STUDY OF SURFACE LAYERS ON PURE TITANIUM PRODUCED BY LASER GAS NITRIDING

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الملخص

إن تقنية النتردة بالليزر أصبحت من الطرق المعترف بها والشائعة في تغيير البنية المجهرية والتركيب الكيميائي لسطح التيتانيوم وسبائكه دون أن تتأثر بقية أجزاء المعدن. في هذا البحث تم دراسة نتردة التيتانيوم النقي باستخدام جهاز باعث لأشعة الليزر ذي قدرة 3 كيلووات بهدف زيادة صلادة التيتانيوم وجعله أكثر مقاومة للبلي والاحتكاك حيث تمت عملية النتردة باستخدام المتغيرات التالية: قدرة الليزر- 2.5 كيلو واط ، سرعة العينة- 15 ملم بالثانية ومعدل سريان غاز النتروجين- 17 لتر بالدقيقة واستخدمت هذه القيم لإعداد طبقات منتردة مفردة و أخرى متراكبة. واستخدم غاز النتروجين النقي والمخفف مع الارجون بنسب محددة لعمل النتردة.بينت النتائج أن صهر سطح التيتانيوم بالليزر في جو من النتروجين يؤدي إلى تكون نتريد التيتانيوم الذي يتميز بالصلادة العالية.البنية المجهرية لهذا النتريد هي شجيرية موزعة بشكل غير متجانس داخل الجزء المنصهر وممتدة بعمق حوالي 0.5 مم من السطح .نتيجة لتكون هذا النتريد فان صلادة السطح ازدادت بشكل كبير. وكلما زادت نسبة النتريدات المتكونة زادت الصلادة. كما أن استخدام النتروجين المخفف مع الارجون يؤدي إلى تقليل نسبة التشققات ولكن من الجهة الأخرى يؤدي إلى تقليل الصلادة.

ABSTRACT

Laser gas nitriding process is a widely accepted technique for modifying the surface structure and composition of titanium and titanium alloys without altering the bulk properties. In the present work, laser gas nitriding of commercial purity titanium with continuous wave 3 kW Co_2 laser has been investigated experimentally. The aim is to increase the surface hardness and hence improve related properties such as wear and erosion. The processing parameters were as follow: 2.5 kW laser power, 15 mm/s specimen scanning rate, and 17 L/min nitrogen gas flow rate. Single and overlapping layers were produced and pure and diluted nitrogen gas was used. The results indicated that laser surface melting of pure titanium in nitrogen atmosphere produced unevenly distributed TiN of dendritic morphology extended to a depth of ~ 0.5mm. The volume fraction of the TiN dendrites decreased gradually with increasing depth from the surface. As a result of TiN formation, the hardness increased substantially. Diluting the nitrogen gas with argon gas was found to have a beneficial effect in decreasing cracking but decreased the resulting hardness level and the nitrided depth.

KEYWORDS: Laser hardening; CP Titanium, XRD; Microstructure.

INTRODUCTION

Titanium and its alloys are a very attractive material due to their high specific strength, excellent corrosion resistance and good formability [1]; they are widely used in aircraft components, chemical processing facilities, and medical implants. However, tribological properties such as wear resistance is low compared to other metals used for medical application. This problem can be overcome by use of suitable surface engineering methods such as nitriding, which can be done by ion implantation [2], plasma nitriding [2-3], physical vapour deposition [4], chemical vapour deposition [5], and laser alloying [6-18].

Surface nitriding by high power laser has several advantages compared to the conventional processes; the process is much faster than conventional nitriding; the thickness of the nitrided layer can be changed from a few micrometers to several hundreds of micrometers; ability to treat very local areas which cannot be treated by conventional methods, and excellent metallurgical bond between the nitrided layer and the substrate. This technique has been developed over the past 20 yeas and involves the use of the intensive optical energy of the laser to melt the surface in nitrogen – containing atmosphere, which forms titanium nitrides. The melted zone consists of dendritic structures of titanium nitride (TiN) which are responsible for the high hardness at the surface.

