Materials Science Forum Vols. 584-586 (2008) pp 49-54
online at http://www.scientific.net

Online available since 2008/Jun/17

Nanostructured SPD Processed Titanium for Medical Implants

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Keywords: nanotitanium, fatigue properties, severe plastic deformation, biological tests, implants.

Abstract
Nanostructured titanium (nTi) with essential enhanced strength and fatigue characteristics is an advanced material for dental implant applications. Nano Ti is commercially pure titanium, that was nanostructured by a special technique of severe plastic deformation. It is bio inert, does not contain even potentially toxic or allergenetic additives and has significantly higher specific strength properties than any other titanium applied in dental implants. Cylindrical threaded screw implants Nanoimplant® sized 2.4 mm in diameter and 12 mm in length were made from nTi. It is the first application of nTi dental implant in the world reported. Recently more than 250 successful clinical applications dealing with surgery on the front teeth were carried out. No complications were noticed during the early postoperative period and early loading. Laboratory cytocompatibility tests undertaken so far on mice fibroblast cells have indicated that nanocrystalline Ti surface has a significantly better property for cell colonisation and healing of tissue consequently.

Introduction

Metallic materials, for example, stainless steel, titanium and its alloys, and tantalum are widely used for medical implants in trauma surgery, orthopaedic and oral medicine. Successful incorporation of these materials for design, fabrication and application of medical devices require that they meet several critical criteria. Paramount is their biocompatibility as expressed by their relative reactivity with human tissues. Another is their ability to provide sufficient mechanical strength, especially under cyclic loading conditions to ensure the durability of the medical devices made therefrom. Finally, the material should be machinable and formable, thereby, enabling device fabrication at an affordable cost.

Numerous clinical studies of medical devices fabricated from commercial purity (CP) titanium for trauma, orthopaedic and oral medicine have proven its excellent biocompatibility [1]. However, the mechanical strength of CP titanium is quite low; therefore, successful adaptation of this material for biomedical devices requires its hardening by either alloying or secondary processing, for example rolling, drawing, etc. These enhancements in mechanical performance normally, however, come with some degradation in biometric response. Recently it has been shown that nanostructuring of CP titanium by SPD processing can provide a new and promising alternative method for improving the mechanical properties of this material [2-6]. This approach also has the benefit of enhancing the biological response of the CP titanium surface [7].

This paper reports the results of the first developments and studies of nanostructured titanium (n-Ti) produced as long-sized rods with superior mechanical and biomedical properties, and demonstrates its applicability for dental implants. Here we also show that nanostructured commercial purity titanium produced by severe plastic deformation (SPD) opens new avenues and concepts for medical implants providing benefits in all areas of medical device technology.

Experimental

The effort was conducted using commercially pure Grade 4 titanium [C – 0.052%, O_2 – 0.34%, Fe – 0.3%, N – 0.015%, Ti-bal. (wt. pct.)]. Nanostructuring involved SPD processing by equal-channel angular pressing (ECAP) followed by thermo-mechanical treatment (TMT) [8] producing 7 mm diameter bars with a 3 m length, Fig. 1.

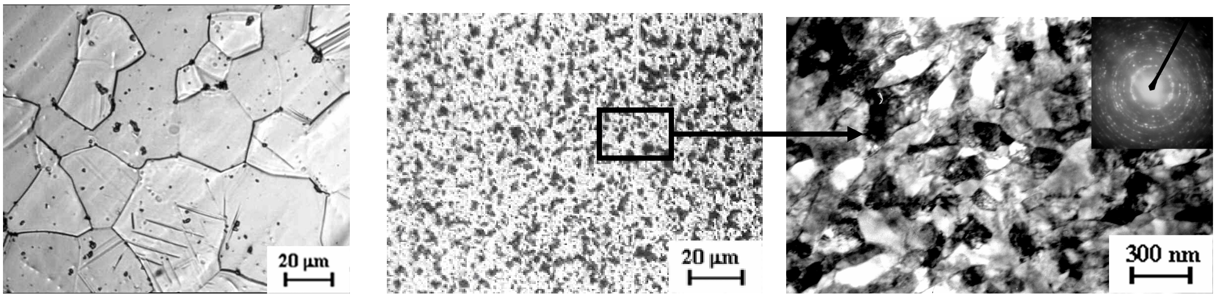
Fig. 1. CP 4 titanium rods after SPD processing

The rod production process comprised a few stages. As received the billets were subjected to ECAP by the following mode: the billet was punched in a special equipment through two intersecting channels of equal cross-sectional area lying at the angle 90° to each other. The deformation was conducted at a temperature of 450°C. The billet was rotated about the longitudinal axis by 90° (route B_c) after each pass, the number of passes 4. The obtained billets were further subjected to forge stretching and drawing with cumulative deformation equal to 80% and finally annealed at 300-350^{0}C.

