Abstract

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 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. Mechanical properties were evaluated using standard tensile tests as well as small punch tests. Correlation between mechanical properties from tensile test and punch test was developed. Depending on imposed strain ($e = 2$ up to $8$) was found that mechanical properties (namely tensile strength) have increased up to 960 MPa. Developed ECAP process enables controlling morphology of microstructures constituents and workability of titanium Grade1. Obtained findings can be used in process of preparing materials for medical application such as dental application where is very important factor their sensitivity to strain.

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 $R_{p0.2}$ at low density $\rho$ 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 polarisation resistance varies around the value $10^3 \text{ R/}\Omega\text{m}$.

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 ($\alpha$ and $\beta$) Ti-6Al-4V. After application of dental implants made of these alloys toxicity of vanadium was confirmed.

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. Single phase $\beta$ Ti alloys were developed at the same time, which are characterised by the low value of the modulus of elasticity. 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.

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: Ti-13Cu-4,5Ni; Ti-20Pd-5Cr; Ti-20Cr-0,2Si. Sensitivity of population to Ni is increasing.

For these reasons pure titanium (CP) 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 nanomaterials 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. 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. 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: \( R_m > 1000 \text{ MPa}, \quad R_{p0.2} > 850 \text{ MPa}. \) 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 \( R_m/\rho \) varies around 70 to 120 (N·m/g), for the alloy Ti6Al4V it varies around 200 (N·m/g), 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), cobalt alloys: \( R_m/\rho = 160 \) (N·m/g), \( \beta \text{Ti (Ti15Mo5Zr): } R_m/\rho = 180 \) (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. At present only few companies in the world manufacture commercially bulk ultra-fine grain materials.
3. EXPERIMENTAL DETAILS

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 Fig. 1-2. Specimens were sectioned along the gauge and grip parts of the deformed sample. The samples were then polished etched using 10 % HF, 10 % HNO₃ and 80 % H₂O for 20 second. Chemical analysis and mechanical properties commercially pure (CP) titanium are given in the Table 1-2.

<table>
<thead>
<tr>
<th>N</th>
<th>O</th>
<th>C</th>
<th>Fe</th>
<th>Al</th>
<th>Cr</th>
<th>Ti</th>
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<td>0.068</td>
<td>0.008</td>
<td>0.03</td>
<td>0.01</td>
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<table>
<thead>
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<th>Rₘ</th>
<th>Rₚ₀.₂</th>
<th>A</th>
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<tr>
<td>[ MPa]</td>
<td>[ MPa]</td>
<td>[%]</td>
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</tr>
<tr>
<td>375</td>
<td>230</td>
<td>51</td>
<td>71</td>
</tr>
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</table>

Table 1. Chemical analysis titanium Grade 1, [weight %]

Table 2. Tensile properties of titanium Grade 1 after annealing 649 °C/1 hour (ASTM E8)

Fig. 1. Initial microstructure of titanium

Fig. 2. Microstructure of titanium after cold rolling
4. RESULTS AND DISCUSSION

Samples from individual heats were processed by the ECAP. The samples for mechanical tests and for micro-structural analyses were prepared from individual variants of processing. On the basis of the results of standard tensile tests (Fig. 3), 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.

![Fig. 3. Stress – strain curve titanium: a) initial sample, b) after 6 passes](image)

Structure of ultra-fine grain titanium after application of the ECAP process is shown in the Fig. 4 and Fig. 5. The structure was analysed apart from light microscopy also by the X-ray diffraction.

![Fig. 4. Microstructure titanium after ECAP](image)  ![Fig. 5. Microstructure of titanium after ECAP 12 passes](image)

**Figure 6** summarises effect of number of passes on mechanical properties. From samples after ECAP were also manufactured specimens for small punch tests (8 mm in diameter, 0.5 mm in thickness) to evaluate new correlation between standard tensile tests and small punch tests for titanium. Small punch tests were carried...
out in MATERIAL & METALURGICAL RESEARCH, Ltd. according to accredited procedure at stroke rate 0,2 mm/min [2]. Results were correlated with tensile test results and are presented in Fig. 7 for yield stress and in Fig. 8 for tensile strength of titanium. In the Figures 7 and 8 is also presented correlations for steels (dashed line), that have been developed for 12 years. From both figures is clearly seen, that origin correlation for steel can not be used for evaluation of mechanical properties of titanium by punch test, new developed correlation changed significantly probably due to friction coefficient effect or lattice effect. Work is still continuing to evaluate reason of this effect as well as to get a more results for titanium and Ti alloys.

4.1 SEM a 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 Fig. 9. 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). 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. 9), 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 [3]. 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 Fig. 5. It reveals dimpled rupture with the dimple depth (3-4 µm) being an order of magnitude larger than the grain size (Fig. 9). 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 Fig. 10 and Fig. 11.

Fig. 9. Fracture area after 6 passes ECAP

Fig. 10. Substructure of titanium in the initial state

Fig. 11. Substructure Ti after ECAP 6 passes

5. CONCLUSION

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. To evaluate mechanical properties of Ti standards tensile tests were carried out as well as very potential method (small punch test) were used. New correlation has been found for titanium that differs significantly from correlation using for steels. Further work is necessary to get more data for new developed correlation on titanium and Ti alloys. Based on the experimental results can be seen that small punch tests can be using to evaluate for titanium especially in the case, when small amount of experimental materials is expected.

Acknowledgement

The authors are grateful to the Grand Agency of the Czech Republic, project No. 106/09/1598

References