Katayama et al. studied the nitriding process of pure titanium and different materials (such as mild steel, nickel, copper and aluminum) by CW Co_2 and Nd: YAG lasers [6]. They indicated that the hardness increased after nitriding up to 600 to 850 HV, but cracks were observed. Walker et al. studied the surface melting and surface nitriding of pure Ti and Ti–15Mo alloy [7]. They indicated that nitrided layers up to 0.3 mm and hardness of around 1000 HV were possible but some cracks were observed. Mordike et al [8] studied the laser nitriding process by means of Co_2 laser. They indicated that the corrosion resistance of the material is very much increased but its fatigue limit decreased. Santos et al [9] have studied the effect of the laser type (continuous or pulsed) on the nature of the nitrided layer on pure titanium. They showed that the nitrided layer produced by continuous wave Co_2 laser is very rough as compared to those layers produced by pulsed Nd-YAG laser; also they indicate that these nitrided layers have detrimental effect on the fatigue strength; the thicker the layer the higher the decrease in fatigue strength. The phases developed by laser nitriding of Ti-6Al-4V alloy have been studied in detail by Hu et al and Kloosterman et al [10-11] using scanning electron microscopy and X-ray diffraction, and X-ray photo-spectrography (XPS); they concluded that the structure consisted of TiN, TiN0.26, and Ti. The volume fraction and distribution of these phases depend on the laser processing conditions. Mridha and Baker [12] have studied the effect of the gas flow rates on the microstructure and properties of the nitrided layer on Ti-6Al-4V alloy. They conclude that crack intensity decreases with decreasing gas flow rate; nitriding at fast speed (50 mm/s) and low flow rate eliminated the cracking.

Surface cracking is still a major problem in laser nitrided layers. The developments of crack- free TiN surface was achieved by diluting the nitrogen content for laser treated commercially pure titanium as reported by Mirdha and Baker [16], Kloosterling et al [11], Weerasinghe et al [14], and for Ti-6Al-4V alloy by Selamat et al [13]. However, this proved to be at the expense of both a lower hardness and a shallower melt depth. Preheating of the substrate is suggested by Hu and Baker [17] and via this process the crack formation at the surface is minimized. Recently Abboud and Fidel [18] have found that the proper selection of the processing parameters may lead to a produce a crack – free nitrided layer with a high hardness.

In this paper, laser gas nitriding of pure titanium by using continuous wave Co_2 laser is presented using pure and diluted nitrogen. The microstructure, chemical composition and microhardness of the nitrided layers formed on commercial purity titanium have been explored.

EXPERIMENTAL WORK

Material and sample preparation

The material used in this study is commercial purity (CP) Ti Grade 2 according to the standard specification ASTM B348. Specimens of dimensions 10 x 10 x 20 mm were cut from a billet by means of a wire electrical discharge cutting machine. The surfaces of all specimens were grinded with abrasive paper of mesh No. 400, to decrease the laser beam reflectively and to yield surfaces of the same topography. Before laser surface processing the specimens were cleaned ultrasonically and dried.

Laser gas nitriding

The laser machine used in this investigation is a Co_2 laser, capable of operating in continuous and pulse modes. The maximum output power is 3 kW. The laser beam is focused by a ZnSe lens with a focal length of 200 mm. The minimum diameter of the focused beam is ~0.5 mm. The relative movement between the laser beam and the work piece is realised by a CNC (computer numerical controlled) X-Y-Z movable head. For alignment procedures, a HeNe laser beam was transmitted along the optical axes.

The experimental set up of the laser gas nitriding process is illustrated schematically in Figure (1).

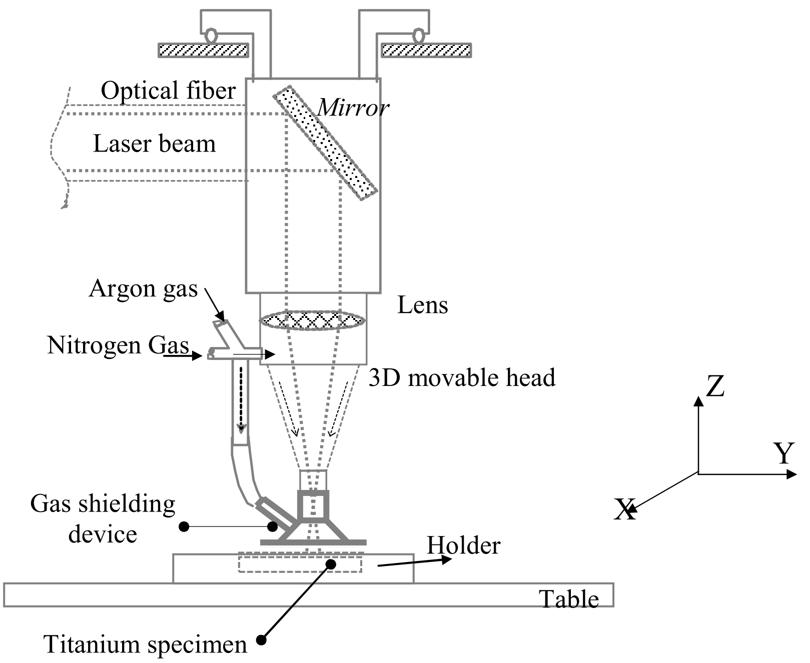


Figure1: A schematic diagram of the laser nitriding experimental setup.

