Chemistry and Materials Research
ISSN 2224- 3224 (Print) ISSN 2225- 0956 (Online)
Vol.3 No.2, 2013


# Corrosion Resistance of AISI 316L after Short Holding Time of High Temperature Gas Nitriding (HTGN)

Agus Suprihanto* Suyitno, R Soekrisno, Rini Dharmastiti
Department of Mechanical Engineering University of Gadjah Mada
*E-mail of the corresponding author:: agusm90@yahoo.com

**Abstract**

Stainless steel AISI 316L is widely used as biomaterial due to its high corrosion resistance. However this property decreases in highly stressed and oxygen depleted environments. Several methods have been developing to increase the corrosion resistance such as low and high temperature gas nitriding. High temperature gas nitriding (HTGN) produces more depth effect than low temperature gas nitriding. Unfortunately HTGN for long holding time results on grain coarsening which reduce its tensile strength. The objective of this research is to determine the effect of HTGN at short holding time on the corrosion resistance, hardness and grain coarsening of AISI 316L.

Specimens were made from as rolled 1 mm thickness AISI 316L plate. Before HTGN process, the specimens were rinsed using ultrasonic cleaner in acetone medium. HTGN process was conducted at temperature 1050$^{o}$C, 1100$^{o}$C and 1200$^{o}$C for short period holding time i.e. 15 and 30 minutes. Micro hardness, microstructure and corrosion tests were conducted in the simulated body fluid (SBF) to evaluate the process.

The results show that hardness and corrosion resistance were increased significantly after HTGN process. Moreover, hardness for holding time of 30 minutes was higher than 15 minutes, however the corrosion resistance were decreased. In addition HTGN process also results on grain coarsening at 30 minutes holding time, however for holding time 15 minutes and temperature 1050$^{o}$C and 1100$^{o}$C did not give significant grain coarsening. Therefore, the HTGN process parameters must be optimized for compromise between hardness and corrosion resistance.

Keywords: high temperature gas nitriding, corrosion resistance, grain coarsening, AISI 316L

## 1. Introduction

The demand of metallic biomaterials has been increasing rapidly since the world population is increasingly older and the elderly people tend to have a high risk of hard tissue failure. Stainless steel of AISI 316L is one of metallic biomaterials which widely used as hard tissue implant materials due to its high corrosion resistance and good mechanical properties (Niinomi et. al. 2012). Unfortunately, corrosion resistance of AISI 316L decrease in highly stressed and oxygen depleted environments (Desai et al. 2008). Stainless steel in implant application are corroded by several ways i.e. pitting, crevice and fretting corrosion. The products of its corrosion can be detrimental to body and cause such as allergy, irritations and infections (Yang & Ren 2010).

The enhancement of corrosion resistance of stainless steel can be achieved by surface treatments such as surface alloying. Surface alloying with nitrogen or carbon must be performed only at relatively low temperature in order to avoid the precipitation of large amounts of chromium compounds, which decrease the corrosion resistance. Low temperature nitriding and carburizing treatments are able to form a modified surface layer that consists of a metastable phase known as S phase, which has high hardness and good corrosion resistance (Martinesi et al. 2006). Another way to improve corrosion resistance of stainless steel is by using high temperature gas nitriding (HTGN).

HTGN is thermo chemical treatment which adds nitrogen into stainless steel. The principle of HTGN is an expose of stainless steel in nitrogen atmosphere at temperature 1050$^{o}$C – 1200$^{o}$C for specific duration and then is followed by quenching. During HTGN process, nitrogen gas is dissociated into nitrogen atom and then diffused into stainless steel. This process will increase nitrogen contents in stainless steel, which improve corrosion resistance and mechanical properties (Berns & Siebert 1996).

