MECHANICAL BEHAVIOUR AND MICROSTRUCTURE EVOLUTION OF SEVERELY DEFORMED TITANIUM

[1]Miroslav GREGER, [2]Ladislav KANDER

[1]*VSB-Technical University of Ostrava, Czech Republic, EU,* *miroslav.greger@vsb.cz*

[2]*Material and Metallurgical Research Ltd, Ostrava*, Czech Republic, *EU,* *ladislav.kander@mmvyzkum.cz*

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Abstract

In this paper the scientific basics for the production of ultra-fine grained titanium using the technology of Equal Channel Angular Pressing (ECAP) deformation to manufacture medical implants for their wide use in trauma treatment and dentistry are presented. Special attention is paid to the physics and mechanics of methods of ECAP deformation leading to the formation of ultra-fine grained structures in titanium. The influence of fine grained on the mechanical and biomedical properties of titanium is studied, and the advantages of applying ultra-fine grained titanium for medical implants are considered in detail.

Keywords: Submicrocrystalline structure, equal channel angular pressing, structure and properties, titanium

1. INTRODUCTION

It is required that a material for dental implants is bio compatible, it must not be toxic and it may not cause allergic reactions. It must have high ultimate strength R_m and yield value R_p at low density ρ and low modulus of elasticity E. Metallic materials used for dental implants comprise alloys of stainless steels, cobalt alloys, titanium (coarse-grained) and titanium alloys. Semi-products in the form of coarse-grained Ti or Ti alloys are used as bio-material for medical and dental implants since the second half of the sixties of the last century. Titanium is at present preferred to stainless steels and cobalt alloys namely thanks to its excellent bio-compatibility. Together with high bio-compatibility of Ti its resistance to corrosion evaluated by polarization resistance varies around the value 10^3 R/Ωm. It therefore occupies a dominant position from this viewpoint among materials used for dental implants. In the past years a higher attention was paid also to titanium alloys due to requirements to higher strength properties. The reason was the fact that titanium alloys had higher strength properties in comparison with pure titanium. Typical representative of these alloys is duplex alloy (α a β) Ti-6Al-4V [1]. After application of dental implants made of these alloys toxicity of vanadium was confirmed. Aluminium, too, can be categorized among potentially toxic elements. During the following development of dental implants the efforts were concentrated on replacement of titanium alloys the toxic and potentially toxic elements by non-toxic elements. That's why new alloys of the type Ti-Ta, Ti-Mo, Ti-Nb and Ti-Zr began to be used [2,3]. Single phase β Ti alloys were developed at the same time, which are characterized by the low value of the modulus of elasticity [4]. Ti alloys with elements with very different density and melting temperature (Ti-Ta, Ti-Mo) require special technology of manufacture, by which they significantly increase production costs and price of semi-products for dental implants [5]. The problem at the development of metallic bio-materials consists not only in their real or potential toxicity, but also in their allergenic potential. Sensitivity of population to allergies keeps increasing. Allergies to metals is caused by metallic ions which are released from metals by body fluids. Share of individual metals on initiation of allergies is different. What concerns the alloying elements for dental implants special attention is paid namely to Ni and Co, as their allergenic effect varies around (13,5%) and Cr (9,5%). Some titanium alloys also contain the elements classified as allergens. These are e.g. the following alloys: Ti-13Cu-4,5Ni; Ti-20Pd-5Cr; Ti-20Cr-0,2Si. For these reasons commercial pure (cp) titanium still remains to be a preferred material for dental applications [6]. Development trend in case of this material is oriented on preservation of low value of the modulus of elasticity and on increase of mechanical properties, especially strength. According to the Hall-Petch relation it is possible to increase considerably strength properties of metals by grain refinement [6,7]. That's why it is appropriate to use for dental implants rather fine-grained Ti instead of coarse-grained Ti. Use of nano-materials concerns numerous fields including medicine. Bulk nano-structural metallic materials are used for dental applications. These are materials with the grain size smaller than approx. 100 to 300 nm [8,9]. High-purity titanium is used for dental implants. Chemical composition of cp Ti for dental implants must be within the following interval. The paper should begin with the introduction in which the present state of the issue relevant to the paper will be presented generally and concisely. It is necessary to quote references taking into consideration the remarks included in the section “References”. It is necessary to present the aim of the research included in the paper and clearly point out the originality of solutions and content-related approach to the issue worked out and described by authors [10].

