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Cyclic deformation fatigue behaviour of Ti6Al4V thermochemically nitrided for articular prostheses

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ABSTRACT: *Titanium and its alloys have many attractive properties including high specific strength, low density, and excellent corrosion resistance. Titanium and the Ti6Al4V alloy have long been recognized as materials with high biocompatibility. These properties have led to the use of these materials in biomedical applications. Despite these advantages, the lack of good wear resistance makes the use of titanium and Ti6Al4V difficult in some biomedical applications, for example, articulating components of prostheses. To overcome this limitation, nitriding has been investigated as a surface-hardening method for titanium. Although nitriding greatly improves the wear resistance, this method reduces the fatigue strength. Low cycle fatigue performance in air of nitrided Ti6Al4V at different deformation amplitudes has been studied. Results show a reduction of low cycle fatigue life of up to 10% compared to the non-treated material. Studies suggest it is not related to the titanium nitride surface layer, but to microstructural changes caused by the high temperature treatment. (Journal of Applied Biomaterial & Biomechanics 2003; 1: 43-7)*

KEY WORDS: *Ti6Al4V, Nitriding, Surface treatment, Fatigue*

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INTRODUCTION

The successful use of titanium and its alloys in medicine stems from its promising effects in trauma treatment (endoprothesis, implants and stability plates etc) and use as parts in equipment and surgical tools. They offer several excellent properties, for example, a good corrosion resistance, high strength to weight ratio and high biocompatibility.
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 enhances wear and friction properties. Thermochemical modification of titanium alloys involving the introduction of carbon, oxygen, nitrogen and other interstitial elements in titanium via a gaseous medium have long been investigated. It produces a hard case, of depths up to 100-200 µm. The treatment studied in this paper is the nitrogen diffusion hardening of Ti6Al4V. The nitrogen diffuses into the titanium, producing an enriched α-case of 20-200 µm width and a layer of nitrides, especially Ti_2N (ε-nitride). Surface hardness and wear properties of the obtained surface layer are greatly improved (1).
Among different surface treatments, nitrogen gaseous diffusion has been shown to improve the wear resistance of Ti6Al4V. By means of this thermochemical process it is possible to obtain a thick and dense nitride layer (1-5 micrometers) on the surface and below this compound layer, a hardened substrate structure (diffusion layer) characterized by a gradually decreasing hardness. The thickness of the modified surface layers is a function of the temperature and the duration of the nitriding treatment. Despite these promising results, it is neces-

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sary to study the fatigue behaviour of thermochemically nitrided Ti6Al4V before its use in biomedical applications.

MATERIALS AND METHODS

The material used in this study was supplied as rods of Ti6Al4V alloy, with a mill-annealed microstructure and an ASTM E112 grain size of 11.8 µm. Both the chemical composition and the microstructure comply with ASTM F136 standard for Ti6Al4V alloy application in surgical implants. Figure 1 shows the mill-annealed microstructure. The material was machined following the ASTM standard E606 to obtain normalized test specimens. Due to the significance of surface finishing on fatigue behaviour, the test specimens were polished with SiC (up to 1200 grit) and aqueous alumina suspension (up to 0.05 µm) until the measure of the surface roughness parameter R_a was under 0.05 µm. Once polished, the samples were cleaned in an ultrasound bath, first, with acetone for 20 minutes, and secondly with isopropilic alcohol for 10 minutes.
When the test specimens were clean, they were thermochemically nitrided at 850 and 900 °C for 1 and 4 hours at each temperature. A batch of non-treated samples and other samples treated in an argon atmosphere at 900 °C for 1 hour were studied at cyclic deformation. Each batch consisted of seven samples and, consequently, 28 fatigue samples were studied. The tests were conducted in a tubular furnace, with an alumina tube, capable of reaching a temperature of 1300 °C. In order to obtain a nitrogen atmosphere, a high-purity nitrogen cylinder was connected to the alumina tube, and the tube was kept closed during tests. An outline is shown in Figure 2. The samples are left to cool down in the furnace after treatment (2, 3).
Strain-controlled fatigue tests were made in an Instron 8500 servohydraulic-testing machine with a 100KN load cell and a coupled extensometer. Tests were conducted with deformation amplitudes of $\pm 5\cdot 10^{-3}$, $\pm 6\cdot 10^{-3}$ and $\pm 7\cdot 10^{-3}$, a ratio R_a = -1 and a load frequency of 0.5-3 Hz. These values were obtained from previous studies in order to assure low cycle fatigue behaviour (2, 4). Both sample fixations allowed for lateral movement during test preparation ensuring for correct alignment. All the tests were conducted in air at room temperature (24 °C).

