



## Effects of Process Temperature and Time on the Properties of Microwave Plasma Nitrided Ti-6Al-4V Alloy

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### ABSTRACT

Titanium alloy (e.g. Ti-6Al-4V) has an excellent combination of properties. However in many cases, the application is limited because of the poor wear property. In this work, a surface modification (plasma nitriding) is carried out to improve the surface properties of Ti-6Al-4V, as a treatment prior to a hardcoating deposition, leading to a duplex coating system. This is an effort to improve the surface and near surface property of Ti-6Al-4V. Plasma nitriding is performed utilizing microwave plasma method in 25% Ar- 75% N<sub>2</sub> atmosphere at temperatures of 600°C and 700°C for different processing times (1, 3 and 5 hours). The phase and microstructure of plasma nitrided substrate were characterized by using X-ray diffraction (XRD) and Scanning electron microscopy (SEM). The plasma nitrided Ti-6Al-4V properties (surface roughness, surface hardness and case depth) were determined using profilometer and microhardness, respectively. Results obtained showed a significant increase on the surface hardness of Ti-6Al-4V. This is due to the formation of TiN and Ti<sub>2</sub>N phases in the form of compound layer. Besides, it shows that the diffusion of nitrogen into the Ti-6Al-4V substrate produces case depth up to 130 µm and this contributes to the improvement of the near surface hardness due to the changes in the microstructures. It was also found that the surface hardness and surface roughness increased with the increases in the process temperature and times.

*Keywords:* Ti-6Al-4V, surface modification, plasma nitriding, microwave plasma

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### INTRODUCTION

Titanium and its alloys have received extensive interest due to their excellent combination of properties, such as excellent corrosion resistance, high strength to weight ratio, high strength at elevated temperatures, low modulus elasticity and biological compatibility. Besides, titanium and its alloys

are widely used for a range of applications in the aerospace, automotive, marine, chemical and biomedical industries.

The most common titanium alloy used is Ti-6Al-4V. The reasons for the success of this particular type of alloy are its beneficial properties (e.g. high strength to weight ratio and corrosion resistance), making it remarkable for technical application varying from construction materials to medical implant materials. However, Ti-6Al-4V is found to be inconsiderably utilized in mechanical engineering applications, as in sliding systems (Ma *et al.*, 2004). This is because of its poor tribological properties such as poor abrasive wear resistance, poor fretting behaviour and high coefficient of friction (Zhecheva *et al.*, 2005). When the untreated titanium alloy surface is in rubbing contact with another material, even though being lubricated, there is a strong tendency for galling to take place leading to severe wear (Bell 1993).

Therefore, surface modifications become a fundamental requirement when Ti-6Al-4V is subjected to wear problem. Some examples of surface modifications of Ti-6Al-4V that are usually carried out are the deposition of hardcoating by chemical vapour deposition (CVD) or physical vapour deposition (PVD) techniques and thermochemical treatment such as diffusion techniques. However, the restriction on common use of hardcoating on Ti-6Al-4V substrate is the load carrying the capacity of the coating-substrate system with correlated to the soft substrate beneath the coating (Ma *et al.*, 2004). As a consequence, delamination and premature failure of the hardcoating on the surface of Ti-6Al-4V components under wear conditions have been observed (Yetim *et al.*, 2008). In order to prevent the failure, a surface modification (e.g. thermochemical treatment) is required intended as a pre-treatment to Ti-6Al-4V substrate before the hardcoating deposition with reference to the duplex coating concept.

Thus, the thermochemical treatment involving diffusion of the substrate material with different elements is an option for improvement in Ti-6Al-4V surface and near surface property. Diffusion treatment like plasma nitriding can increase the wear resistance, decrease the coefficient of friction and certainly harden the surface of materials (Yetim *et al.*, 2009). The high reactivity of titanium with respect to nitrogen, oxygen and carbon is an advantage to produce high hardness of surface layer, making the diffusion treatment particularly interesting to improve the wear property of Ti-6Al-4V. Processes such as oxidation, carburizing and nitriding are among popular thermochemical treatments used to improve the surface properties of titanium alloy, especially Ti-6Al-4V (Holmberg & Matthews, 2009).

In conducting thermochemical treatment on the substrate, the utilization of plasma advantageously reduces the duration of process. This is due to the diffusion of high energy ions and intensification of the elements (nitrogen, oxygen, carbon) transportation from the surface to the substrate core. Besides, the process parameters such as temperature and time are available for the modification to improve the surface properties such as phase composition, microstructure and surface morphology (Zhecheva *et al.*, 2005).

