Formation of S phase layer on Medical Grade AISI 316LVM via Low-Temperature Hybrid Gas Diffusion Process

J. Saedon, M. F. M. Azmi, M. S. Adenan[1]*
Faculty of Mechanical Engineering, Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia
** juri41@yahoo.com*

ABSTRACT

The low-temperature thermochemical hybrid process below 450°C will result in the formation of a thin layer of supersaturated nitrogen/carbon interstitial solid solution known as the S phase layer. This work focuses on development and characteristics analysis of the S phase layer on AISI 316LVM (ASTM F138) stainless steel using hybrid gas diffusion techniques. The hybrid heat treatment process performed at 425°C for 6 hours of treatment time with the hybrid gas composition of NH_3, CH_4, and N_2 at 80%, 5%, and 15%, respectively. Based on the XRD analysis and optical microscope micrograph, the gas diffusion techniques are capable of forming the S phase layer on the stainless steel. However, the thickness is not as significant as plasma techniques. The hardness of the material is increased by about 52% compared to the untreated material, and the unavailability of the chromium nitride precipitates to ensure that the corrosion resistivity of AISI 316LVM does not deteriorate. In conclusion, the hybrid gas diffusion process capable of improving the stainless-steel properties by the formation of the S phase layer.

Keywords: *Hybrid S phase, gas diffusion, low-temperature heat treatment, 316LVM.*

Introduction

Stainless steel type 316L is most widely used for implant material due to its low cost compared to titanium and cobalt alloy (Galván et al., 2016). The use of 316L stainless steel as a temporary implant also is approved by the Food and Drug Association of the United States (US FDA) (Ibrahim et al., 2017).

ISSN 1823- 5514, eISSN 2550-164X
Received for review: 2019-06-10
Accepted for publication: 2019-07-01
Published: 2020-06-30

Austenitic stainless steel type 316L is utilized in orthopedic implants departments such as bone fracture plates and screws, intramedullary nail, and total hip replacements (Chen & Thouas, 2015). However, the critical problem confronted by the clinician on a 316L stainless steel implant is the failure of the implant due to the corrosion in adverse human body conditions (Manam et al., 2017). To resolve the problem, low-temperature nitriding or carburizing could be considered as an appropriate method as nitriding process below 500°C will result in an interstitial-saturated thin layer that is saturated with nitrogen/carbon atoms (Lo et al., 2009). The thin layer called the S phase layer or expanded austenite. The interstitial layer improves the 316L stainless corrosion resistance, enhanced hardness, and wears resistance (Menthe & Rie, 1999).

S phase formed when austenitic stainless steel or other S phase forming materials exposed to a large amount of nitrogen, carbon, or combination of both carbon and nitrogen at low-temperature heat treatment in the absence of chromium nitrides or carbides precipitation (Gontijo et al., 2006). The formation of the S phase can be obtained from nitriding (Leyland et al., 1993), carburizing (Rotundo et al., 2014), and the hybrid process of nitrocarburizing (M.S. Adenan et al., 2013). There are four different techniques used to develop the S phase, which is plasma diffusion process (Sun, 2005), ion implantation process (Williamson et al., 1994), physical vapor deposition (PVD) process (Parsapour et al., 2012) and gas and liquid diffusion process (Haruman et al., 2006). The targeted surface of austenitic stainless steel should be activated by removing the oxide layer to permit the diffusion process (Shih et al., 2004). There are a few techniques used by the previous authors to remove the oxide layer such as cathodic sputtering (Baranowska, 2004), using fluoride solution (T. L. Christiansen & Somers, 2013) and using hydrochloric acid (Paijan et al., 2012). The removal of the oxide layer denied the claim of the inefficiency of gas diffusion techniques and proved to successfully develop the S phase layer via low-temperature gas nitriding and carburising process.

