Investigation of surface properties of high temperature nitrided titanium alloys

E. Koyuncu [a,*], F. Kahraman [a], Ö. Karadeniz [b]

[a] Department of Mechanical Engineering,
Dokuz Eylül University, 35100 İzmir, Turkey
[b] Department of Physics,
Dokuz Eylül University, 35100 Izmir, Turkey
* Corresponding author: E-mail address: emre.koyuncu@deu.edu.tr

Properties

ABSTRACT

Purpose: The purpose of paper is to investigate surface properties of high temperature nitrided titanium alloys.

Design/methodology/approach: In this study, surface modification of Ti6Al4V titanium alloy was made at various temperatures by plasma nitriding process. Plasma nitriding treatment was performed in 80% N_2-20% H_2 gas mixture, for treatment times of 2-15 h at the temperatures of 700-1000°C. Surface properties of plasma nitrided Ti6Al4V alloy were examined by metallographic inspection, X-Ray diffraction and Vickers hardness.

Findings: Two layers were determined by optic inspection on the samples that were called the compound and diffusion layers. Compound layer contain TiN and Ti_2N nitrides, XRD results support in this formations. Maximum hardness was obtained at 10h treatment time and 1000°C treatment temperature. Micro hardness tests showed that hardness properties of the nitrided samples depend on treatment time and temperature.

Practical implications: Titanium and its alloys have very attractive properties for many industries. But using of titanium and its alloys is of very low in mechanical engineering applications because of poor tribological properties.

Originality/value: The nitriding of titanium alloy surfaces using plasma processes has already reached the industrial application stage in the biomedical field.

Keywords: Plasma nitriding; Titanium nitriding; Surface treatments

1. Introduction

The combination of high strength-to-weight ratio, excellent mechanical properties, and corrosion resistance makes titanium the best material choice for many critical applications [1]. Titanium and titanium alloys are very attractive materials because of their excellent combination of properties that give them the possibility to be used in many industries. However, they have some disadvantages that reduce the number of possible applications, especially those which require good tribological properties. These problems can be overcome using such surface engineering technologies like different thermal treatments, coatings and thermochemical treatments to obtain desirable properties. Thermochemical treatments such as oxidation, carburizing and nitriding are quite effective because they change the chemistry of the surface layers. Different types of nitriding such as plasma, laser and gas nitriding are among the most popular methods for thermochemical treatment used for this purpose [11].

Titanium exists in two crystallographic forms. At room temperature, unalloyed (commercially pure) titanium has a hexagonal close-packed (hcp) crystal structure referred to alpha (α) phase. At 883°C (1621°F), this transforms to a body-centred cubic (bcc) structure known as beta (β) phase. Based on the phases present, titanium alloys can be classified as either α alloys, β alloys, or α+ β alloys. Most common α + β alloy is Ti-6Al-4V. Titanium's corrosion resistance is based on the formation of a stable, protective oxide layer. This passivating behaviour makes the metal useful in applications ranging from chemical processing equipment to surgical implants and prosthetic devices [1].

Plasma nitriding is a method for thermochemical treatment that has many advantages such as control of the phase formation and the depth of the nitrided layer. It requires short periods of nitriding time and it avoids oxidation. One disadvantage of plasma nitriding is that it reduces the fatigue strength of titanium alloys; however, this problem can be overcome by reducing the processing [11].

Titanium has the following advantages:

- Good strength
- Resistance to erosion and erosion-corrosion
- Very thin, conductive oxide surface film
- Hard, smooth surface that limits adhesion of foreign materials.

The use of titanium has expanded in recent years to include following applications:

- Applications where titanium is used for its resistance to corrosion, such as chemical processing, the pulp and paper industry, marine applications, and energy production and storage
- Biomedical applications that take advantage of the metal's inertness in the human body for use in surgical implants and prosthetic devices
- Special applications that exploit unique properties such as superconductivity (alloyed with niobium) and the shape-memory effect (alloyed with nickel) [1].

Plasma nitriding is a diffusional process, and produces a continuous hardness profile. During nitriding, the hard layer including TiN and Ti_2N is formed on the surface, and the outermost TiN layer is known to improve wear and corrosion resistance [10]. In Ti6Al4V it is observed that when the ion-nitriding treatment was carried out at 973 and 1073 K the diffusion layer microstructure showed a preferred formation of separate α phase crystals in the α-β matrix. If the ion nitriding was performed at 1173 and 1273 K, the prior layer consisted of two regions: an outermost continuous layer of α phase and a zone of coarse columnar α phase crystals embedded in the α-β underlying matrix. In other words, the morphology of the surface layers is determined by nitriding temperature relative to the α- and β-transus of the alloy [7].

