

# HIGH DENSITY PLASMA NITRIDING OF PURE TITANIUM

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**ABSTRACT** Pure titanium in the industrial grade has been widely utilized, but its products suffered from low wear and erosion resistance. The plasma nitriding was selected as a tool to harden the pure titanium products; high temperature processing was necessary to attain high hardness. In the present study, high density plasma nitriding system was applied to make low temperature plasma nitriding at 723 K (or 450°C) for 14.4 ks (or 4 hours). The average measured hardness reached to 490 HV. This high hardness of plasma-nitrided pure titanium at low temperature was attributed to formation of fine TiN precipitates and nitrogen solid solution into vacancy sites in HCP crystalline structure of titanium.

## 1. INTRODUCTION

Titanium is a very attractive metal, such as lightweight, high strength by alloying, and high performance in structuring. Pure titanium in the industrial grade has been widely utilized for structural and mechanical parts. For an example, the pure titanium in the first grade has high specific strength to be utilized for artificial bone materials. However, it suffers from poor tribological properties (Zhecheva, et al, 2005). Titanium has two crystallographic forms: at room temperature, it has a hexagonal close-packed (HCP) crystal structure which is referred to  $\alpha$ -phase, and, at 883°C, this transforms to a body-centered cubic (BCC) structure, so-called as a  $\beta$ -phase (Koyuncu, 2009). The surface protection by a stable oxide layer improves its corrosive resistance. However, these pure titanium products often suffer from wear and erosion in practice because of low hardness, even though they have sufficiently high strength by grain size reduction.

That low hardness of titanium is improved by nitriding with the thermochemical methods. There are several methods in this nitriding: the gas nitriding, the laser nitriding and the plasma nitriding. Yoshida, et al. (2013) reported that the hardness of pure titanium increased to 620 HV by the gas nitriding process at 1073 K for 18.0 ks with flow rate of 1.5 l/min.

Other researcher (Yilmazer, et al., 2009) reported that titanium surface was modified to have hardness of 2050 HV down to 250  $\mu\text{m}$  in depth by the DC glow discharge with 2 kV voltage at 1073 K for 9 hours. That high hardness was also concluded to come from fine precipitation of  $\epsilon$ -Ti<sub>2</sub>N and  $\delta$ -TiN in the nitrided surface layer. Nevertheless, high temperature treatment also drives the grain growth to deteriorate the original structure. It has a risk of contamination by surface oxidation in parallel with nitriding. Furthermore, the leading time for production is much prolonged by heating and cooling as well as long nitriding time. Plasma nitriding is available in commercial. Large energy consumption still presents a challenge to surface engineers and researchers, serving as a driving force for optimization on plasma nitriding process (Tong, et al., 2008).

In the present study, low temperature high density plasma nitriding is applied to increase the hardness of pure titanium at 723 K. The RF-DC plasma system together with the hollow cathode device plays a role to attain the high hardness. The plasma processing parameters are optimized to determine the appropriate conditions for a low temperature plasma nitriding; e.g. the RF voltage is set to be 250 V, and, the DC bias, -600 V. Under this condition, the present plasma nitriding at 723 K for 14.4 ks (or 4 hours) provides high hardness up to 490 HV.

## 2. EXPERIMENTS

### 2.1 High Density Plasma Nitriding System

High density RF-DC plasma system was utilized for the present low temperature plasma nitriding. It consists of RF dipole electrodes and DC bias cathode plate. The glow discharge plasma is generated by RF around 2 MHz in frequency. The input-output matching is automatically adjusted in the frequency. A mixture gas of nitrogen and hydrogen is used; each flow rate is controlled to adjust the total pressure in processing. The titanium specimen with the size of  $18 \times 40 \times 0.3 \text{ mm}^3$  is placed in the inside of the rectangular hollow cathode. Figure 1 shows a typical experimental set-up for the present plasma nitriding.