Unfortunately, HTGN process results grain coarsening especially for longer holding time (Kuroda et al. 2003). Grain coarsening cannot be avoided because of temperature process of HTGN is higher than the recrystalization temperature. The phenomenon have consequence on reducing its tensile strength. Several methods have been developed to overcome grain coarsening during HTGN process such as optimizing the grain size by hot and cold rolling before process (Kuroda et al. 2003) and grain refinement after process (Onomoto et al. 2009). Another way to reduce grain coarsening effect is by shorten the holding time. These research studies the effect of short holding time in the HTGN process on the corrosion resistance and hardness for AISI 316L.

**2. Experimental procedures**

Specimens were made from 1 mm thickness plate of AISI 316L. The chemical compositions of AISI 316L are shown in Table 1. Specimens were rinsed by ultrasonic cleaner and soaking in acetone before treatment. HTGN process was conducted at temperature 1050$^{0}$C, 1100$^{0}$C and 1200$^{0}$C and holding time 15 and 30 minutes and the followed by quenching process in water. Table 2 shows the process parameter of HTGN of this experiment. Figure 1 depicts the test equipment of HTGN process. Before heater was turned on, the tube furnace was flushed by argon gas at flow rate 1000ml/min for 20 minutes. After flushing, the heater was turned at heating rate 10$^{o}$C/min. During heating process, nitrogen gas flowed into tube furnace at flow rate 100ml/min and pressure inside tube is maintained at 1 atm.

After treatment, specimens were processed in grinding machine using emery paper and then were polished to get mirror-like surface. Vickers micro hardness test was performed to determine hardness distribution at cross sectional of specimens. Potentiodynamic corrosion test was also carried out using simulated body fluid (SBF) which has 0,9%NaCl. In this corrosion test, the temperature was kept to be constans at 37$^{o}$C. In addition a light optical microscope (LOM) was used to evaluate the microstructure of specimens before and after HTGN process.

**3. Result and Discussion**

Figure 2 shows the cross sectional hardness distribution before and after treatment. The hardness of specimens after treatment was increased significantly. The hardness of the surface specimens was higher than at the middle section. The higher temperature and the longer holding time results the increasing of hardness.

Nitrogen gas will dissociate into nitrogen atoms at temperature above 1050$^{o}$C. This property can be utilized in HTGN process through diffusion of nitrogen atoms on surface of specimens. Nitrogen atoms occupy in the interstitial site of the face-centered cubic (FCC) lattice of working specimens. The increasing of nitrogen contents after treatment causes the increasing of its hardness. This mechanism is similar to the role of carbon in strengthening mechanism in the steel.

Figure 3 shows the grain coarsening captured by LOM before and after HTGN process. The grain coarsening were significantly produced during HTGN process on specimens. The grain changed and its growth was controlled by temperature and holding time. Grain starts to grow due to the temperature of process is above recrystalization temperature ($T_{rec}$) of AISI 316L, that is about 600$^{o}$C. In this research the heating rate was set to 10$^{o}$C/min and the temperature of specimens reaches $T_{rec}$ after 65 minutes. The durations of specimens exposed to the temperature above $T_{rec}$ were 40, 45 and 55 minutes for temperature process of 1050$^{o}$C, 1100$^{o}$C and 1200$^{o}$C, respectively. Grain size for temperature process of 1050$^{o}$C and 1100$^{o}$C and holding time 15 minutes was not significantly different, because the duration of specimens exposed to the temperature above $T_{rec}$ were also not significantly different. The grain size of temperature process of 1200$^{o}$C and 30 minutes holding time was coarser than another parameter HTGN process due to the highest temperature and longest holding time. Increasing the process temperature cause grain more easily to growth and the final size of grain is determined by holding time.

The result of corrosion test is shown in Table 3. Corrosion rate was significantly reduced after treatment. Reducing in the corrosion rate means that after treatment the specimens have more corrosion resistance. It has generally accepted that nitrogen improves the resistance to pitting corrosion and passivity. The beneficial effect of nitrogen on the pitting corrosion can be predicted by pitting resistance equivalent number (PREN). The PREN gives indication of beneficial effect of chromium, molybdenum and nitrogen on the pitting corrosion resistance. The formula of PREN is %Cr + 3.3%Mo + x%N, where x varies from 10 to 30. Nitrogen has more effective to pitting corrosion than chromium and molybdenum.