The laser beam is reflected towards the specimen by use of a mirror. Before the laser beam reaches the specimen, it is focused through a lens. The focal point of the laser beam is ~ 10 mm below the nozzle and 10-15 mm above the specimen surface. Due to the high affinity of titanium to oxygen, titanium nitriding by laser requires an efficient shroud to prevent oxidation. A gas shielding device is made to serve three purposes; first to prevent oxidation, second to supply the nitrogen gas to the melted zone and thirdly to push away the plasma, which forms, above the melted zone. The formation of plasma prevents the absorption of laser beam and in some cases; it may cause breakage of the lens.

The flow rate of the nitrogen gas was controlled using two calibrated flow meters, one for nitrogen and another for argon. The axial nozzle is used to supply the nitrogen atmosphere. The side flow is necessary to prevent plasma formation and to protect the molten metal from oxidation. All nozzle diameters are at least several times the melt pool diameter. In order to prevent mixing with air, the gas flow must never become turbulent. The specimen was fixed on the table by means of a holder to prevent any movement during the process.

Surface characterization methods

Microstructural characterisation and microanalysis was carried out on transverse sections using optical microscopy, scanning electron microscopy and X-ray EDS. Nitrogen contents were obtained from the EDS data. A D5005 diffractometer was used for XRD structural analysis of the different phases and compounds formed. Microhardness measurements were obtained using a Shimadzu micro-hardness tester HMV-2, across the nitride layer, toward the unaffected region.

RESULTS AND DISCUSSION

Microstructure of the nitride layer

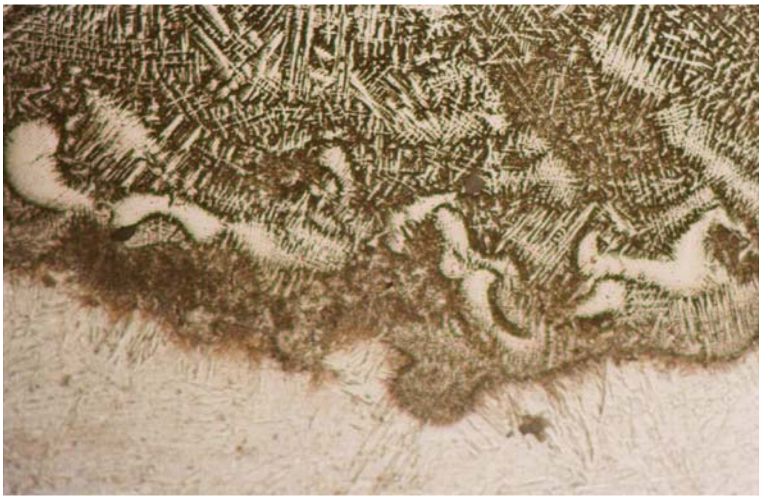
Within the range of parameters studied; an optimum set of laser power, scanning speed and nitrogen flow rate which produced a smooth and relatively crack-free surface layer, were found to be at 2.5 kW, 15 mm/s and 17 L/min, respectively. With these parameters, both single and overlapping nitrided layers were produced. Figure (2a) shows a typical cross section of a single laser nitrided track; the track has a melted width of ~ 2 mm and a depth of 0.5 mm. The microstructure is dendritic, with the volume fraction of dendrites decreasing gradually with increasing the depth from the nitrided surface (Figure 2a). In the inter-denderitic zones as well as in some areas within the nitrided layer a dark micro-constituent is observed. These dendrites have been previously identified as titanium nitride [18]. It is believed that they are produced by a reaction between the melting pool and the dissolved nitrogen during the process of laser heating and subsequent rapid cooling. According to the Ti-N binary phase diagram presented by Murray [19], TiN forms either directly from the melt when the solubility limit is exceeded or as a result of a peritectic reaction of the type:

$\alpha + \ell \rightarrow \mathrm{TiN}$

Several flow loops are viewed in the track section (Figure 2b). These loops are distinguished by small needles (martensite) at the centre and a dense array of dendrites at the periphery of the loops, i.e. along the capillary flow lines.

(a)

(b)



(c)

Figure 2: Optical micrographs showing: (a) cross section of the nitrided layer (2.5KW, 15 mm/s, 100%N_2) ((b) the upper and central part of the nitrided layer, (c) the lower part of the nitrided layer

Because of the convectional flow which developed, the nitrogen distribution in the melt pool is believed to remain inhomogeneous; the rapid solidification further retards extensive nitrogen diffusion throughout the melt. Therefore in a single melt pool, different TiN population was observed.