A common method used for thermochemical process of Ti-6Al-4V is plasma nitriding. The nitrogen used has high solubility in  $\alpha$ -Ti phase, and it therefore strengthens the surface layer significantly. Modification on the surface layer of plasma nitride Ti-6Al-4V consists of a compound layer on top of the surface with TiN and Ti<sub>2</sub>N phases. The presence of TiN and Ti<sub>2</sub>N phases has significant effect on the surface hardness of Ti-6Al-4V (Yildiz *et al.*, 2008; Lakshmi, 2002). Underneath the compound layer is the diffusion layer which consists of an

interstitial solution of nitrogen in the  $\alpha$ -Ti phase (Yildiz *et al.*, 2008). The diffusion layer is also known to improve the hardness properties of Ti-6Al-4V with the formation of case depth profile (Yildiz *et al.*, 2008).

Various methods have been used by other researchers to ensure the success of the plasma nitriding process including Direct Current (DC) and Radio Frequency (RF) methods. DC plasma nitriding method is the most widely used. In this method, plasma is created by an electrical discharge between the two electrodes. According to Yildiz *et al.* (2008), the DC technique formed dense TiN phase as process temperature and time were increased, while the Ti<sub>2</sub>N phase disappeared when the process temperature and time were increased. Besides, Yilbas *et al.*, (1996) utilised the DC plasma nitriding method and also found that the diffusion of nitrogen increased with the increase in the surface temperature.

Another method used by researchers for the plasma nitriding process is RF plasma nitriding method. In this method, plasma is produced when the electrons absorb power from the RF field, and then transmit it through collisions of electrons with the gaseous atoms. The installation of RF is per the industrial band standard (13.56 MHz) in order to avoid interference with communication network (Chattopadhyay, 2004). The RF plasma nitriding also produces TiN and Ti<sub>2</sub>N phases with significant improvement on the surface hardness of Ti-6Al-4V. These also lead to the improvements of wear resistance (Fouquet *et al.*, 2004; El-Hossary *et al.*, 2006).

Another method that can generate plasma for the nitriding process is microwave plasma nitriding method. The advantages of this method are due to its efficiency in generating the plasma and it is also readily available at low cost of 2.45 GHz microwave generators (Chattopadhyay, 2004). Besides, it requires low pressure as compared to the DC and RF methods. In addition, it applies magnetic field to encourage the formation of plasma. This study aimed to understand the effects of process parameters (e.g. temperature and time) on the microstructure and mechanical properties of microwave plasma nitride Ti-6Al-4V substrate.

## EXPERIMENTAL

The samples used for this study is Ti-6Al-4V, with the following chemical compositions (wt %): Al (6), V (4) and Ti (balance). The samples were cut from a long rod, with 10mm × 25mm (thickness × diameter) and mechanically polished for surface roughness, Ra < 0.5. After polishing, the sample was cleaned using ultrasonic cleaning in ethanol bath for 15 minutes and then dried using hot air dryer.

The sample was put inside the chamber and evacuated by a rotary pump until the pressure reached 10<sup>-2</sup> mTorr (Fig.1), and subsequently cleaned by hydrogen plasma with an overall pressure of 15 mTorr for 5 minutes. The samples were then heated to the required temperature (600°C, 700°C) and nitrogen along with argon gas was introduced into the microwave source (1kW, 2.45GHz) to produce plasma. The operating pressure in the chamber was fixed at 30 mTorr, and the flow rates of the N<sub>2</sub> and Ar gas mixtures were set at 25% (Ar): 75% (N<sub>2</sub>). The nitriding temperatures were monitored and performed for 1hr, 3hr and 5 hr.

X-ray diffraction (XRD) for phase identification was carried out with X'Pert PRO system with monochromatic Cu K $\alpha$  radiation in  $\theta$  - 2 $\theta$  geometry. All the XRD patterns were obtained with scan steps of 0.01° and a counting time of 40s. The surface roughness of the samples was

