

# Nitrided Ti-13Nb-13Zr in wear applications

N. Axén, G. Akdogan, S. Luyckx,<sup>1</sup> E. Johansson<sup>2</sup> and L. Klintberg<sup>3</sup>

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*The possibility of forming a thin hard titanium nitride layer on a titanium alloy with 13% Nb and 13% Zr using a thermally enhanced diffusion process is investigated. In particular, the tribological performance of the surface treated titanium alloy in unlubricated and saline solution lubricated sliding contact is evaluated. The effects of the surface treatment on hardness, surface roughness and the microstructure of the surface zone are also studied. It was found that thin hard layers of titanium nitride compounds were formed on the surface of the alloy during the diffusion process. Although the properties of the surface layers were strongly dependent on the processing parameters, the friction and wear properties were considerably improved compared to the untreated alloy. In general terms, the choice of surface treatment parameters is a compromise between optimisation of surface or bulk properties.*

## Introduction

The most prominent characteristics of titanium and titanium based alloys as construction materials are their corrosion resistance (e.g. off-shore industry) and the favourable strength to weight ratio (aviation). This group of materials has been used for engineering applications over the past 50 years and is constantly expanding its field of applications, particularly in competition with stainless steels and aluminium alloys.<sup>1</sup>

Although not a mass consumer of titanium, the bio-technical industry find increasing use of titanium as an implant material due to unique bio-compatibility properties.<sup>2</sup> This field of use includes orthopaedic, oral, plastic and cardiovascular surgery. It is the unusual combination of excellent corrosion resistance in biological environments, tissue compatibility and mechanical properties that gives titanium its unique potential as a bio-material.<sup>3</sup>

The use of titanium in applications involving surfaces in sliding contact is limited because of its low hardness and poor friction and wear properties, characterised by low seizure resistance and high friction. Suitable alloying in combination with heat treatments improves the mechanical properties of titanium. The most common alloying elements are aluminium and vanadium, as in the popular Ti-6Al-4V material. Some researchers, however, have

coupled these elements to observed adverse tissue reactions, and the search for alloys more suitable for implants is therefore progressing.<sup>1</sup>

An alternative bio-material with more bio-compatible ingredients may be the Ti-13Nb-13Zr alloy, being designed to have a low modulus of elasticity, enhanced bio-compatibility, high strength, toughness, fatigue endurance, and corrosion resistance.<sup>4,5</sup> This material is a promising candidate for orthopaedic implants.

It is desirable to improve the tribological properties of titanium and its alloys. The deposition of thin, hard coatings or the formation of hard top-layers by chemical methods are alternatives to improve the surface properties of a material. The chemical reactivity of titanium allows the formation of wear protective titanium nitride compounds on the surface by nitriding at moderate temperatures.<sup>1,6</sup> Such diffusion based techniques form nitrides which are integral parts of the base material, thus avoiding the adhesion problems of deposited coatings.

Nitriding of titanium and its alloys (most commonly the technically pure grade 2 and the Ti-6Al-4V, grade 5) is today an industrial process. Applications include human implants, off-shore applications and various wear parts.<sup>6,7</sup>

Nitriding of titanium takes place somewhere between 600 and 900°C and produces a surface layer of stoichiometric TiN at the outer 0.1–5 µm depending on temperature and nitriding time. Further down from the surface, layers of complicated structures including Ti<sub>2</sub>N and other nitrides appear, followed by diffusion layers with dissolved nitrogen in the titanium structure. The diffusion layers may reach 10–15 µm down into the material.<sup>6</sup>

In the present paper, the prospects of nitriding the Ti-13Zr-13Nb alloy for optimised friction and wear performance is investigated. The effects of nitriding parameters on hardness, grain size, and surface topography as well as on wear and friction characteristics in sliding contact are evaluated.

## Experimental procedures

### Materials and processes

The properties of titanium alloyed with 13% niobium and 13% zirconium (Ti-13Nb-13Zr) is compared with CP (pure) titanium (ASTM grade 2), a single  $\alpha$ -phase material (hcp) with a  $\beta$ -transus temperature of 885°C (transition to bcc). Ti-13Nb-13Zr is an alloy in the near- $\beta$  subgroup of the  $\alpha + \beta$  class, with  $\beta$ -transus of 735°C.<sup>5</sup>

As-delivered the Ti-13Nb-13Zr alloy was in the

<sup>1</sup>School of Process and Materials Engineering, University of the Witwatersrand, P.O. Wits, 2050 South Africa

<sup>2</sup>Tisurf Int. AB, Kungsängsvägen 25, 753 23 Uppsala, Sweden

<sup>3</sup>Uppsala University, The Angstrom Laboratory, Box 534, . . . S-751 21 Uppsala, Sweden

quenched but un-aged condition, i.e. with a completely martensitic structure. Before nitriding the samples were mechanically ground and polished to mirror finish using oxide polishing (silica) in the last step.