Christiansen (T. Christiansen & Somers, 2005) use a custom built furnace with ammonia (NH_3) as nitriding gas and hydrogen (H_2) as the carrier gas. Meanwhile, for the carburising process, carbon monoxide (CO) and H_2 was used as carburising and gas carrier respectively. The S phase was effectively developed without the existence of carbides or nitrides. Another study by Adenan (Mohd Shahriman Adenan et al., 2014) successfully developed S phase layer on 2205 Duplex stainless steel. The low temperature thermochemical hybrid heat treatment performed at 450°C for 30 hours. During the heat treatment process, nitrogen and carbon elements were simultaneously introduced to the furnace. The process successfully produced a high hardness S phase layer; however, the result also found the presence of chromium precipitation, which may affect the corrosion resistance of the treated steel.

According to a study by Cheng, the hybrid S phase is a superposition of nitrogen and carbon S phase profile (Cheng et al., 2005). Thus, the hybrid S phase receives the same benefits as both nitrogen and carbon S phase (T. L. Christiansen & Somers, 2009).

This research focuses based on fundamental investigations on the development and characteristics of the S phase layer on AISI 316LVM stainless steel using hybrid gas diffusion techniques. The investigation helps to prove the formation of the S phase layer on AISI 316LVM to obtain improved hardness without the presence of precipitation of CrN using a low-cost horizontal tube furnace.

Experimental procedure

Medical grade AISI 316LVM stainless steel was selected as the specimen due to it complies with the standard EN1811 to be used for prolonged and direct contact bio-implant. Table 1 shows the material and its alloying composition of AISI 316LVM used in this study in weight percent. The preparation process includes sectioning, grinding, polishing, and drying. The sectioning process of the hot-rolled bar of 316LVM into 6mm x 10mm (length x diameter). The specimen surface then ground using SiC paper grit size of 240, 320, 600, 800, 1000, and 1200 respectively. To achieve the mirror finish surface of the specimen, it was polished using 3µm and 1µm of alumina oxide, Al_2O_3 powder in water solution using a cloth-covered rotating wheel. The specimen is then washed and cleaned using an ultrasonic cleaner where it is immersed in acetone for 15 minutes and rinsed with distilled water. The specimen is dried using a dryer and stored in a closed dry cabinet to avoid environmental contamination.

Table 1. Composition of AISI 316LVM

316LVM Composition (wt%)										
C	Si	Mn	P	S	Cr	Ni	Mo	Cu	N	Fe
0.021	0.49	1.68	0.018	0.001	17.43	14.22	2.77	0.082	0.055	Bal.

The hybrid treatment was performed using a conventional tube furnace involving a simultaneous hybrid introduction of ammonia (NH_3) for nitriding, methane (CH_4) for carburizing process and nitrogen (N_2) as a gas carrier. The flow of the gases was controlled by the flow meter and went to the mixing chamber for the blending process before entering the furnace. The specimen is placed on a porcelain boat positioned in the centre of the horizontal tube furnace to ensure the optimum diffusion during the heat treatment process. The

gases then flowed out through the outlet and channeled into the water for the scrubbing process before released into the atmosphere. This process is precisely monitored and controlled to obtain an accurate experimental result. The gas diffusion hybrid heat treatment performed at 425°C at 6 hours of treatment time. The composition of NH_3, CH_4, and N_2 during the process is 80%, 5%, and 15%, respectively. After the treatment, the specimen then cooled to room temperature

X-Ray Diffraction (XRD) method is utilized to analyze and examine the crystalline structure of the material. The phase constituent of the hybrid treated specimen analyzed using the Geiger Diffractogram of Rigaku brand. During the analysis, Cu-Kα radiation was used with applied voltage and current at 45kV and 40mA, respectively. The data obtained from XRD was analyzed using PXRD software provided by Rigaku. Microhardness test was employed to measure the hardness of heat-treated specimens by using the indentation method. For this study, the Vickers hardness test machine of model MVK-H, Mitutoyo, is used for the hardness test. The cross-sectional of the heat-treated specimen is prepared by bake lite hot mounting, grinding up to 1200 grit paper, and polished up to 1μm.

