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NITRIDING OF PURE TITANIUM BY HIGH DENSITY PLASMA USING H_2-N_2 GAS MIXTURE AT LOW TEMPERATURE

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ABSTRACT: Most plasma nitriding of titanium was successfully carried out at a temperature higher than 500 ºC. A lower temperature process is needed to save energy. The experiment was carried out by varying the substrate temperature from 350 to 450 ºC. The plasma was generated in a vacuum chamber by a 2 MHz RF power supply. A gas mixture of nitrogen and hydrogen was introduced into the chamber resulted in a significantly effective nitriding of the titanium. The plasma was intensified to a higher density by utilizing a combination of DC bias technique and a hollow cathode. At the optimum mixture of 80% N_2 and 20% H_2, by the pressure of 35 Pa, a four-hour nitriding resulted in a 20 µm nitrided layer. The hardness of the treated surface was varied between 550 and 1990 HV depending on the process temperature. XRD measurements showed that the nitriding leads to the formation of Ti_2N and TiN precipitates. Expansion of the original hcp-structured lattices was also noticed. The hardening was a result of a lattice straining induced by the precipitates and also a possible small percentage of nitrogen solid-solution.

Keywords: Plasma nitriding, High-density plasma, Low temperature, Titanium, Hardening

1. INTRODUCTION

Titanium has been tremendously the interest in many fields of applications, such as aerospace[1], automobile industries [2], home appliances, and medical implants [3]. The metal is lightweight and yet performs high mechanical performances. It has high stability at high temperature and high corrosion resistance. Alloying the titanium with other metals such as aluminum, vanadium, and molybdenum produces a wider range of application [4].

However, the drawback of the utilization of the titanium is due to its poor tribological properties, i.e., low surface hardness, low wear resistance, and high friction coefficient. It is important to enhance the tribological properties so that even wider utilization is possible in the future. The enhancement should also consider the durability and usage life especially when frictions cannot be avoided [5].

There have been many efforts to enhance the tribological properties of pure titanium. One of the methods is carried out by nitriding modifications of the surface. It is well known that the nitriding process can increase the surface hardness and hence the wear resistance of metals [6]. From the history of titanium nitriding, it has been learned that the metal can be hardened effectively by incorporating the nitrogen into the hcp structured or the α-phase. A number of methods and techniques have been proposed such as a gas nitriding by a nitrogen thermo-diffusional treatment [7] or depositing a layer of nitride by physical vapor deposition (PVD) [8].

Recently, a plasma nitriding is utilized to modify the titanium's surface. It is a common nitriding method which has been established for metals [9]. The method has proven itself to be efficient due to its shorter process time and reduction of gas usage. In addition, it is an environmentally friendly process [10]. Other advantages of the plasma nitriding come from its flexibility for selective nitriding and high possibility to be implemented in industrial scale.

A study of the plasma nitriding for a titanium alloy Ti_6Al_4V, show that the process carried out at a temperature of 1000 ºC for 10 hours was able to increase the hardness up to 1365 HV [11]. Another researcher successfully hardened a $Ti_5Al_4V_2Mo$ titanium alloy by plasma nitriding at 1173 K for 4 hours. The surface hardness was 1.7 times higher than the original hardness. The thickness of the nitrided layer was 30 µm containing nitride precipitates [12]. Researchers found that the increase of the surface hardness in the plasma nitriding was related to the increase of nitrogen concentration in the surface and subsurface in the form of a solid solution and TiN [13]. Despite the many advantages of the plasma nitriding technique, the high-temperature thermo-chemical process for titanium may cause a deprivation of fatigue strength and a damaging of microstructural changes in the titanium substrates [14].

Further advancements of the technique should be undertaken to reduce the holding temperature during the process which can minimize the degradation of the fatigue strength and the microstructural deterioration. The low-temperature process is also desirable for reducing the usage of energy.