The lower part of the melt track showed a sharp, non-uniform and irregular interface Figure (2c). Such non –uniform melt profile was not observed when melting was performed in un-reactive gas such as argon [14]. It has been reported that due to great affinity of Ti for nitrogen, besides the diffusion of nitrogen into the liquid Ti there was an exothermic reaction between the nitrogen and the liquid Ti, by which the TiN phase was produced [15].

$$\mathrm{Ti} + \tfrac{1}{2}\mathrm{N} = \mathrm{TiN}$$

The formation of TiN releases heat energy, the dissipation of which might give a non-uniform melt profile. It has been reported by Mridha [12] that the non-uniform pattern of the melt zone could be attributed to the Maragoni forced convection flow of the liquid containing dissolved nitrogen to form the high melting point TiN.

More details about the microstructures can be seen from the SEM micrographs taken at different locations in the melted zone. Figure (3a) shows a very thin continuous layer of about 5 μm of thickness at the top surface of the nitrided tracks. From this layer the dendrites grow inward perpendicular to the melt zone. This type of structure was also reported by many authors [11-13]. Below the top surface (Figure 3b and c), massive dendrites are randomly distributed throughout the melted zone.

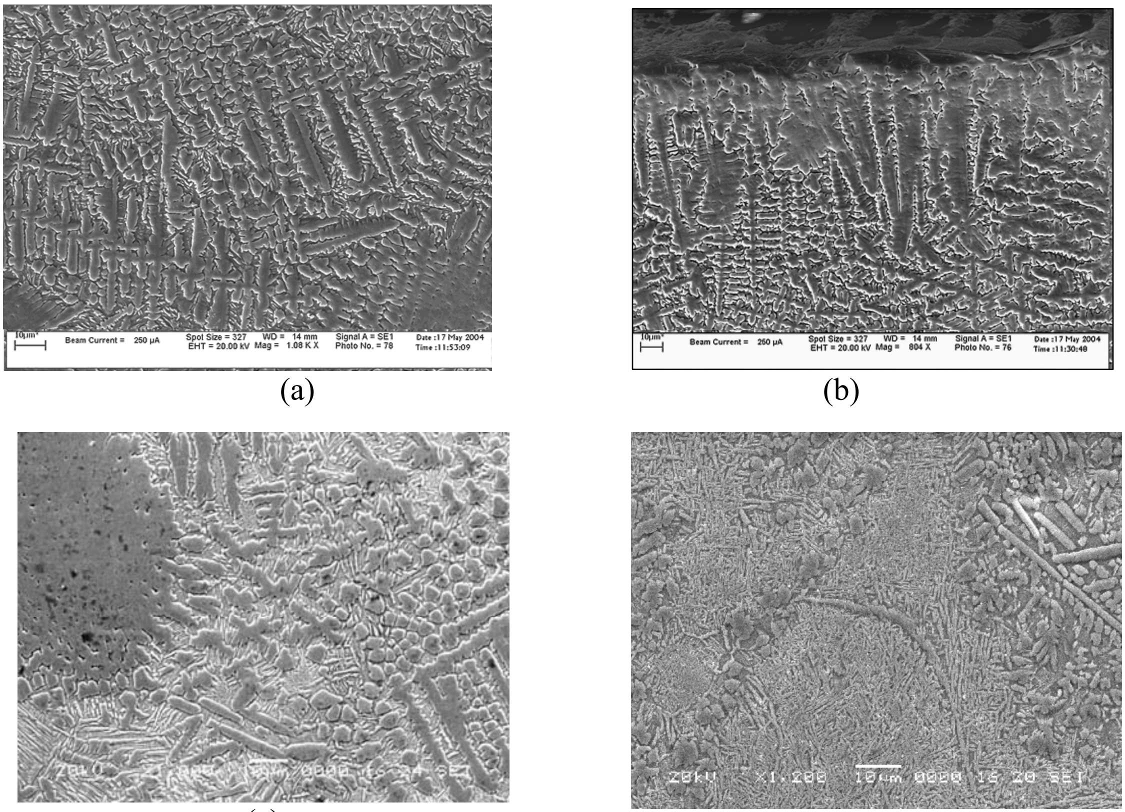
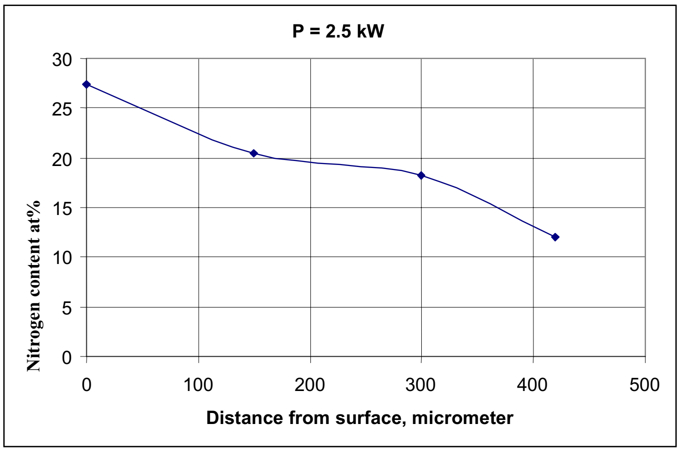


