Ultra-fine grained $\beta$-type TNZT ELI alloy with high strength and low elastic modulus

A V Polyakov$^1$, I P Semenova$^1$, E Ivanov$^2$, R Z Valiev$^1$

$^1$ Ufa State Aviation Technical University, Institute of Physics of Advanced Materials, 12 K. Marx str., Ufa, 450008, Russian Federation

$^2$ Tosoh SMD Inc., 3600 Gantz Road, Grove City, OH 43123, USA

E-mail: alex-v.polyakov@mail.ru

Abstract. This work deals with the improvement of mechanical properties of medical alloy Ti-34Nb-7Zr-4.6Ta ELI (TNZT) by severe plastic deformation (SPD) techniques at temperatures below the temperature of the onset of phase transformations in order to maintain a low modulus of elasticity. For the formation of a nanostructured state, high pressure torsion (HPT) at room temperature and equal channel angular pressing (ECAP) at 200 °C, that is, below the onset of diffusion $\omega$-transformation, were used. It is shown that HPT leads to the formation of the UFG structure in the alloy with the grain size of about 110 nm without changing in the alloy phase composition. The ECAP processing allowed forming a subgrain structure with an average size of grains/subgrains of 500 nm and an ultimate tensile strength of 745 MPa, which exceeded the ultimate tensile strength after the standard aging in the (\(\alpha + \beta\)) area (686 MPa). The issues of the effect of SPD on changes in the structure, phase transformations in the alloy and ways of maintaining a low modulus of elasticity in this alloy are discussed.

1 Introduction

Titanium and its alloys are the best ones to be applied in medicine as materials for long-term application implants due to their excellent biocompatibility, corrosion resistance and high specific strength [1]. However, the elastic modulus of the bone, in which implants from such materials are usually integrated, is from 30 GPa and below [2]. Therefore, $\beta$- and near $\beta$ Ti alloys have been recently the most promising ones. For example, the elastic modulus of Ti-15Mo alloy is 80 GPa, whereas $\alpha$-Ti or ($\alpha + \beta$) alloys Ti-6Al-4V and Ti-6Al-7Nb have an elastic modulus over 110 GPa [3,4]. A large difference between the elastic modulus of the implant material and the bone could lead to stress shielding, bone resorption and, as a consequence, implant loosening and need for repeated surgery [1]. Alongside, the alloys of this system have a relatively low mechanical strength, which usually does not exceed 550 MPa [4]. It is known that modern implants are produced from Ti alloys, the strength of which is over 1000 MPa, which positively effects the service lifetime of items [1]. Thus, the strength enhancement in $\beta$-Ti alloys with retention of the ductility reserve and low elastic modulus is an urgent problem.

The lowest elastic modulus is demonstrated by the Ti-Nb-Ta-Zr (TNZT) system alloys, the value of which can achieve 50 GPa depending on the content of elements in the alloy [3,4]. TNZT alloys are biocompatible, as they have only biotolerant elements in their composition. Alongside, Ti alloys of the TNZT system can have different contents of alloying elements, greatly impacting the phase
transformations and elastic modulus. For example, it is known that Zr is a neutral element, however, it significantly impacts phase transformations in the alloys of the Ti-Nb system [5]. In particular, Zr suppresses formation of martensite $\alpha'$ and $\alpha''$ phases, and it can play the role of $\beta$-stabilizer in the presence of other strong $\beta$-stabilizers (e.g. Nb) [5,6]. Therefore, the choice of the alloy composition of this system is an important aspect for achieving the required properties. In this work the research object is medical alloy Ti-34Nb-7Zr-4.6Ta ELI with an extremely low content of oxygen (224 ppm) and enhanced content of Zr as compared to the alloy studied in [7,8]. This alloy is the stable $\beta$-phase alloy with an elastic modulus of about 55 GPa [4].

A strengthening of $\beta$-Ti alloys by conventional thermomechanical treatment (TMT) usually result in simultaneous increase of strength and elastic modulus due to precipitation of secondary $\omega$ and $\alpha$-phases [4,9]. The severe plastic deformation (SPD) techniques, allow forming nanocrystalline and ultrafine-grained (UFG) structures in metals and alloys, which could cardinaly change their physical and mechanical properties [7,10]. SPD can be performed at relatively low temperatures, lower than phase transformation temperatures. For example, formation of a nanostructured state in $\beta$-Ti alloy by HPT at room temperature allows increasing the strength with retention of a low elastic modulus as reported in [8]. Besides, the grain boundary area has lower values of the elastic modulus as compared to the grain volume, therefore the increase of the extension of non-equilibrium boundaries in the microstructure after SPD can reduce the total elastic modulus [11]. Two SPD techniques - high pressure torsion (HPT) and equal channel angular pressing (ECAP) - were used in order to form a UFG state in it. The aim of this study was to investigate the peculiarities of microstructure changes in the alloy, their impact on the mechanical behavior of the alloy.

2 Experimental methods

The material for the research was the stable $\beta$-alloy Ti-34Nb-7Zr-4.6Ta ELI (oxygen content 224 ppm) obtained by electron beam melting. In the initial (as received) state the billets of the alloy were machined only. Discs with a diameter of 10 mm and 1.6 mm thick were subjected to HPT in the press with grooved anvils under a pressure of 6 GPa at room temperature. The number of turns was 1, 5 and 10. The rods with a diameter of 10 mm and 80 mm long were subjected to ECAP in the die-set with the angle of channels intersection of 120° at the temperature of 200 °C. The Vickers microhardness measurements were performed on the Duramin Struers unit under a load of 0.5 kg with a dwelling time of 10 sec. At least three indentations were carried out per point of the length.

