



## MICROSTRUCTURAL CHARACTERIZATION OF LASER NITRIDED TITANIUM

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### Introduction

Titanium and titanium alloys possess several excellent properties like a good corrosion resistance and high strength to weight ratio. Its light weight and ability to withstand extreme temperatures make it suitable for aircraft applications. However a disadvantage of titanium is its high friction and poor wear resistance. This problem can be tackled by nitriding the surface which results in a hard ceramic surface layer and as a consequence enhance both wear and friction properties. [2-5,8] Nitriding techniques like chemical vapor deposition (CVD) and physical vapor deposition (PVD) have a limited surface layer of a few micrometers. In contrast, laser nitriding may result in a modified layer of several hundreds of micrometers. [1-6]

For that purpose, laser gas alloying experiments were done on cp-Ti with a 1.5 kW CO<sub>2</sub> laser in a nitrogen atmosphere at various laser scan velocities. This paper concentrates on the characterization of the microstructural features. The basic concepts are the following: during laser processing the Ti will melt and a difference in surface tension, as a consequence of temperature gradients, causes a convective flow in the liquid Ti. This flow, which in fact is directly controlled by the intensity distribution of the laser beam, increases the amount of Ti in which nitrogen diffusion takes place and results in a modified surface layer of a few hundred micrometers. The advantage of melting the Ti with respect to solid state diffusion is that the intake of nitrogen goes much faster. Besides nitrogen diffusion TiN will be formed by the exothermal reaction:  $Ti + 1/2N_2 \Rightarrow TiN$ .

The binary phase diagram (Fig. 1) shows that  $\alpha$ -Ti is stable as an interstitial solid solution until the intake of 23 atomic percent nitrogen. [10] Furthermore there exist a Ti<sub>2</sub>N and a  $\delta'$  phase with a specific nitrogen concentration but these are expected to be absent due to the high cooling rates. TiN possesses a high melting point and is stable from 30 to 55 atomic percent nitrogen.

If the temperature of molten Ti is somewhat lower than the melting point of TiN, the reaction product TiN will almost immediately nucleate. If the temperature is high enough, TiN can be present in the liquid phase. At the same time, the increase of TiN in the melt enhances its viscosity which may influence the final surface morphology. Because of constitutional supercooling there is no flat solidification front but protrusions will develop leading to a dendritic microstructure. Since these hard ceramic TiN dendrites are embedded in a ductile Ti matrix better wear properties are expected.

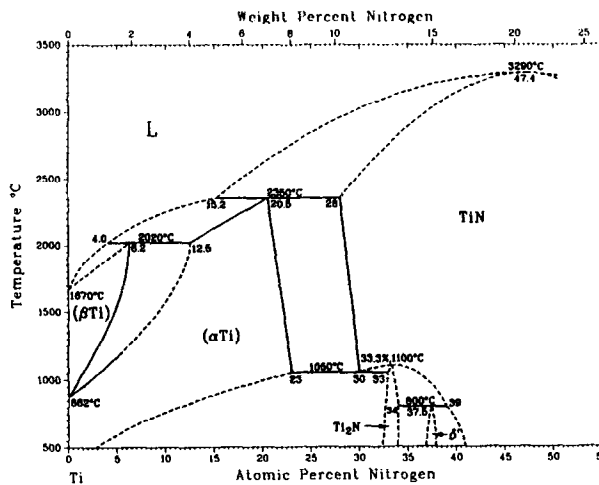


Figure 1. Ti-N equilibrium phase diagram. [10]

### Experimental Techniques

The experiments were carried out with the use of 1.5 kW Spectra Physics 820 CO<sub>2</sub> laser. This laser operates in a TEM<sub>00</sub> mode which results in a Gaussian intensity distribution. The laser beam hits the surface 4 mm out of focus with scan velocities in the range of 1.5-15 m/min. The laser output power varies between 300 and 1500 W. The laser beam diameter amounts 0.6 mm. Besides an axial N<sub>2</sub> flow there was also a small side flow. This was applied to have a small drift in order to decrease the possibility of plasma formation. The total gas flow amounts 10 l/min.

Commercially pure (grade 4) Ti sheets with a thickness of 5 mm were laser treated. Before processing the samples were sand blasted to increase the absorption of the laser beam. During laser processing the Ti samples were attached with heat sink pasta on a water-cooled copper block.

After laser processing cross sections were made by embedding the material followed by several sandpaper and polish steps. Finally the polished samples were chemically etched in a solution of 0.3 % HF and 1% HNO<sub>3</sub> in water. Microstructural analyses were carried out by optical microscopy, scanning electron microscopy (SEM) and Vickers hardness measurements with 50 g load.

### Results

#### Surface

There appeared a transition from a partially covered surface with TiN to completely covered. This transition can be distinguished quite easily by a yellow and a shiny yellow golden colour, respectively. For laser power densities (LPD) above  $\sim 2.5 \cdot 10^3$  W/mm<sup>2</sup> (this is an average value for the Gaussian beam distribution) the surface will be covered with a thin TiN layer starting from the middle of the track extending almost to the complete width of the beam for higher LPD's.