Samples of both grades were nitrided in a vacuum furnace at temperatures of 500, 650, 720, 790 or 820°C, the nitriding time being 6 h for all temperatures. During nitriding the sample surfaces were exposed to a 0.04 cm/s linear flow of pure N<sub>2</sub> gas (N52). The process pressure was 400 mbar. Further details on the process are given by Johansson.<sup>6</sup> The nitriding was performed at TiSurf International AB (Sweden).

The temperature of 500°C results in a hardly distinguishable nitride layer. This temperature was chosen since ageing at 500°C for 6 h has been shown to produce optimal hardness and fatigue properties to the Ti-13Nb-13Zr alloy.<sup>5</sup> The higher temperatures were chosen to produce thicker layers of nitrides and better wear resistance. 820°C has produced promising wear resistance results on CP titanium in works.<sup>6</sup>

### Characterisation techniques

Metallographic investigations were performed with optical (OM) and scanning electron microscopy (SEM) on polished and etched (Kroll's reagent) surfaces. The thickness of the nitride layers was measured by cross-section SEM. The morphology of the nitrided surfaces was investigated by SEM and surface profilometry and their chemical composition by glow discharge optical spectroscopy (GDOES).

The Vickers hardness of the bulk material was measured using a 50 g load and the film hardness was assessed with loads of 10 g and 50 g. The lower load was more sensitive to the hardness of the top layers. Surface roughness was assessed as R<sub>a</sub>-values with an Alfa Step Instrument using a 12.5 μm radius diamond stylus.

The tribological behaviour of the nitrided surfaces in sliding contact was studied with a pin-on-disc tribometer (manufactured by VTT, Finland) in which the friction was continuously registered with a PC. The tribotests were used to characterise the materials in terms of what loads (contact pressures) they could resist without seizure. A large increase in the friction coefficient was used as an indication of the occurrence of seizure.

In all tribo-tests the surfaces were self-mated. A stationary mushroom shaped pin with a spherical hat of 50 mm radius was loaded against a rotating flat with an 11° inclination (see Figure 1). By rotation of the mushroom this configuration permits many tests on the same pin. The sliding speed was held constant at 15 mm/s, and the load was varied between 1 and 60 N. The highest load corresponds to hertzian contact pressures between 50 and 200 MPa for un-nitrided Ti-13Nb-13Zr, depending on hardness, and was enough to cause failure of all coatings, even in lubricated sliding.

The wear track radii on the flats were between 5 and 10 mm and the tests were performed both dry and with a 3.5% saline solution simulating sea water as lubricant. All