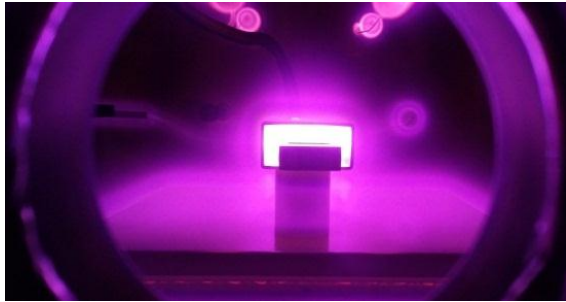


Fig. 1 Experimental set-up of specimen in the hollow cathode in the chamber.

### 2.2 Experimental procedure

In preparation, the strain-wrought specimen was degreased with industrial soap (alkali solution) at ultrasonic cleaner system for 5 minutes. After that, the sample was rinsed and drained.

Titanium specimen was introduced into the chamber and then the pressure chamber is evacuated down to the base pressure of 0.7 Pa. After that, the sample was heated until the temperature of 723 K or 450°C in nitrogen gas atmosphere. Before nitriding process, the specimen was pre-sputtered by DC bias voltage of -500 V with nitrogen gas flow rate of 160 ml/min for 1.8 ks. This pre-sputtering process was followed by the nitriding process under the mixture gas flow of 160 ml/min nitrogen and 40 ml/min hydrogen gas for 14.4 ks or 4 hours. In the following experiment, the RF voltage was fixed constant by 250 V; the DC bias was varied from -500 V to -600 V. In order to understand the effect of the pressure on the hardening process, the pressure of mixture gas was also varied by 150 Pa, 75 Pa and 50 Pa, respectively.

### 2.3 Observation and Measurement

The specimen surface morphology was observed by the microscope (Keyence VW-9000). The hardness was measured by the micro-Vickers hardness tester (Mitsutoyo, Co. Ltd.) with the applied load of 0.5 N or 50 gf. The average surface hardness was calculated from the measured data at five different positions. X-ray diffraction (XRD) system (Rigaku Ultima IV, Rigaku,

Co. Ltd.) by the monochromated Cu K $\alpha$  radiation with  $\lambda = 1.545980 \text{ \AA}$  was utilized for structural analysis. The diffraction angle,  $2\theta$ , was controlled to vary from 3° to 90°, with the scanning step of 0.02° and the counting time for 4 deg/min. The profile parameters were obtained using Rietveld refinement with program Crystalsleuth. Starting lattice parameters were taken from ICSD#44390 (for  $\alpha$ -Ti), and ICSD#152807 (for TiN).

## 3. RESULTS

The top surface morphology before and after nitriding process was compared in Fig. 2. The surface morphology of pure titanium changes from the wrought structure to the granular structure with the bigger black spots. This change must be attributed to structural change during the plasma nitriding,

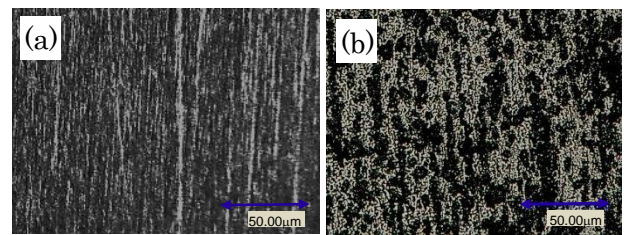


Fig. 2 Surface morphology of (a) pure titanium, (b) nitrided sample at 723 K for 14.4 ks by 50 Pa

In each specimen, five points were selected in Fig. 3 for hardness distribution on the nitrided titanium specimen.



Fig. 3 Positions for surface hardness testing by 50 gf or 0.5 N in loading.

The average surface hardness for the initial pure titanium sample and nitrided samples for 14.4 ks at 723 K was summarized in Table 1.

Table 1 Average surface hardness for the initial pure titanium and five plasma nitrided specimens.

No.	Sample Condition	Average Hardness (HV)
1.	Pure Titanium	310
2.	Nitrided at 150 Pa, 500 V DC bias	330
3.	Nitrided at 75 Pa, 500 V DC bias	420
4.	Nitrided at 50 Pa, 500 V DC bias	470
5.	Nitrided at 75 Pa, 600 V DC bias	470
6.	Nitrided at 50 Pa, 600 V DC bias	490

Among several plasma nitriding parameters, the pressure plays an important role to increase the hardness; e.g. even using the same DC-bias of -500V or -600V, the

hardness increases by lowering the pressure from 75 Pa to 50 Pa. This might be because the mean free path for activated species in the plasmas becomes longer with decreasing the pressure enough to penetrate the nitrogen atoms into the depth of titanium specimen.