The sub-layer with titanium nitrides only (TiN and Ti_2N) forms the compound layer, while α (N) is a diffusion zone. The phase transitions of the sample surface during nitriding can be written as [11]:

α-Ti→ α (N)-Ti → Ti_2N→ TiN
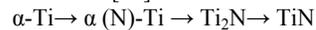
The aim of this research is to investigate the effects of plasma nitriding treatments on the mechanical properties of Ti6Al4V subject to microstructures, X-ray diffraction (XRD), hardnesses, thicknesses of surface layers formed on the titanium alloy. The working conditions of ion-nitriding process have a remarkable influence on the microstructure and on the mechanical properties of the hardened layers. The thickness of the modified surface layers is a function of temperature, of time and the volumetric ratio of N_2 in the plasma atmosphere of N_2+H_2 gaseous mixture as process parameters.

In this investigation, Plasma nitriding was performed in a gas mixture of 20% H_2-80% N_2, temperatures of 700-1000 °C and process times of 2-15 h.

2. Experimental details

A number of widely known analytical techniques such as X-ray diffraction (XRD), optical microscopy (OM), were used when studying the phase transformations and microstructure changes taking place during the process of nitriding. Hardness measurements, using Vickers indentation geometries were extensively used.

2.1. Material

Ti6Al4V titanium alloy was used as the test material and its mechanical properties are listed in Table 1. Ti6Al4V titanium alloy specimens (with the following chemical composition: Ti 89.3, Al 6.3, V 4.0, C 0.004, Fe 0.15, O 0.11, N 0.03, H 0.002) were 10 mm in diameter and 10 mm long.

Table 1.
Mechanical properties of Ti6Al4V alloy

Density (g/cm^3)	Tensile Strength (MPa)	Yield Strengths (MPa)	Young Modulus (GPa)	% Elongation
4.5	965	895	110	12

2.2. Ion-nitriding procedures

The samples were treated in a laboratory glow discharge, ion nitriding system, where the sample was the cathode, and the anode was a filament. The following process parameters were used: gaseous mixture composed of 80% nitrogen and 20% hydrogen; pressure of 2, 5 mbar; feed voltage of 400–800 V; nitriding temperature of 700-1000°C; 2-15 h of nitriding time. All of the ion-nitriding procedures were carried out at various temperatures and times. Gas composition (N_2/N_2+H_2) was constant. Ion-nitriding process conditions were given in Table 2.

The plasma nitriding process was performed as follows: First of all, the chamber was evacuated to 2 mbar and washed by nitrogen into the vacuum chamber in 1 hour. Prior to the nitriding process, the work pieces were cleaned by hydrogen sputtering under a pressure of 3.5 mbar. This process continued until 200°C. The work pieces were preheated using Eddy current. Because of plasma nitriding is a vacuum process, conventional heat transfer (convection, transmission, radiation) is not possible at this vacuum environment. At this plasma nitriding treatment's heating system was a coil. This coil adds to nitriding the temperature about 150°C using Eddy current. Additional temperature was obtained feeding 9 V voltage to the coil. At this process heat producing occur directly on the material. Filament wrap on ceramic pipe to generate a bobbin which has Ra resistance. Thus, heating the substrate with Eddy current which is generated in the substrate exists in the Ceramic pipe. After these processes the working gas was introduced into the chamber, and then the discharge of plasma was started. The flow rates of the N_2–H_2 gas mixture were fixed at %80 and %20, respectively. The ratio of H_2 gas to N_2 gas in the mixture was varied using mass flow controllers. Nitrogen was given into the vacuum chamber until 2 mbar at the pointer of vacuum gauge. After stability was reached, hydrogen was given into vacuum chamber until 2.5 mbar at the pointer of vacuum gauge. Gas mixture containing predetermined volume of nitrogen and hydrogen was allowed to flow into the chamber.

The pressure inside the chamber was controlled continually. The fed voltage changes between 400-800 V according to the process temperature. The specimen temperature was controlled by a Ni-Cr-Ni thermocouple inserted through a hole at the bottom of a specimen holder. Time for the process was started as soon as the process temperature was reached what took about 40 minutes after the formation of plasma. After the process was finished, nitrogen was given into the vacuum chamber. The samples were held until room temperature in vacuum chamber was reached.

2.3. Microhardness testing and optical microscope

The morphology of the layers was analysed by metallographic cross sections. The nitrided samples were characterised by optical microscopes as first. After ion-nitriding process was completed, the samples were taken in polyester. The sample surface was ground using SiC emery papers (from 800 to 2000) and polished using 0.25-1 μm grain size diamond (Al_2O_3) paste until all micro scratches were eliminated then washed with ethanol. In the microscopic structural examination, the composition of the etching solution used Ti6Al4V titanium alloy goes as follows: 1 ml HF, 2 ml H_2NO_3 and 50 ml pure water. The samples were exposed to the etching solution and left exposed to it for 10-15 seconds enough to reveal a discernible microstructure. Subsequently, the samples were taken out of the solution, washed in ethanol, dried in hot air in order not to leave any reactant. The experimental set-up for plasma nitriding is shown in Table 2. The structures were observed and photographed using an optical microscope. The thickness of layers was measured in NS-Elements D 2.30 image analysis program. The surface hardness was measured by using Vickers indentation geometries at a constant load of 0.98 N and loading time of 15 s.

