Journal of Achievements in Materials and Manufacturing Engineering
VOLUME 40
ISSUE 1
May
2010

Mechanical properties of ultra-fine grain titanium

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Received 27.02.2010; published in revised form 01.05.2010

Properties

ABSTRACT

Purpose: The main goal of the presented paper was to describe deformation behaviour of the commercial purity titanium during the ECAP method. Attention was paid particularly on reached mechanical properties of above mentioned material.

Design/methodology/approach: Design of experiments rested in extrusion at temperature in range from room temperature up to 280°C. The way of approach was planned in investigation of imposed strain accumulation ability. Among used methods for determination of intended aims were tensile tests, TEM, SEM.

Findings: Depending on imposed strain (e = 2 up to 8) was found that mechanical properties (namely tensile strength) have increased up to 960 MPa.

Research limitations/implications: Developed ECAP process enables controlling morphology of microstructural constituents and workability of commercially pure titanium.

Practical implications: Obtained findings may be used in process of preparing materials for medical application such as dental application where is very important factor their sensitivity to strain.

Originality/value: Value of paper is mainly in observed findings that can be used in determination of process conditions at submicro or ultra-fine crystalline materials.

Keywords: Mechanical properties; Ultra-fine grain materials; Titanium; ECAP

Reference to this paper should be given in the following way:
M. Greger, M. Widomská, L. Kander, Mechanical properties of ultra-fine grain titanium, Journal of Achievements in Materials and Manufacturing Engineering 40/1 (2010) 33-40.

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 [1]. It must have high ultimate strength R_m and yield value $R_{p0,2}$ at low density ρ 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/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 [6]. Typical representative of hese alloys is duplex alloy (α and β) Ti6Al4V [7]. After application of dental implants made of these alloys toxicity of vanadium was confirmed [8]. 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 [9]. 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. Sensitivity of population to allergies keeps increasing. Allergies to metals are 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 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 [10]. 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.

2. Structure and properties of commercial pure titanium

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. Microstructure of deformed specimens after testing is shown in Figs. 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 Tables 1-3.

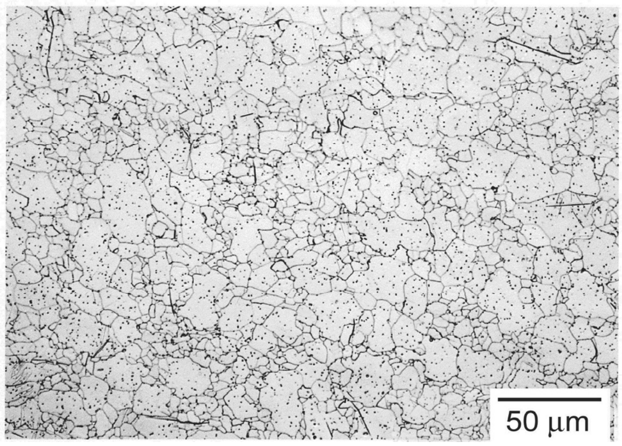


Fig. 1. Initial microstructure of commercial pure titanium (longitudinal direction)

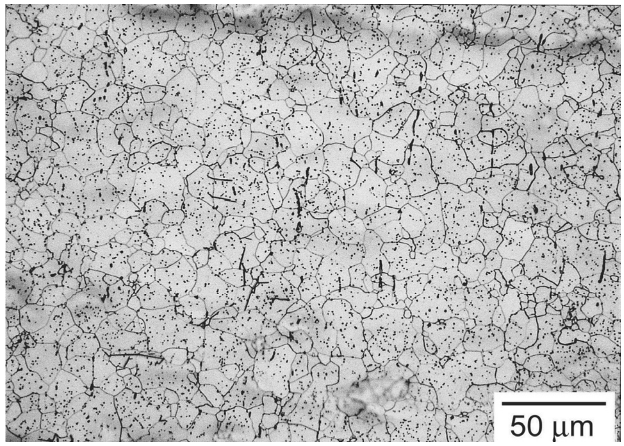


Fig. 2. Initial microstructure of titanium (transverse direction)

Table 1.
Chemical analysis pure titanium (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)

R_m [MPa]	$R_{p0.2}$ [MPa]	A [%]	Z [%]
365	212	51	71

Table 3.
Hardness of CP titanium 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