Figure 4 compares the XRD diagrams for the initial pure titanium and two nitrided samples by the DC bias voltage of -600 V. In the XRD analysis, the Rietveld procedure was used to adjust each directional indices to each measured peak. Direct comparison of initial pure titanium and nitrided samples shows that the peak position shifts itself in the plane  $[2\bar{1}\bar{1}1]$ ,  $[2\bar{1}\bar{1}3]$  and  $[11\bar{2}2]$ ; e.g. the peak from the plane  $[2\bar{1}\bar{1}1]$  shifts by  $0.739^\circ$  in  $2\theta$  from  $40.271^\circ$  to  $39.532^\circ$  for nitrided Ti at 50 Pa. Near the peak  $[0002]$ , a new peak of TiN with the plane  $[111]$  is detected in Fig. 4, and, also near the peak  $[11\bar{2}0]$ , found the plane  $[220]$  of TiN. The new peak with plane  $[200]$  of TiN also found at  $43.2^\circ$  at the nitrided surface.

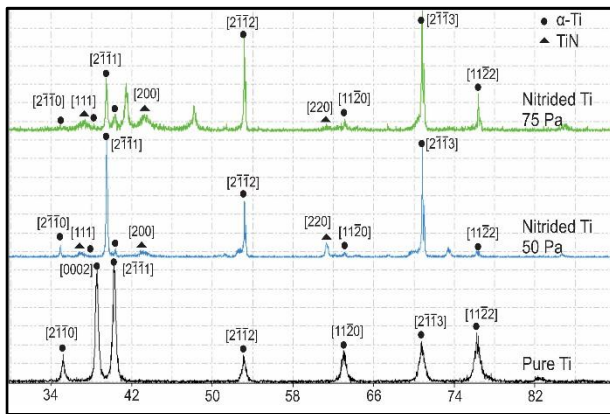


Fig. 4 XRD diagrams of original titanium and two nitrided titanium specimens.

The lattice parameters and the micro-strains for the plasma-nitrides specimens are summarized in Table 2. The crystalline micro-strain is defined by  $e_a = (a_1 - a_0)/a_0$  in the a-axis and  $e_c = (c_1 - c_0)/c_0$  in the c-axis, respectively.

Table 2 Lattice Parameter and Microstrain from XRD data of samples

No.	Sample Condition	Lattice parameter (Å)	Microstrain (-)
1.	Pure Titanium	$a_0 = 2.9473$ $c_0 = 4.6714$	
2.	Nitrided at 50 Pa, 600 V DC bias	$a_1 = 2.9617$ $c_1 = 4.7261$	$e_a = 4.886 \times 10^{-3}$ $e_c = 1.171 \times 10^{-2}$
3.	Nitrided at 75 Pa, 600 V DC bias	$a_2 = 2.9605$ $c_2 = 4.7158$	$e_a = 4.479 \times 10^{-3}$ $e_c = 9.505 \times 10^{-2}$

## 4. DISCUSSION

The obvious differences in Fig. 2 before and after nitriding indicates that the compound layer is formed on the nitrided sample including the titanium (III) nitride or TiN at the surface. The new peaks are detected in Fig. 4 at  $2\theta = 37.0^\circ$ ,  $43.2^\circ$  and  $63.1^\circ$  corresponding to plane  $[111]$ ,  $[200]$  and  $[220]$  in the cubic structure of TiN. From the Scherrer equation, the size of TiN precipitation is extended to be 10-20 nm. It means there are formed fine precipitation of TiN occurs due to the reaction of nitrogen and titanium at the surface of nitrided sample.