Table 2.
Ion-nitriding process conditions

Group	TimeE(h)	Temperature (°C)	Nitrogen (%)
700-2	2	700	80
700-4	4	700	80
700-7	7	700	80
700-10	10	700	80
700-15	15	700	80
800-2	2	800	80
800-4	4	800	80
800-7	7	800	80
800-10	10	800	80
800-15	15	800	80
900-2	2	900	80
900-4	4	900	80
900-7	7	900	80
900-10	10	900	80
900-15	15	900	80
1000-2	2	1000	80
1000-4	4	1000	80
1000-7	7	1000	80
1000-10	10	1000	80

2.4. X-ray diffraction analysis

The microstructure of the treated samples was examined by X-ray diffraction analysis to identify the surface phases. XRD was carried out with a scanning angle range of 10–100° and a scanning rate of $3.5°min^{-1}$ using Cu K-ALPHA1 radiation at the current of 10mA and voltage of 30 kV.

3. Results and discussion

3.1. Microstructure of Ti6Al4V after plasma nitriding

The cross-section of Ti6Al4V subjected to plasma nitriding was observed by optical microscopy (Figure 1). In every specimen, three kinds of regions compound layer, diffusion layer and matrix of Ti6Al4V are formed. A layer with a thickness of a few micrometers is formed on the outermost surface (compound layer). On the inner side of this layer, fine acicular phases are precipitated (diffusion layer), followed by equiaxed grains that are present as a matrix of Ti6Al4V. The region where the acicular

phases are precipitated is wide, and the size of the equiaxed grains is coarsened with an increase in the plasma nitriding temperature.

Diffusion layer and a matrix of Ti6Al4V comprise a mixture of the acicular and equiaxed phases.

The thicknesses of the compound and diffusion layers are given in Table 3. The surface hardness and thickness of the layers increase, as both the treatment time and temperatures increase. The highest hardness value and modified layer thickness was obtained from the specimens nitrided at 1000°C-10 h. Typical microstructure of Ti6Al4V contains completely α-Ti and β-Ti phases. It was found that β-Ti phase has lamellar shape and darker than α-Ti phase in the structure. When Figure 1was examined, it was observed that a distinct and continuous compound layer was formed on the surface. Initially ε-Ti$_2$N, then δ-TiN phases is formed in the compound layer. The thickness of the compound layer formed at the temperatures higher than 700°C is too thin to be observed.

Microstructure of the nitrided specimens was examined by an optical microscope. Surface layers grown on specimens nitrided at higher temperature were separated into two sublayers, namely TiN on the top and Ti$_2$N below. Below the compound layer, diffusion layer is formed which corresponds to the solid solution of nitrogen in titanium. It was observed that the diffusion layer formed beneath the compound layer did not separate with a distinct line from the substrate. Both diffusion layer and matrix of Ti6Al4V comprised a mixture of the acicular and equiaxed phases.

Fig. 1. Optical micrograph of the cross-section of ion-nitrided Ti-6Al-4V samples (x200 magnification)

The optical micrograph shown in Fig 1 reveals the cross-section of the specimen nitrided at different temperature and time.

It was found that Ti$_2$N and diffusion layer had existed for treatments group of 700-2, but TiN layers had not been grown at this treatment. Thickness of diffusion layer at group of 700-15 was determined 28.74 μm. It was seen that TiN layer existed for 700°C treatments after 4 hours of nitriding process. It was grown that TiN layer existed for 700-15. TiN, Ti$_2$N and diffusion layers grew together in group of 700-15. Thickness of layers (TiN, Ti$_2$N and diffusion) in group of 700-15 was determined respectively 1.95 μm, 2.53 μm, 28.74 μm. It is clearly seen three layers (TiN, Ti$_2$N and diffusion layers) on specimens after 2 hours at 800°C as parameter of nitriding process. At this parameter, thickness of diffusion layer was 55.42 μm. The thickness (respectively TiN, Ti$_2$N and diffusion layers) of group of 800-15 was determined

3.91 μm, 5.09 μm and 90.85 μm. And it was found that TiN layer existed at 800°C and 900°C with only 2 hours of nitriding time. Also it was seen that TiN layer was developing quickly depending on increasing time. The thickness (respectively TiN, Ti$_2$N and diffusion layers) of group of 900-15 was determined 5.12 μm, 8.89 μm and 285.13 μm and these were the best values at this temperature.