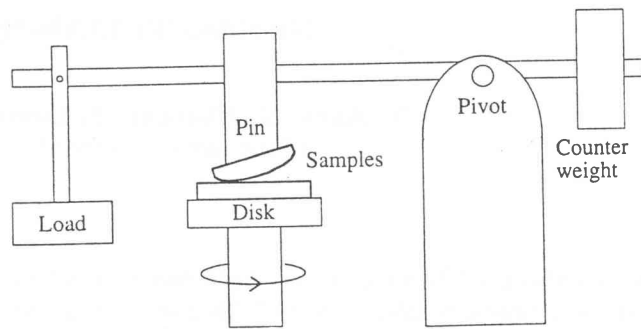


Figure 1 Schematics of the pin-on-disc set-up with the mushroom-shaped pin

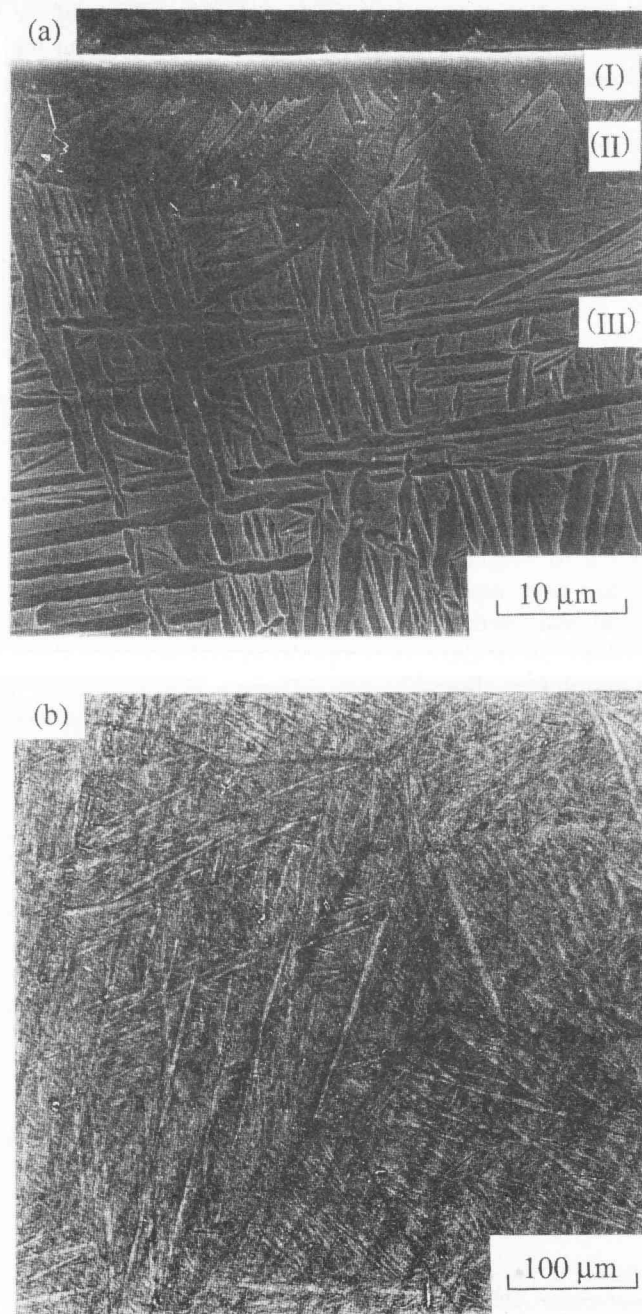


Figure 2 Cross-section of polished and etched (a) and a top view (b) of Ti-13Nb-13Zr nitrided at 790°C (SEM)

tests were run at room temperature. The sample flats were attached to the bottom of a little reservoir containing the lubricant which covered the flats. The wear tracks were investigated in a SEM.

## Results

### Microstructure

Cross-section SEM of nitrided layers on Ti-13Nb-13Zr typically revealed three different zones (see Figure 2). The thin first zone (I) appears homogeneous in the SEM and corresponds to a nitrogen rich TiN outer layer found in the GDOES analysis. For nitriding at 790°C, zone (I) became 2–3 μm thick. Further down a second zone (II), 5–10 μm thick for 790°C nitriding, was observed. Zone (II) contains much less nitrogen than (I) and is believed to consist mainly of the titanium alloy with dissolved nitrogen, possibly with small amounts of nitrides. Below these diffusion layers (I + II), the titanium alloy, free from nitrogen but solution treated and aged as a result of the nitriding process, can be seen (III). The microstructure of both zone (II) and (III) is acicular but a clear difference between the zones in the orientation of the needles can be seen. The acicular structure can also be seen on the top of the layer, as exemplified in Figure 2b.

Cross-section SEM of nitrided CP titanium revealed similar zone patterns and comparable layer thicknesses, although the single phase microstructure ( $\alpha$ ) of CP titanium makes the diffusion zone (II) less distinct in microscopy.

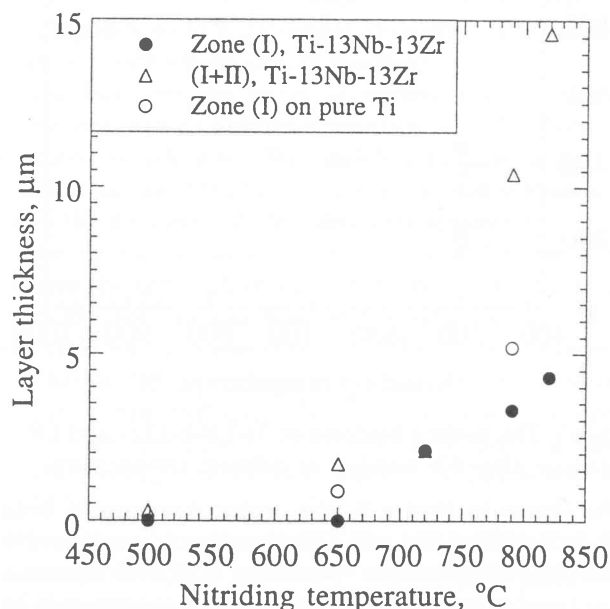


Figure 3 Estimated thickness of the nitrided layers (I) and (II) on Ti-13Nb-13Zr and CP titanium after nitriding for 6 h

The thickness of the nitrided layer is a function of the nitriding temperature and time. Figure 3 shows how the thicknesses of zones (I) and (II) vary with temperature after nitriding for 6 h. This nitriding time resulted in very

thin surface zones for temperatures below 650°C (< 0.1 μm for zone (I)), whereas for temperatures around 820°C it resulted in considerable film growth (3–4 μm for zone I). Considering only the top zone (I), there is no clear difference in film thickness comparing CP titanium and Ti-13Nb-13Zr. The (II) zone, however, increased faster in thickness above 720°C for Ti-13Nb-13Zr than for CP titanium.

Both the microstructure and the grain size of the Ti-13Nb-13Zr bulk is affected by the nitriding process. With increasing nitriding temperature the thickness of the acicular needles increases and the prior-β grain size reaches values close to 1 mm, as measured from SEM micrographs. For temperatures above 800°C, see Figure 4.