Partially covered surfaces with TiN exhibited a considerable roughness compared with a completely covered one. In the case of a complete covered surface, the morphology of the TiN layer can be characterized by a combination of lamellae and ripples in the radial direction (Fig. 2 and 3). These ripples represent the solidification fronts which can be seen more clearly by laser melting Ti in an Ar atmosphere. It is found that surface rippling decreases with increasing scan velocities and the lamellae become larger at increasing laser



Figure 2. Optical micrograph of laser nitrided surface showing lamellae and ripples.

power. In the case of two successive laser treatments, both with a high scan velocity and a high laser power, there arose very big lamellae and there was nearly no rippling anymore.

Besides lamellae and ripples, cracks are observed which depend on laser power and scan velocity. The cracks can be distinguished in two different types, namely tiny cracks with different orientations and cracks which partially or completely cross the laser track perpendicular to the scan direction. (Fig.3) The width of these cracks is much larger than the width of these microcracks. After careful examination it appeared that the microcracks penetrate only a few (~2-10) micrometers whereas the larger cracks possibly penetrate to the bottom of the melt pool. At the surface the cracks tend first to propagate along the border between two lamellae and then to cross the lamellae perpendicularly.

It is found that there exists a correlation between the periodicity of the cracks, the laser power and scan velocity. The large cracks return periodically with a periodicity changing upon scan velocity and laser power. With increasing scan velocity the density of cracks increases, i.e. become densely spaced and do not always cross the complete track width anymore. With increasing laser power the number of cracks decrease. However after studying the longitudinal cross sections the penetration depth changes also depending on laser parameters.

### **Transversal Cross Sections**

The cross sections taken in the transverse direction with respect to the laser track reveal the inhomogeneity of the melt pool.(Fig. 4 and 5) If the laser power is high enough a flat thin TiN layer of a few (1-3) micrometers is created on top of the melt pool. Below this thin layer TiN dendrites are observed which are oriented almost perpendicular to the surface.(Fig. 6) The TiN dendrites are surrounded by nitrogen rich Ti. Energy dispersive X-ray (EDS) measurements appeared to be not adequate enough to measure the nitrogen concentration because of its low yield. In addition, the energy peaks of nitrogen and Ti (L-peak) do overlap due to its bad



Figure 3. Optical micrograph showing microcracks with different orientations and one crack perpendicular to the scan direction.



Figure 4. Optical micrograph of cross section of lasertrack. ( $P=1.5$  kW,  $v=9$  m/min)

resolving power. Better results concerning the nitrogen concentration can be obtained by electron probe micro analysis (EPMA). [4,8] The structure of the surrounding Ti is needle like which locally seem to have two preferable, almost perpendicular directions. The microstructure below the TiN dendritic region is a composition of "needle like" structures, "coarse" structures and eventual groups of TiN dendrites, which are swept away by the convective flow from the edge of the melt pool where a pile up of TiN dendrites exists. Although the different microstructures below the TiN dendritic layer are not always situated on the same spot in different cross sections of the same laser track, the general observation is that TiN dendrites are always surrounded by a "needle like" structure. Further the amount of a "needle like" structure increase with increasing duration of the convective flow. This can be explained by the fact that with increasing duration the amount of N in the melt pool increases which probably result in a needle like structure after solidification.

The thickness of the TiN dendritic layer increases with increasing interaction times and even can be present throughout the complete resolidified molten zone. However at the same time there is an increase in surface roughness caused by the fast convective flow. Besides the position of the different microstructures, the shape of the melt pool also changes for different laser parameters. At higher interaction times the shape of the melted zone indicate the presence of capillary flows.

At some places small cracks are observed which can be correlated to the microcracks observed at the surface. Besides perpendicular also cracks are running parallel to the surface.(Fig. 7) At increasing thickness of the TiN dendritic layer and consequently increasing width of dendrites cracking occurs parallel to the surface and even parts of the layer were broken out after preparing cross sectional samples. So there exists a transition where besides lateral stresses also stress gradients perpendicular to the surface becomes predominant.

### **Longitudinal Cross Sections**

A noticeable variation of the thickness of the TiN dendritic layer within the same laser track was found. When the power is 1.2 kW and laser beam scan velocity is 12 m/min, the thickness varies over 10-25mm. Also in the longitudinal cross section there were no specific areas or periodicities observed that correlate with a particular microstructure.

The penetration depth of the periodic cracks observed at the surface were found to change upon laser power. With increasing laser power the cracks penetrate deeper into the melt pool until they reach the bottom where they terminate. However at the same time the number of cracks per unit length becomes less.