2. STRUCTURE AND PROPERTIES OF PURE TITANIUM

Commercially pure titanium (cpTi) bars and sheets were used in this study. The average grain size of the as received cp Ti is ASTM no. 4. Tensile specimens with a gauge of 50 mm length, 10 mm width and 3,5 mm thickness were machined with the tensile axis oriented parallel to the final rolling direction [11,12]. The specimens were deformed at room temperature with different initial strain rates. After testing, the deformed specimens in order to preserve the microstructure **Figure 1.** Specimens were sectioned along the gauge and grip parts of the deformed sample. The samples were then polished etched using 10 % HF, 10 % HNO_3 and 80 % H_2O for 20 second. Chemical analysis and mechanical properties CP titanium are given in **Table 1-3**.

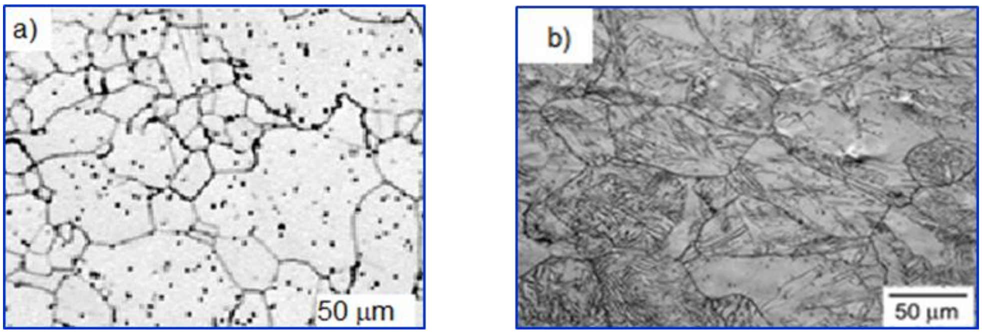

Figure 1 Microstructure of cp Ti: a) initial structure, b) after cold rolling

Table 1 Chemical analysis commercially pure titanium, (weight %)

N	**O**	**C**	**Fe**	**Al**	**Cr**	**Ti**
0.004	0.068	0.008	0.03	0.01	0.01	Rest.

Table 2 Tensile properties of cp Ti after annealing 649 °C/1 hour (ASTM E8)

R_m (MPa)	**$R_{p0,2}$ (MPa)**	**A (%)**	**Z (%)**
365	212	51	71

2.1. Properties of ultra-fine grain titanium

Ultra-fine grain titanium is characterized by exceptional mechanical properties, among which high ultimate strength and high yield value are of utmost importance. Strength properties of ultra-fine grain titanium must have the following values: $R_m > 1000$ MPa, $R_{p0,2} > 850$ MPa. Apart from the strength, another important properties of dental implants is their so called specific strength (strength related to density). Mechanical properties of metallic material for implants are evaluated in relation to its density as soalled specific properties.

Table 3 Initial hardness of commercially pure titanium and hardness after cold rolling

Label	Diagonal of indention *d* (μm)	HV30
Sample nr. 1 *(initial hardness)*	659	128
	632	139
	652	131
Sample nr. 2 *(initial hardness)*	658	128
	655	130
	658	128
Sample nr. 3 *(cold rolling)*	527	200
	525	202
	535	194

In case of classical coarse-grained titanium, the relation (R_m/ρ) varies around 70 to 120 (N·m/g), for the alloy Ti-6Al-4V it varies around 200 (N·m/g) [13,14], and for titanium it is possible to predict the values $R_m/\rho = 270$ (N·m/g). As a matter of interest, it is possible to give the specific strength also for some other dental materials:

- steel AISI 316L; $R_m/\rho = 65$ (N·m/g),
- cobalt alloys; $R_m/\rho = 160$ (N·m/g),
- βTi (Ti-15Mo-5Zr); $R_m/\rho = 180$ (N·m/g).

Disadvantage of dental implants based on steel or cobalt alloys is their high tensile modulus of elasticity: E = 200 to 240 GPa, while in case of titanium and its alloys this value varies between 80 and 120 GPa [15]. At present only few companies in the world manufacture commercially bulk nano-materials.

2.2. The technology for manufacture of ultra-fine grain titanium

The main objective of experiments was manufacture of ultra-fine grain Titanium, description and optimization of its properties from the viewpoint of their bio-compability, resistance to corrosion, strength and other mechanical properties from the viewpoint of its application in dental implants [16-18]. Chemical purity of semi products for titanium was ensured by technology of melting in vacuum and by zonal remelting. The obtained semi-product was under defined parameters of forming processed by the ECAP technology. The output was nano-structural titanium with strength about 1050 MPa). The obtained ultra-fine grain titanium was further processed by technology (of rotation forging) and drawing to the shape suitable for dental implants. Sequence of production of ultra-fine grain titanium is described in the **Table 4**.