Before the specimen placed on the Vickers hardness test machine, the specimen placed under an optical microscope to ensure the quality of the surface. When the specimen is fixed on the machine, the 10g load is applied to the specimen for 10 seconds at ten different depth point (Naragino et al., 2016). Hardness measurement was conducted according to ASTM E384 (Standard Test Method for Vickers Micro-Hardness of Metallic Material) (*ASTM E384-17, Standard Test Method for Microindentation Hardness of Materials*, 2017).

Results and Discussion

Phase Analysis

The phase composition of untreated and hybrid treated specimens determined by X-ray diffractogram analysis are plotted as in Figure 1. The diffraction pattern comparison between the samples shows that the peaks of the hybrid treated specimens are shifting towards the lower 2θ angles compared to the untreated material. The peak shift indicates the formation of expanded austenite or the S phase (Sun et al., 1999). The peak shifting and broadening of the XRD pattern are insignificant due to the low amount of nitrogen and carbon-containing solid solution as the S phase layer is very thin. The diffraction results also show there is no formation of chromium nitride (CrN) precipitation in the hybrid S phase layer. The formation of CrN precipitation on top of the featureless bright white S phase layer will deteriorate the specimen's corrosion resistivity.

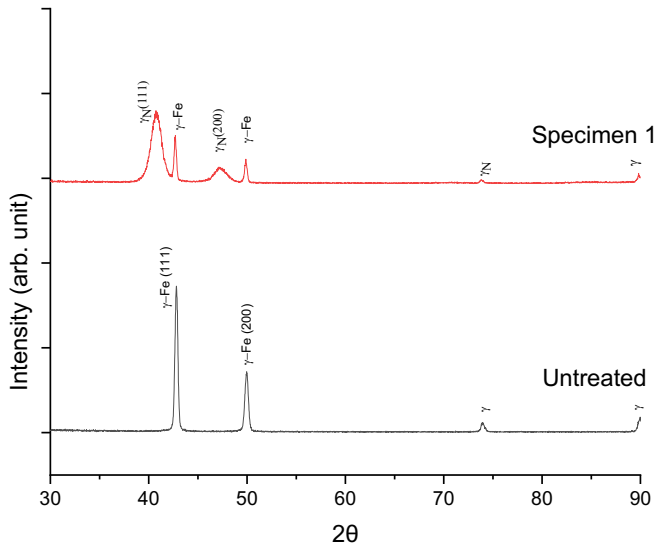

Figure 1: XRD of Untreated and Hybrid Treated Specimen

Morphology Analysis

Based on the visual observation using an optical microscope on the specimen cross-sectional microstructure (Figure 2), it was found that a layer is formed uniformly on the surface of the host material. The surface layer appears to be in bright white without any dark area on the top of the layer. The presence of the featureless bright white layer indicates the formation of the S phase layer (expanded austenite) (Sun, 2010).

The average layer thickness for the specimen was taken at three different locations. For the specimen with the lowest parameter setting, the layer thickness obtained is 1.2µm. The layer thickness obtained is not as thick as recorded by the plasma nitrocarburizing process, which about 10µm at 430°C (Cheng et al., 2005) and up to 40µm (Buhagiar & Dong, 2012) as the temperature increased. The difference in layer thickness between gas diffusion and plasma process is related to the oxide film of stainless steel. During plasma nitrocarburizing, the oxide film of stainless steel is eliminated by the sputtering of the plasma gas towards the oxide film. This action activates the stainless-steel surface for the diffusion process. Thus, the formation of the S phase on stainless steel by plasma nitriding becomes more efficient.