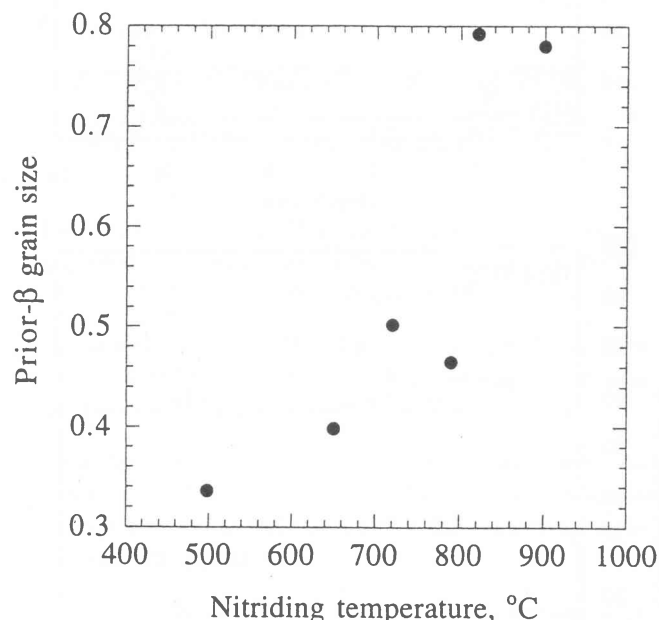


Figure 4 Estimation of the prior-β grain size of Ti-13Nb-13Zr after 6 h nitriding at different temperatures

### Chemical composition

The GDOES analysis of the nitrided surfaces revealed compositional changes beneath the surface which could be interpreted in terms of the surface zones described above. At depths exceeding about 5–7 μm for the surfaces nitrided at the higher temperatures only Ti, Zr and Nb were detectable with the resolution of the equipment (see Figure 5). At depths less than about 1 μm for the surfaces nitrided at 500°C (Figure 5a), and about 4–5 μm for the surfaces nitrided at 820°C (Figure 5b), the amounts of Nb and Zr fell and simultaneously oxygen and nitrogen became noticeable. At this depth an increase in titanium content was recorded for the high temperature surfaces, as in Figure 5b.

For all surfaces except those nitrided at 500°C there was much more nitrogen than oxygen present in the outer layers. At a depth of approximately 0.1 μm for the 500°C surfaces and about 1 μm for the 820°C surfaces, a strong

increase in the nitrogen content was measured, accompanied by a fall in the amounts of Ti, Nb and Zr (see Figure 5).

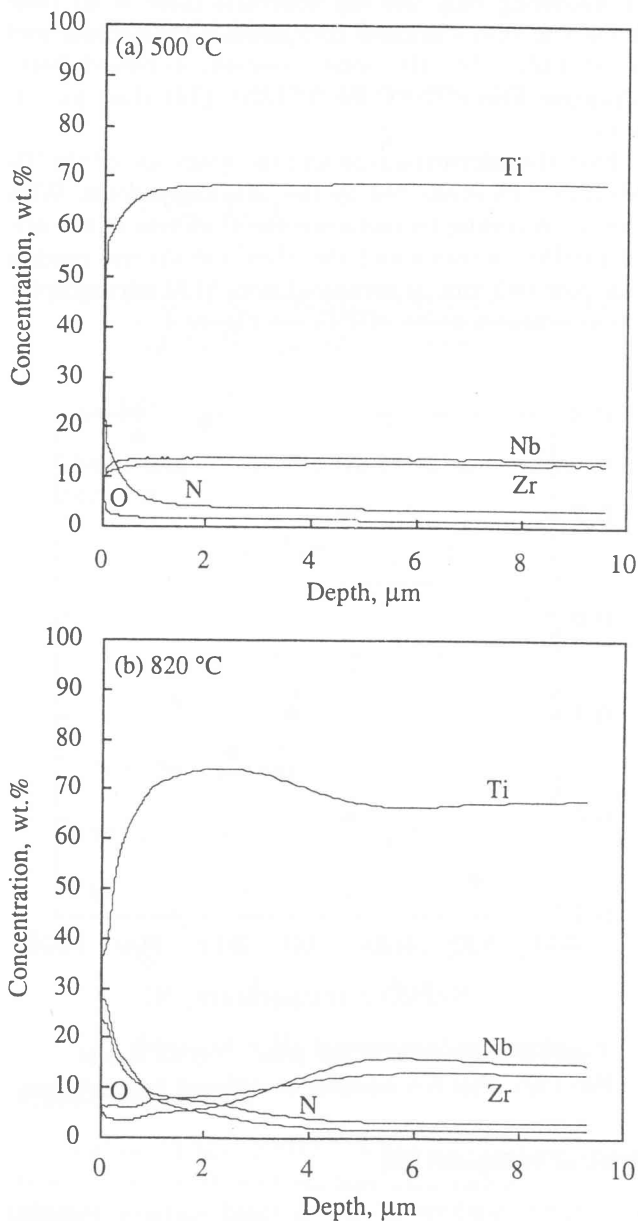


Figure 5 Chemical Composition as a function of depth for Ti-13Nb-13Zr nitrided at 500°C (a) and 820°C (b)

### Hardness

The substrate hardness of CP titanium was about 180 HV and remained unaffected by the nitriding process. The hardness of solution treated and quenched but unaged Ti-13Nb-13Zr was 240 HV. Nitriding at 500°C for 6 h resulted in ageing which produces a close to optimal substrate hardness (~310 HV). Higher temperatures rapidly decreased the hardness to between 240–260 HV, due to over-ageing below 735°C and phase transformation above 735°C. There were only minor differences in the hardness resulting from nitriding temperatures between 650 and 820°C (see Figure 6).