This work was focused on the plasma treatment of pure titanium to gain fundamental knowledge of an alternative high-density plasma utilized for surface hardening. Other researchers reported that at a relatively low holding temperature of 500 ºC, the hardening was controlled by the nitrogen solid solution. On the other hand, at higher holding temperature the hardening was also affected by the formation of TiN and Ti_2N precipitates [15]. The application of the alternative high-density plasma was intended to compensate the lower holding temperature. A combination of a DC bias voltage and a hollow cathode was employed to produce the high-density nitrogen plasma. Other than the combination, the previous study has shown that incorporation of a small amount of hydrogen in the nitrogen plasma produced active nitrogen species in the plasma which resulted in highly effective nitriding [16]. The amount of the hydrogen inclusion was determined by means of optical emission spectroscopy (OES) and Langmuir impedance measurement. It was found that the appropriate concentration of the hydrogen to be around 17%. The ratio resulted in nitrogen plasma containing a large density of N2*, N2+ and NH complexes behaving as positively charged species. The species are chemically active and are able to produce a high concentration of high energy atomic nitrogen which diffuses into the metal uniformly via complex surface reactions.

2. EXPERIMENTS

A high-density nitrogen plasma reactor was utilized to achieve the successful low-temperature nitriding. The reactor consists of a vacuum chamber, an RF generator a high voltage DC generator. The nitrogen plasma was generated by applying the RF generator on the two floating electrodes (anodes) in the chamber. The base frequency of the RF was 2 MHz. The reflected power was minimized by an electronic matching system shifting the frequency around the base. A high DC voltage was applied to a cathode to accelerate ions toward it. The application of the DC bias increased the density of the plasma in the cathode area [6]. Further enhancement of the plasma density was achieved by setting up a hollow rectangular metal tube on the cathode. Due to the electrical connection, the tube functioned as a hollow cathode. The cathode assembly was equipped with a controlled heater providing a constant temperature. The system is described in Figure 1.

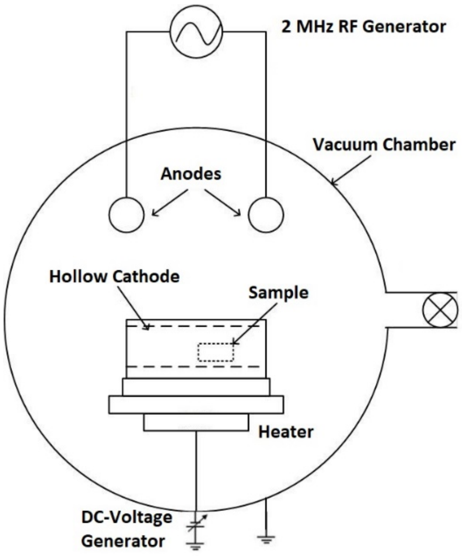


Fig. 1 A schematic representation of the hollow cathode plasma nitriding system.

After the loading procedure, the chamber was pumped down to 0.5 Pa to evacuate the air. The heater was then turned on to increase the substrate temperature to the process temperature, i.e., 350, 375, 400, 425 or 450 ºC. Before the main plasma treatment process, the samples underwent a pre-treatment for 1 hour. The pre-treatment process was carried out by applying a 100% nitrogen plasma at the process temperature and at the chamber pressure of 70 Pa. The RF and DC bias voltage during the pre-treatment process was 250 and 500 volts respectively. The main plasma nitriding treatment was carried out immediately at the RF and DC bias voltage of 250 and 600 volts respectively for 4 hours. The pressure of the chamber was lowered to 35 Pa with a mixture of 80% N_2 and 20% H_2.