Figure 3: SEM micrographs of various zones of the nitride track cross-section: (a) the upper zone; (b) the central zone; (c) the left side; (d) the N-free zone.

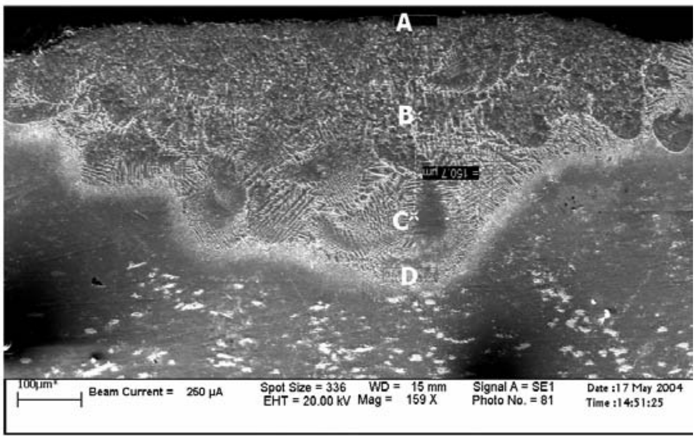
A characteristic feature of the nitrided layer is fine TiN denderites originating from the massive ones (Figure 3c). These regions represent a high concentration of nitrogen driven by fluid flow. Due to the constitutional super-cooling and the high nitrogen concentration, branching of fine dendrites from massive ones may occur. The dark micro-constituent situated in the inter-dendritic regions consists mainly of α'-titanium martensite needles (Figure 3c). Another interesting feature of the nitrided layer is the presence of a nitrogen-free zone within the nitrided layer. The microstructure of this zone shows long needle like martensitic structure of a hardness approaching that of the un-reacted titanium. Because of the rapid cooling, not all the molten titanium had enough time to react with nitrogen, and some area within the melted zone underwent martensitic transformation after solidification (Figure 3d);

Nitrogen content of the nitrided layer

Nitrogen content across the alloyed depth, processed at 2.5 kW power, 15 mm/s scanning speed, and 17 l/min N-flow rate, determined by EDS, is shown in Figure (4).



(a)



(b)

Figure 4: (a) Nitrogen concentrations measured as a function of depth along a line as shown in the micrograph in (b).

Near the surface, the concentration of nitrogen is very high at an excess of 27 at %. It decreases slowly inward, remaining around 20 at% for more than 70% of the total nitrided layer depth. Within this area the structure is largely denderitic, comprising a large volume fraction of TiN. Below this zone the nitrogen concentration was found to decrease rapidly. Above the heat affected zone, a needle-like structure was displayed with a nitrogen concentration ~10%. This decrease in nitrogen concentration is due to the decrease in the available nitrogen gas from the surface and the temperature gradient across the depth giving rise to decreasing solubility and diffusivity.

X-ray diffraction analysis

X-ray diffraction was utilized to identify the possible phases resulting from the laser gas nitriding process. For a single nitride track the 2 mm width is not enough for XRD analysis. A wider nitrided surface layer on the titanium substrate was produced by overlapping single tracks at a 50% melted width intervals, using the same set of parameters, identified previously. A series of such overlapped layers were produced. Figure (5) shows the diffraction pattern taken from the surface of the nitride layer after removing a layer ~ 100 um of the surface by grinding. Two crystallized phases were identified; one is a cubic titanium nitride (TiN) and the other as hexagonal alpha-titanium with higher peaks for TiN. Figure (8) shows another diffraction pattern taken from the same sample after removing 300μm from the surface. The peaks due to TiN diminished, while those, corresponding to α′-Ti grew.