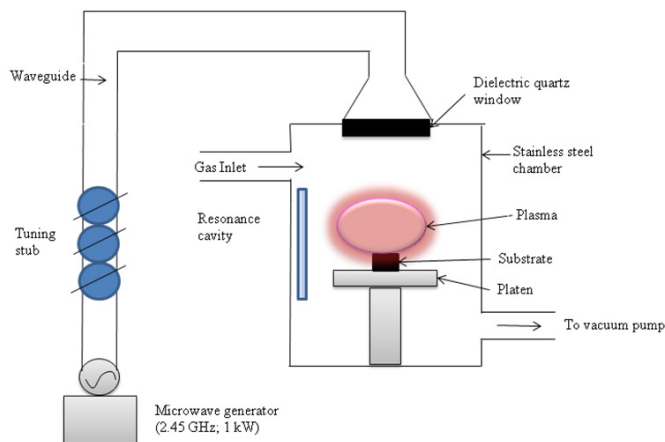


Fig.1: A schematic diagram of the Microwave plasma reactor

measured using Mitutoyo SJ 301 surface profilometer with SR10 tip type. Cross sectional metallographic examination was carried out using a scanning electron microscope (Zeiss). Prior to that, the cross sectioned area was ground and polished to produce mirror-like finish surface and the surface was etched using Kroll's reagent to reveal the microstructures. For the purpose of mechanical property study, Mitutoyo microhardness tester with Vickers indenter was employed with 100g load to measure the surface hardness and 25g for the case depth profile for the cross sectioned samples. The choice of load was based on the measurable indentation size produced during the experimental work. The lower load used for the case depth profiling was to avoid overlapping of indentation.

## RESULTS

### *As received*

The XRD patterns of as received Ti-6Al-4V revealed that the sample consisted of  $\alpha$ -Ti (ICDD: 00-001-1198) and  $\beta$ -Ti (ICDD: 00-044-1288), as shown in Fig.2 and the SEM cross-sectioned micrograph is shown in Fig.3. It shows that the microstructures consist of equiaxed  $\alpha$  phases and fine acicular shape for the  $\beta$  transform phases. As for the surface roughness, the average Ra value obtained was  $0.23 \pm 0.03 \mu\text{m}$  and the surface hardness value was  $349.04 \pm 4.77 \text{HV}_{0.1}$ .

### *The Effects of Process Temperature and Time*

#### **Phase Composition**

The XRD pattern of plasma nitride surface of the substrate revealed the formation of TiN phases with cubic structures (ICDD: 01-087-0633) and  $\text{Ti}_2\text{N}$  phases with tetragonal structure (ICDD: 01-0076-0198) (Fig.4). In addition, the diffraction peaks show that the TiN phases has a dominant (highest intensity) at [111] plane, while  $\text{Ti}_2\text{N}$  phases have a dominant at [111] plane. It was also observed that the diffraction pattern at both process temperatures (600°C and 700°C), the  $\alpha$ -Ti of [100], [002] and [101] peaks were shifted to lower  $2\theta$  side. Whereas, the  $\beta$ -Ti

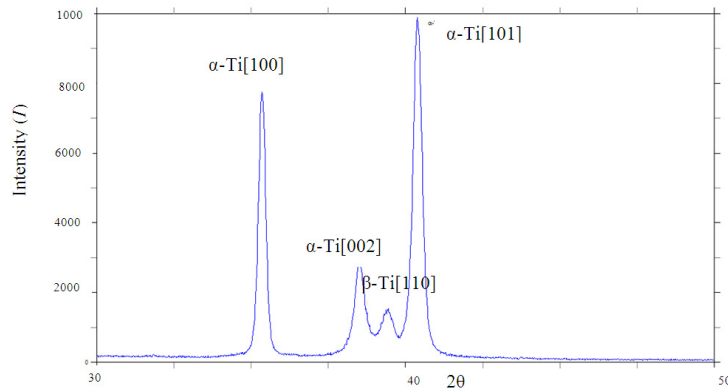


Fig.2: The XRD patterns of as received Ti-6Al-4V substrate

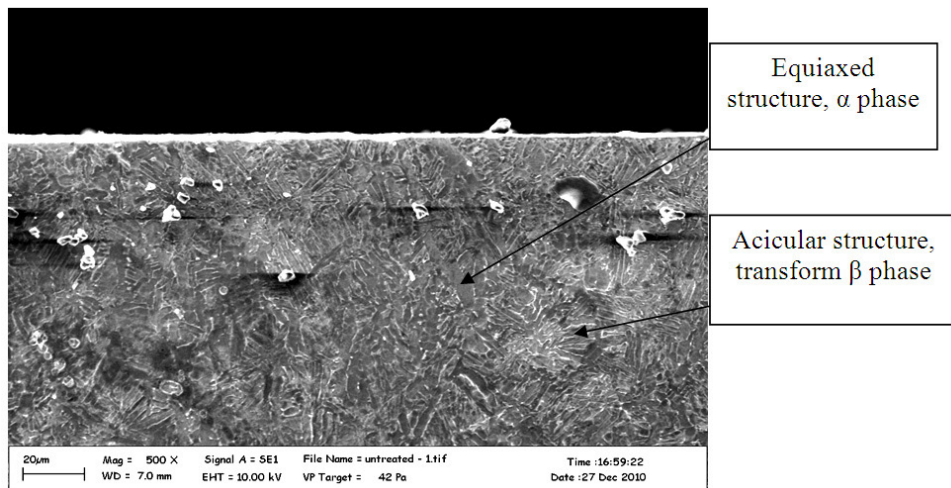
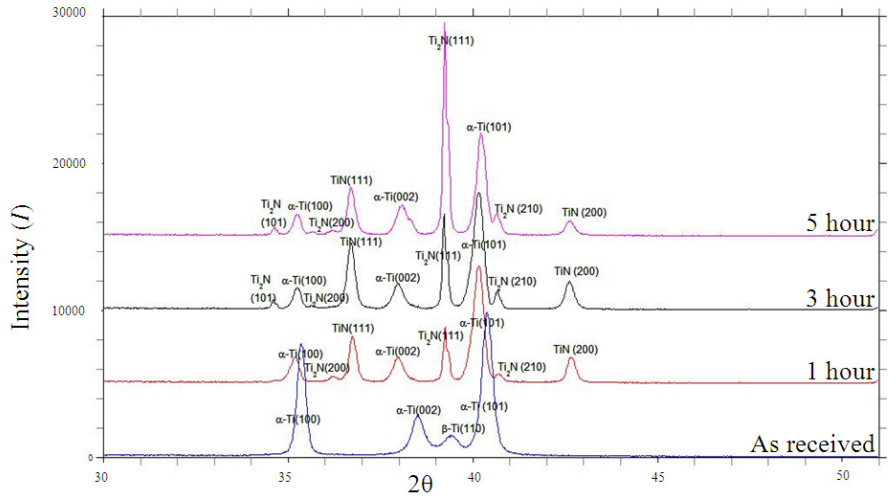