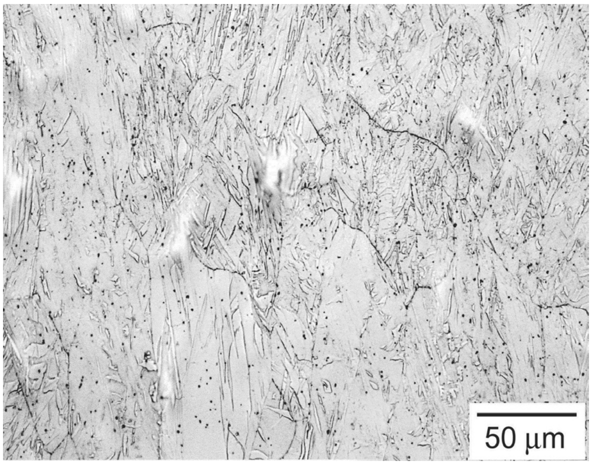


Fig. 3. Microstructure of titanium after cold rolling (longitudinal direction)

2.1. Properties of ultra-fine grain titanium

Ultra-fine grain titanium is characterised 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 [11]. Apart from the tensile strength, another important property 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 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) [12], 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 316 L: $R_m/\rho = 65$ (N·m/g) [13, 14], cobalt alloys: $R_m/\rho = 160$ (N·m/g) [15, 16], βTi (Ti15Mo5Zr): $R_m/\rho = 180$ (N·m/g) [17, 18]. 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 [19-21].

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

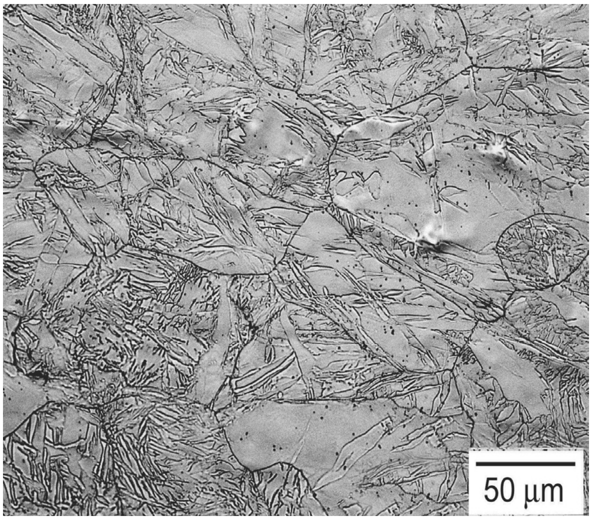


Fig. 4. Microstructure of titanium after cold rolling (transverse direction)

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 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 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 Equal Channel Angular Pressing (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 titanium

n	Operation
1.	Melting and casting of titanium 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 Stress : P_{max} = 1500 MPa, Temperature : t = 280 °C
4.	Mechanical properties: • R_m = 960 MPa, A = 12 %,
5.	Rotation re-forging and drawing of (n) titanium to a wire: D_d = 6 mm, R_m ≥ 1030 MPa,

3. Obtained results and their analysis

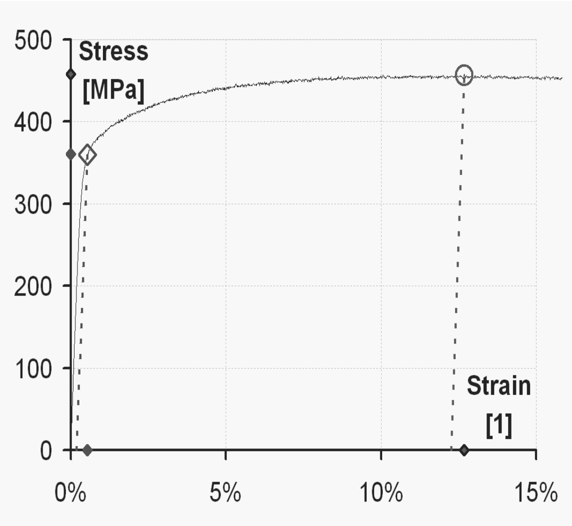
Semi products from individual heats were processed according to modified programs by the ECAP technology and then drawn to a wire. Wire diameter varied about 4 - 5 mm [22-23].