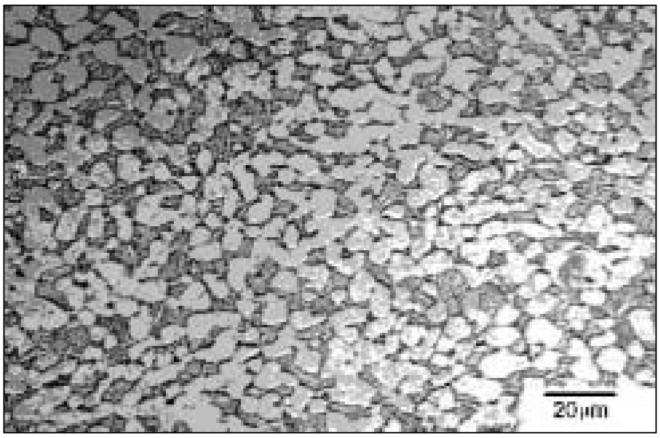

Fig. 1 - *Ti6Al4V mill-annealed microstructure.*

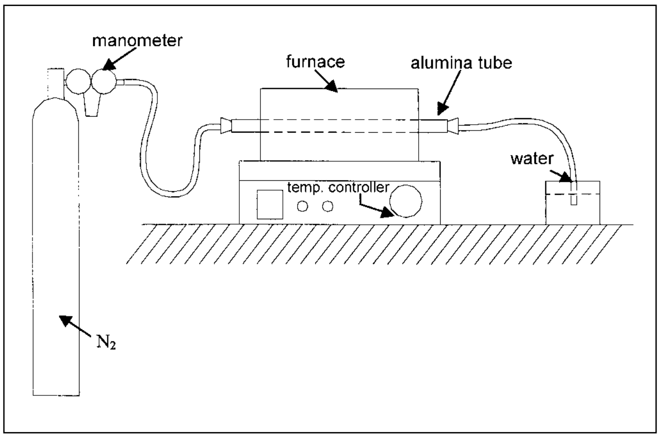

Fig. 2 - *Scheme of the furnace used.*

TABLE I - CYCLES TO FAILURE OF SAMPLES TESTED TO LOW CYCLE FATIGUE

Load (kN)	σ_{norm}[1]	$\Delta\varepsilon/2$	**Cycles ± σ (n = 3)** NT	**900 °C 1h Ar**	**850 °C 1h**	**850 °C 4h**	**900 °C 1h**	**900 °C 4h**
11.8	0.926	$\pm 5\cdot 10^{-3}$	69229 ± 5115	19204 ± 1989	12423 ± 2132	8841 ± 1.526	10702 ± 1374	5383 ± 636
14.9	1.169	$\pm 6\cdot 10^{-3}$	11128 ± 435	1950 ± 421	3313 ± 549	1511 ± 385	3026 ± 522	1178 ± 257
16.7	1.311	$\pm 7\cdot 10^{-3}$	5033 ± 550	156 ± 47	207 ± 55	138 ± 37	191 ± 57	102 ± 29

[1] Monotonic yield stress in air: 649 MPa (2)