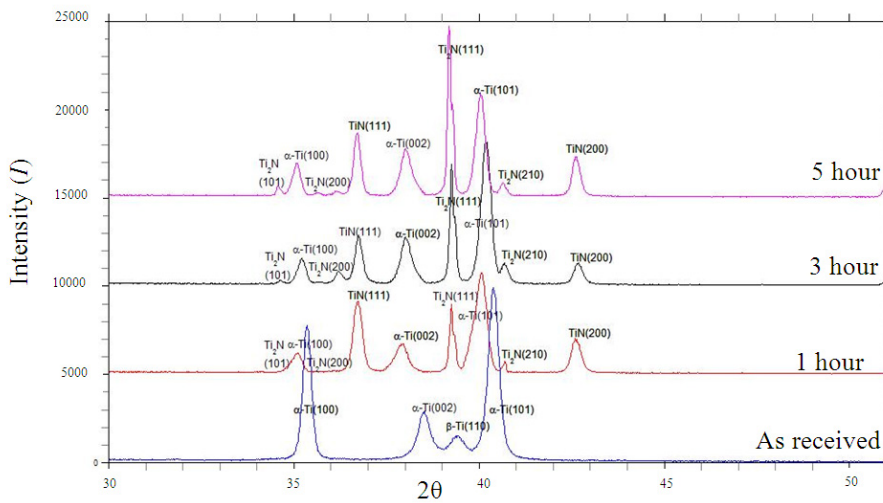
Fig.3: The SEM micrograph of the cross-sectioned of as-received Ti-6Al-4V substrate

peak (Observed in the as received Ti-6Al-4V) was not detected in the plasma nitrided samples.

In general, as the temperature increased, changes on the peak intensities of TiN [111] and [200] and Ti<sub>2</sub>N [210] peaks were observed. The intensity of TiN [111] peak of the sample 600°C 3 hours was double the intensity of α-Ti [002], but for the 700°C 3 hours sample, the intensity was almost the same. The intensity of TiN [200] was almost the same with that of Ti<sub>2</sub>N [210] peak for 600°C 5 hours sample, but for the 700°C 5 hours sample, the intensity of TiN [200] was more than 2 times higher than Ti<sub>2</sub>N [210]. However, these changes did not affect conclusion made on the type of phase present in the samples. While the intensity of Ti<sub>2</sub>N [111] peak showed increases with the decrease of the process temperature. This is evident in the samples nitrided for 5 hours at 600°C and 700°C. In contrast, as the process time increased, the intensities of TiN [111] and [200] and Ti<sub>2</sub>N [210] peaks showed irregular changes in the intensities. Meanwhile, the Ti<sub>2</sub>N [111] peak intensities increased as the process time increased.



(a) 600°C



(b) 700°C

Fig.4: The XRD pattern of microwave plasma nitrided at various process temperatures and times

### Microstructures

The SEM micrographs on the cross-sectioned plasma nitride samples revealed that the variation in the microstructure is visible at the depth of 120  $\mu\text{m}$  (Fig.5). Throughout this depth, 3 distinct regions with different microstructures were observed. As the process temperature and time increased, the outermost layer was apparently observed. Underneath this continuous outermost layer, a distinct layer with lamellar and acicular structures was found to exist. These lamellar and acicular structures grew bigger with the increase of process temperature. Besides, the distinct layer was observed broadening with the increase of process time.