Table 4 Basic diagram of manufacture of ultra-fine grain Ti

n	Operation
1.	Melting and casting of Ti in vacuum furnace. Semi product in the form of a bar: D_{min} = 35 mm. L_{min} = 130 mm.
2.	Refining - production of high purity semi product for ECAP. Chemical composition - **Table 1**.
3.	ECAP process: Bar with ϕ 30 mm; number of passes 8. Load on extruding punch: P_{max} = 1500 MPa, T = 280 °C
4.	Mechanical properties: R_m = 960 MPa, A = 12 %, $E \approx$ 100 GPa, $d_z \approx$ 100 to 300 nm.
5.	Rotation re-forging and drawing of (n)Ti to a wire: D_d = 6 mm, $R_m \geq$ 1030 MPa.

3. OBTAINED RESULTS AND THEIR ANALYSIS

Semi products from individual heats were processed according to modified programs by the ECAP technology and then drawn to a wire. Wire diameter varied about 4 - 5 mm.

ECAP technology and drawing was made in several variants:

a) 2 to 5 passes ECAP at a temperature of 450°C.
b) 2 to 5 passes ECAP at a temperature of 370°C.
c) passes ECAP at a temperature of 280°C; with annealing between individual passes.
d) rotation re-forging to a diameter of 10 mm: (deformation cold forming: *e* = 2,2).
e) rotation re-forging to a diameter of 6 mm: (deformation cold forming: *e* = 1,02).
f) the following technology of drawing was realized at increased temperatures (**Table 5**).

The samples for mechanical tests **(Figure 2)** and for micro-structural analyses were prepared from individual variants of processing. On the basis of the results, particularly the obtained strength values, several variants were chosen for more detailed investigation of developments occurring in the structure at application of the ECAP and subsequent drawing after heat treatment. Structure of ultra-fine grain titanium after application of the ECAP process is shown in the **Figure 3.** The structure was analyzed apart from light microscopy also by the X-ray diffraction. **Table 5** summarizes the obtained basic mechanical properties.

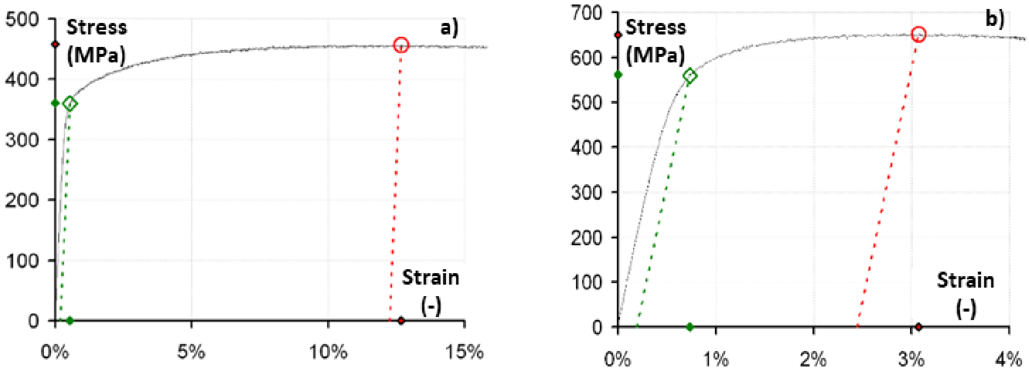

Figure 2 Stress - strain curve cp Ti: a) initial sample, b) after 4 passes

Table 5 Mechanical properties of ultra-fine grain titanium after ECAP and drawing

Forming processed	R_m (MPa)	*A* (%)	*E* (GPa)	d_z (nm)
ECAP (2 passes)	579.4	14.7	80.1	430
ECAP (5 passes)	610.6	17.3	99.7	-
ECAP (8 passes)	960.3	12.1	100.2	100 to 300
Drawing (D_d = 6 mm)	1030 to 1050	9.3	100.2	100 to 300

3.1. SEM analyze of fracture surfaces

For detailed investigation of the samples after tensile test SEM JEOL JSM 6490L was used. Details of fracture areas at selected grains size are shown in **Figure 4**. The evolution of damage and final fracture in ultra-fine grains titanium is only beginning to be understood. The absence of substantial macroscopic tensile ductility in ultra-fine grains titanium together with the observation of dimpled rupture on fracture surfaces leads to the hypothesis that deformation is localized). Fracture surfaces resulting from tensile tests have frequently shown dimpled rupture in microcrystalline titanium. Further, it has been shown that the dimple size is significantly larger than the average grain size; in addition, a pair of mating fracture surfaces was shown that clearly illustrated the presence of significant stretching of the ligaments between the dimples that was taken to be indicative of appreciable local plasticity. An example of a fracture surface obtained from a tensile specimen of ultra-fine grained titanium with a grain size of around 250 - 300 nm. It reveals dimpled rupture with the dimple depth (3 - 4 μm) being an order of magnitude larger than the grain size. Furthermore, the dimple size is uniform and extends across most of the specimen cross-section**.** When the grain size is reduced to 0,1 μm or less an in the case of titanium after 8 passes ECAP, the resulting fracture surface from a tensile specimen still continues to show what appears to be dimpled rupture with the important difference that the dimple diameter on an average is finer in size relative to those seen in **Figure 4c.**