ECAP technology and drawing was made in several variants [24, 25] :

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 (Fig. 5) 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 [26]. Structure of ultra-fine grain titanium after application of the ECAP process is shown in the Figs. 6, 7 and Fig. 8. The structure was analysed apart from light microscopy also by the X-ray diffraction. Table 5 summarises the obtained basic mechanical properties.

a)



b)

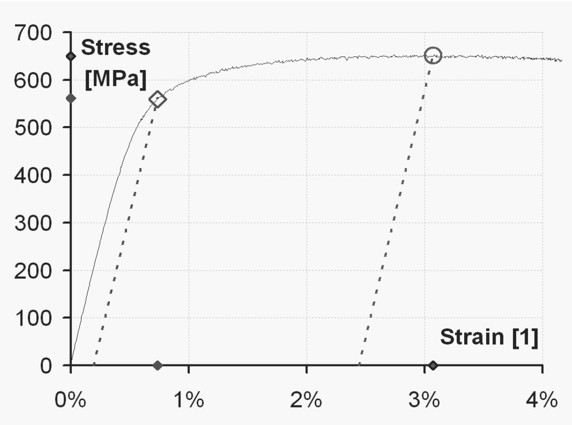


Fig. 5. Stress - strain curve titanium: a) initial sample, b) after 6 passes

Table 5.
Mechanical properties 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 (10 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

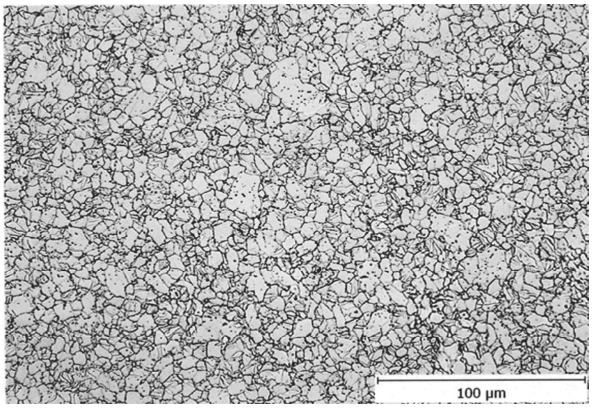


Fig. 6. Microstructure of ultra-fine grain titanium after ECAP (2 passes; longitudinal direction)

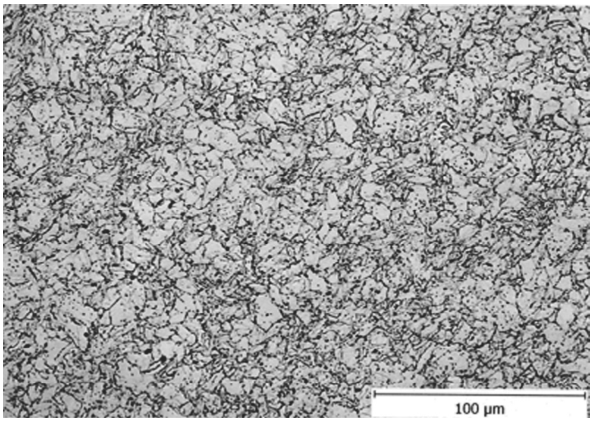


Fig. 7. Microstructure of ultra-fine grain titanium after ECAP (2 passes; transverse direction)

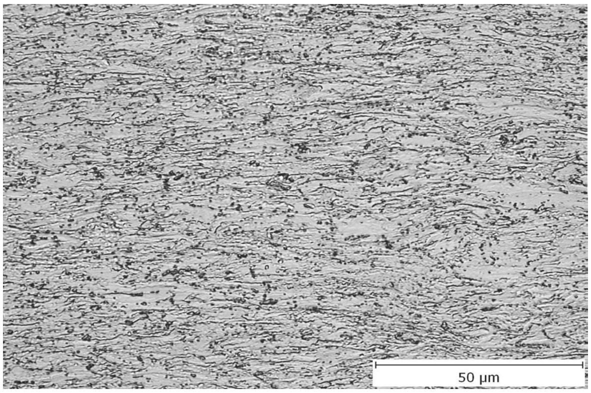


Fig. 8. Microstructure of ultra-fine grain titanium after ECAP (4 passes; longitudinal direction)

