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STRUCTURE AND PROPERTIES OF TITANIUM FOR DENTAL IMPLANTS

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This paper describes manufacture of nano-structural titanium, its structure and properties. Nano-titanium has higher specific strength properties than ordinary (coarse-grained) titanium. Nano-titanium was produced by the equal-channel angular pressing (ETAP) process. The research it self was focused on physical base of strengthening and softening processes and developments occurring at the grain boundaries during the ECAP process at half-hot temperature. Strength of nano-titanium varies around 960 MPa, grain size around 300 nm.

Key words: submicrocrystalline structure, severe plastic deformation (SPD), ECAP, structure and properties, titanium

Struktura i svojstva titana za zubne umetke (implantate). Rad opisuje proizvodnju nanostrukturnog titana te njegovu strukturu i svojstva. Nanotitan se odlikuje višom čvrstoćom od običnog, krupnozrnatog, i proizveden je kanalno kutnim prešanjem (KKP). Samo istraživanje bilo je usmjereno na fizikalne osnove procesa očvršćavanja i omekšavanja na granicama zrna tijekom procesa kanalno kutnim prešanjem (KKP) na srednjim temperaturama. Čvrstoća nanotitana varira oko 960 MPa, a veličina zrna je oko 300 nm.

Ključne riječi: submikrokristalne strukture, intenzivna plastična deformacija (JPD), KKP, strukture i svojstva, titan

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 [1]. It must have high ultimate strength R_m and yield value R_p at low density and low modulus of elasticity E [2]. Metallic materials used for dental implants comprise alloys of stainless steels, cobalt alloys, titanium (coarse-grained) and titanium alloys [3]. 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 [4]. Titanium is at present preferred to stainless steels and cobalt alloys namely thanks to its excellent bio-compatibility [5]. Together with high bio-compatibility of Ti its resistance to corrosion evaluated by polarisation resistance varies around the value 10^3 R/Ω·m [6].

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 [7]. Typical representative of these alloys is duplex alloy (α a β) Ti6Al4V [8]. After application of dental implants made of these alloys toxicity of vanadium was confirmed [9]. Aluminium, too, can be categorised 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 TiTa, TiMo, TiNb and TiZr began to be used. Single phase β Ti alloys were developed at the same time, which are characterised by the low value of the modulus of elasticity [10]. Ti alloys with elements with very different density and melting temperature (TiTa, TiMo) require special technology of manufacture, by which they significantly increase production costs and price of semi-products for dental implants.

The problem at the development of metallic bio-materials consists not only in their real or potential toxicity, but also in their allergenic potential [11]. 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: Ti13Cu4,5Ni; Ti20Pd5Cr; Ti20Cr0,2Si. Sensitivity of population to Ni is increasing.

For these reasons pure titanium still remains to be a preferred material for dental applications. Development

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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. 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 [12]. High-purity titanium is used for dental implants. Chemical composition of CP Ti for dental implants must be within the following interval [3].

STRUCTURE AND PROPERTIES OF CP Ti

Commercially pure titanium (CP) bars and sheets were used in this study. The average grain size of the as-received CP titanium 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. 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- 4. 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 commercially pure (CP) titanium are given in the Table 1-3.

PROPERTIES OF NANO-TITANIUM (N)Ti

Nano-titanium is characterised by exceptional mechanical properties, among which high ultimate strength and high yield value are of utmost importance. Strength properties of (n)Ti must have the following values: $R_m >$ 1000 MPa, $R_{p0,2} >$ 850 MPa [6]. 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

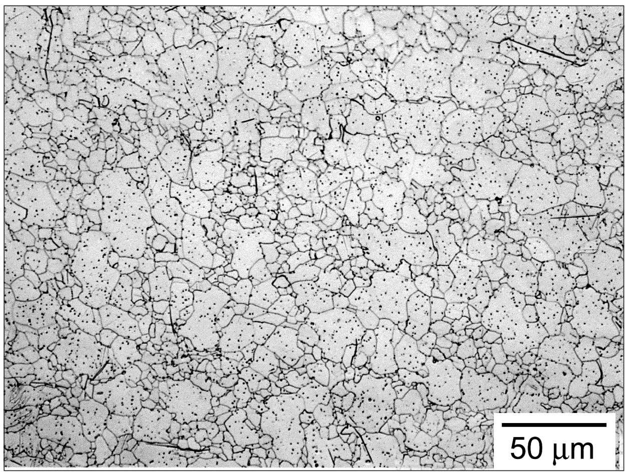

Figure 1. Initial microstructure of CP Ti (longitudinal direction)