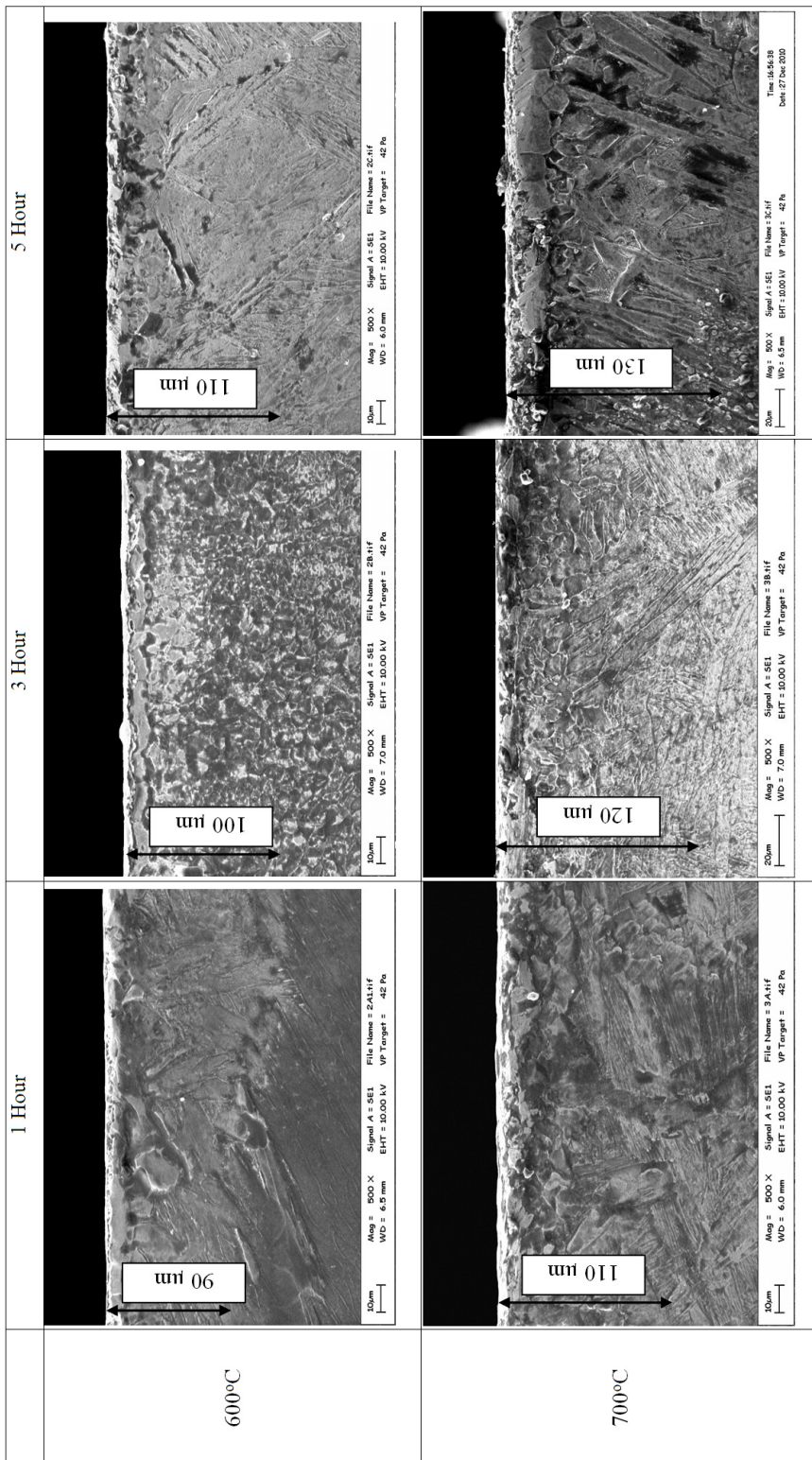


Fig.5: The SEM micrograph of the cross-sectioned microwave plasma nitrided Ti-6Al-4V at various of process temperatures and times, indicating the case depth obtained for each sample

### Surface Roughness

The surface roughness, Ra of the as received and microwave plasma nitrided Ti-6Al-4V alloy at various temperatures and time is shown in Fig 6. It shows that the plasma nitriding process increased the Ra value of the nitrided samples as compared to the as received alloy. In general, the Ra value increased as of the process temperature and time increased. However, the increase of Ra value was less obvious for the samples nitrided at 700°C for 3 hours and 5 hours.