Table 3.
Thickness (μm) of the surface layer on specimens nitrided at different temperatures

| Group	Diffusion Layer (μm)	Ti$_2$N (μm)	TiN (μm)
700-2	8.26	0.94	none
700-4	12.28	1.17	0.63
700-7	14.8	1.36	0.81
700-10	19.81	1.61	1.08
700-15	28.74	2.53	1.95
800-2	55.42	2.33	1.03
800-4	59.1	2.71	1.92
800-7	67.5	3.28	2.38
800-10	82.08	3.7	2.83
800-15	90.85	5.09	3.91
900-2	75.11	4.68	2.41
900-4	88.35	6.35	3.45
900-7	146.15	7.42	3.91
900-10	214.7	8.22	4.39
900-15	285.13	8.89	5.12
1000-2	156.86	6.09	3.38
1000-4	204.89	6.53	3.98
1000-7	286.91	8.84	4.78
1000-10	341.11	9.33	6.84
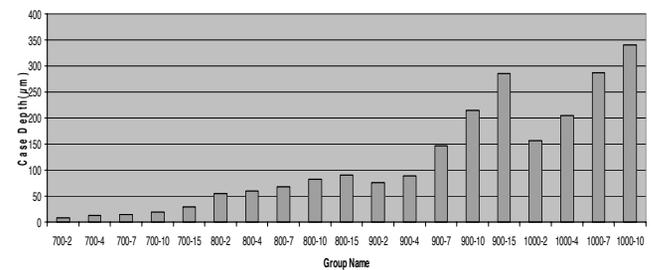
Fig. 2. Average case depth of our specimen groups

The best desirable surface properties of Ti6Al4V were obtained in the group of 1000-10. At 1000°C which was the highest temperature in this study, required layers were grown at a very short period of time. The thickness of layers (respectively TiN, Ti$_2$N and diffusion layers) was 6.84 μm, 9.33 μm and 341.11 μm. Case depth and compound layer thickness increased with increasing process temperature. It was shown clearly that temperature effected on titanium and its alloys as a nitriding parameter. The thickness of layer increases along with quick increase of temperature. Table 3 shows the effect of the nitriding temperature and time on the surface each layer thickness after plasma nitriding of Ti-6Al4V. Increase of temperature and nitriding time results in greater case depth. Average diffusion layer

thicknesses are represented in Table 3, Figure 2. It is clearly seen from the Figure 2, the case depth increase at increasing temperature. Also the case depth increased at increasing time. Case depth of group 1000-10 is the highest depth.

3.2. Microhardness of Ti6Al4V after plasma nitriding

Figure 3 shows the depth profile of the Vickers hardness of Ti6Al4V subjected to plasma nitriding. The Vickers hardness of the surface of Ti6Al4V increases significantly at plasma nitriding. The degree of hardness is the highest at the specimen surface and decreases rapidly with distance from the surface. This trend is derived from the titanium nitride formation. The hardness outermost surface of $1000^{o}C$ is higher than that of $900^{o}C$ because it is considered that the thickness of the diffusion layer formed on Ti6Al4V is thicker than that on $900^{0}C$, as shown in Fig. 3.
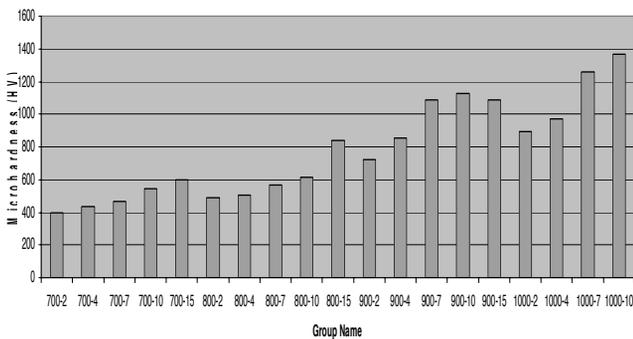

Fig. 3. Average case depth of our specimen groups

Near the surface of the nitrided layer, the maximum hardness was found at 1000°C-10 h, to have a value 1365 HV which is roughly four times higher than the hardness of the non-nitrided samples (341 HV). This high hardness value was only observed for short distance (15 μm) from the top nitrided surface. The presence of TiN phase was confirmed by the XRD and the cross-sectional optical investigation of the nitrided samples. Due to the presence of the diffusion layer below the compound layer, the hardness value decreased gradually from the top compound layer. Near to the interface between the diffusion layer and the core materials, hardness values were nearly the same as values for the untreated samples (341 HV). The presence of nitrogen in a solid solution enriching α-Ti phase in the diffusion layer, resulted in an increase in the hardness value for this layer. Figure 3 showed a case of hardness profiles of specimens.

There is an increase of hardness after nitriding that is caused by the increase of the nitrogen concentration and the formation of new phases like TiN and Ti_2N on the surface of the material. For example, the plasma nitriding at temperatures between 700 and $1000^{o}C$ for 1.5–14 h increases the surface hardness of Ti–6Al–4V to 1700 HV [11].