Table 1. **Chemical analysis commercially pur etitanium (CP), (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 titanium after annealing 649 C °/1 hour (ASTM E8)**

Tensile strength R_m	$R_{p0,2}$ Yield strength	Elongation 2“ gage	Reduction of area
/ MPa	/ MPa	/ %	/ %
365	212	51	71

Table 3. **Initial hardness of commercially pure Ti and hardness after cold rolling**

Label	Diagonal of indention d / μm	HV30
Sample nr. 1	659	128
	632	139
	652	131
Sample nr. 2	658	128
	655	130
	658	128
Sample nr. 3.	527	200
	525	202
	535	194

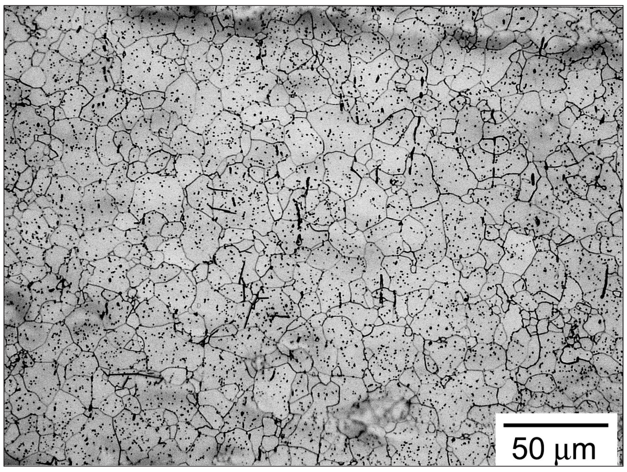

Figure 2. Initial microstructure of Ti (transverse direction)

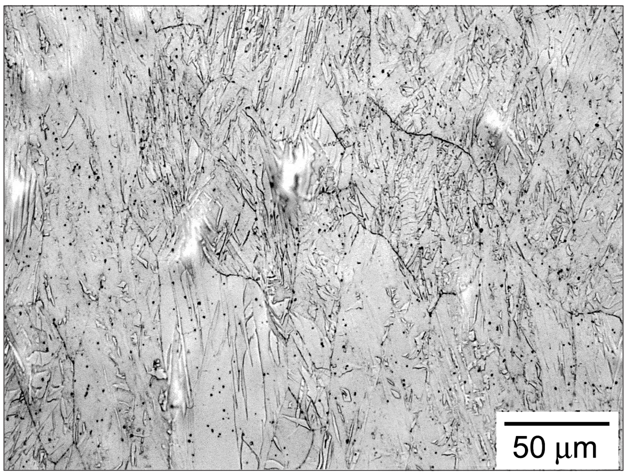

Figure 3. Microstructure of Ti after cold rolling (longitudinal direction)

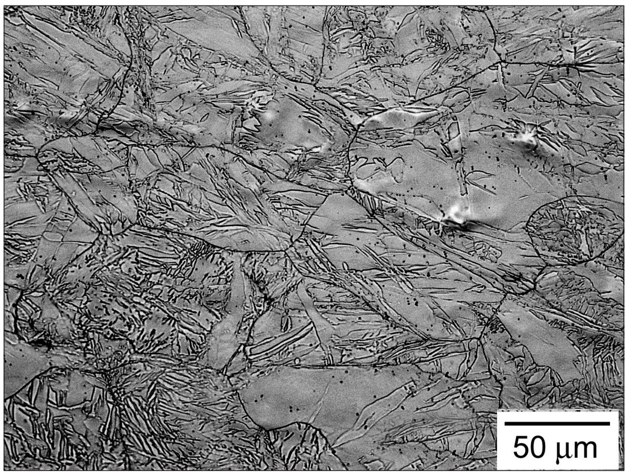

Figure 4. Microstructure of Ti after cold rolling (transverse direction)

are evaluated in relation to its density as so called specific properties. In case of classical coarse-grained titanium the relation (R_m/ρ) varies around 70 to 120 N·m/g, for the alloy Ti6Al4V it varies around 200 N·m/g [13,14], and for (n)Ti it is possible to predict the values $R_m/$ = 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/ρ = 65 N·m/g, cobalt alloys - R_m/ρ = 160 N·m/g, βTi (Ti15Mo5Zr) - R_m/ρ = 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, 16].

At present only few companies in the world manufacture commercially bulk nano-materials.

