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PROPERTIES OF PURE TITANIUM AND ULTRA FINE GRAINED TITANIUM

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Preliminary Note – Prethodno priopćenje

The properties of ultra fine grained nano Titanium made by ECAP technology and pure cold drawn Titanium are analyzed in this contribution. Mechanical properties, resistance to wear by a ZrO_2 ball friction test, corrosion in a Hank solution by the Tafel's method at temperatures 21 °C and 37 °C, and fatigue properties in torsion were evaluated and compared. The fatigue fracture started with crack formation parallel to the specimen axis and it was finalized by cracking in the angle of maximum shear stress. Titanium powder has been observed on the sample surfaces which indicated the crack initiation. Nano structure Titanium showed higher resistance to corrosion less wear by friction, and to a limited number of cycles higher fatigue strength.

Key words: fatigue in torsion, biocompatibility, nano Titanium, resistance to corrosion, wear

Svojstva čistog titana i ultra fino zrnatog titana. Članak analizira svojstva ultrafino zrnatog nanotitana ECAP tehnologijom i čistog, hladnim vučenjem. Izučavana su i uspoređivana mehanička svojstva, otpor habanja sa pokusom trenja kuglicama ZrO_2, korozija u Hank otopini sa Tafel' metodom na temperaturama 21 °C i 37 °C, te svojstva zamora torzijom. Zamorni prijelom je započinjao sa obrazovanjem pukotine, usporedno sa osi uzorka i finalizirana je pucanjem pod kutom maksimalnih smicajnih naprezanja. Titanin prašak je zapažen na površini uzorka koji označava inicijalnu pukotinu. Nanostrukturni titan pokazuje visoku korozijsku otpornost, otpornost na habanje te povećani broj opterećenja na čvrstoću zamaranjem.

Ključne riječi: zamor torzijom, bioprihvatljiv, nanotitan, otpornost koroziji, habanje

INTRODUCTION

Medical applications are a new field for Titanium known for its high biocompatibility in living bodies. In some cases the medical replacements should be very small in size, bearing high loads. That is why, new technologies are sought to improve the load carrying capacity of used materials. Pure Titanium 99,9 % is a preferred material for medical application. The actual life span of the applied materials depends first on the correct loading, strain, environment, and adverse effects assessment in the design.

Materials with high mechanical properties are preferred with low Young's modulus not exceeding 100 GPa. This time the solid nano structure Titanium (nTi) with the ultra fine grained structure is tested for applications in dental implants. The ultra fine grain means material with grain size from 1 to 100 nm.

As testing showed, proteins can adhere to nTi more than 30 % more than can to common Titanium of the same [1]. In the field of implants there are very strict rules prescribing the safe, nontoxic quality of the used material. All other properties of the used material which can be important during service life in the human body should be inspected. Corrosion resistance is one of them.

Fragments released by corrosion can be harmful or toxic [2,3]. The human body is self-controlled to keep the acidity around pH 7,4 and all the degradations are processed at body temperature 37 °C. Good electric conductivity is secured by the high content of dissolved salts in the fluids of the human body, supporting the electro chemical mechanism of corrosion and hydrolysis.

The tested material showed excellent resistance to corrosion. It can last for supposed service life in the human body, without harm. The biocompatibility and corrosion resistance of Titanium is achieved by natural passive TiO_2 films 2 to 6 nm thick formed in the surface of Titanium [1,2,4-6].

There are a few works reported only dealing with the micro structure and the properties of nano Titanium made by severe plastic deformation during angular extrusion. The technology is known as Equal Channel Angular Pressing (ECAP). Common static mechanical properties test results of pure commercial Titanium are compared to the results of Titanium after severe plastic deformation in works [1,7]. As mentioned the wide range application of Titanium is calling for a better knowledge of the fatigue properties, too. Fatigue test results in tension are in works [8-10].

The aim of this contribution is to update the information about fatigue properties in torsion, compare the cor-

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rosion properties of nano Titanium and commercial pure Titanium (cp Ti) and test the tribology in their surfaces.