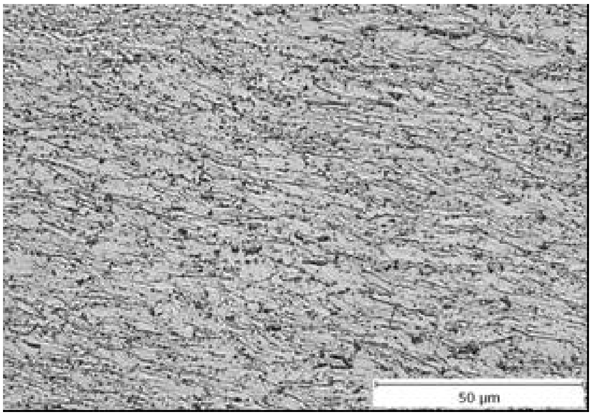


Fig. 9. Microstructure of ultra-fine grain titanium after ECAP (5 passes; longitudinal direction)

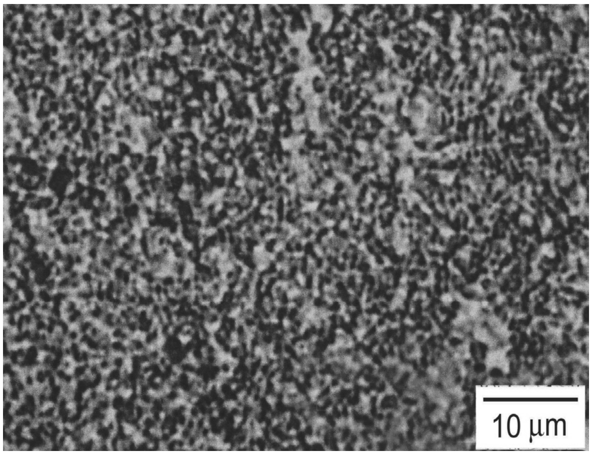


Fig.10. Microstructure of ultra-fine grain titanium after ECAP (12 passes)

3.1. SEM and TEM analyse 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 Figs. 11 up to 13.

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 localised).

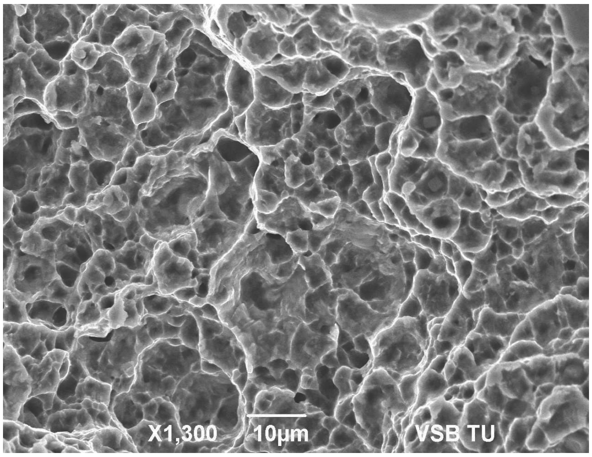


Fig. 11. Fracture area of the sample after 2 passes ECAP

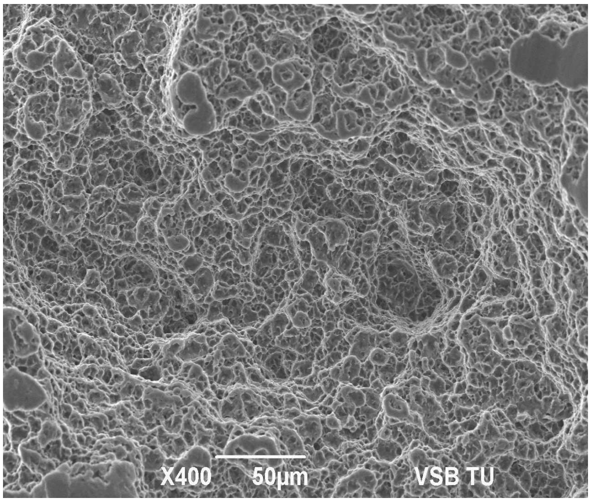


Fig. 12. Fracture area of the sample after 4 passes ECAP

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 (Fig. 11), 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 is shown Figure 10. It reveals dimpled rupture with the dimple depth (3-4 μm) being an order of magnitude larger than the grain size (Fig. 12). Furthermore, the dimple size is uniform and extends across most of the specimen cross-section (Fig. 13).