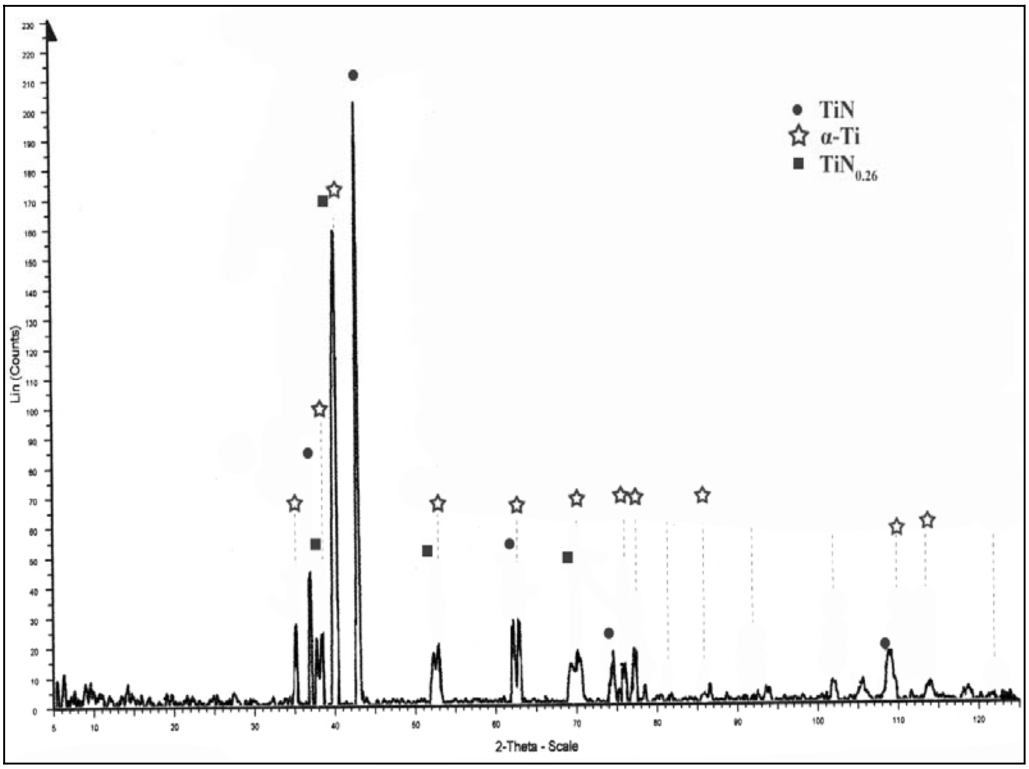


Figure 5: X-ray patterns taken from the nitride layer at a depth 100 μm from the surface (2.5kW, 17 l/min. 900 mm/s, and 100% nitrogen).

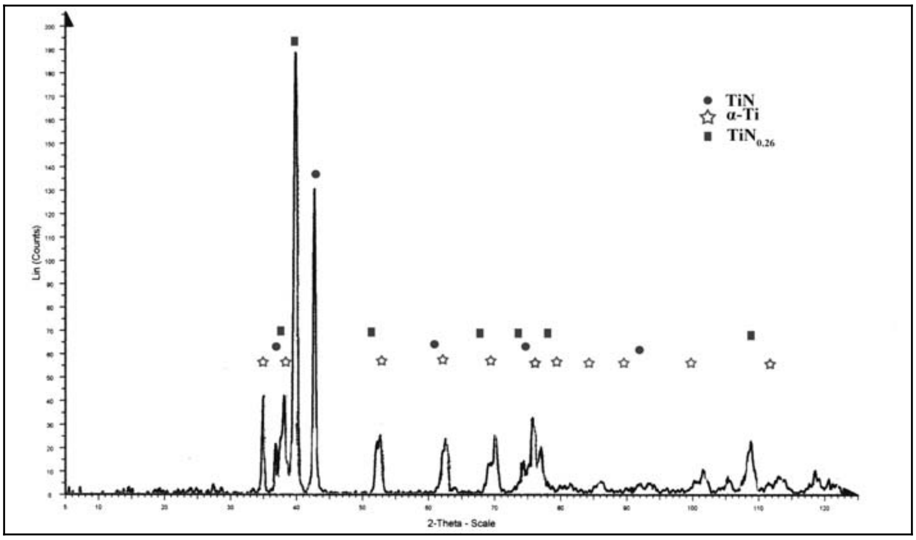


Figure 6: X-ray patterns taken from the nitride layer at a depth 300 µm from the surface.

Moreover, some peaks, corresponding to $TiN_{0.26}$ became noticeable. This indicates that TiN is the dominant phase on the surface while α′-Ti and $TiN_{0.26}$ may be found in the underlying nitrided layer. The high concentration of nitrogen and the high hardness at the surface supports this conclusion. These results are in good agreement with the work done by Hu et al [10], Selamat et al [13] and Kloosterman and De Hosson [11]. Their results showed that the top layer consists of TiN dendrites embedded in a mixture of $TiN_{0.3}$ and α′-Ti

Microhardness profile

The microhardness profile across the nitride layer is shown in Figure (7). The maximum hardness of 1100 HV was identified near the surface and decreased as the depth increased.