The enhancement corrosion resistance and hardness after HTGN process indicates that nitrogen is diffused into stainless steel. The longer holding time results more nitrogen diffused. Although the increasing of nitrogen contents can increase the PREN, however, the corrosion rate for 30 minutes holding time is higher than 15 minutes. Nitrogen will have beneficial effect for corrosion resistance of stainless steel if is alloyed under its solubility limit, but if not, it will reduce the corrosion resistance. Moreover, nitrogen in the large amount forms precipitate and results chromium depleted zone along grain boundary which reduce corrosion resistance. The mechanism nitrogen affects corrosion resistance of stainless steel was discussed Bayomi et al. (2005) and Levey et al. (1995). This fact becomes the reason why the nitrogen contents in stainless steel must be limited. Nevertheless the corrosion rate after short holding time of HTGN was significantly reduced when compared with the raw materials.

The corrosion resistance of specimens after treatment was increased, but for higher temperature and longer holding time the corrosion resistance was decreased slightly. The reason of this phenomenon is higher temperature and longer holding time caused more nitrogen diffusion on the specimens.

## 4. Conclusion

HTGN process enhance the hardness and the corrosion resistance of AISI 316L. The higher temperature and longer holding time result increasing hardness but corrosion resistance was reduced slightly. The parameter of its process must be optimized for compromise between increasing of hardness and corrosion resistance which reduce susceptibility to fretting corrosion.

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Table 1. Chemical composition AISI 316L

| C | Cr | Ni | Mo | Mn | S | P | Si | Cu | Fe |
|---|---|---|---|---|---|---|---|---|---|
| 0,014 | 15,5 | 11,8 | 1,24 | 1,23 | 0,005 | 0,003 | 0,47 | 0,42 | Balance |

Table 2. Process parameter of HTGN process

| No | Specimens code | Temperature | Holding time |
|---|---|---|---|
| 1 | Raw materials | - | - |
| 2 | 1.1 | 1050°C | 15 minute |
| 3 | 1.2 | 1050°C | 30 minute |
| 4 | 2.1 | 1100°C | 15 minute |
| 5 | 2.2 | 1100°C | 30 minute |
| 6 | 3.1 | 1200°C | 15 minute |
| 7 | 3.2 | 1200°C | 30 minute |

Table 3. Effect of HTGN treatment on the corrosion rate in SBF medium

| Specimens code | HTGN process parameter | | Corrosion rate (mpy) |
|---|---|---|---|
| | Temperature | Holding time | |
| Raw materials | - | - | 0.0228 |
| 1.1 | 1050°C | 15 minutes | 0.0011 |
| 1.2 | 1050°C | 30 minutes | 0.0144 |
| 2.1 | 1100°C | 15 minutes | 0.0005 |
| 2.2 | 1100°C | 30 minutes | 0.0202 |
| 3.1 | 1200°C | 15 minutes | 0.0028 |
| 3.2 | 1200°C | 30 minutes | 0.0174 |