### Surface Hardness

The surface hardness of plasma nitrided Ti-6Al-4V samples was found to be higher as compared to the as received sample (Fig.7). This means that the surface hardness for the plasma nitrided samples increased as the process temperature and time increased. The highest value was observed for the sample nitrided at 700°C for 5 hours and the lowest value was observed at

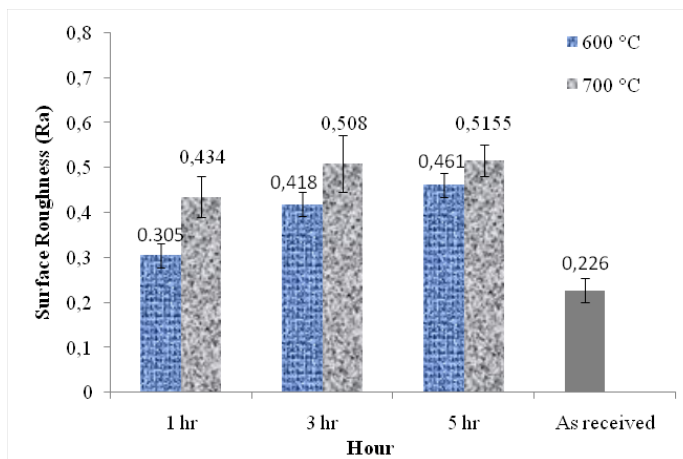


Fig.6: The surface roughness of the as received and microwave plasma nitrided Ti-6Al4V at various temperatures and times.

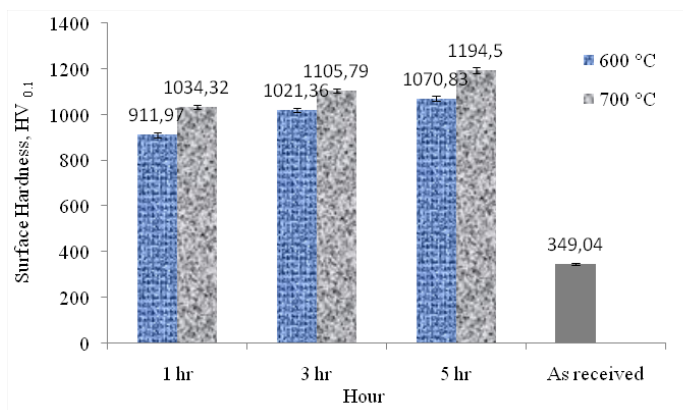


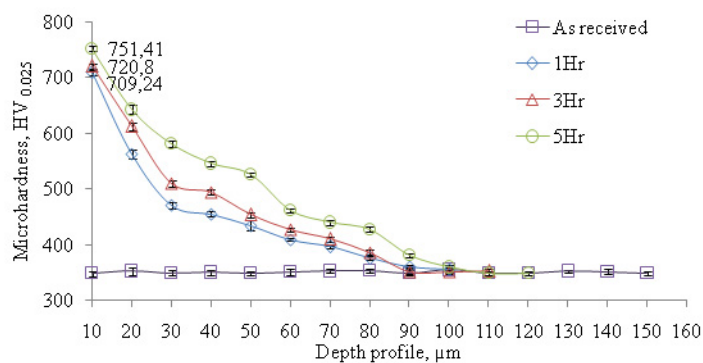
Fig.7: The surface hardness results of the as received and microwave plasma nitrided Ti-6Al-4V at various temperatures and times



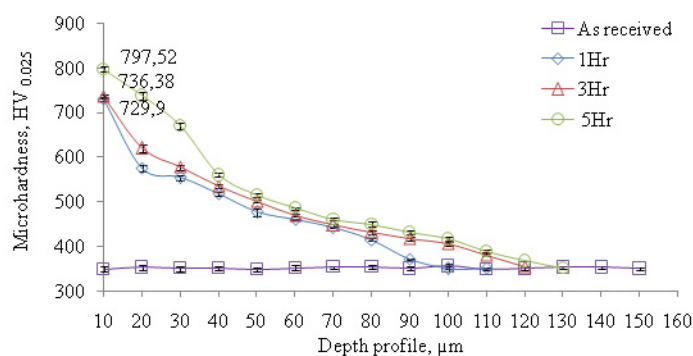
the sample nitrided at 600°C for 1 hour. It should be noted that major increment on the surface hardness is due to the increase of temperature. This is evident for the sample nitrided for 1 hour at 600°C and 700°C, whereby the surface hardness of the sample was  $911.97 \pm 9.45 \text{ HV}_{0.1}$  at 600°C and  $1034.32 \pm 7.98 \text{ HV}_{0.1}$  at 700°C, respectively. In contrast, less significant increment of the surface hardness was observed for the sample nitrided at the same temperature, namely, the sample nitrided at 700°C for 3 hours the surface hardness was  $1105.79 \pm 9.84 \text{ HV}_{0.1}$  and with 5 hours, the surface hardness was  $1194.5 \pm 11.8 \text{ HV}_{0.1}$ .