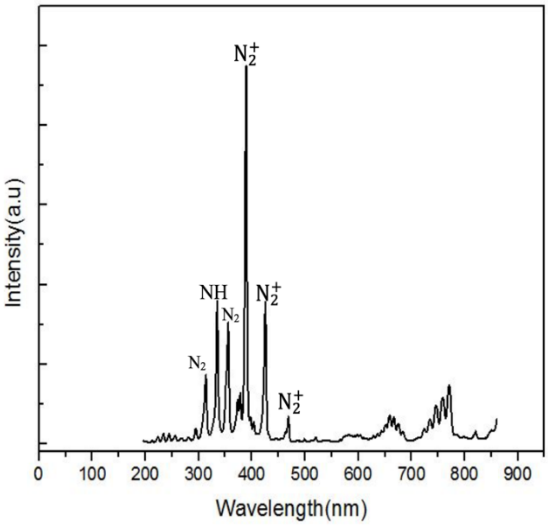


Fig. 2 Optical emission spectrum of the mixture of H_2-N_2 plasma.

The species of the plasma was observed by means of an optical emission spectrometer (OES). Figure 2 shows the peaks related to the active species during the nitriding process which has been studied earlier.

Surface hardness characterization of the specimens was carried out using a Vickers micro-hardness testing system (Akashi MVK-H1). The measurement was taken at five different points on every specimen with the applied load of 1N or 100 gfs. Cross-sectional hardness measurements were conducted to obtain a hardness depth profile characteristic of the specimens. The measurements were taken at points having the distance of 10, 20, 30, 40, 50 and 60 μm from the surface. Accompanying the depth profiling measurement, cross-sectional micrograph observations were conducted using a scanning electron microscope (JEOL JSM-7100 F).

An X-ray diffractometer (XRD, Rigaku SmartLab) was utilized to identify the crystallographic phases of the specimens. The observation was carried out under a monochromated Cu Kα radiation with λ = 1.54598 Å at a range of diffraction angle of 30 to 90 degrees with a step angle of 0.010 degrees.

3. RESULTS AND DISCUSSIONS

The high-density nitrogen plasma treatment by the application of a combination of DC bias voltage and a hollow cathode resulted in an effective hardening of pure titanium. The original hardness of the titanium was 319.4 HV. Depending on the sample temperature during the plasma treatment, the surface hardness was increased up to 1989 HV (at 450 °C). Measurement of the hardness on the cross-sectional surface revealed the depth hardness profile due to the plasma treatment as shown in Figure 3.

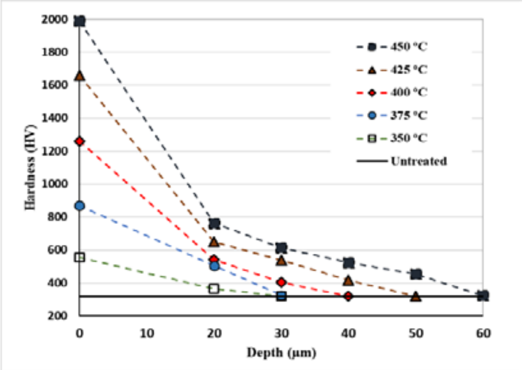


Fig. 3 Hardness depth profile of pure titanium specimens treated with the high-density plasma at various temperature for 4 hours.

It can be seen from the Figure 3, the hardness profile shows preservation of a relatively high hardness to the deep and abruptly decrease at around 20 μm depth. The SEM micrographic observation confirmed that the profile is related to the nitrogen distribution in the nitriding area.

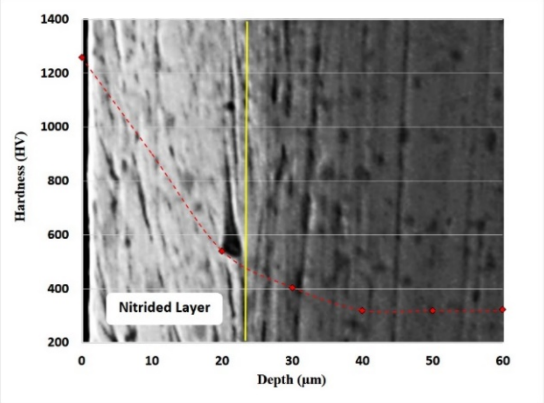


Fig. 4 SEM micrograph observation related to the hardness depth profile of pure titanium specimen treated with the high-density plasma at a temperature of 400 °C for 4 hours.