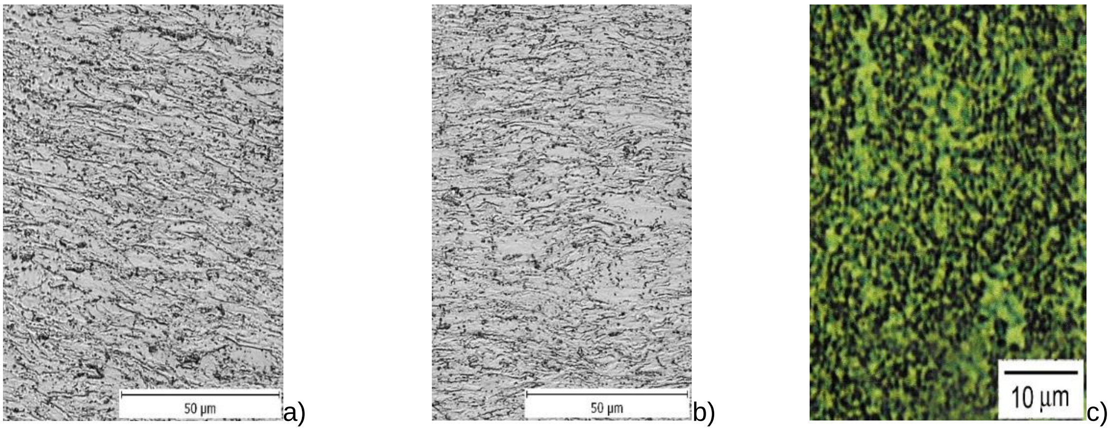

Figure 3 Microstructure of ultra-fine grain Titanium after ECAP: a) 4 passes; b) 5 passes, c) 8 passes+700°C/1h

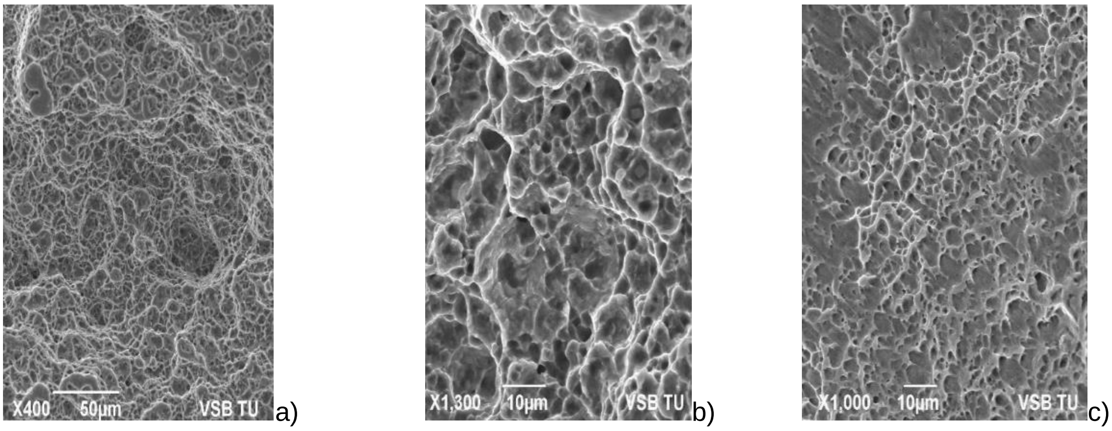

Figure 4 Fracture area of the sample after: a) tensile test, 2 passes ECAP, 8 passes ECAP

4. CONCLUSION

Technology of manufacture of nano-titanium was proposed and experimentally verified. Grain refinement in input materials was obtained using the ECAP process. In conformity with the Hall-Petch, relation the strength properties of Ti increased significantly as a result of grain refinement. The obtained mechanical properties correspond with the declared requirements. Nano-titanium has higher specific strength properties than ordinary titanium. Strength of nano-titanium varies around 1050 MPa, grain size around 300 nm.

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