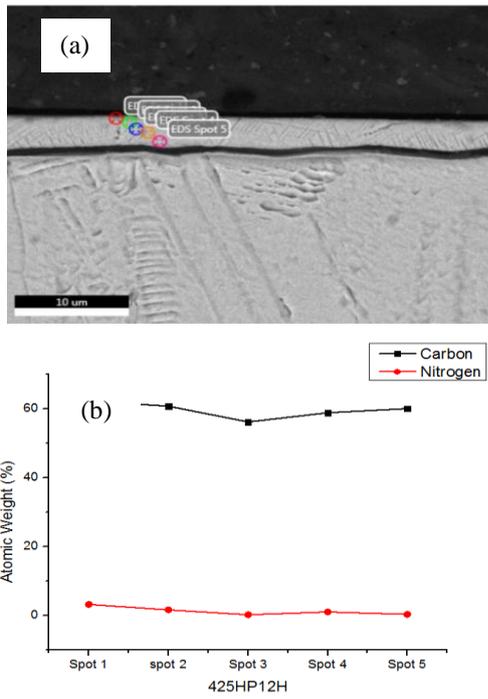


Fig. 5: The s-phase spots of elementary profiling of carbon and nitrogen atomic weight on 425HP12H. (a) Spots of evaluation (b) Graph of atomic weight between C and N respects to the spots.

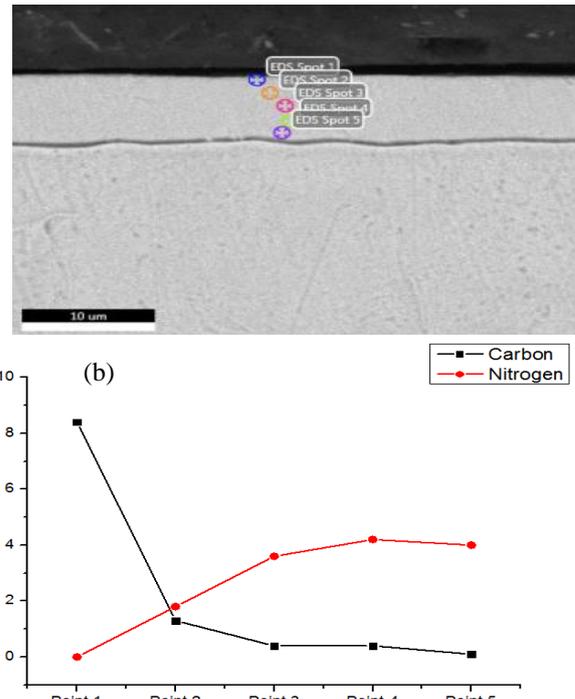


Fig. 7: The s-phase spots of elementary profiling of carbon and nitrogen atomic weight on 475HP12H. (a) Spots of evaluation, (b) Graph of atomic weight between C and N respects to the spots.

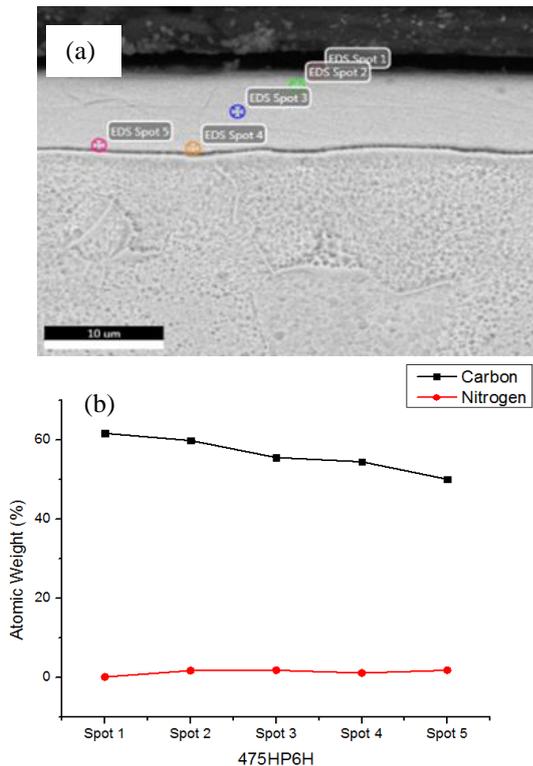


Fig. 6: The s-phase spots of elementary profiling of carbon and nitrogen atomic weight on 475HP6H. (a) Spots of evaluation (b) Graph of atomic weight between C and N respects to the spots.

D. Surface hardness

According to Fig 5, the highest value of microhardness at the surface area was 475HP12H with the value 1170.0 HV<sub>0.05</sub>. The microhardness value was 5 times harder than untreated, 210.9 HV<sub>0.05</sub>. Specimens 425HP6H, 425HP12H and 475HP6H presented a gradual increase with respect to thickness which were 282.6 HV<sub>0.05</sub>, 336.1 HV<sub>0.05</sub> and 521.5 HV<sub>0.05</sub> respectively. The extreme hardness in s-phase can be attributed to the high concentration of carbon introduced by diffusion process to the austenite phase [11][12][13]. The microhardness increases as the temperature increases.

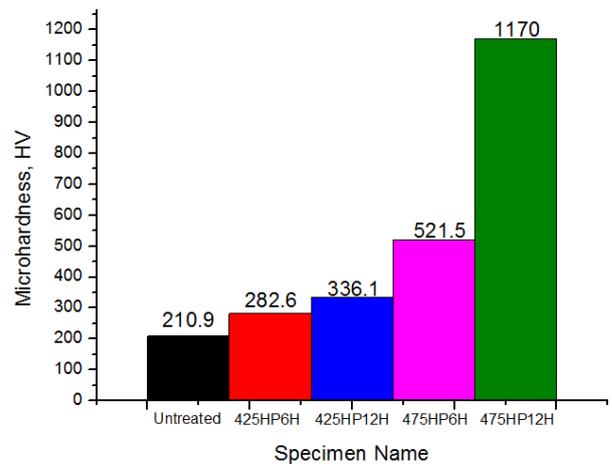


Fig 8: Microhardness of the surface area

#### IV. CONCLUSION

The present experiment on austenite stainless steel specimen with respect to different temperature at 425°C and 475°C and different time at 6 hours and 12 hours had evidently influenced the result outcome. Specimen 475HP12H showed that heat treatment at 475°C and 12 hours can produce a better uniform thickness and hardness. The expended austenite layer by hybrid treatment in the tube furnace was slightly identical to the outcome of plasma process. Based on the result at present, the tube furnace can also perform effectively by incorporating simultaneous gas ammonia and methane of hybrid treatment. As conclusion, the thickness correlation might be depended with increasing in both temperature and holding time.

#### ACKNOWLEDGMENT

A very special appreciation goes to Ministry of Education with grant number FRGS/1/2016/TK05/UITM/02/4 and special assistance by Mr. Yuki Hamada from Ube College, Japan

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