The billets microstructure analysis was conducted by the methods of scanning and transmission electron microscopy. For stretching tests standard billets notched out of the rod central part in long axis direction were used 3 mm in working part diameter and 15 mm in gauge length (GOST 1498-84). More than three billets were tested for each condition. Tensile tests were conducted on an Instron tensile machine with the loading speed 1mm/min.

Results

The SPD processing procedure resulted in a major reduction in grain size, the initial titanium rods having 25 μm equiaxed grain structure which was reduced to 150 nm after combined SPD and TMT processing, as shown in Fig. 2. The selected area electron diffraction pattern (Fig. 2c) further suggests that the ultra fine grains contained predominantly high-angle grain boundaries with non-equilibrium distorted structure leading to their excess energy [9].



a) b) c)

Fig. 2. Optical and transmission electron microscopy illustrating microstructure of CP Grade 4 titanium: (a) Conventional;(b,c) ECAP + TMT.

A similar structure for CP Ti can be produced in small discs using other SPD methods, for example – high pressure torsion (HPT) as studied in detail [6]. In the present work it was essential to produce homogeneous ultrafine-grained structure throughout a three-meter length rod to enable the production of pilot implants and provide sufficient material for thorough mechanical and bio-medical tests of nanostructured titanium.

Table 1 illustrates mechanical property benefits attainable by nanostructuring CP titanium, for example, the strength of the nanostructured titanium has almost doubled vis-a-vis conventionally processed CP titanium. Notably this improvement has been achieved without the drastic ductility reductions normally seen after rolling or drawing.

Table 1. Mechanical properties of conventionally processed and nanostructured CP Grade 4 titanium.

State	Processing/treatment conditions	UTS, MPa	YS, MPa	Elongation, %	Reduction in Area, %
1	Conventional Ti Warm rolled	700	530	25	52
2	nTi ECAP + TMT	1240	1200	12	42

Further room temperature, laboratory air fatigue studies of nanostructured and conventional CP titanium were performed according to ASTM E 466-96 at R ($\sigma_{min}/\sigma_{max}$) = 0.1 and 20 Hz . Fig. 3 shows that the fatigue strength of nanostructured CP titanium at 10^6 cycles is almost 80% higher than conventionally processed CP titanium and approaches that of the Ti-6Al-4V alloy [10].

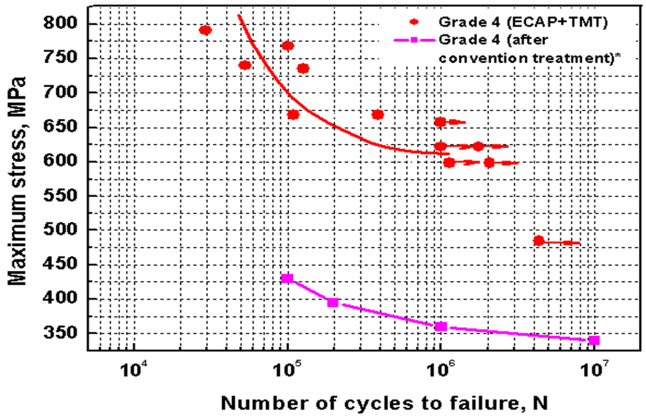


Fig. 3. Results of room temperature, laboratory air (R=0.1 at 20 Hz) fatigue study for conventional and nanostructured CP Grade 4 titanium.

Cytocompatibility tests utilizing fibroblast mice cells L929 were undertaken to verify the previously reported benefits of nanostructured CP titanium vis-a-vis conventionally processed coarse-grained CP Ti. The recent research proved that titanium nanostructuring changes the morphology and composition of oxide film [12, 13], which significantly increases protein interaction and the following cytoadherence, improving, in its turn, nanostructured titanium osteointegration parameters. This study was performed as described elsewhere [11], with hydrofluoric acid surface etching being performed prior to cell exposure. Fig. 4 shows the etched conventionally processed and nanostructured titanium surfaces, respectively. The differences in surface roughness of these materials are easily seen, a homogeneous and nanometer-sized roughness being apparent for nanostructured titanium vis-a-vis a much coarser structure for conventionally processed CP Grade 4 titanium.

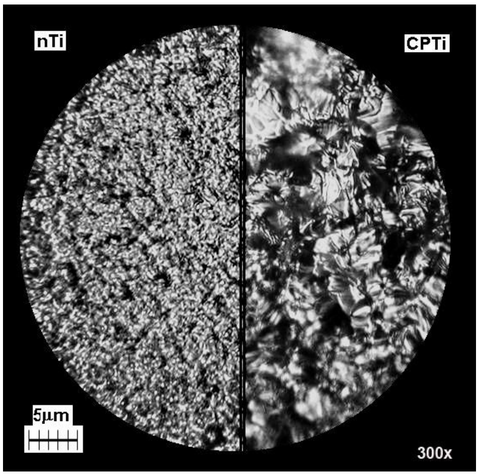


Fig. 4. Surface relief after hydrofluoric acid treatment of nanostructured (left) and conventionally processed (right) CP Grade 4 titanium (right) surfaces.