Figure 4 shows a relational illustration of the SEM micrograph and the hardness depth profile measurement. The SEM image shows a whitish area indicated the existence of a nitrided layer reaching the depth of 23 μm. The thicker layer was observed on the specimen treated at higher holding temperature.

Further study was carried out by examining the change of the titanium phase before and after the treatment by means of XRD measurements as shown in Figure 5.

Pure titanium used in this work has an ideally hexagonal close-packed (hcp) structure. This untreated α-titanium can be confirmed by the peaks shown in Figure 5 which match the database for the pure titanium (α-Ti). In the plasma treated specimens, some of these line peaks are shifted to the lower angles. The shift of the peak indicates the occurrence of lattice straining of the α-Ti due to the interstitial nitrogen resulted in α'(N)-Ti. The expansion can be observed from the shift of peak at 40.5 degrees toward 39.5 degrees. The peak is assigned to $[101\bar{1}]$ the plane as seen in Figure 5.

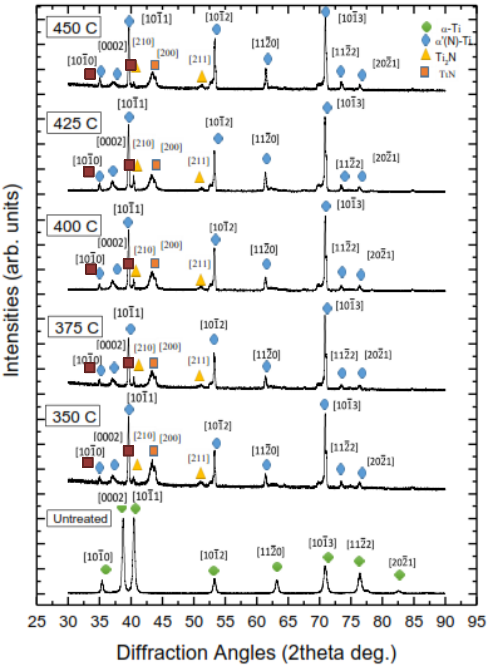
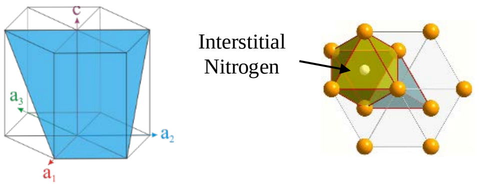


Fig. 5 X-ray diffractogram of untreated and plasma treated specimens.

The solid solution interstitial nitrogen can reside at either octahedral or tetrahedral site in the hcp structure. However, the expansion of the $[101\bar{1}]$ plane indicated that the interstitial nitrogen prefers the octahedral vacancy sites as shown in Figure 6.



(a) **(b)**

Fig. 6 Illustration of: (a) the $[101\bar{1}]$ plane in the hcp structure; and (b) interstitial nitrogen residing at the octahedral vacancy site.

The radius of nitrogen solute or r_N is 0.92 Å, while the size of the octahedral r_o and tetrahedral r_T vacancy sites are = 0.6 Å and 0.33 Å respectively. The relative available space size of the vacancy and the replacement solute size determine the possibility of site occupation for the solute to vacancy [17]. Generally, the wider size of octahedral vacancy site is preferable for the nitrogen solute occupation in the localization process. Since the $r_N > r_o$, the occupation of the nitrogen is accompanied with lattice expansions, especially in the c-axis.

Other than the shift, new peaks were observed in the diffractogram of the treated specimens. The peaks are related to the phase of TiN and Ti_2N. The peak at 37.15 and 43.4 degrees are related to the TiN diffraction plane, while the Ti_2N phase was indicated by the peaks at 51.3 degrees and 40.3 which overlap with the previous $[101\bar{1}]$ plane reflection. The previous study suggested a possibility of the occurrence of a phase transformation from α-Ti to ω-Ti which was indicated by the peak at 37.15 degrees [18]. However, the transformation should include the ω-Ti which was not observed in the diffractogram. This is due to the plasma treatment process was conducted far below the α to β transformation temperature, i.e., 1156 K (883ºC) [15]. The effect of the holding temperature during the plasma nitriding on the lattice straining is summarized in Table 1.