Effects of process parameters such as treatment temperature and duration on the hardening characteristics of the specimens have been discussed. The effect of treatment time on the hardness behaviour of ion nitrided samples from $700^{o}C$ is shown in Figure 4. It seems that little valuable hardness increase from $700^{o}C$ treatments. Because of this $700^{o}C$ is not a good ion-nitriding process parameter for Ti6Al4V alloy. Average microhardness values as well as case depths, case hardness are represented in Table 4, Fig. 3 for all groups.

Table 4.
Average values of microhardness correspond to the distance from the surface of all specimen groups

MICROHARDNESS (HV)											
DISTANCE FROM SURFACE (μm)											
GROUP	15	25	35	45	55	65	75	85	95	105	150	200
700-2	394	360	341	341	341	341	341	341	341	341	341	341
700-4	435	356	341	341	341	341	341	341	341	341	341	341
700-7	465	390	355	341	341	341	341	341	341	341	341	341
700-10	540	432	399	381	380	366	344	341	341	341	341	341
700-15	601	455	381	392	377	363	341	341	341	341	341	341
800-2	488	423	357	389	385	353	341	341	341	341	341	341
800-4	505	468	420	389	383	372	355	341	341	341	341	341
800-7	568	477	432	394	388	377	370	345	341	341	341	341
800-10	614	557	456	435	469	436	402	377	371	363	350	341
800-15	842	703	637	602	568	478	437	391	399	371	364	341
900-2	724	708	658	684	544	570	467	452	433	431	386	341
900-4	852	817	689	623	474	468	459	423	413	402	379	341
900-7	1087	835	784	689	642	616	586	580	540	465	398	344
900-10	1124	901	863	736	702	590	573	504	556	456	402	357
900-15	1091	791	692	608	658	549	502	455	417	397	382	345
1000-2	893	615	602	591	576	512	496	431	404	417	393	361
1000-4	972	745	722	656	637	510	485	497	448	441	418	386
1000-7	1255	1092	913	860	772	748	684	697	589	561	503	441
1000-10	1365	1119	955	849	897	646	599	559	550	503	494	431
untreated	341	341	341	341	341	341	341	341	341	341	341	341

Near the surface of the nitrided layer, the maximum hardness was found at 1000°C-10 h, to have a value 1365 HV which is roughly four times higher than the hardness of the non-nitrided samples (341 HV). This high hardness value was only observed for short distance (15 μm) from the top nitrided surface. The presence of TiN phase was confirmed by the XRD and the cross-sectional optical investigation of the nitrided samples. Due to the presence of the diffusion layer below the compound layer, the hardness value decreased gradually from the top compound layer.

Near to the interface between the diffusion layer and the core materials, hardness values were nearly the same as values for the untreated samples (341 HV). The presence of nitrogen in a solid solution enriching α-Ti phase in the diffusion layer, resulted in an increase in the hardness value for this layer. Figure 3 showed a case of hardness profiles of specimens.

There is an increase of hardness after nitriding that is caused by the increase of the nitrogen concentration and the formation of new phases like TiN and Ti_2N on the surface of the material. For example, the plasma nitriding at temperatures between 700 and 1000°C for 1.5–14 h increases the surface hardness of Ti–6Al–4V to 1700 HV [11].

Effects of process parameters such as treatment temperature and duration on the hardening characteristics of the specimens have been discussed. The effect of treatment time on the hardness behaviour of ion nitrided samples from 700°C is shown in Fig. 4. It seems that little valuable hardness increase from 700°C treatments. Because of this 700°C is not a good ion-nitriding process parameter for Ti6Al4V alloy. Average microhardness values as well as case depths, case hardness are represented in Table 4, Fig. 3 for all groups.

In Figure 4, the effects of treatment time on the microhardness behaviour of ion nitrided samples from 700°C are given. The hardness is increased with the increase of process time. Required surface hardness is not obtained at groups of 700°C. The hardness value at 700-15 is 601 HV.
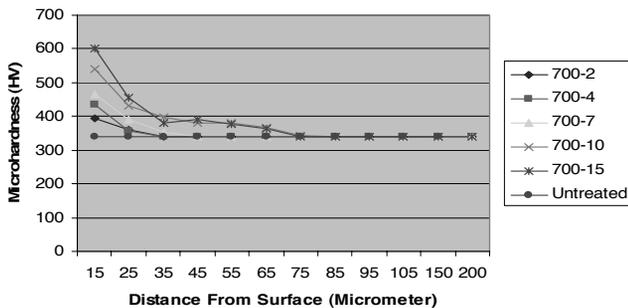

Fig. 4. The effect of treatment time on the hardness behaviour of the ion nitrided samples treated at 700°C

