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Research Article

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Evaluation of hardness, wear, corrosion resistance and magnetic properties of Austenitic Stainless Steel 316LVM by means short high temperature gas nitriding

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ABSTRACT

High temperature gas nitriding (HTGN) for austenitic stainless steel 316LVM is successfully done. Specimens are treated at temperature 1323, 1373 and 1573 K for 15 minutes holding time at 0.3 atm nitrogen gas pressures. As received and treated specimens were evaluated by means vickers micro hardness test, metallographic examination, abrasive wear test, corrosion test and vibrating sample magnetometer test. Hardness, wear resistance and grain size increase with temperature. However, the corrosion resistance at ringer solution decreases with temperature. HTGN treatments at 1323 K for 15 minute holding time are able to improve the hardness, wear resistance, corrosion resistance and increase the non-magnetic stability of 316LVM.

Keywords: short HTGN, 316LVM, hardness, wear non-magnetic, corrosion resistance

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INTRODUCTION

Stainless steel 316LVM is austenitic stainless steel that has been processed by vacuum melting. The corrosion resistance significantly enhance compared to its predecessor 316L due to the excellent micro cleanliness and structural homogeneity [1, 2]. This stainless steel is suitable for the production of both temporary and permanent implants. As other metallic biomaterials, 316LVM is more susceptible to corrosion under body fluid compared to the titanium and titanium alloy. Stainless steel implants are corroded by several ways such as pitting, crevice and fretting corrosion [3, 4]. The corrosion products are detrimental to the body and cause such as allergy, irritation, inflammation and infection [5].

Various techniques have been developed to enhance its corrosion resistance and mechanical properties such as surface treatment and modification of its chemical compositions. The well-known surface treatments and commonly applies are surface passivation, sandblasting, ion sputtering, nitriding, carbonitriding. Surface passivation is only able to improve its corrosion resistance [6, 7]. Sandblasting is able to enhance its hardness but reduce its corrosion resistance [8, 9]. Nitriding and carbonitriding are able to improve both its corrosion resistance and hardness due to the formation of thin layer about few micrometer of S-phase/expanded austenite phase [10, 11].

The expanded austenite phase generates the weakly ferromagnetic properties, because this phase is ferromagnetic [12, 13]. The presence of ferromagnetic should be avoided due the requirement of magnetic resonance imaging (MRI) environments. Because the MRI is widely used as clinical imaging tools, metallic biomaterials should have stable non-magnetic properties due to the MRI safety and compatibility issues [14]. In the past, implant and medical devices from austenitic stainless steel meet the MR system below the 1.5 Tesla (T), but the newest MR system -3.0 T and above- their MR compatibility decrease [15, 16].

Another promising technique which able to improves the mechanical properties, corrosion resistance and avoids the magnetic phase is high temperature gas nitriding (HTGN) [17]. HTGN is thermo chemical treatments which add nitrogen by diffusion mechanism. The principle process is holding the stainless steel at temperature 1323 – 1573 K in the nitrogen gas atmosphere prior quenching [18]. Nitrogen is well known as addition elements that improve the mechanical properties, corrosion resistance and austenite stabilizer elements for stainless steel [19, 20]. The properties obtained after treatments depends on the amounts of nitrogen. The increasing nitrogen contents is controlled by chemical composition of stainless steel, heating temperature, holding time and nitrogen gas pressure [21, 22]. Although HTGN have been carried out for various series of stainless steel [23-25], but the studies of HTGN for 316LVM are limited. This paper discusses the effect of short holding time of HTGN treatments on the hardness, wear resistance, corrosion resistance and magnetism properties of 316LVM.