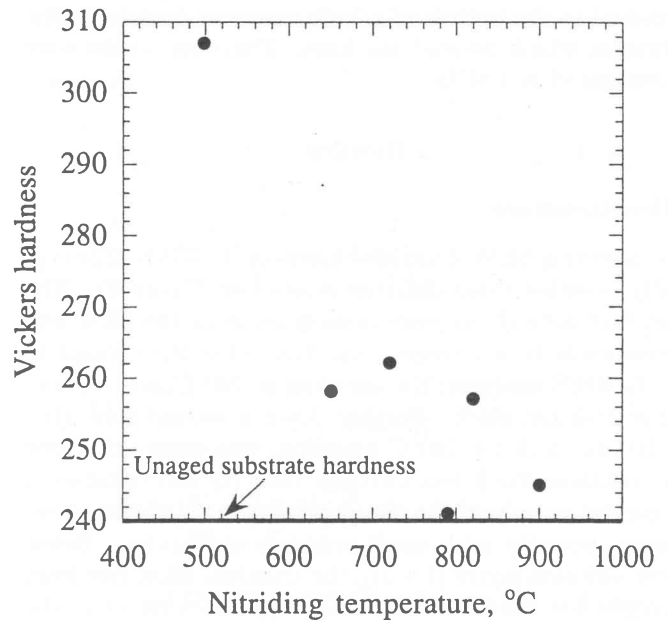


Figure 6 The substrate hardness of Ti-13Nb-13Zr after 6 h nitriding at different temperatures

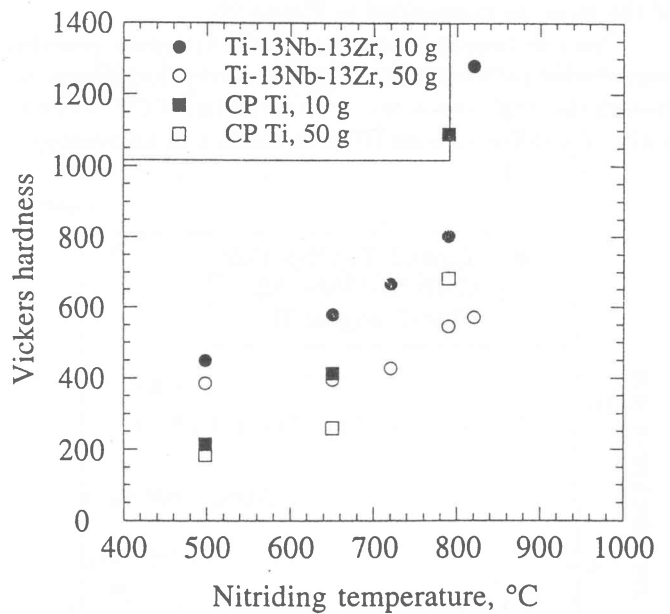


Figure 7 The surface hardness of Ti-13Nb-13Zr and CP titanium after 6 h nitriding at different temperatures

As shown in Figure 7, the surface hardness of both nitrided Ti-13Nb-13Zr and CP titanium increased with the nitriding temperature. Nitriding at 500°C increased the hardness of the Ti-13Nb-13Zr surface considerably as measured both with the 10 g and 50 g loads. Higher nitriding temperatures resulted in larger increases in hardness for the surface compared to the bulk. However, for CP titanium there was not much difference between the surface and the bulk hardness at a nitriding temperature of 500°C, whereas for higher temperatures the surface became increasingly harder than the substrate.

## Surface roughness

The polished alloys had an  $R_a$ -value of about 200 before nitriding. This value rose with the nitriding temperature. For nitriding at 650°C and above, the surface roughness increased more for the Ti-13Nb-13Zr alloy than for CP titanium (see Figure 8).

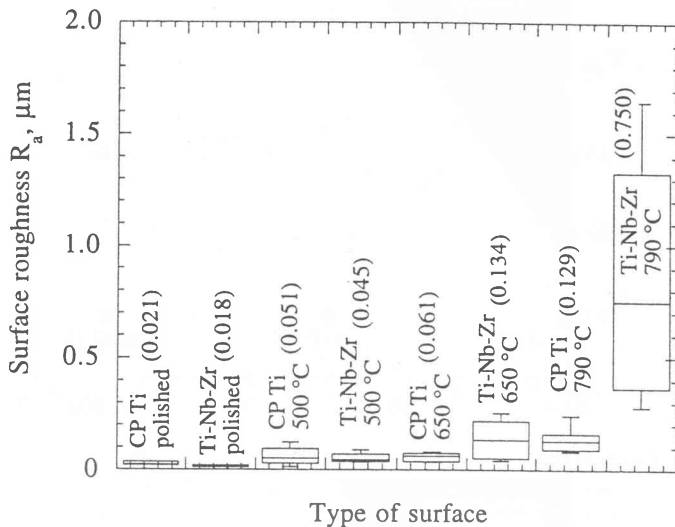


Figure 8 Surface roughness ( $R_a$ ) of Ti-13Nb-13Zr and CP titanium before and after 6 h nitriding at different temperatures

## Wear and friction

Dry friction tests with self-mated, unmodified titanium typically resulted in friction coefficients (ratio between friction force and load) of between 0.4 and 0.5. Such high friction coefficients are to be interpreted as seizure; the resulting wear rates are high and the worn surfaces rough. The nitriding process reduced the friction coefficient to 0.1–0.2, as long as the nitride layers resisted the wear. With such low friction coefficients the wear is very low and the tests can go on for long sliding distances.