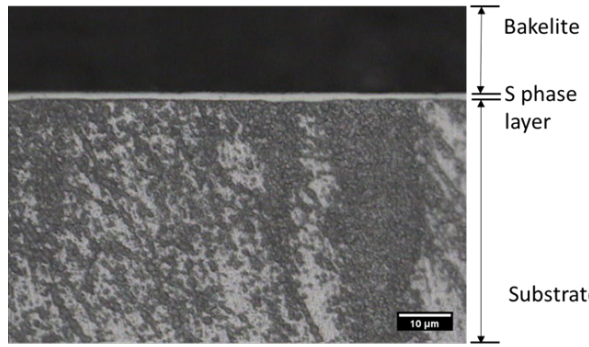

Figure 2: Optical micrograph of S phase layer

Hardness

The heat-treated samples show the improvement on the hardness in comparison with untreated AISI 316LVM SS. The ammonia and methane introduction during the heat treatment process has formed a thin hardened hybrid S phase layer on the host material. According to the microhardness result obtained as in Figure 3, it is evidence that the hardness of the treated specimen has improved. The maximum hardness of the hybrid treated specimen obtained is 442$Hv_{0.001}$. The recorded 52% increment of hardness proved that the hybrid heat treatment enhanced the hardness of the material.

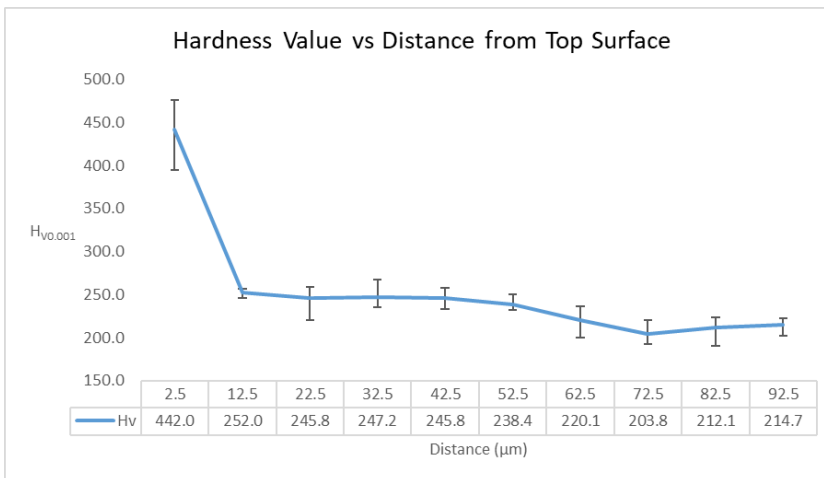

Figure 3: Micro-hardness test of the hybrid treated specimen

The graph trends for the specimen show a steep reduction of hardness between 5 to 10µm and gradually reduced to substrate hardness at about 210

$HV_{0.001}$. The variance graph trends are due to the S phase layer thickness and nitrogen/carbon diffusivity. The hybrid S phase layer contains a very high amount of nitrogen, and its concentration is gradually reducing from the surface. Thus, the thicker layer gives more advantages to the material hardness due to the hard nitrogen-rich layer on the material surface.

Conclusion

In conclusion, it is possible to develop the S phase layer using gas diffusion hybrid low-temperature heat treatment via a horizontal tube furnace. The hardness increments up to 52% show the S phase layer can be beneficial in aggressive condition application such as a biomedical implant. The S phase layer thickness obtained is not significant (1.2 μm) due to low parameter heat treatment of temperature and holding time. The formation of the S phase is confirmed by the XRD pattern, where the peak is slightly shifted to the left. The peak shift is not significant due to the low amount of carbon and nitrogen-containing solid solution as the S phase layer is very thin. The XRD analysis also shows the absence of chromium nitride precipitates on the saturated interstitial solid solution of the S phase layer. It is a requirement to ensure the unavailability of the chromium nitride precipitate on the S phase layer to preserve the corrosion resistivity of the hybrid treated material.

Acknowledgements

The authors wish to show highest gratitude to the faculty of Mechanical Engineering (AMTEX), Research Management Institute Universiti Teknologi MARA (600-IRMI/DANA 5/3/BESTARI(P)(038/2018)) and Ministry of Education, Malaysia for funding the research.