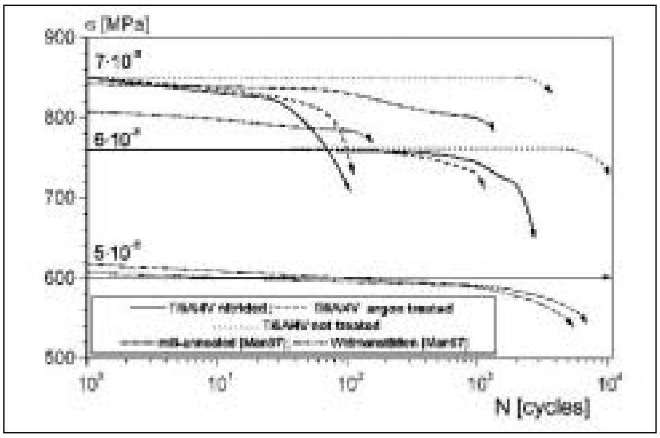

Fig. 3 - ***Cyclic softening curves for the sample Ti64-900-1 and samples of Ti6Al4V with mill-annealed and Widmanstätten structures.***

Fig. 4 - ***α-grains with α-Widmanstätten plates microstructure.***

RESULTS

The data obtained from the fatigue tests (Tab. I) show a low cycle fatigue behaviour for tests carried out with deformation amplitudes of $\pm 6 \cdot 10^{-3}$ and $\pm 7 \cdot 10^{-3}$, whilst tests conducted with an amplitude control of $\pm 5 \cdot 10^{-3}$ show a longer fatigue life. Differences between nitrided and non-treated samples are also evident. A comparison of the tests also indicate a softening effect in the specimens tested with strains over $\pm 5 \cdot 10^{-3}$. Figure 3 shows a comparison of cyclic softening of non-treated Ti6Al4V and nitrided samples tested at 900 °C for 1 hour at different strain values compared to data from (2). In the Ti6Al4V microstructures differences can be observed, in the non-treated samples. The microstructure is mill-annelaed as in Figure 1 and when the samples are treated at 850 or 900 °C a partial growth of α-Widmanstätten colonies is formed. This microstructure can be observed in Figure 4.
Cyclic softening is observed in all cases when the different microstructures are cyclically deformed at the different total strain amplitudes. Figure 3 shows the cyclic softening curves for the materials at the different total strain amplitudes, where the maximum stress has been plotted against the number of cycles. It should be noted that the for the "mill-annealed" microstructure (as supplied) softening occurred from the first cycle, whilst for the partial Widmanstätten samples hardening takes place during the first two to five cycles, which was followed by subsequent softening until fracture.
It should also be noted that the proportional limit is much lower than the yield stress for the Widmanstätten microstructures. The proportional limit has been measured by means of an extensometer with a sensibility of 10^{-5} per mV. The Widmanstätten microstructures exhibit proportional limits (≈ 570 MPa) and they yield macroscopically at 0.2% at stress from 820- 860 MPa for Widmanstätten. Therefore, irreversible plastic deformation is occurring between the proportional limit and the yield stress. In fact, plastic deformation starts to occur at much lower stresses than for the "mill-annealed" material.
The cyclic softening increases as the total strain amplitude increases and the highest rate of softening was observed for the martensitic microstructure.
Although the behaviour of the nitrided samples is similar to the non-nitrided samples, fractography shows clear differences between them in the external layer. The nitrided layer suffers brittle transgranular fracture propagation, whilst the non-treated samples show a usual fatigue crack propagation. Non-nitrided and argon-treated samples exhibit, for all the strain range studied, a fatigue starting point in the border of the samples, usually from a machining surface defect. The nucleated crack grows with load cycling. However, nitrided samples show a different fractography. A transgranular brittle fracture appears in the outer layer of the sample (50 µm), which corresponds to the nitrided layer. A transition to common fatigue mechanism is observed (Fig. 5a) and the crack progresses until a ductile fracture appears. The brittle fracture of the nitrided layer can be observed (Fig. 5b).
The fatigue crack in the mill-annelaed titanium formed within a grain on the surface (Fig. 6). A featureless facet of one grain size inclined at 45° was found at the initial crack site on the fractured surface. The above data shows that the fatigue cracks form through an ordinary stage-1 growth caused by irreversible slip within a grain. On the other hand, the initial crack of the nitrided titanium formed in