In Figure 5, the effects of treatment time on the hardness behaviour of the ion nitrided samples treated at 800°C are given. The effect of treatment time on the hardness behaviour of ion nitrided samples from 900°C is shown in Figure 6. Surface hardness does show an increasing trend at increasing time. This temperature for ion-nitriding can be a good parameter. For a treatment temperature of 900°C, hardness in the nitrided region is increased from the bulk value 341 to 1124 HV at group of 900-10.
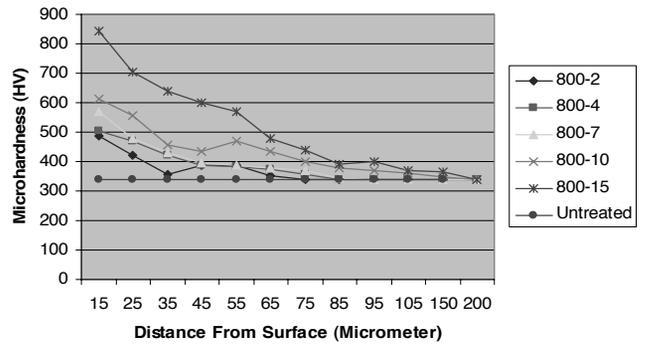

Fig. 5. The effect of treatment time on the hardness behaviour of the ion nitrided samples treated at 800°C
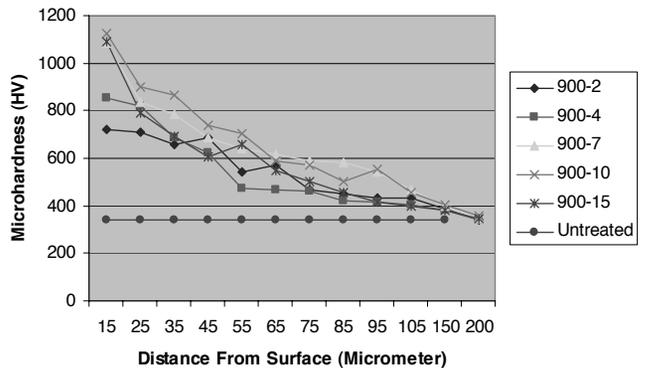

Fig. 6. The effect of treatment time on the hardness behaviour of the ion nitrided samples treated at 900°C
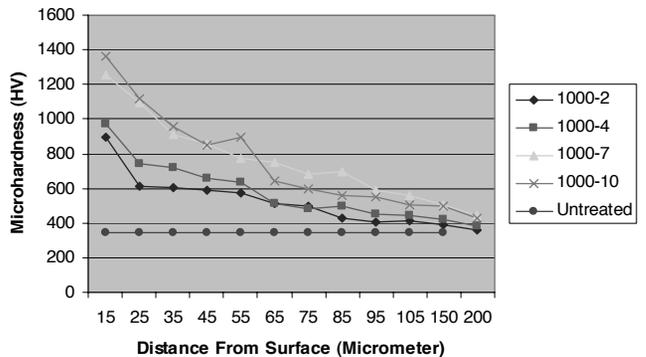

Fig. 7. The effect of treatment time on the hardness behaviour of the ion nitrided samples treated at 1000°C

This is significant and sufficient hardness value, but process time is too long. The highest temperature in this study was 1000°C. At this temperature desired layers were grown at a very short period of time. The best microhardness results were obtained at the group of 1000-10. The surface hardness was 1365 HV (Fig. 7). The effect of treatment time on the hardness behaviour of ion nitrided samples from 900 and 1000°C is shown in Fig. 8.
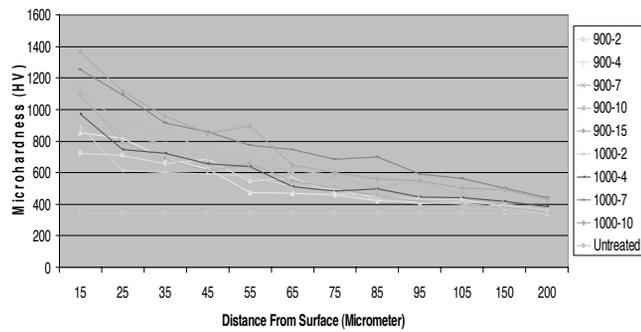
Fig. 8. The effect of treatment time on the hardness behaviour of the ion nitrided samples treated at 900 and 1000°C

3.3. Phase analysis by X-ray diffraction

The microstructure of the treated samples was examined by X-ray diffraction analysis. This analysis was performed to identify the surface phases.