EXPERIMENTAL SECTION

Specimens were prepared from 4 mm thick plate of austenitic stainless steel 316LVM. The chemical compositions of the specimens (%wt) are 0.01 C, 17.30 Cr, 15.5 Ni, 1.73 Mo, 1.67 Mn, 0.42 Si and Fe (balance). Specimens were rinsed using ultrasonic cleaner in acetone as soaking medium prior HTGN treatments. Specimens were inserted to the furnace tube then vacuumed to 10 Pa for 15 minute and flushed using nitrogen gas at 1000 ml/min for 15 minute prior heated. Nitrogen gas flowed continuously at 100 ml/min until treatment temperatures achieve. The treatment temperatures were chosen at 1323, 1373 and 1573 K. During treatments, the nitrogen gas pressure maintained at 0.3 atm for 15 minute holding time prior quenching in water. HTGN treatments was carried out at modified three zone heating chamber of vertical furnace (Carbolite type TZF 15/50/610) which equipped with a precision digital pressure controller as shown schematically at Figure 1.

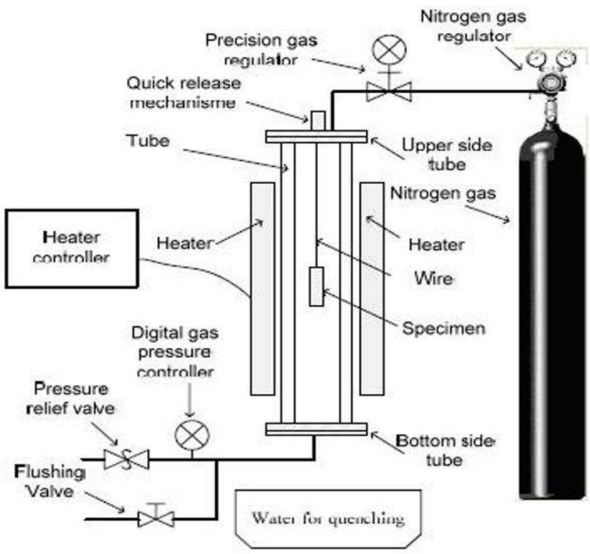

Fig. 1. Schematic of modified vertical furnace

As received and treated specimens were gently polished in order to remove the scale using metal polish prior hardness, wear resistance and corrosion resistance test. The Vickers micro hardness test was carried out at cross sectional specimens at sub surface till a distance of 1000 μm at Buehler micro hardness tester. The applying load for micro hardness test was 300 gr. The wear test was performed at the surface of specimens using Ogoshi high speed universal wear testing machine type OAT-U. The pressure load and abrasion distance was 12.72 kg and 7.8m respectively. The corrosion resistance test was carried out at polarizations resistance corrosion techniques in ringer solution as corrosion medium at temperature 310 K.

The specimens were cut, mounted, grinded, polished and etched using 5% $FeCl_3$ solution prior micrographic examination with light optical microscope. The examination of micro structure was focused for the evolution of grain size. The average grain size was calculated by means an image analysis software Image-J version 1.47.

Magnetism property was carried out at Oxford type 1.2h vibrating sample magnetometer (VSM). As-received and treated specimens were made in to powder using low speed saw prior VSM test. The powder was exposed to the magnetic field from -1T to 1T and magnetic moments was recorded. The results of VSM test were hysteresis curve of magnetic field (T) versus magnetic moments (emu).

RESULTS AND DISCUSSION

The evolution of the micro structure of as received and treated specimens depicted in Fig. 2. As received micro structure show the very fine grain which has average grain size 10 μm. Figure 3 show the effect of treatment temperatures on the grain size of the specimens. The grain size is increase with temperature. Although the grain size of treated specimen at treatment temperatures 1323 K slightly increase, but treated specimens at treatments temperature 1373 and 1573 K the grain size increase. The grain size of treated specimens at 1573 K is four times than as-received specimens. The grain size increases with temperature.