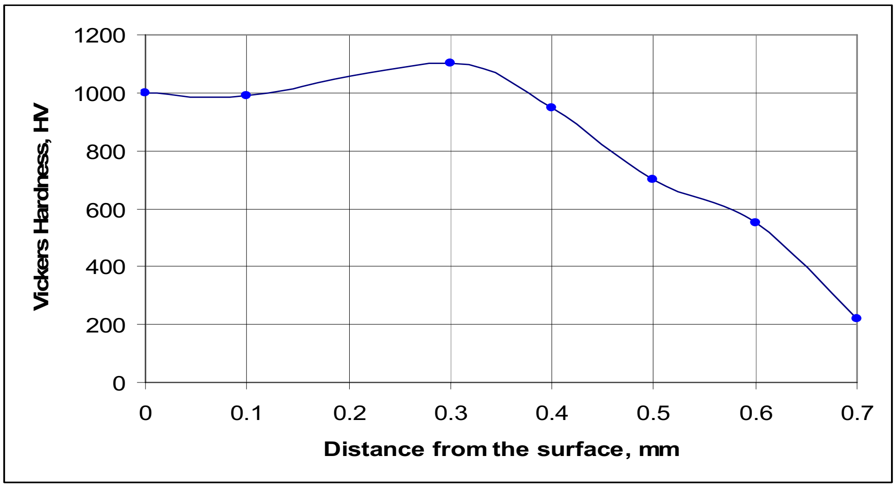


Figure 7: Microhardness profile across the nitrided layer produced on CP titanium by a laser power of 3 kW, 100 % N_2 and a scanning rate V = 900 mm/min.

It reached ~ 200 HV, which is the value of the un-treated Ti, at a depth of 0.7 mm. This tremendous increase of hardness is attributed to the formation of hard TiN phase in the nitrided layer. The development of hardness is directly related to the higher nitrogen dissolution into the over-heated melt that has been created by melting utilising the higher energy intensity of the laser beam. This high nitrogen concentration in the melt resulted in the formation of higher TiN population and larger dendrite arms during subsequent solidification eventually causing the hardness to increase. The results of the X-ray analysis support this explanation. The gradual decrease in the hardness values towards the matrix is attributed to the gradual replacement of TiN by a mixture of α'–Ti and TiN0.3 at deeper depths of the melted zone.

Nitriding with diluted nitrogen

Cracking is one of the serious problems occurring during laser nitriding of titanium alloys. It is associated with the formation of hard and brittle nitride phases of lower linear expansion coefficient, compared with the Ti substrate material. It is also enhanced by the residual stresses induced by the rapid cooling after TiN formation at the end of the laser processing. To overcome crack problem, several approaches have been tried. Mridha and Baker [16], and Kloosterman and De Hosson [11] used diluted nitrogen environment to obtain crack free surfaces. They attributed the elimination of cracking to a reduction in the rate of TiN formation reaction. In this work, no cracks have been observed in a single track. However, when overlapping was performed, longitudinal cracks were seen running along the laser track. In order to decrease cracking of the nitrided layers, diluted nitrogen atmosphere was tried with different parameters.

Figure (8) shows transverse sections of nitride layers produced at a constant power, speed and flow rate but with different levels of nitrogen concentration.