### Case Depth Profile

Fig.8 shows the case depth profile of the microwave plasma nitrided samples in varying process temperatures and times. The hardness of as received Ti-6Al-5V is  $350 \pm 4.26 \text{ HV}_{0.025}$ . Thus, it is considered as the hardness limit (core hardness). It was found that the highest hardness obtained was at the near surface area region. The hardness gradually decreased with the depth of the sample and finally reached the hardness limit (core hardness). This represents the case depth profile for each sample. It was also observed that the case depth profile increased with the increases of process temperatures and times. In particular, the highest case depth was obtained (130 $\mu\text{m}$ ) in the sample nitrided at 700°C 5 hours.



(a) 600°C



(b) 700°C

Fig.8: The case depth profile of microwave plasma nitrided Ti-6Al-4V at various of process temperatures and times

## DISCUSSION

During microwave plasma nitriding, process parameter (temperature and time) plays a significant role on the microstructures and mechanical properties of the plasma nitrided Ti-6Al-4V substrate. The new phases, such as TiN and Ti<sub>2</sub>N, were observed at 600°C for 1 hour. This parameter (600°C 1 hour) was lower processing parameter compared to other study (utilizing RF plasma) where a moderate parameter, 700°C 4 hours was required to form the TiN phase (Fouquet *et al.*, 2004). This finding is in agreement with suggestion made by Yildiz *et al.* (2008), whereby it was mentioned that the Ti<sub>2</sub>N phase is formed at the temperature < 700°C. However, there is an increase in the Ti<sub>2</sub>N peak intensities with the process time increases, and this is in contrast with the result by Yildiz *et al.* (2008) which indicated that the intensity of Ti<sub>2</sub>N decreased as the process time increased using the DC plasma method.

The determination of TiN and Ti<sub>2</sub>N phases indicates that the compound layer is formed on the plasma nitrided Ti-6Al-4V surface at the process parameter of 600°C 1 hour. The formation of this particular compound layer during nitriding of titanium is as per in the schematic presentations of the kinetics of formation and the growth of surface layers during nitriding of titanium suggested by Zhecheva *et al.* (2005) (see Fig.9). This is also supported with the SEM micrograph cross section of the samples (Fig.5), where the existence of compound layer was observed on the outermost layer. The compound layer thickness increased as the process temperature and time increased.

The XRD pattern of the nitrided samples at 600°C and 700°C shows that the TiN phase has a dominant peak at [111] and [200] planes. This is in agreement with the findings by Yildiz *et al.* (2008) and Fouquet *et al.* (2004). Besides, Ti<sub>2</sub>N phase has dominant planes at [111] and

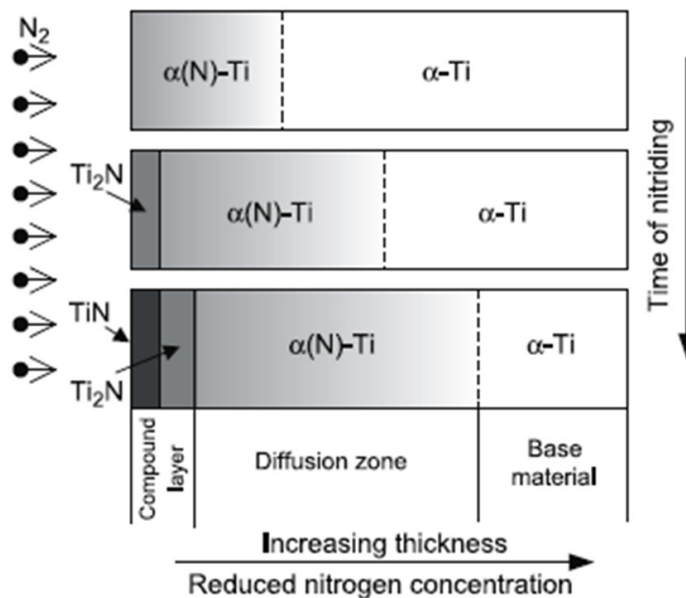


Fig.9: A schematic presentation of the kinetics of formation and growth of surface layers during nitriding of titanium (Zhecheva *et al.*, 2005)

[210], but these findings contradict with the results obtained by Raaif *et al.* (2007) and Fouquet *et al.* (2004), where the  $Ti_2N$  dominant planes at [210] and [111]. This variation seems to be due to the different types of nitriding gases used, such as Raaif *et al.* (2007) who utilized pure nitrogen plasma and Fouquet *et al.* (2004) who utilized hydrogen. It was also observed that the  $Ti_2N$  phase is highly oriented and depending on the composition of gas (Raveh *et al.*, 1989). Besides, the diffraction pattern of  $\alpha$ -Ti phases with [100], [002] and [101] planes shifted to lower  $\theta$  side and the peaks were broadened as the process time increased. This is due to the enlargement of  $\alpha$ -Ti cell caused by the nitrogen atoms, where the compressive residual stresses occur (Yildiz *et al.*, 2008). This also explains the undetected  $\beta$ -Ti peak as suggested by Yildiz *et al.* (2008).