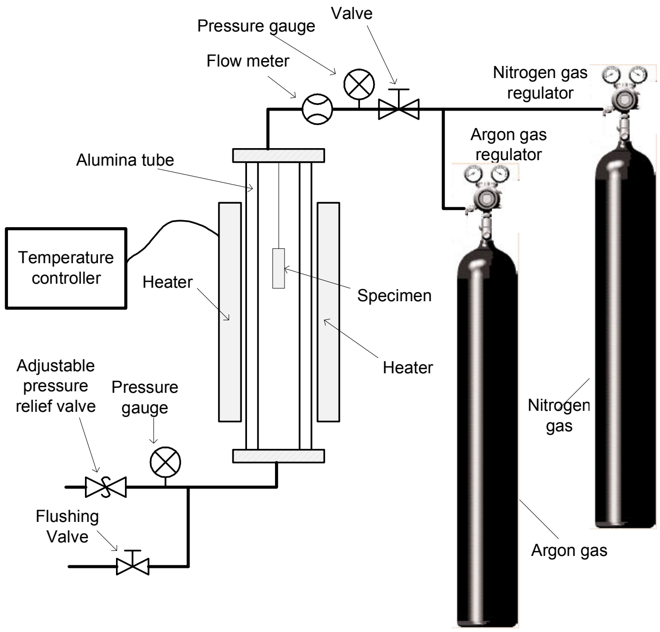
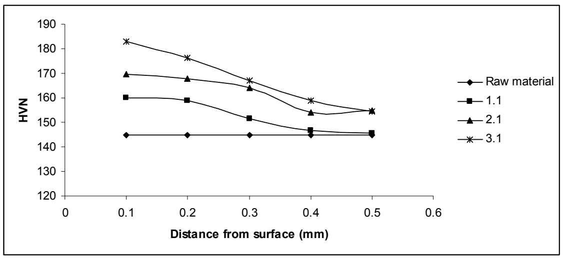
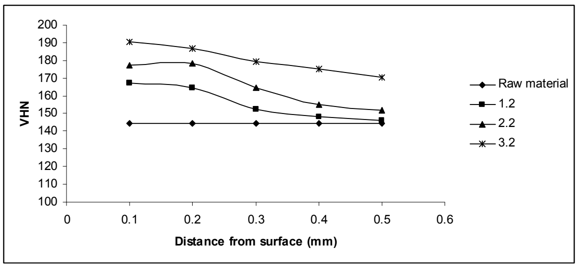



Figure 1. Experimental devices and equipments




a. holding time 15 minutes




b. holding time 30 minutes

Figure 2. Hardness distribution along cross section

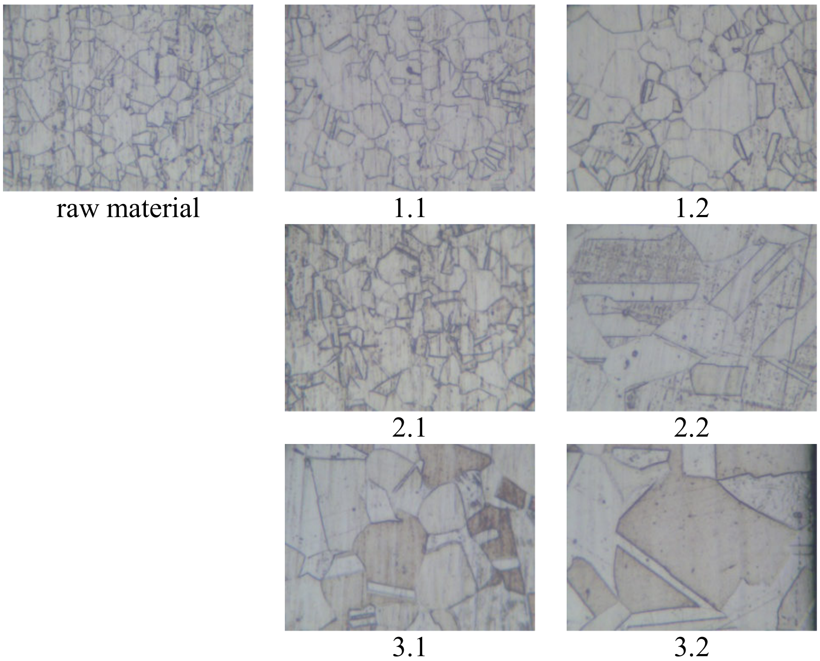



Figure 3. Microstructure of AISI 316l before and after HTGN process