When the grain size is reduced to 0.1 μm or less an in the case of titanium after 8 passes ECAP (Fig. 13), the resulting fracture surface from a tensile specimen still continues to show what appears to be dimpled rupture with the importat difference that the dimple diameter on an average is finer in size relative to those seen in Fig. 14 and Figs. 15 - 18.

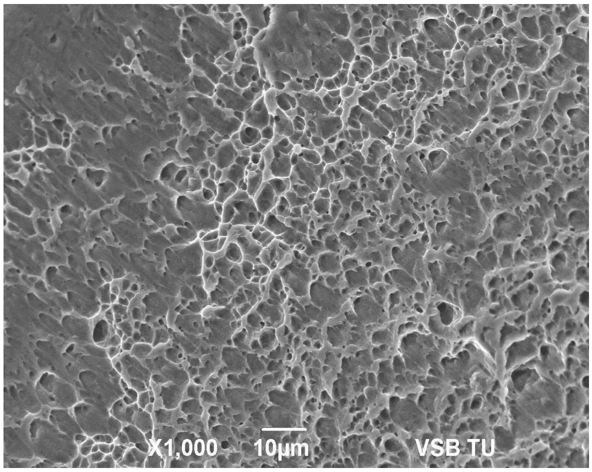


Fig. 13. Fracture area of the sample after 8 passes ECAP

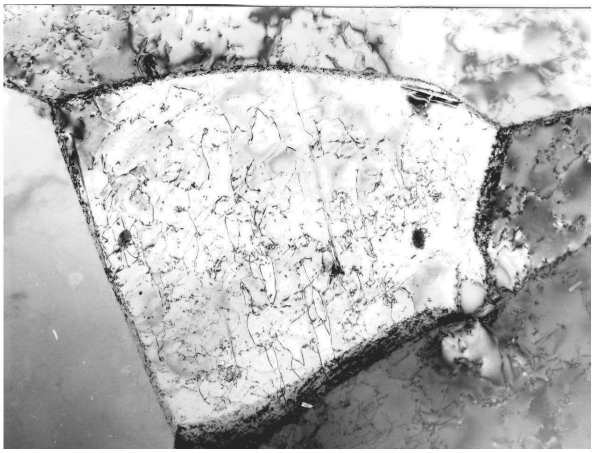


Fig. 14. Substructure of CP titanium in the initial state

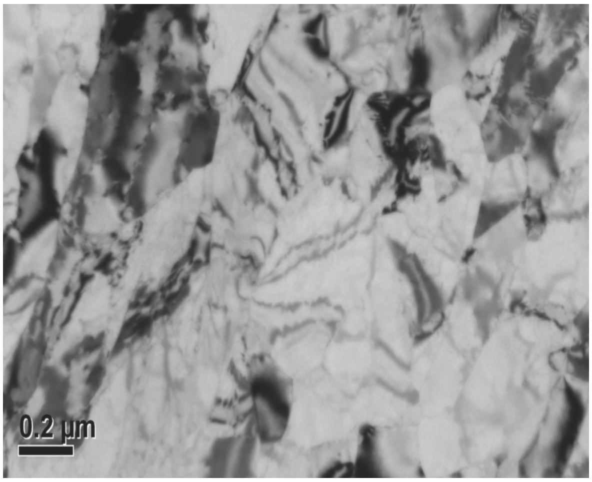


Fig. 15. Substructure of the sample after 3 ECAP passes

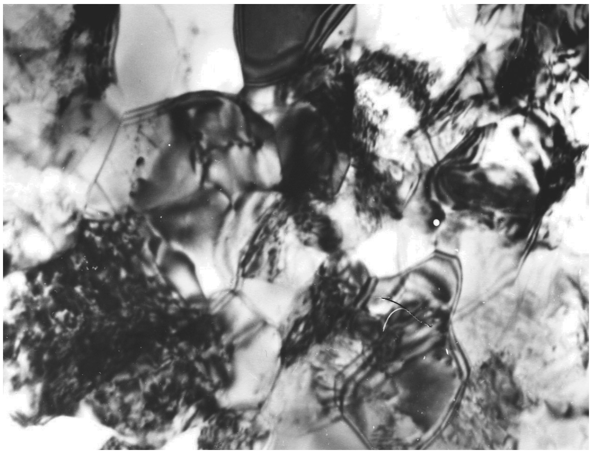


Fig. 16. Substructure of the sample after 4 ECAP passes

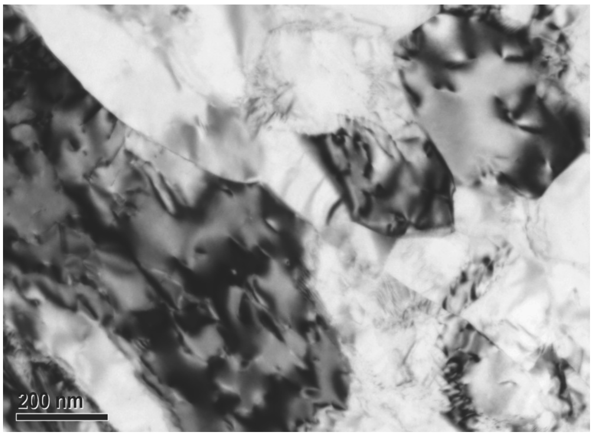


Fig. 17. Substructure of the sample after 6 ECAP passes

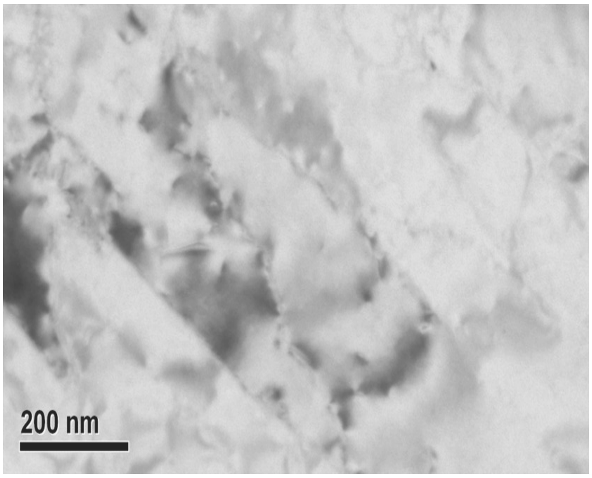


Fig. 18. Substructure of the sample after 8 ECAP passes

4. Conclusions

Technology of manufacture of ultra-fine grain titanium was proposed and experimentally verified. Grain refinement in input materials was obtained using the equal channel angular pressing process. In conformity with the Hall-Petch, relation the strength properties of commercially pure titanium increased significantly as a result of grain refinement. The obtained mechanical properties correspond with the declared requirements. Ultra-fine grain has higher specific strength properties than ordinary titanium. Strength of ultra-fine grain varies around 1250 MPa, grain size around 300 nm.