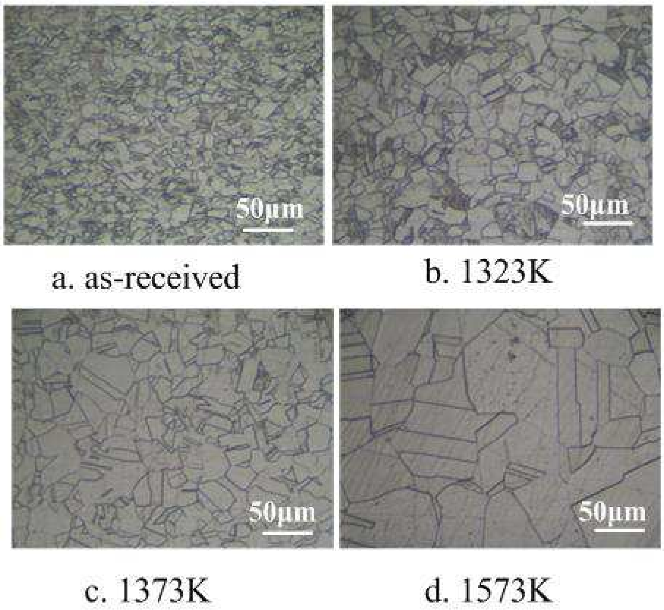

Fig. 2. Microstructure of specimens 316LVM

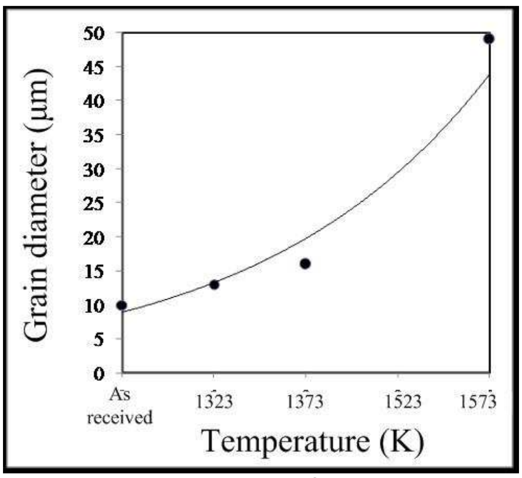

Fig. 3. The evolution of grain size

The distribution of micro hardness across the specimen after treatments is shown in Figure 4. The hardness also increases with temperature. The surface hardness of all treated specimens increases significantly compared to the as received. The distributions of hardness for all treated specimens show that the hardness at surface decreases sharply until 400 μm of depth. The rest are the same as the received specimens. It indicates that nitrogen atoms from dissociation of nitrogen gas molecules at above temperature 1323 K immediately diffuse into surface but below the surface the diffusion process is slowly.

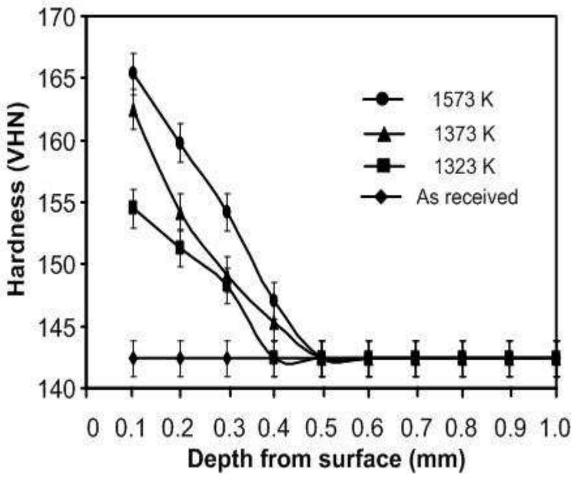

Fig. 4. Hardness distribution of as received and treated specimens

The results of abrasive wear test are plotted together with hardness at the surface as shown at fig. 5. The magnitude of specific wear (Ws) of as received specimens is 0.29 mm2/kg and treated specimens are 0.28, 0.2 and 0.15 mm^2/kg for treatments temperature 1323, 1373 and 1573 K respectively. The magnitude of Ws is decline as the hardness at the surface increase. The magnitude of Ws decreases sharply at treatment temperature 1373 and 1573 K. It indicates that treated specimens are more wear resistance than as-received.