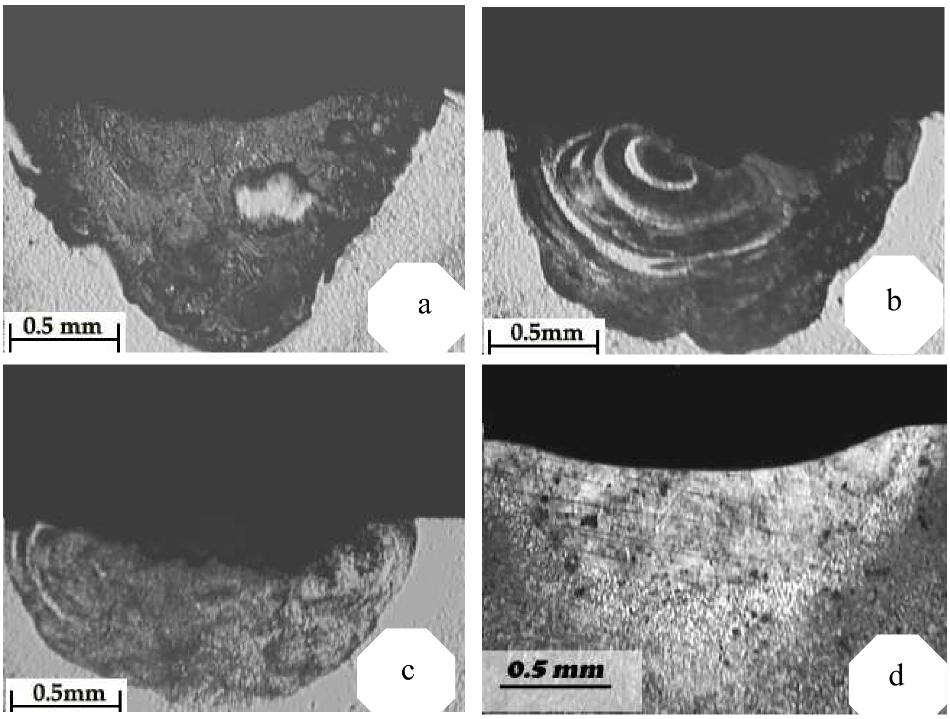


Figure 8: Optical micrographs of nitride layers at different nitrogen content in the nitrogen/argon gas mixture (a) 100% N_2, (b) 60% N_2 (c) 40% N_2, and (d) 100% Ar.

It is evident that decreasing nitrogen concentration leads to decrease of the melted depth and width. Furthermore, decreasing nitrogen concentration produced smoother interfaces. However, cracking and other defects such as pores and surface rippling still appear. Microstructural examinations showed a decrease in the TiN dendrites with a decrease in nitrogen concentration. In the track produced at 60% nitrogen, the volume fraction of the TiN dendrites was much reduced and the needle like structures was increased. This decrease in TiN dendrite volume fraction is clearly reflected in the microhardness profiles (Figure 9). When 100% nitrogen was used, the surface hardness was very high with some fluctuation between 1000 and 1300 HV extending to a depth exceeding 0.4mm. With decreasing the nitrogen concentration to 60%, the surface hardness decreased to ~ 800HV. With further decrease of nitrogen ratio to 40%, the surface hardness decreased to ~600 HV extending to a depth of 0.3mm. When surface melting was performed using 100% argon gas, the microhardness did not increase. This experiment shows the role of nitrogen in increasing the surface hardness of titanium.

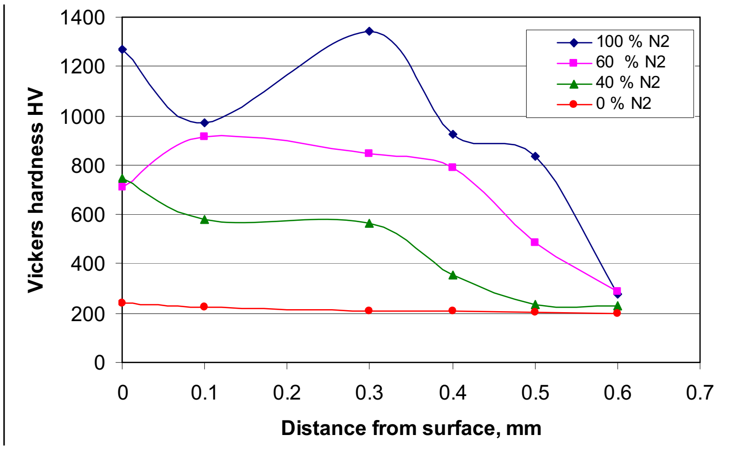


Figure 9: Microhardness profiles across the nitrided layer produced on CP Ti at different nitrogen concentrations.

CONCLUSIONS

- Laser surface melting of commercial purity titanium in nitrogen containing atmosphere leads to the formation of TiN dendrites. The volume fraction and the distribution of TiN are strongly influenced by the processing parameters.
- Microstructure and XRD analysis showed that the laser nitride layer consisted of dendritic TiN and needle-like $TiN_{0.26}$ and α′ Ti phases.
- The nitrogen concentration changes with the depth, showing a maximum of ~30 at %N at the surface, promoting TiN phase formation. The amount of titanium nitride produced depends on the nitrogen concentration. The lower the nitrogen concentration, the less the titanium nitride formed.
- The micro-hardness of the treated surface varied over a wide range of 500–1100 HV, the surface micro-hardness level of the nitride layers is related to the amount of titanium nitride formed. The micro-hardness of the nitride surface decreased significantly with the reduction of the nitrogen content.
- The higher the surface micro-hardness, the more severe the cracking in the laser nitride layer.
- Dilution of nitrogen with argon reduces the tendency to cracking and improves the surface morphology; simultaneously, the volume fraction of TiN denderites, and consequently the surface micro-hardness are noticeably lowered.

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