References

[1] Adenan, M.S., Berhan, M. N., & Haruman, E. (2013). Surface Modification of 2205 Duplex Stainless Steel by Low Temperature Thermochemical Hybrid Heat Treatment at 450° C. *Advanced Materials Research*, *845*, 408–411. https://doi.org/10.4028/www.scientific.net/AMR.845.408

[2] Adenan, Mohd Shahriman, Berhan, M. N., & Haruman, E. (2014). Formation of Expanded Austenite Using Hybrid Low Temperature Thermochemical Heat Treatment on 2205 Duplex Stainless Steel. *Advanced Materials Research*, *970*, 244–247. https://doi.org/10.4028/www.scientific.net/AMR.970.244

[3] *ASTM E384-17, Standard Test Method for Microindentation Hardness of Materials*. (2017). ASTM International.

[4] Baranowska, J. (2004). Characteristic of the nitride layers on the stainless steel at low temperature. *Surface and Coatings Technology*, *180–181*, 145–149. https://doi.org/10.1016/j.surfcoat.2003.10.056

[5] Buhagiar, J., & Dong, H. (2012). Corrosion properties of S-phase layers formed on medical grade austenitic stainless steel. *Journal of Materials Science: Materials in Medicine*, *23*(2), 271–281. https://doi.org/10.1007/s10856-011-4516-z

[6] Chen, Q., & Thouas, G. A. (2015). Metallic implant biomaterials. *Materials Science and Engineering R: Reports*, *87*, 1–57. https://doi.org/10.1016/j.mser.2014.10.001

[7] Cheng, Z., Li, C. X., Dong, H., & Bell, T. (2005). Low temperature plasma nitrocarburising of AISI 316 austenitic stainless steel. *Surface and Coatings Technology*, *191*(2–3), 195–200. https://doi.org/10.1016/j.surfcoat.2004.03.004

[8] Christiansen, T. L., & Somers, M. A. J. (2009). Low-temperature gaseous surface hardening of stainless steel: The current status. *International Journal of Materials Research*, *100*(10), 1361–1377. https://doi.org/10.3139/146.110202

[9] Christiansen, T. L., & Somers, M. A. J. (2013). Low-temperature surface hardening of stainless steel. *Advanced Materials and Processes*, *171*(11), 52–53. https://doi.org/10.3139/105.110091

[10] Christiansen, T., & Somers, M. A. J. (2005). Low temperature gaseous nitriding and carburising of stainless steel. *Surface Engineering*, *21*(5–6), 445–455. https://doi.org/10.1179/174329405X68597

[11] Galván, J. C., Larrea, M. T., Braceras, I., Multigner, M., & González-Carrasco, J. L. (2016). In vitro corrosion behaviour of surgical 316LVM stainless steel modified by Si+ ion implantation - An electrochemical impedance spectroscopy study. *Journal of Alloys and Compounds*, *676*, 414–427. https://doi.org/10.1016/j.jallcom.2016.03.162

[12] Gontijo, L. C., Machado, R., Miola, E. J., Casteletti, L. C., Alcântara, N. G., & Nascente, P. A. P. (2006). Study of the S phase formed on plasma-nitrided AISI 316L stainless steel. *Materials Science and Engineering A*, *431*(1–2), 315–321. https://doi.org/10.1016/j.msea.2006.06.023

[13] Haruman, E., Sun, Y., Malik, H., Sutjipto, A. G. E., Mridha, S., & Widi, K. (2006). Low Temperature Fluidized Bed Nitriding of Austenitic Stainless Steel. *Solid State Phenomena*, *118*, 125–130. https://doi.org/10.4028/www.scientific.net/SSP.118.125

[14] Ibrahim, M. Z., Sarhan, A. A. D., Yusuf, F., & Hamdi, M. (2017). Biomedical materials and techniques to improve the tribological, mechanical and biomedical properties of orthopedic implants – A review article. In *Journal of Alloys and Compounds* (Vol. 714, pp. 636–667). https://doi.org/10.1016/j.jallcom.2017.04.231

[15] Leyland, A., Lewis, D. B., Stevensom, P. R., & Matthews, A. (1993). Low temperature plasma diffusion treatment of stainless steels for improved wear resistance. *Surface and Coatings Technology*, *62*(1–3), 608–617. https://doi.org/10.1016/0257-8972(93)90307-A