Table 1 The effect of holding temperature during plasma nitriding process on lattice straining

Nitriding Temp. (°C)	**α-Ti phase**			**Lattice Straining (%)**
	a (Å)	**c (Å)**	**c/a**	
Unprocessed	2.9421	4.6703	1.5874	-
350	2.9642	4.8669	1.6419	4.21
375	2.9658	4.8681	1.6414	4.24
400	2.9658	4.8694	1.6419	4.26
425	2.9658	4.8707	1.6423	4.29
450	2.9658	4.8719	1.6427	4.32

It can be seen from the table, the plasma nitriding treatment resulted in lattice strains. However, the expansion was anisotropic since the crystalline strains in the c-axis is larger than those in the a-axis. The straining in the a-axis was not changed at the temperature above 375 ºC. On the other hand, the straining in the c-axis continues to grow with the increase of the holding temperature. The relation between the lattice straining in c-axis and the hardening as a function of the holding temperature is shown in Figure 7.

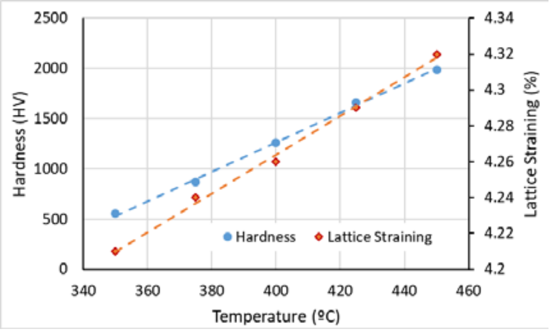


Fig.7 The effect of holding temperature on hardness and lattice straining

The hardening was evidently controlled by the lattice straining. In this low-temperature process, the nitrogen diffuses into the α-Ti matrix forming fine precipitation of TiN and Ti_2N and also the interstitial solid solution, i.e., α’(N)-Ti. The combination of the three phases was varied with the change of the holding temperature. In the high-temperature nitriding, the hardening was strongly controlled by both the precipitation reaction and also the α to β phase transformation [11, 14]. Closely observation on the peak at 43.4 degrees for the [200] plane of the TiN and 61.5 degrees for the $[11\bar{2}0]$ the plane of the α’(N)-Ti in Figure 4 reveals that the increase of the increase of the holding temperature decreases the TiN population. At the same time, the intensity of the α’(N)-Ti was increased. This indicates that the formation of the solid solution phase was related to nitrogen super-saturation state in the hcp structure. The hardening of the pure titanium by means of the low-temperature nitriding is strongly affected by the presence of the interstitial nitrogen in the hcp structure.

4. CONCLUSION

The high-density plasma nitriding using a mixture of 80% nitrogen and 20% has effectively hardened the pure titanium at low temperature. The nitrogen diffused deep into **the α**-Ti matrix forming TiN, Ti2N and α’(N)-Ti phases. A nitrided layer with the thickness of 30 µm was obtained with the holding temperature of 425 ºC resulted in surface hardness of 1696 HV. The hardness of the surface reached 1989 HV after the nitriding with the temperature of 450 ºC.

The nitrided layer was anisotropically strained in the c-axis. The lattice straining which was noticeably increased with the increase of the increase of the α’(N)-Ti phases. The nitrogen solid solution resides at the octahedral vacancy sites. Although the high hardness is usually attributed to fine precipitation of Ti_2N and TiN, evidently the existence of nitrogen super-saturation in the α-Ti lattices greatly affect the hardness.

Further study of the diffusion and the formation of phases related to the high-density nitrogen plasma will open new possibilities in hardening titanium and its alloy efficiently.

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