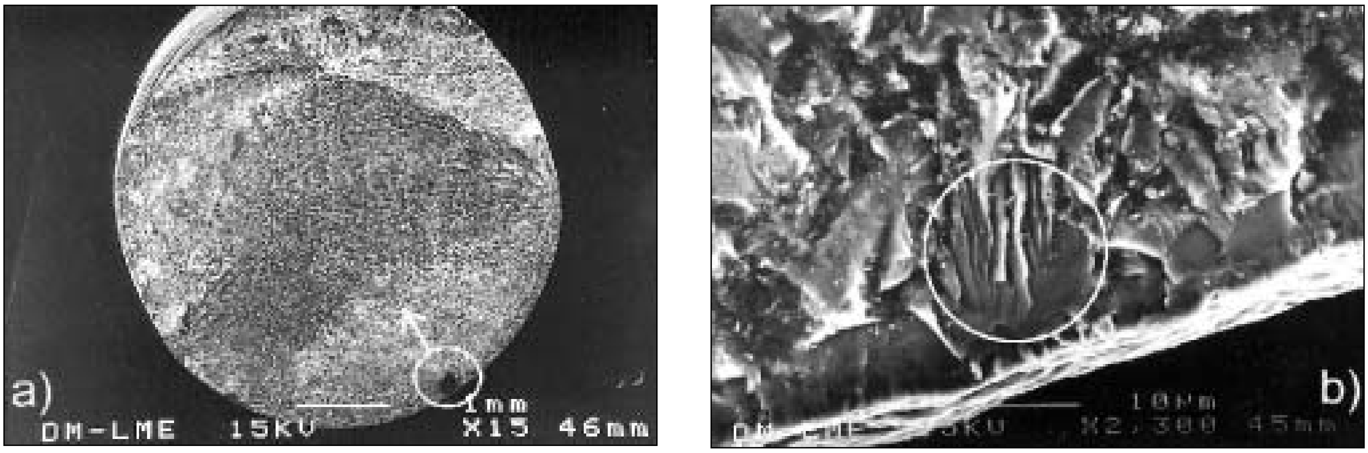

Fig. 5 - ***a) General view and b) detail of the fractography of the sample Ti6Al4V treated at 900 °C for 1 hour tested with a deformation of $\pm 5 \times 10^{3}$. b) transgranular brittle fracture of the nitrided layer.***