MATERIAL AND EXPERIMENTAL METHODS

Nano structure Titanium nTi was used for the experiments prepared by the ECAP technology. Rods were produced Ø 7,56 mm in diameter. For comparison commercial pure Titanium was used delivered as cold drawn rods Ø 9,96 mm purified by zonal refinement. Metallographic images of polished samples and foils were studied by electron microscopy.

Sub micro structures were studied by the method of thin foils in a transition electron microscope (TEM) JEOL JEM 2000 FX with acceleration voltage 200 kV. The thin foils were prepared by electrolyte thinning in a stream of $HClO_4$: methanol alcohol: butyl alcohol = 6:59:35 at 11 V.

Resistance to corrosion was tested by immersion in the Hank solution (simulated body fluid SBF) using the Tafel's evaluation method [11] of polarization curves at two temperatures 21 °C and 37 °C. The common 3 electrode circuit was used with the main electrode (Ti sample), with the saturated calomel electrode (SCE) and a Platinum keep alive electrode, all connected to a Potentiostat VOLTALAB 21 controlled by a PC. The electro chemical characteristics were evaluated using VOLTAMASTER 4.0 software. The main electrode working surface was 0,7 cm^2 exposed to the Hank solution.

Tribology by a ball tester was tested at the following conditions:

- ZrO_2 ball, diameter 6 mm, dry surfaces, speed 10 cm/s, runway radius 2 mm, distance 50 m, load 1 N and 2N.

Fatigue properties were tested by cyclic loading in torsion using the PWOG tester from Carl Schenck. The used asymmetry rate was R= -1 and the loading frequency was 35 Hz. Test pieces for fatigue tests were machined to shape shown in Figure 1.

RESULTS AND DISCUSSION

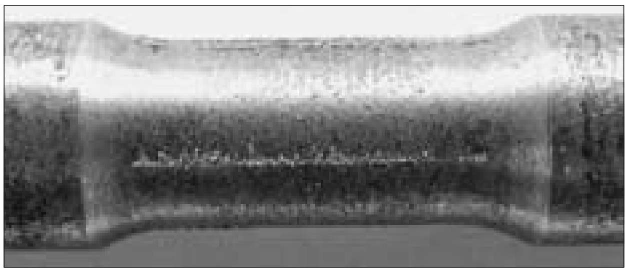

Figure 1 Fatigue test sample with logitudinal surface crack covered by Titanium powder

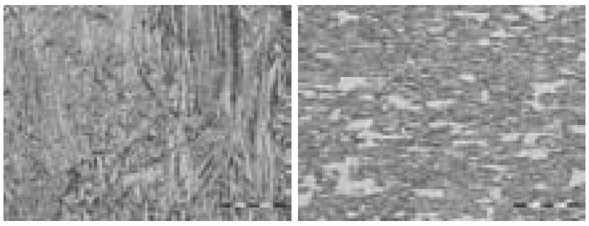

Figure 2 Micro structure of nTi and cpTi

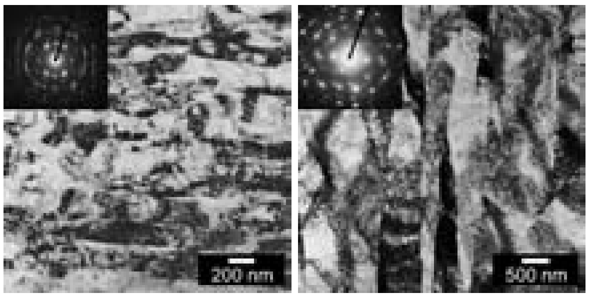

Figure 3 Sub micro structure of nTi and cpTi

Micro structures in the longitudinal direction shown [11] by scanning electron microscope (SEM) are in Figure 2. The nano structure of nTi (a) is finer and more homogeneous than the micro structure of cp Ti (b).

The sub micro structure for both tested materials is documented in Figure 3a,b.