In term of surface roughness, it was observed that it increased with the increases of the process temperature and time. This is consistent with findings by Yildiz *et al.* (2008) using the DC method and Fouquet *et al.* (2004) who used the RF method. The increase of the surface roughness of plasma nitrided Ti-6Al-4V alloy was probably due to the cones formed by the effect of ions bombardment during the nitriding process (Yildiz *et al.*, 2008). This increment might also be caused by the enlargement of the  $\alpha$ -Ti structures, as shown in the SEM micrograph of cross-sectioned microwave plasma nitrided samples (Fig.5). The  $\alpha$ -Ti structures were observed to have enlarged during the plasma nitriding process and grown as the process temperature increased. Consequently, this contributed to the roughness of the outer layer. In addition, it was also observed that when the process time increased, the growth  $\alpha$ -Ti structure was more prominent leading to the agglomeration of the TiN grain forming a compound layer. As a result, a less significant increase in the surface roughness was observed. For example, at 700°C for 3 hours, Ra is  $0.508 \pm 0.063$ , while for 5 hours Ra is  $0.515 \pm 0.035$ .

The improvement of microwave plasma nitrided surface hardness samples is suggested by the existence of  $Ti_2N$  and TiN phases in the form of compound layer, the finding which has also been observed by El-Hossary *et al.* (2006). Besides, the increase in the surface hardness is also parallel with the increase of  $Ti_2N$  and TiN peak intensities. It was observed that the highest surface hardness of  $1194.5 \pm 11.81 HV_{0.1}$  was obtained in this study when the microwave plasma method at 700°C for 5 hours was used. As a comparison, another study conducted by El-Hossary *et al.* (2006) utilizing the RF plasma method produced the hardness of nearly 600  $HV_{0.1}$  at 725°C. Meanwhile, Yildiz *et al.* (2008) utilized the DC plasma method to produce a hardness of 1180  $HV_{0.1}$  at 700°C for 4 hours. Thus, it can be seen that the microwave plasma method is able to produce a high surface hardness of plasma nitrided Ti-6Al-4V at a comparable of process parameter. Also, it was observed that the increase in the surface hardness is in conjunction with the increase of the compound layer thickness. This is evident when looking at the SEM micrographs of the cross-sectioned samples (Fig.5) where the thickest compound layer observed for the sample nitrided at 700°C for 5 hour yielded the highest surface hardness of  $1194.5 \pm 11.81 HV_{0.1}$ .

Generally, the case depth hardness is high at near surface area ( $<700HV_{0.025}$ ) and gradually decreases until it reaches the core hardness; more than  $550HV_{0.025}$  at the diffusion zone beneath the compound layer and  $350 \pm 4.26 HV_{0.025}$  at the core hardness. This is explained by the diffusion of nitrogen into the Ti-6Al-4V surface to form solid solution or precipitation hardening which results in the increase of the diffusion layer strength (Zhecheva *et al.*, 2005).

In addition, the case depth profile is in agreement with the cross-sectioned plasma nitrided samples observed in the SEM micrograph (Fig.5). To make a comparison with the other method, Yildiz *et al.* (2008) who had utilized DC reported the case depth of 50  $\mu\text{m}$  for the sample nitrided at 700°C for 1 hour. In this study, the case depth was found to be 100  $\mu\text{m}$  for the sample nitrided at 700°C for 1 hour.

## CONCLUSION

In the current work, the plasma nitriding process of Ti-6Al-4V alloy was conducted utilizing the microwave plasma technique. The following conclusions are made based on the findings of this study:

1. The TiN and Ti<sub>2</sub>N phases in the form of compound layer were observed for the sample nitrided at the temperature as low as 600°C for 1 hour. The thickness of this compound layer increased with the increases in the nitriding temperature and time.
2. The surface hardness increased with process temperature and time and is related to the formation of the compound layer.
3. The diffusion of nitrogen into the Ti-6Al-4V substrate produced a case depth up to 130  $\mu\text{m}$ . This contributes to the improvement of hardness value of near surface area and causes changes in the microstructure.
4. The surface roughness of the plasma nitrided Ti-6Al-4V samples increases with the increases in process temperature and time.

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