THE TECHNOLOGY FOR MANUFACTURE OF NANOSTRUCTURE TITANIUM (N)Ti

The main objective of experiments was manufacture of (n)Ti, description and optimisation 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. Chemical purity of semi products for (n)Ti 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 (n)Ti was further processed by technology (of rotation forging) and drawing to the shape suitable for dental implants. Sequence of production of (n)Ti is described in the Table 4.

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 [17-19].

Table 4. Basic diagram of manufacture of (n)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: 12 • Load on extruding punch – P_{max} = 1500 MPa, • T = 280 °C • Time = 120 s.
4.	Mechanical properties: • Rm = 960 MPa, • E = 100 GPa, • A = 12 %, • d_z = 100 to 300 nm.
5.	Rotation re-forging and drawing of (n)Ti to a wire: D_d = 6 mm.
6.	Mechanical properties: • $R_m \geq$ 1030 MPa, • Structure strengthened by deformation.

ECAP technology and drawing was made in several variants:

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

The samples for mechanical tests 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 (n)Ti after application of the ECAP process is shown in the Figure 5, 6 and Figure 7. The structure was analysed apart from light microscopy also by the X-ray diffraction. Table 5 summarises the obtained basic mechanical properties.

Table 5. Mechanical properties (n)Ti after ecap and drawing

Forming processed	R_m /MPa	A /%	E /GPa	d_z /nm
ECAP (10 passes)	960	12	100	100 to 300
Drawing (D_d = 6 mm)	1030 to 1050	9	100	100 to 300

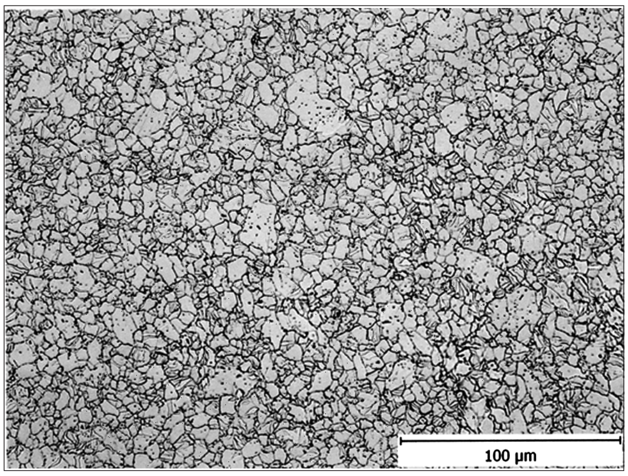

Figure 5. Microstructure of (n)Ti after ECAP (2 passes; longitudinal direction)

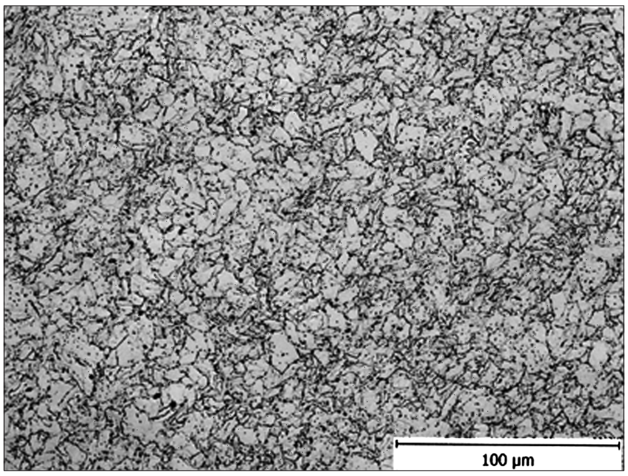

Figure 6. Microstructure of (n)Ti after ECAP (2 passes; transverse direction)

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 1250 MPa, grain size around 300 nm.

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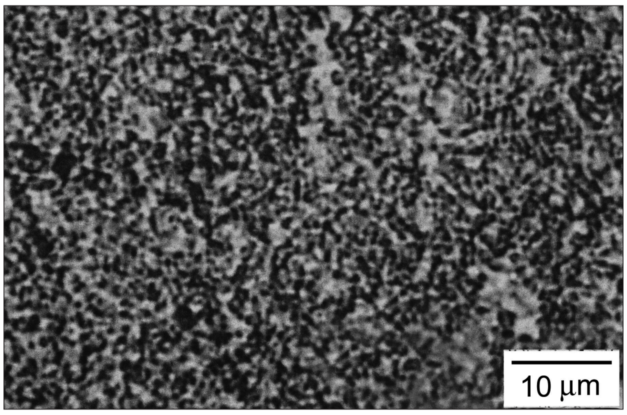

Figure 7. Microstructure of (n)Ti after ECAP (10 passes)

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