It was found that, depending on how the layers were worn through, the friction results from the pin-on-disc tests could be classified into three different characteristic modes. In the first mode, the friction coefficient remained stable at a low value (0.1–0.2) for a prolonged sliding distance. This behaviour is associated with a nitrided layer that resists the wear conditions produced by the corresponding test parameters. That the low friction of this first friction mode was maintained for long sliding distances, was confirmed in a few prolonged tests (approximately 10 h). But to save time most of the tests were not run further than 10 m (about 10 min).

In the second mode, the friction coefficient rose slowly but continuously towards 0.3–0.4 with sliding distance. This friction behaviour is interpreted as a slow but continuous wear-through of the surface film.

In the third friction mode, the surface zone was worn through almost immediately, resulting in a rapid rise of the friction coefficient to about 0.4–0.5, a value that corresponds to dry, self-mated sliding of untreated titanium. Examples of the first two friction modes are given in Figure 9.

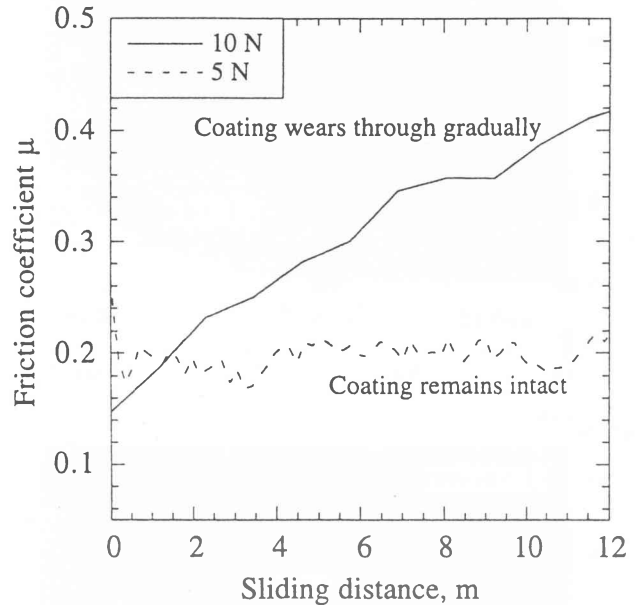


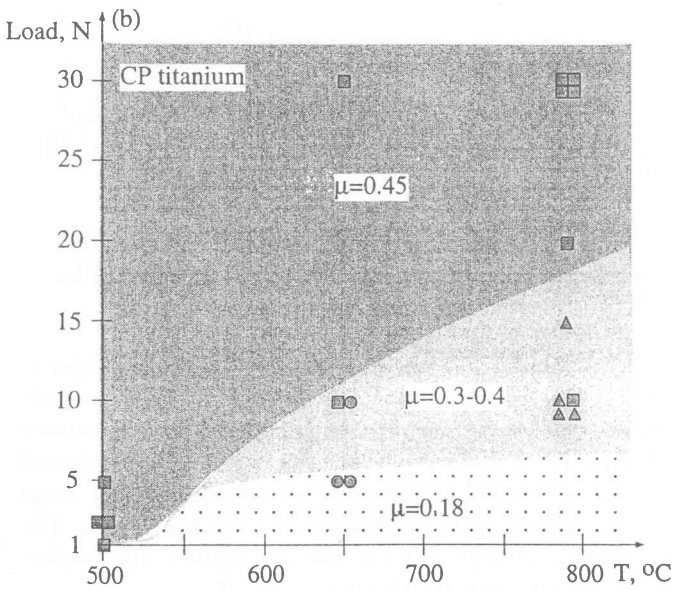
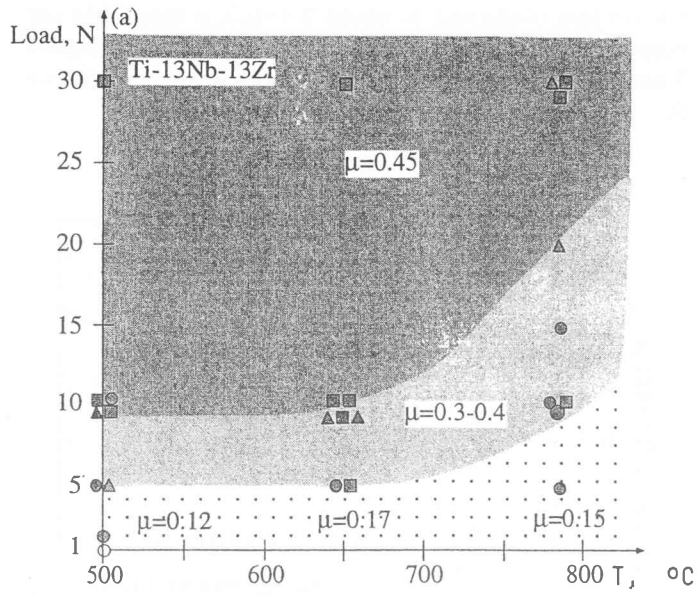
Figure 9 Examples of steadily low and continuously increasing friction as a function of sliding distance for CP titanium nitrided at 650°C

The transition between these friction modes depends both on the processing parameters and on the test conditions as well as on the type of substrate, as can be seen in Figure 10, where the test results from the unlubricated tests are presented in the form of schematic wear maps showing approximate borders for the friction modes. The data points correspond to actual test results; the borders between the modes are sketched.