Since the nitriding process is performed at 723 K, which is much lower than transition temperature of  $\beta$ -Ti, the nitrided layer also consists of the solid solution  $\alpha$ -Ti(N). From the XRD analysis on the initial pure titanium before nitriding, the pure titanium of  $\alpha$ -Ti phase has hexagonal closed-pack crystalline structure with the lattice parameters of  $a_0 = 2.9473$  Å and  $c_0 = 4.6714$  Å, respectively. After plasma nitriding at 723 K for 14.4 ks by 50 Pa with the DC bias voltage of -600 V, this lattice parameter increases: e.g.,  $a_0$  increases to  $a_1 = 2.9617$ , and,  $c_0$  to  $c_1 = 4.7261$ , respectively. This suggests that the original HCP-structured crystals should expand both in the a-axis and c-axis by the nitrogen solid solution, in correspondence of the peak shift in the direction of small  $2\theta$  in Fig. 4. In both nitrided specimens, the crystalline strains in the c-axis is larger than those in the a-axis; the above expansion of  $\alpha$ -Ti lattice is anisotropic.

In case of the solid solution into  $\alpha$ -Ti lattice, the nitrogen solutes diffuse interstitially to HCP structure of titanium. There are two possible interstitial positions in HCP crystal, i.e. the octahedral vacancy site or the tetrahedral vacancy site, as illustrated in Fig. 5.

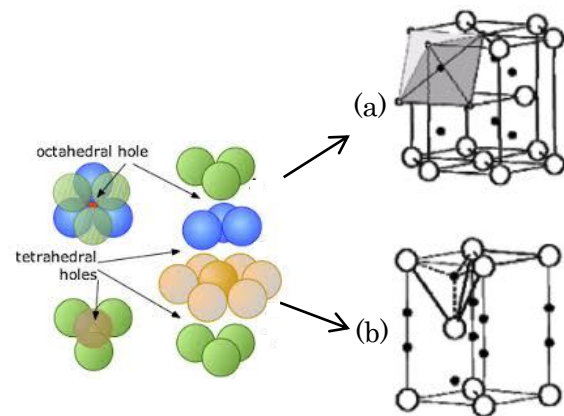


Fig. 5 Possibility of interstitial diffusion at HCP-crystal (a) Octahedral sites, (b) Tetrahedral sites.

The interstitials are shown as black dots.

Considering the chemical potential gradient in the HCP structured crystals, the most preferable nitrogen solute diffusion site is an octahedral vacancy. In the  $\alpha$ -titanium HCP crystal, the radius of nitrogen solute or  $r_N$  is 0.92 Å. On the other hands, the octahedral vacancy site is sized by  $r_O = 0.6$  Å, and, the tetrahedral one,

$r_T = 0.33 \text{ \AA}$ . Gicoel, et al. (1990) discussed that relative dimension between the vacancy size and the replacement solute size should determine the possibility of site occupation for solute to vacancy. Wider size of octahedral vacancy site is selected for nitrogen solute occupation in the diffusion process. Since  $r_N > r_T$ , the nitrogen solute occupation to octahedral vacancy sites accompanies with the lattice expansion in the c-axis.

Both the fine precipitation of TiN into  $\alpha$ -Ti matrix and the nitrogen solid solution into  $\alpha$ -Ti matrix drive the low temperature nitriding. As reported in Yoshida, et al. (2013), Yilmazer, et al. (2009) and Koyuncu, et al. (2009), the precipitation reaction between BCC-structured titanium and nitrogen or the formation of TiN surface layer drove the hardening of titanium by high temperature nitriding. This reveals that low temperature nitriding is characterized by nitrogen solid solution into HCP-structured titanium for hardening.

## CONCLUSION

The high density RF-DC plasma system is applied to low temperature nitriding of the pure titanium at 723 K. Formation of fine TiN precipitates and the nitrogen solid solution into  $\alpha$ -Ti matrix drives this nitriding process. The hollow cathode device with high DC bias voltage addition at low pressure plays a role to increase the surface hardness. The average hardness up to 490 HV is attained in low temperature without the phase transition to BCC  $\beta$ -titanium. Further study is necessary to delineate the role of TiN precipitation in the hardening of nitrided titanium from the role of nitrogen solid solution.

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