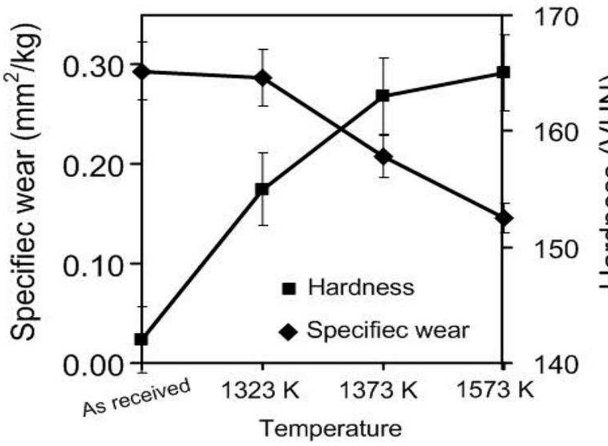

Fig. 5. Specific wear and hardness at the surface

The polarization curve of specimens before and after treatments is shown in fig. 6. The E_{corr} of treated specimens increase while the I_{corr} decrease compared to the as-received specimens. It indicates that the corrosion resistance of treated specimens increases. Table 1 summarizes the corrosion rates at ringer solution. Corrosion rate increases with treatment temperatures. The corrosion rate of as received specimens is 1.3 x 10^{-3} mpy. After HTGN treatments the corrosion rate is 2 x 10^{-4}, 8 x 10^{-4} and 1.1 x 10^{-4} mpy. for treatments temperature at 1323 K, 1373 K and 1573 K respectively. HTGN at treatment temperatures 1050^{o}C and 1100^{o}C significantly enhance the corrosion resistance of AISI 316 LVM. Corrosion rate of treated specimens at 1573 K is the same of as received specimens.

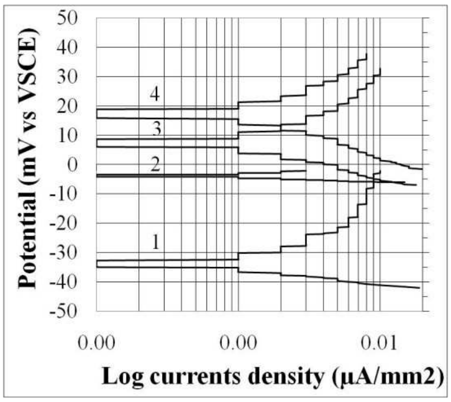

Fig. 6. Polarization curve. 1. as received, 2. 1323 K, 3. 1373 K & 4. 1573 K

Table 1. Corrosion resistance AISI316LVM in ringer solution medium

No	Specimens	E_{Corr} (mV)	Corrosion rate (mpy)
1	As received	-33.43	0.0013
2	1323 K	-39.11	0.0002
3	1373 K	17.1	0.0008
4	1573 K	7.32	0.0011

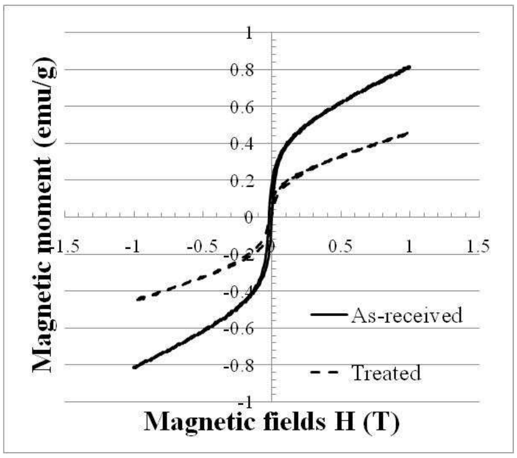

Fig. 7. Magnetization curve of specimens

Table 3. Magnetic properties obtained from VSM test

	As-received	Treated at 1323K For 15 minutes
M_s	0,78 emu/gr	0,431 emu/gr
M_r	0,16 emu/gr	0,079 emu/gr
H_c	9,92 x10^{-2} Oe	8,17 x10^{-2} Oe
κ	0,0006	0,0002
μ_r	1,0006	1,0002

Fig. 7 shows the magnetization curve of as-received and treated specimens at temperature 1323 K. Magnetic moments of treated specimens reduce about a half compared to as-received specimens. Table 2 shows the magnetic properties obtained from hysteresis curve namely magnetic saturation (*Hs*), magnetic remanence (*Mr*), coercivity (*Hc*), magnetic susceptibility (κ) and relative permeability (μ_r). The magnitude of relative permeability (μ_r) both as-received and treated at 1323K is less than 1.004 that is maximum μ_r requirement for MR safe and compatibe. It indicates that the treated specimen has more stable non-magnetic properties than as received ones. In the view of MR environment, metallic biomaterial should have not only biocompatible but also MR safe and compatible.