Figure 9 shows the XRD patterns obtained from the surfaces of Ti6Al4V subjected to plasma nitrided for 10 h at (a) untreated, (b) 700°C, (c) 800°C, (d) 900°C and (e) 1000°C. The microstructure of the untreated Ti6Al4V completely consists of α-Ti and β-Ti phases. The XRD surface analysis of each kind of treated sample showed the presence of TiN (fcc) and Ti_2N (tetragonal) phases formed during the treatment. It is observed that, in these samples, the intensity of the peaks related to the nitride phases, in comparison with Ti peak intensity, increases as the plasma nitriding temperature increases (Fig. 9). As it is seen in Figure 9, the intensity of Ti_2N phase is low and it is formed at the higher temperatures than 700°C. δ-TiN phase was mainly observed in the modified layer formed at the temperatures above 700°C. For the specimen nitrided at 700°C, the low intensity of TiN phase shows that the treatment temperature limits the formation of TiN phase. As both the treatment temperature and time increases, the intensity of the δ-TiN phase increases. The most intense δ-TiN peak was obtained in the specimen nitrided at 1000°C (Fig. 9). In addition, it was observed that as both the treatment temperature and time increase, the intensity of both α-Ti and β-Ti phases decreases and relatively disappears. If TiN phase was formed in the compound layer, the wear resistance increased.
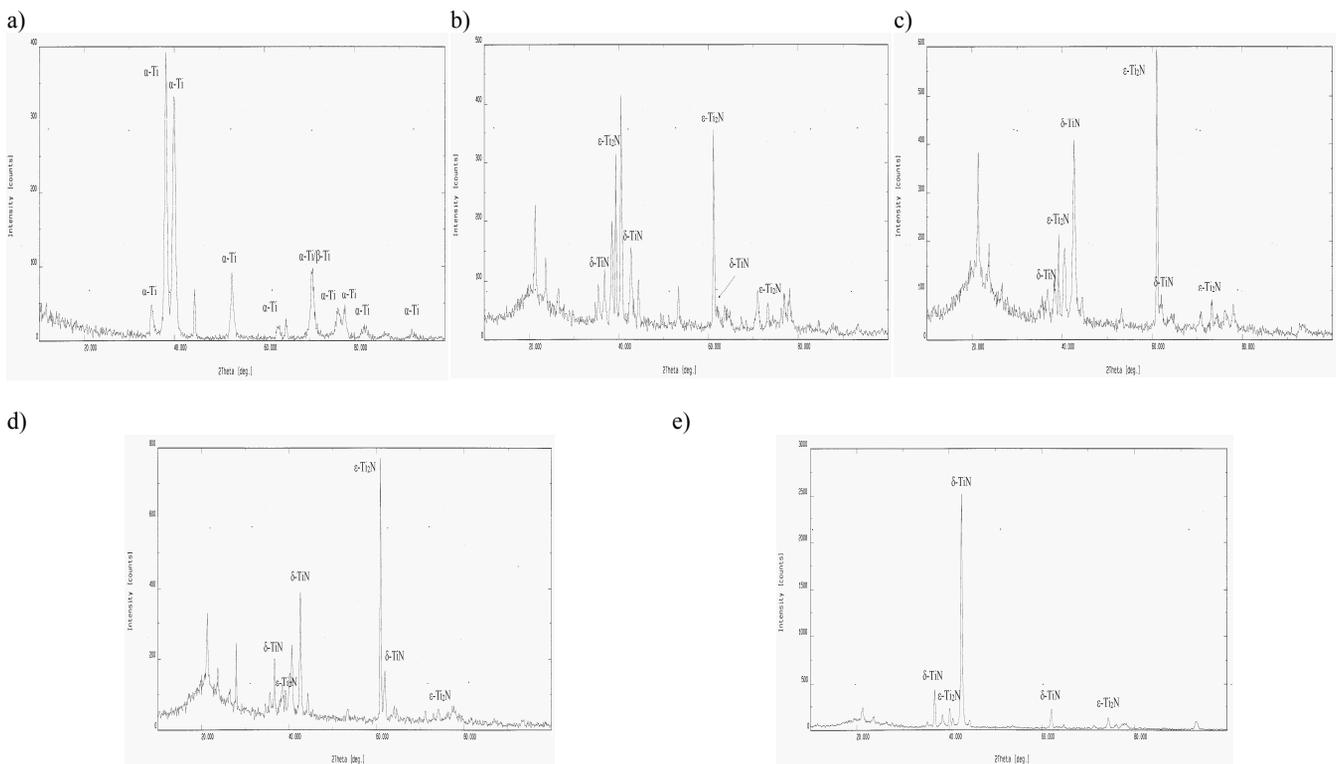

Fig. 9. X-ray diffraction patterns of Ti–6Al–4V plasma nitrided for 10 h at (a) untreated, (b) 700°C, (c) 800°C, (d) 900°C and (e) 1000°C

In this analysis, the effect of δ-TiN phases appears more clearly at increasing temperature. In Ti6Al4V, strong TiN peaks are obtained at the highest temperatures (900 and 1000 °C). The intensities of TiN peaks increase at increasing temperatures. These results indicate that the titanium nitride layer formed on the surface of Ti6Al4V consists of the outer TiN layer and the inner Ti_2N layer. The weak intensities of TiN peaks are obtained at the lowest temperatures (700 and 800°C). The TiN layer formed at the highest temperatures (900 and 1000°C) is thicker than that formed at lowest temperatures (700 and 800°C).