Acknowledgements

The authors are grateful to the Grand Agency of the Czech Republic, project No. 106/09/1598 and the Czech Ministry of Education, Project No. VS MSM 619 891 0013 and No. VS MSM 258 708 0701.

References

[1] J. Marciniak, Biomaterials, Edited by Silesian University of Technology, Gliwice, 2002.
[2] M. Gierzyňskia-Dolna et al., Titanium and its alloys. Processing and application in technology and medicine, Edited by Czestochowa University of Technology, Czestochowa, 2002.
[3] R. Hunter, F. Alister, J. Mőller, J. Alister, A new approach to modelling and designing mono-block dental implants, Journal of Achievements in Materials and Manufacturing Engineering 22/1 (2007) 77-80.
[4] G.I. Raab, R.Z. Valiev, Obtaining a nanostructure in titanium by equal channel angular pressing, Metal Science and Heat Treatment 42 (2000) 361-365.

[5] D. Krupa, J. Baszkiewicz, J. Sobczak, A. Bilinsk, A. Barcz, Modifying the properties of titanium surface with the aim of improving its bioactivity and corrosion resistance, Journal of Materials Processing Technology 143-144 (2003) 158-163.

[6] M. Metikos-Hukovic, A. Kwokal, J. Piljac, The influence of iobium and vanadium on passivity of titanium-based implants in physiological solution, Biomaterials 24 (2003) 37-65.