The cell investigation shows that fibroblast colonization of the CP Grade 4 titanium surface dramatically increases after nanostructuring, Fig. 5. For example, the surface cell occupation for conventional CP Ti was 53.0% after 72 hours in contrast to 87.2% for nanostructured CP Grade 4. The latter observations also confirm the previous study [7], cell-adhesion on nanostructured titanium being greater than on conventionally processed CP Grade 4 titanium and suggest that a high osteointegration rate should be expected with nanostructured CP Grade 4 titanium when compared to conventionally processed material.

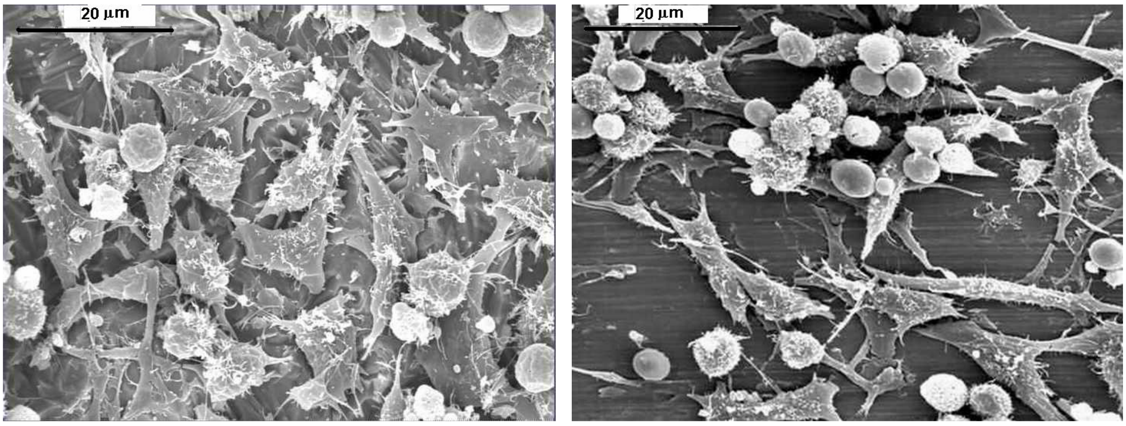


Fig. 5. Occupation of the mice fibroblast cells L929 after 24 hours;
Nanostructured (left) and conventionally processed (right) CP Grade 4 titanium.

The objective of this effort was also to design, fabricate and implant a nanostructured CP Grade 4 dental post to clinically demonstrate the benefits associated with nanostructuring outlined previously. This resulted in fabrication of a reduced diameter implant, or Nanoimplant®. This implant sustains the same load as a conventional 3.5 mm diameter titanium implant, the former having the added capability of being used as a pillar in cases of insufficient thickness of the alveolar bone.

The certified system of Timplant® manufactured according to standard EN ISO 13485:2003 was used during development of the Nanoimplant® implant. The implants shown in Fig. 6a are the intraosseal nanoimplants 2.4 mm in diameter. The strength characteristics of these implants are equivalent to the conventional of 3.5 mm diameter implant (Fig. 6b).

a

b

Fig. 6. 2.4 mm diameter Nanoimplant® (a); 3.5 mm diameter Timplant® (b).

To date, over 250 Nanoimplants® have been implanted, most of them as immediate load implants, with all results indicating the excellent primary stability of Nanoimplants® when compared to other implant types [http://www.timplant.cz/e_stomatolog.asp]. For example, a 55-year-old male with edentulous mandible and maxilla was treated by insertion of conical implants laterally and Nanoimplants® in the narrow anterior part. Primary retention of all implants was very good; on the day of surgery the patient received a complete provisional bridge. Post-operation healing at the surgery site occurred without complications, with subsequent attachment of a definitive metalloceramic bridge completing the treatment.

Conclusions

Thus, nanostructuring of titanium by SPD processing leads to a material with significantly superior mechanical performance when compared to conventionally processed CP Grade 4 titanium. Furthermore cytocompatibility studies with fibroblast mice cells L929 have indicated that the nanostructured Ti surface has significantly higher cell colonization, suggesting more rapid osseointegration.

Nanostructured (Nanoimplants®) implants have been successfully designed, and fabricated. Clinical trials with over 250 patients, most of them receiving immediate load implants, have shown no adverse effects, preliminary results being extremely encouraging. Further clinical studies are presently underway with an enlarged, 1000 patients, population.

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