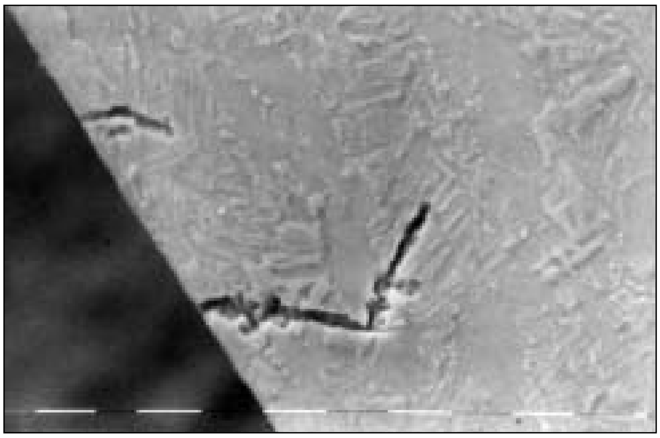

Fig. 6 - ***Crack nucleation in the mill-annealed microstructure.***

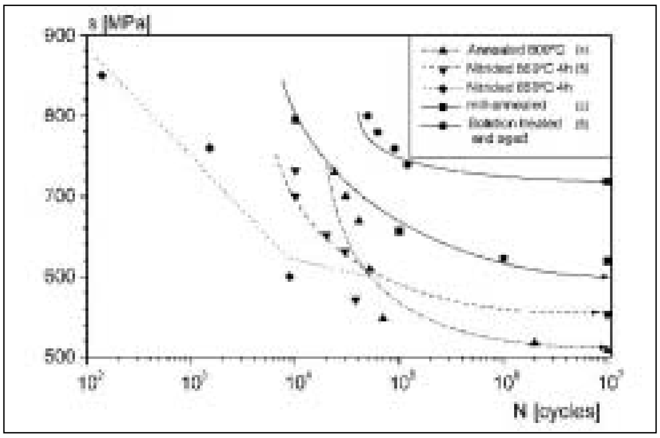

Fig. 7 - ***Comparison of fatigue behaviour results.***

the compound layer. When the surface of the fracture was examined, with attention focused on the crack site, a facet exhibiting brittle features with "river-like" lines was found just under the compound layer. These findings indicate that a sharp crack formed in the compound layer induces a brittle fracture of the entire case. The brittle fracture of the compound layer limits the fatigue strength of the nitrided titanium.

There is a contradiction in that the fatigue strength of the nitrided titanium does not improve in spite of the compressive residual stress. The stress concentration caused by the misfit of Young's moduli may be a cause. Since Young's modulus of the compound layer (E_{layer}= 426 GPa) is higher than that of the substrate (E= 100GPa) the magnitude of the real stress generated in that layer is E_{layer}/E = 4.3 times. This stress concentration is the most likely reason why the effect of the compressive residual stress is cancelled.

DISCUSSION

The low cycle fatigue data obtained were compared to existing S-N curves for Ti6Al4V (2, 5) in Figure 4 and some interesting characteristics appeared. Low cycle fatigue resistance of nitrided Ti6Al4V is reduced when compared to samples of Ti6Al4V that were not treated, but it is similar to the values presented by Ti6Al4V treated in a vacuum, and it is even better for fatigue over 10^5 cycles. This result could be due to the change of microstructure from mill-annealed to Widmanstätten. The effects of the nitrided layer could be positive, as the residual stress in the sample surface could slow down crack nucleation. A better explanation is the important difference of Young's modulus between Ti6Al4V (100 GPa) and titanium nitrides (300-400 GPa) (5). When high strains are imposed in a nitrided sample the nitrided layer cannot follow the strain because of its brittleness, and a crack nucleates and grows in

this layer. When the imposed strains are lower, the nitrided layer withstands the strain. In this case, the compressive forces of the layer prevent crack nucleation on the surface, improving the fatigue resistance of the nitrided sample.
A comparison of the nitrided sample results with fatigue tests of solution treated and aged (STA) sample results (5) shown in Figure 7, exhibits a clear disadvantage for the nitrided samples, because STA treatment offers increased improvements in fatigue life for the Ti6Al4V alloy (4).
It is important to note that methods exist in order to improve Ti6Al4V fatigue life. The formation of more suitable microstructures (STA-like) by means of heat treatment after the nitriding process could prove interesting, as it could combine the best properties of both treatments.
Another method for improving fatigue life is the application of a “shot peening” treatment (1, 6). This treatment produces beneficial improvements in fatigue life, but it also increases surface roughness. However, the effect on the nitrided layer should be studied.
The beneficial properties of the nitrided Ti6Al4V, combined with its excellent resistance to corrosion in saline medium (7) allows us to consider some applications of nitrided Ti6Al4V alloy as a biomaterial, mainly for the use in prostheses and dental implants, in order to improve wear resistance without a significant reduction of other properties.

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