[16] Lo, K. H., Shek, C. H., & Lai, J. K. L. (2009). Recent developments in stainless steels. *Materials Science and Engineering R: Reports*, *65*(4–6), 39–104. https://doi.org/10.1016/j.mser.2009.03.001

[17] Manam, N. S., Harun, W. S. W., Shri, D. N. A., Ghani, S. A. C., Kurniawan, T., Ismail, M. H., & Ibrahim, M. H. I. (2017). Study of corrosion in biocompatible metals for implants: A review. *Journal of Alloys and Compounds*, *701*, 698–715. https://doi.org/10.1016/j.jallcom.2017.01.196

[18] Menthe, E., & Rie, K. T. (1999). Plasma nitriding and plasma nitrocarburizing of electroplated hard chromium to increase the wear and the corrosion properties. *Surface and Coatings Technology*, *112*(1–3), 217–220. https://doi.org/10.1016/S0257-8972(98)00793-2

[19] Naragino, H., Egiza, M., Tominaga, A., Yoshitake, T., Murasawa, K., Gonda, H., & Sakurai, M. (2016). Fabrication of Ultrananocrystalline Diamond/Nonhydrogenated Amorphous Carbon Composite Films for Hard Coating by CoaxialArc Plasma Deposition. *EVERGREEN Joint Journal of Novel Carbon Resource Sciences & Green Asia Strategy*, *03*(01), 1–5. https://doi.org/10.7567/JJAP.55.030302

[20] Paijan, L. H., Berhan, M. N., Adenan, M. S., Yusof, N. F. M., & Haruman, E. (2012). Structural development of expanded austenite on duplex stainless steel by low temperature thermochemical nitriding process. *Advanced Materials Research*, *576*, 260–263. https://doi.org/10.4028/www.scientific.net/AMR.576.260

[21] Parsapour, A., Khorasani, S. N., & Fathi, M. H. (2012). Effect of Surface Treatment and Metallic Coating on Corrosion Behavior and Biocompatibility of Surgical 316L Stainless Steel Implant. *Journal of Materials Science and Technology*, *28*(2), 125–131. https://doi.org/10.1016/S1005-0302(12)60032-2

[22] Rotundo, F., Ceschini, L., Martini, C., Montanari, R., & Varone, A. (2014). High temperature tribological behavior and microstructural modifications of the low-temperature carburized AISI 316L austenitic stainless steel. *Surface and Coatings Technology*, *258*, 772–781. https://doi.org/10.1016/j.surfcoat.2014.07.081

[23] Shih, C.-C., Shih, C.-M., Su, Y.-Y., Su, L. H. J., Chang, M.-S., & Lin, S.-J. (2004). Effect of surface oxide properties on corrosion resistance of 316L stainless steel for biomedical applications. *Corrosion Science*. https://doi.org/10.1016/S0010-938X(03)00148-3

[24] Sun, Y. (2005). Enhancement in corrosion resistance of austenitic stainless steels by surface alloying with nitrogen and carbon. *Materials*

Letters, *59*(27), 3410–3413. https://doi.org/10.1016/j.matlet.2005.06.005
[25] Sun, Y. (2010). Production of nitrogen and carbon S phases in austenitic stainless steels by hybrid plasma surface alloying. *Surface Engineering*, *26*(1–2), 114–122. https://doi.org/10.1179/174329409X451065
[26] Sun, Y., Li, X. Y., & Bell, T. (1999). X-ray diffraction characterisation of low temperature plasma nitrided austenitic stainless steels. *Journal of Materials Science*, *34*(19), 4793–4802. https://doi.org/10.1023/A:1004647423860
[27] Williamson, D. L., Ozturk, O., Wei, R., & Wilbur, P. J. (1994). Metastable phase formation and enhanced diffusion in f.c.c. alloys under high dose, high flux nitrogen implantation at high and low ion energies. *Surface and Coatings Technology*, *65*(1–3), 15–23. https://doi.org/10.1016/S0257-8972(94)80003-0