Metallic biomaterials should have stable non magnetic properties. Fig. 7 show that HTGN treatment is also able to enhance the stability of the non-magnetic properties.

The changes in grain size during heat treatments depend on heating temperature, holding temperature and degree of cold work. The grains start to grow above recrystallization temperature (T_{rec}). The T_{rec} is about a half of melting point of metals in Kelvin. Austenitic stainless steel has melting points around 1673 K, thus it has T_{rec} around 835 K [26].

In this study, HTGN treatments are carried out above temperature T_{rec} and heating rate 10 K/min. The treated specimens are exposed to the temperature above T_{rec} for 60, 65 and 75 minutes for treatments temperature 1323, 1373 and 1573 K respectively. The different temperature and exposing time above T_{rec} for treatment temperatures at 1323 and 1573 K are only 150 K and 15 minutes respectively, but the grain size changes from fine into coarse grain. It indicates that grain growth is strongly influenced by treatment temperature.

Treated specimens at 1573 K actually is exposed to a temperature above nitrogen gas molecules start to dissociation and diffuse 15 minutes longer than treated specimens at 1323 K due to heating rate is controlled at 10 K/min. It produces the highest nitrogen concentrations at the surface which results in highest hardness. Despite the grain size of specimens are different, hardness at section above 400 μm are the same. It indicates that increasing of hardness is solely influenced by increasing of nitrogen concentrations. Thus HTGN treatments for 15 minutes holding time produce 400 μm diffusion depths which deeper than another common surface treatments such as nitriding and carbonitriding at the same holding time.

Wear resistance is expressed by specifics abrasion wear (Ws) in mm^2/kg. Ws is proportional constant expressing the abrasion characteristic of material that is contact with a specific abrasive materials. Ws for the same condition test such as pressure loads, distance to abrasion, speed of abrasion test and temperature can be used as comparative wear resistance of tested materials.

At common polycrystalline metals, increasing grain size reduce the wear resistance due to the reduced its hardness [27]. Despite treated specimens at 1573 K show large grain size, the wear resistance increase. It can be concluded that wear resistance is only influenced by the hardness of specimens. The wear test shows that the HTGN treatment is also able to increase wear resistant. Wear resistance increase with temperature as indicate with decrease in Ws. This is in accordance with hardness of specimens.

The increasing hardness due to the increasing of nitrogen contents is also improving the corrosion resistance. The corrosion resistance of austenitic stainless steel correlates with the magnitude of pitting resistant equivalent number (PREN). PREN has formula %Cr + 3.3%Mo + (20-30)%N. It shows from PREN formulae, the nitrogen atoms more effective to enhance the corrosion resistance of stainless steel. In this study, hardness increase with treatments temperature, but corrosion resistance decrease. The corrosion resistance is also increase with grain size [28]. Larger grain size tends to be more corrosion resistance.

The contradictive results may explain by the fact that nitrogen is able to improve the corrosion resistances of stainless steel unless it does not form compounds such as nitride. The nitrogen atom is easily diffuse along grain boundary due the large vacancy. The metallic nitride such as (Fe, Cr, Mo)N is also possible to form at grain boundary. It reduces the free chromium which produces oxide layer that acts as surface passivation. The difference free Cr contents in the grain and along grain boundary produces chromium depleted zone. It acts as galvanic corrosion couple which is susceptible to corrosion. The same phenomenon is also obtained at previous study for austenitic stainless steel 316L [29].

CONCLUSION

HTGN at short holding time enhance the hardness, wear resistance, corrosion resistance and stabilization of non-magnetic properties of austenitic stainless steel 316LVM. The treatments temperature 1323 K is able to improve the properties of 316LVM without produce the excessive grain coarsening. Therefore treated specimen at 1323 K has more not only biocompatible but also more MR safety and compatibility than as-received.

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