The cpTi material was before drawing purified by zonal refining. During purification elongated needle like grains were formed with typical signs of the Widmanstätten morphology. The dislocation density in the matrix was increased by cold work after the refinement, but not to the extent of forming cellular sub micro structure. There were in some grains areas with a different diffraction contrast, characteristic for different angles of the crystalline lattice a sign of a start to build cellular sub micro structure.

Diffraction spectra made on cp Ti showed the alignment of the sub micro structure, again a sign of some start to build cellular sub micro structure. The cp Ti material had a coarse Widmanstätten grain morphology, no signs of cellular sub micro structure and this way higher ductility and lower strength properties. On the other hand sever plastic deformation and strengthening of the nTi sub micro structure, along with the high dislocation density in the ultra fine micro structure resulted decrease of ductility and a significant increase of yield point and ultimate tensile strength.

The resistance to corrosion was evaluated by differences in the potentials for the tested materials or micro structures in the SBF solution at two vital temperatures and they are listed in Table 1. To improve the possibility of comparison, to the corrosion resistance data in Table 1 data for Ti_6Al_4V were added. The last one is a material most frequently used for implants in medicine nowadays.

Sever plastic deformation by ECAP formed high density of grain boundaries in nTi. This led to the increase of passive film adhesion by penetration of pro-

Table 1 **Corrosion potentials in simulated body fluid (SBF)**

Material	E /mV	
	21 °C	37 °C
Ti_6Al_4V	-403	-434
cpTi	-283	-294
nTi	-94	-213

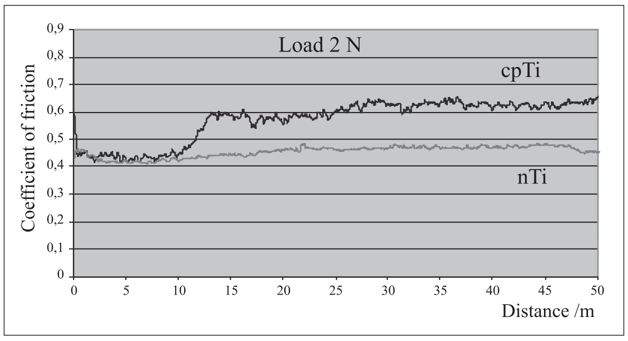

Figure 4 Coefficient of friction for nTi and cpTi

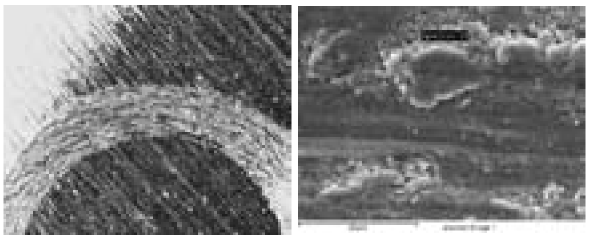

Figure 5 Wear track and the track damage mechanism in more detail

truding oxide parts into the grain boundaries [3,12]. At the human body temperature 37 °C the behavior of the Titanium materials changed. The order of nobility did not change, but there was a more negative voltage for nTi than it was at room temperature 21 °C. Also, the protective character of the passive films is significantly lower for cp Ti and nTi materials at the human body temperature.

The resistance to wear is an important characteristic for implants. Coefficients of friction were calculated from the results of the ZrO_2 ball rolling at two load levels. Comparison of wear results at the load of 2N for the tested materials on 50 m distance is in Figure 4. In Figure 5 is documented the track of wear. In more detail it is described in [13].

Track profiles were measured after wear tests. The lost material volumes were calculated in dependence on the unity distance and unity load and they can be found in Table 2.

Static tensile testing was used to evaluate the mechanical properties. The results are in Table 3 and show the improvement of strength by the ECAP technology.

The fatigue test results in torsion are in dependence of stress on the number of cycles to fracture in Figure 6.