### **Hardness**

The layer with TiN dendrites and N-rich  $\alpha$ -Ti exhibits a hardness that depends basically on the concentration of the dendrites. It varies from 700 to 1800 Vickers for very closely compacted dendrites at the edge of the melt pool. The "needle like" structure has a hardness of  $560 \pm 60$  Vickers and the "coarse structure" of  $300 \pm 20$  Vickers. Probably, the "needle like" structure is nitrogen enriched Ti because laser melting Ti in an argon

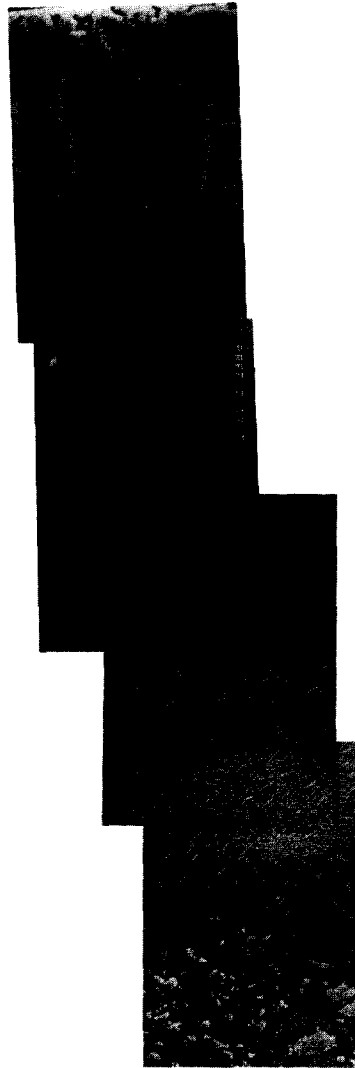


Figure 5. (right) SEM micrograph of cross section revealing different microstructures. TiN dendrites on top, "needle like" structures (A), "coarse" structures (B) and below the heat affected zone.

atmosphere does not increase the hardness that much. Different nitrogen contents possibly explain the large standard deviation. The "coarse structure" corresponds to resolidified nearly pure Ti because for Ti melted in Ar same hardnesses were found. The heat affected zone is a little harder than the substrate material,  $nl. 230 \pm 30$  against  $180 \pm 50$  Vickers.

### **Discussion**

Due to the continuous intake of nitrogen in Ti, even shortly after the interaction with the laser beam, the solidification temperature will increase. First of all a thin TiN layer will solidify out of which dendrites will grow into the melt due to constitutional supercooling. These dendrites grow by rejecting Ti into the melt. At the same time there will be a solidification front at the bottom of the melt pool and somewhere these fronts

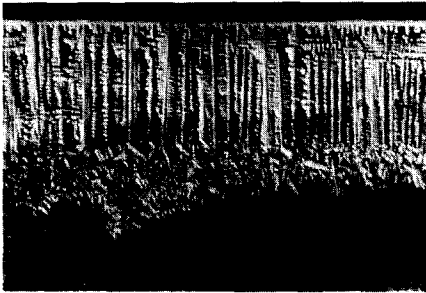


Figure 6. Optical micrograph of dendritic TiN region with on top a flat TiN layer.



Figure 7. Optical micrograph showing cracks parallel to the surface.

meet each other. If the cooling rate is fast enough and the nitrogen concentration in Ti lies below 6.2 atomic percent, a martensitic transformation from the b-phase is possible during cooling down. [9]

For the case that TiN has been present in the liquid phase, a smoothly varying surface layer will formed depending on the viscosity and velocity of the convective flow. However, a disadvantage of the presence of this top layer is that the nitrogen diffusion into the Ti is controlled by the diffusion through the TiN layer, which goes much slower. Further it is not clear if this thin ceramic TiN layer could be of practical use because of the height variation at the surface. Nevertheless the combination of hard TiN dendrites which are very well embedded in a ductile material is likely to improve the surface properties. Preliminary wear test indeed confirm this, the results of which will be reported separately.

Generally, laser treatment of materials induce tensile stresses in the material. In the case of a metal, these stresses can be relieved by elastic and plastic deformation. However a ceramic material shows a more brittle behavior and laser treatments may cause cracking. In these experiments cracks in the laser track indicate the build up of a tensile stress in the scan direction which will be relieved by perpendicular cracking if it exceeds a critical stress. For single lasertracks, crack formation in the scan direction only occur for very high laser energy densities. However for overlapping tracks periodic cracking occurs in the scan direction, which can be explained by a stepwise increase in the residual stress with each successive, overlapping laser track up to a maximum value.[7] Parallel cracking probably takes place if the dendritic layer thickness and the dendrite density become too high. In that case stress gradients perpendicular to the surface become significant and result in parallel crack formation. Cracks may be circumvented by preheating the sample or by using diluted nitrogen.[6] The mechanism of prevent cracking by preheating is that it increases the ductility of Ti and enhances the possibility of stress relieve by plastic deformation. Diluted nitrogen by argon results in less cracking due to a decreased reaction rate and thus a decreased presence of TiN. However a disadvantage is that at the same time the TiN dendrite layer also decreases.

### Conclusions

Laser gas alloying of Ti in a nitrogen atmosphere results in a modified surface layer consisting of hard ceramic TiN dendrites embedded in a ductile substrate with on top a thin TiN layer. Hardness as high as 1800 Vickers has been measured. However after laser processing, as a consequence of residual stresses, cracking occurs. These cracks can be prevented by preheating the sample or by using diluted nitrogen.

### Acknowledgment

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