The CP titanium nitrided at 500°C resisted hardly any load at all without giving a high friction coefficient. This alloy needs to be nitrided at temperatures exceeding 650°C for the nitriding process to improve the wear properties noticeably. Also for higher nitriding temperatures, the effect on the wear resistance was lower than for Ti-13Nb-13Zr, see Figure 10b.

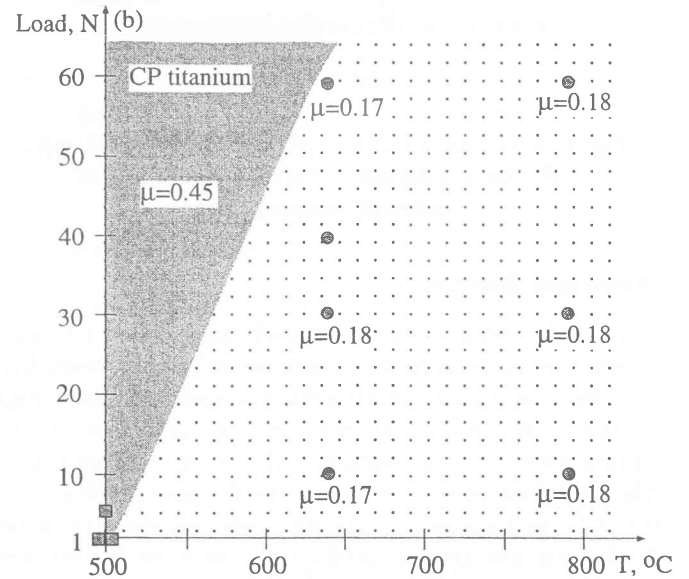
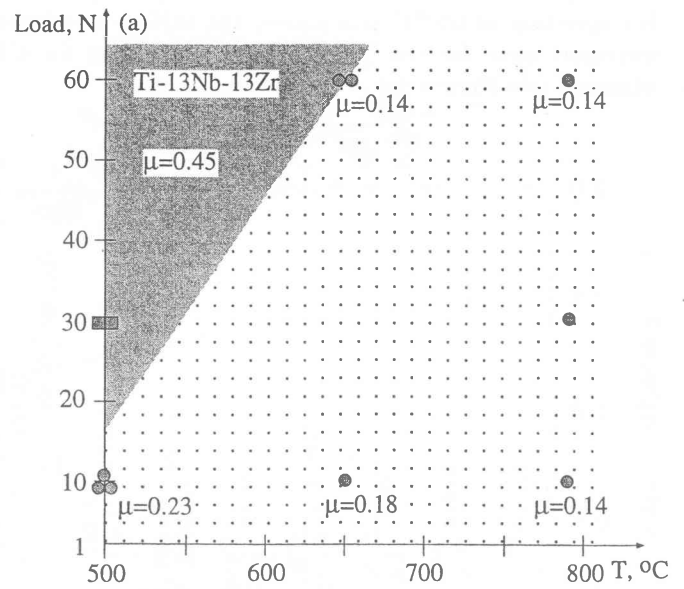
For the Ti-13Nb-13Zr alloy, however, even nitriding at 500°C had a clearly beneficial effect on the wear behaviour. Nitriding at this low temperature made this alloy perform much better than CP titanium (compare Figures 10a and b). The wear performance was even more improved as a result of nitriding at higher temperatures, and a great improvement was achieved by nitriding at 790°C (see Figure 10a).

With saline solution as lubricant, a run-in behaviour was typical for most materials and test conditions. Initially, the friction coefficient was about 0.15–0.20, but



- Immediate failure, friction coefficients of 0.4-0.5
- ▲ Continuously increasing friction as the coating is worn through
- Coating remains intact and the friction stays low

Figure 10 Wear maps of the dry friction results for Ti-13Nb-13Zr (a) and CP titanium (b)



- Immediate failure and friction of 0.4-0.5
- Coating remains intact and the friction is low

Figure 11 Wear maps of the lubricated friction results for Ti-13Nb-13Zr (a) and CP titanium (b)

then dropped to a value below 0.15 for the Ti-13Nb-13Zr alloy. This behaviour was probably a result of a run-in wear phenomenon of surface asperities and was more pronounced for the surfaces nitrided at higher temperatures and also for tests run with higher loads.