Table 2 **Wear rate**

Load /N	Wear rate / $mm^3.m^{-1}.N^{-1}$	
	cpTi	nTi
1	1,148 x 10^{-3}	0,892 x 10^{-3}
2	0,896 x 10^{-3}	0,584 x 10^{-3}

Table 3 **Mechanical properties**

Material	$Rp_{0,2}$ / MPa	R_m /MPa	A_5 /%	Z %	HV
nTi	1290	1310	10	51	327
cpTi	645	665	17	66,5	210

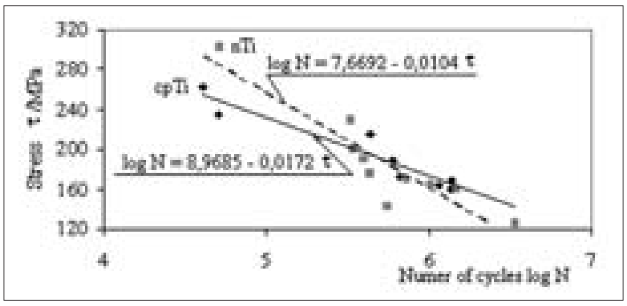

Figure 6 Wöhler curves for cp Ti and nTi in torsion

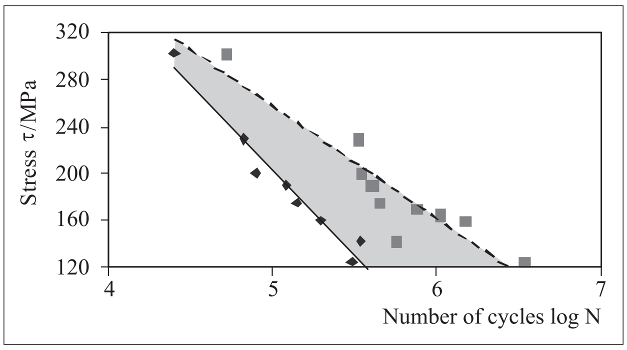

Figure 7 Wöhler curve for nTi in torsion

The crack initiation was monitored at fatigue test of Titanium with nano structure. It became evident by the appearance of Ti powder on the surface of the tested sample (as can be seen in Figure 1). The fatigue process products on the test piece surface are the remnants of repeated extrusions. With a small delay it is the time of crack initiation and it is marked with green marks in Figure 7. On a few samples multiple initiation areas were observed around the sample stem. The cracks grew with the number of cycles in the longitudinal direction. The cracked sample is in Figure 8.

After crack propagation in longitudinal direction the failure ended with final cracks angled 45° to the axis of the sample.

The semi logaritmic plots of points at different stess levels τ in torsion defined by the number of cycles to fracture log N were plotted and a straight line across the points was calculated by the method of mean squares. The parametric equations of the lines for nTi and cpTi are in Figure 6.

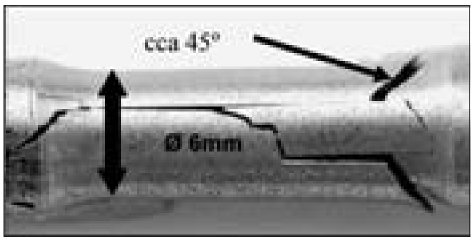

Figure 8 Longitudinal cracks, final fracture in 45° in the sample of nTi

CONCLUSION

From the results obtained by testing samples of pure Titanium with nano structure nTi and commercial pure Titanium cpTi the following can be concluded:

– Pure nTi prepared by ECAP technology has an ultra fine microstructure with high dislocation density and a low occurrence of preferred sub structure orientation.

– In pure cpTi micro structure the Widmanstätten morphology of grains was found with signs of a start to build cellular sub micro structure.

– Polarization curves both 21 °C and 37 °C showed higher nobility of nTi when compared to cp Ti.

– The protective character of the passive films of nTi was 5 times more efficient than that for cpTi materials at room temperature.

– At 37 °C was the protective character of the passive films about equal, though for both materials decreased, compared to 21 °C

– Wear at friction was for nTi about 35 % lower than that of cpTi.

– Nano Titanium made by ECAP had about 2 times higher strength properties, at the decrease of ductility from 18 % to 10 %.

– Nano structure Titanium showed to a limited number of cycles $5{,}7 \cdot 10^5$ higher fatigue strength, over this number of cycles it was lower

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