[7] M. Žitňanský, L. Čaplovič, M. Greger, The influence of rolling on the structure of Ti6Al4V, Proceedings of the 10th Scientific International Conference “Achievements in Mechanical and Materials Engineering” AMME ´2002, Gliwice - Zakopane, 2002, 631-636.

[8] A. Kieizkowska, E. Krasicka-Cydzik, M. Jenek, Characteristic surface layer of Ti6A14V alloy after deformation by bending, Biomaterials Engineering 47-53 (2005) 146-148.

[9] M. Kozłowski, E. Czerwosz, P. Dłużewski, E. Kowalska, J. Radomska, H. Wronka Nanostructural C-Pd coatings obtained in 2-steps PVD/CVD technological process, Journal of Achievements in Materials and Manufacturing Engineering 37/ 2 (2009) 304-308.

[10] M.J. Tan, X.J. Zhu, Dynamic recrystallization in comercially pure titanium, Journal of Achievements and Manufacturing Engineering 18 (2006) 183-186.

[11] D. Kuroda, M. Niomi, M. Morinaga, Y. Kato, T. Yashiro, Design and mechanical properties of new β titanium alloys for implant materials, Materials Science and Engineering A243 (1998) 244-249.

[12] A. Baron, D. Szewieczek, R. Nowosielski, Selected manufacturing techniques of nanomaterials, Journal of Achievements in Materials and Manufacturing Engineering 20 (2007) 83-86.

[13] Ch. Leinenbach, D. Eifler, Fatigue and cyclic deformation behaviour of surface-modified titanium alloys in simulated physiological media, Biomaterials 27 (2006) 1200-1205.

[14] A. Vinogradov, S. Hashimoto, Fatigue of severely deformed metals. Advanced Engineering Materials 5 (2003) 351-358.

[15] J. Żmudzki, W. Chladek, J. Krukowska, Attachments of implant retained tissue supported denture under biting forces, Achievements in Materials and Manufacturing Engineering 20 (2007) 83-86.

[16] T.S. Hin, Engineering materials for biomedical applications, World Scientific Publishing Co, Singapore, 2004.

[17] Y.T. Zhu, T.C. Lowe, Observation and issues on mechanism of grain refinement during ECAP process, Materials Science and Engineering A 291 (2000) 46-50.

[18] Y.T. Zhu, T.C. Lowe, R.Z. Valiev, V.V. Stolyarov, V.V. Latysh, G.J. Raab, Ultra-fine grained titanium for medical implants, United States Patent No. US 6,399,215 B1

[19] M. Žitňansky, L. Čaplovič, L. Rehák, F. Makai, Investigation and implantation of endo-prosthesis in biological experiment on animals, Journal of Achievements in Materials Manufacturing Engineering 24/1 (2007) 146-152.

[20] I. Kim, J. Kim, D.H. Shing, K.T. Park, Effects of grain size an pressing speed on the deformation mode of commercially pure Ti during equal channel angular pressing, Metallurgical and Materials Transactions A: 34A (2003) 1555-1557.

[21] D.H. Shin, I. Kim, J. Kim, Y.T. Zhu, Shear strain accommodation during severe plastic deformation of titanium using equal channel angular pressing, Materials Science and Engineering A 334/1-2 (2002) 239-245.

[22] M. Greger, V. Vodárek, L. Kander, M. Černý, Working steel P2-04BCH by Equal channel angular extrusion, Metallurgy 48/4 (2009) 263-266.

[23] M. Greger, L. Kander, Mechanical Properties of Titanium after Severe Plastic Deformation, Hutnické listy 62/4 (2009) 50- 55.

[24] M. Greger, R. Kocich, L. Čížek, L.A. Dobrzański, M. Widomská, Influence of ECAP technology on the metal structures and properties, Archives of Materials Science and Engineering 28 (2007) 709-716.

[25] M. Greger, R. Kocich, L. Čížek, Grain rafining of Cu and Ti-Ni shape memory alloys by ECAP process, Journal of Achievements in Materials and Manufacturing Engineering 20 (2007) 247-250.

[26] M. Greger, M. Kursa, L. Drápala Formation of ultra fine grained structure and mechanical properties by ECAP deformation, Rare Metals 28/1 (2009) 770-773.