In the saline solution lubricated tests, only the wear modes corresponding to immediate wear-through of the nitrided layer and the mode of continuous low level friction could be observed. With saline solution lubrication the surface layers failed at considerably higher loads. Also in the lubricated tests, nitriding at 500°C had almost no effect on CP titanium, but strongly improved the performance of Ti-13Nb-13Zr. Higher nitriding temperatures improved the performance for both substrates (see Figure 11).

After tests with a load of 60 N and a sliding distance of 60 m, the surfaces resulting from 790°C nitriding on Ti-13Nb-13Zr seemed unaffected. For CP titanium some wear damage could be found on the nitride layer of the rounded mushroom shaped pin after such a test. This was the only difference in performance between high temperature nitrided CP titanium and Ti-13Nb-13Zr alloy in the lubricated tests.

For the tests where total wear-through of the nitrided layers occurred, this appeared to take place simultaneously on both pin and disk, despite the wear scar on the pin being focused to a point and the wear on the disk being distributed over a circular track. The friction coefficient was slightly lower for Ti-13Nb-13Zr than for CP titanium (see Figure 11). This difference was small but consistent.

## Discussion

The nitride layer thickness of Ti-13Nb-13Zr appears to be fairly constant for nitriding below 720°C, whereas for higher temperatures a large increase in the nitride as well as the solid solution hardened layer thickness is obtained (see Figure 3). This can be due to the phase change from hcp ( $\alpha$ ) to bcc ( $\beta$ ) occurring at 735°C. Since the lattice structure of the  $\beta$ -phase is more open, the diffusion may proceed more easily, resulting in the large increase in the affected zone thickness. That this phase transformation occurs at a higher temperature for CP titanium and the different diffusion rates in the two phases can explain why the surface roughness increased more on Ti-13Nb-13Zr than on CP titanium during nitriding at 790°C.

From the GDOES analysis no conclusions about the chemical bonding in the zones affected by the nitriding could be made. Therefore no statements about the amounts of nitrogen forming nitrides or the amounts being interstitially dissolved can be made in this work. However, the results support the interpretation that there is an outer layer of nitrides (I), consisting primarily of TiN at the top and Ti<sub>2</sub>N further down, but probably also of small amounts of niobium and zirconium nitrides. Beneath the nitride layers a thicker region (II) with dissolved nitrogen is present. A similar layer structure is found for CP titanium.

The tribological evaluation shows that Ti-13Nb-13Zr is much more wear resistant than CP titanium after nitriding at temperatures as low as 500°C, both in the dry and the lubricated tests. Nitriding of CP titanium at this temperature does not significantly increase the load carrying capacity. The Ti-13Nb-13Zr alloy, in contrast, holds for more than 5 N unlubricated and more than 15 N in the lubricated tests. This may be a result of the higher substrate hardness of Ti-13Nb-13Zr, and of the thicker diffusion-hardened zone formed beneath the nitride layer in this material, both giving the thin nitride layer better support.

After nitriding at higher temperatures Ti-13Nb-13Zr is more wear resistant than CP titanium, although the difference is not as pronounced as for the lower temperatures. The thicker diffusion hardened zone produced in the Ti-13Nb-13Zr may be attributed to the presence of zirconium, which is a larger atom than titanium and thus creates a more open lattice, enhancing diffusion. Further, zirconium is a more reactive element and has a greater affinity for nitrogen than titanium.

Lubrication enhanced the loads that the surface layers could resist without seizure. The fact, that the nitriding process affected the seizure resistance also in the lubricated tests, indicates that full-film lubrication was not achieved. Instead some mechanical contact between surface asperities took place, as in boundary lubrication. This may also explain why the second friction mode was not observed in the lubricated tests; for loads high enough to totally squeeze out the plasma lubricant from sliding surfaces, the nitride layer was also quickly worn through. In addition, the lubricant may have helped to remove wear debris from the surfaces, also increasing the resistance to seizure.

The test shows that thicker nitride layers are preferable for optimisation of the tribological qualities. To strongly enhance the growth of the nitrided layer a temperature above the  $\beta$ -transus should be chosen. Such high temperatures, however, may result in overaging and an excessive grain growth in the bulk material, which in turn may reduce its mechanical properties. The choice of nitriding conditions for optimal performance is therefore a compromise between conditions giving optimal bulk properties and parameters giving more seizure resistant surfaces.

## Conclusions

For CP titanium, nitriding at 500°C for 6 h does not result in a sufficiently thick nitride layer to significantly improve the tribological properties. For Ti-13Nb-13Zr, however, these processing conditions strongly improved the wear properties.

For both CP titanium and the Ti-13Nb-13Zr alloy, the surface hardness and the wear resistance increases with the thickness of the nitride layer. The wear properties of the Ti-13Nb-13Zr alloy, however, benefit more from nitriding at both high and low temperatures than CP titanium.

For higher nitriding temperatures, the surface roughness of Ti-13Nb-13Zr increases more than for CP titanium.

With the investigated nitriding process, one set of nitriding parameters cannot result in both optimal wear properties and substrate hardness. Therefore the choice of processing parameters is a compromise between optimisation of tribological properties and the mechanical properties of the bulk.

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