4. Conclusions

In this study, plasma nitriding treatment of biomedical titanium alloy Ti6Al4V was performed in $20\%H_2$–$80\%N_2$ gas mixture, for treatment times of 2–15 h at the temperatures of 700–1000°C. The nitriding of titanium alloy surfaces using plasma processes has already reached the industrial application stage in the biomedical field. After plasma nitriding, the results of the examinations of microstructures, hardnesses, thicknesses of surface layers formed on the orthopaedic materials of Ti-6Al-4V titanium alloy were examined. X-ray diffraction was used to examine the treated materials. The following results were obtained;

- The plasma nitriding process results in three distinct zones in the vicinity of the treated surface. These include formation of δ-TiN and ε-Ti_2N phases in the compound layer on the surface of the materials; thick diffusion layers consisting mainly of α-Ti solid solution enriched with nitrogen.
- For plasma nitriding, the most important parameters that can be varied to obtain desirable surface properties of titanium and titanium alloys are temperature and time. Hardness level, case depth and compound layer thickness increased at increasing process temperature and time.
- The results of maximum layer thicknesses (TiN, Ti_2N and diffusion layers) were obtained at the group of 1000-10. The thickness of layers (respectively TiN, Ti_2N and diffusion layers) was 6.84 μm, 9.33 μm and 341.11μm.
- High values of surface hardness depending on the processing parameters; the surface hardness of ion nitrided samples at 1000°C increased min. 261 % percent and max. 400 % percent according to matrix structure. The maximum surface hardness at group of 1000-10 was shown. The hardness value was 1365 HV.
- The plasma nitriding at temperatures between 700 and 1000°C for 2–15 h increases the surface hardness of Ti–6Al–4V to 1365 HV. The plasma nitriding at temperature 700°C on Ti–6Al–4V alloys did not show a good parameter as process temperature. The process time was too long for ion-nitriding on titanium alloys at 800°C as process temperature. At 900 and 1000°C, desired layers were grown at a very short period of time.
- The XRD analysis showed the presence of TiN and Ti_2N phases. The intensity of the related peaks increases as the plasma nitriding temperature increase. The complete nitriding layer can be confirmed to be δ-TiN, ε-Ti_2N and the α-titanium by using XRD. As both the treatment temperature and time increases, the intensity of the δ-TiN phase increases. The most intense δ-TiN peak was obtained in the specimen nitrided at 1000°C.

Additional information

The paper was published also in the Archives of Materials Science.

References

[1] ASM International Handbook Committee, ASM Handbook-Vol. 2 Properties and Selection, Nonferrous Alloys and Special-Purpose Materials, ASM International, United States of America, 1990.

[2] T. Bacci, F. Borgioli, E. Galvanetto, F. Galliano, B. Tesi, Wear resistance of Ti–6Al–4V alloy treated by means of glow-discharge and furnace treatments, Wear 240 (2000) 199-206.

[3] K.C. Chen, G.J. Jaung, D.C. diode ion nitriding behaviour of titanium and Ti-6Al-4V, Thin Solid Films 303 (1997) 226-231.

[4] A. Çelik, S. Karadeniz, S. Kaymaz, Plazma destekli modern yüzey işlemleri, Proceedings of the 6th Denizli Malzeme Sempozyumu, 1995, 134-142.

[5] F. Gallianoa, E. Galvanettoa, S. Mischler, D. Landoltb, Tribocorrosion behaviour of plasma nitrided Ti 6Al 4V alloy in neutral NaCl solution, Surface and Coatings Technology 145 (2001) 121-131.

[6] S. Karadeniz, Plazma Tekniği, TMMOB Makine Mühendisleri Odası Yayınları, Yayın, 137, 1990 (in Turkey).

[7] A. Molinari, G. Straffelini, B. Tesi, T. Bacci, G. Pradelli, Effects of load and sliding speed on the tribological behaviour of Ti6Al4V plasma nitrided at different temperatures, Wear 203-204 (1997) 447-454.

[8] O.T. Inal, C.A. Zimmerly, H. Akbulut, Ion nitriding of explosively-clad titanium/steel tandems. Journal of Materials Science 34 (1999) 1641-1652.

[9] T. Telbizova, S. Parascandola, F. Prokert, Ion nitriding of Al: Growth kinetics and characterisation of the nitride layer, Surface and Coatings Technology 142-144 (2001) 1028-1033.

[10] F. Yildiz, A.F. Yetim, A. Alsaran, A. Çelik, Plasma nitriding behaviour of Ti6Al4V orthopaedic alloy, Surface and Coatings Technology (2007) 2472-2476

[11] A. Zhecheva, W. Sha, S. Malinov, A. Long, Enhancing the microstructure and properties of titanium alloys through nitriding and other surface engineering methods, Surface and Coatings Technology (2005) 2192-2207.