The microstructures of the specimens were analyzed by transmission electron microscopy (TEM) on the JEOL JEM 2100. The foils were cut out using electrical discharge machining, and mechanically thinned for electro-polishing using the TenuPol-5 Struers facility. Solution of 5% perchloric acid, 35% butanol, and 60% methanol was used at a polishing temperature within the range from –20 to –35 °C. The diffraction patterns were taken from the areas having diameters of 120 and 240 nm.

Cylindrical samples with a gauge length of 15 mm and diameter of 3 mm (ISO 6892) were subjected to tensile testing on the Instron 5982 tensile machine with the strain rate $\dot{\varepsilon} = 10^{-3}$ s$^{-1}$ at room temperature. At least 3 samples were tested for each state.

3 Results and their discussion

3.1 HPT

In the as-received state the structure of TNZT samples consisted of coarse grains of the $\beta$ phase, the size of which was from 100 to 250 $\mu$m (Figure 1a). The TEM images of the structure display well-resolved dislocations, which points to the fact that internal areas of $\beta$-grains have a very low dislocation density (Figure 1b). The identification of diffraction patterns confirms the presence of one $\beta$-phase (Figure 1b).
Figure 1. SEM-image (a) and TEM image (b) of the microstructure of TNZT alloy samples in the as-received state.

High pressure torsion after 1 turn results in considerable refinement of β-grains (Figure 2a). Judging by the dark-field images of the microstructure, the average size of subgrains achieves 150 nm. The microdiffraction pattern points to multiple elements with different crystallographic orientation of atomic planes. This is testified by spots located along the concentric circles.
Figure 2. TEM-images of TNZT alloy sample after 1 (a), 5 (b) and 10 (c) HPT turns at 6 GPa and RT, where (a), (c) and (e) – bright field, (b), (d) and (f) – dark field images.

The deformation by 5 and 10 turns results, on the one hand, in additional reduction of grain/subgrain sizes to 130 and 110 nanometers, respectively (Figure 2b, c). On the other hand, the structure becomes more homogeneous, which is testified by the contrast in the dark-field images and more uniform distribution of spots on the concentric circles in the diffraction patterns. It should be noted that no additional spots from secondary phase precipitates were observed in the diffraction patterns. Alongside, precipitation of ω-phase particles is possible in the alloy of the given system under high pressure (6 GPa), which is induced by severe deformation [5,11]. Probably, lack of its spots in the diffraction patterns after HPT is connected with implementation of reverse transformation ω→β, as reported in [11].

Figure 3 displays the change of the microhardness over the radius of discs from the center to the edge. The highest increment of the microhardness from 176±5 to 236±17 HV was observed after 1 turn due to a cardinal decrease of the size of β-grains to 150 nm. The microhardness value after 5 and 10 turns increases slightly and is 253±11 and 257±10 on the average, respectively (Figure 3). It is seen from Figure 4 that on the periphery of samples the microhardness is higher than that in the center, which is conditioned by the HPT deformation scheme and typical of different materials subjected to this type of deformation [7,12]. It should be noted that with the number of turns increasing, i.e. accumulated strain degree, the HV values over the disc section are leveled (Figure 3). Such behavior was observed in near-β Ti-15Mo alloy processed by HPT at room temperature [12].
Figure 3. Distribution of microhardness over the TNZT sample radius subjected to HPT to a strain degree corresponding to 1, 5 and 10 turns.

3.2 ECAP
As it is known, the ECAP technique allows producing bulk billets with a UFG structure [7,10]. Alongside this deformation scheme applied to Ti alloys usually suggests processing at elevated temperatures, which can lead to $\beta \rightarrow \alpha$ and $\beta \rightarrow \alpha$ transformation and, as a consequence, to increase of the elastic modulus. Therefore, in this work the alloy was processed by ECAP at $200^\circ$C, which was lower than the temperature of the start of diffusion precipitation of $\omega$- and $\alpha$-phases [5].

The study of coarse-sized TNZT samples with a diameter of 10 mm shows that after 6 ECAP passes a microstructure forms that is different from the HPT one (Figure 4). The TEM images display a weakly pronounced grain-subgrain structure, which is testified by the image of diffraction patterns with grouped position of spots. The shape of subgrains is non-equiaxed and elongated especially in the longitudinal section of the billet (Figure 4b). Judging by the dark-field images of the structure, the average size of grains/subgrains was 500 nm.

Figure 4. TEM images of the TNTZ alloy microstructure after 6 passes of ECAP at $200^\circ$C, where (a) cross section; (b) longitudinal section.

Table 1 lists the mechanical properties of the studied alloy samples in the initial state and after ECAP. As a result of grain structure refinement the ultimate tensile strength increased from 550 to 745 MPa, and the relative elongation changed insignificantly (from 20 to 15%). The mechanical properties achieved by ECAP are higher than the properties of the alloy after standard heat treatment that includes ageing at temperatures of secondary $\alpha$-phase precipitation [4].

| Phase composition | UTS, MPa | YS, MPa | Elongation, % | HV  |
|-------------------|----------|---------|---------------|-----|
| Initial TNZT      | $\beta$  | 550     | 530           | 20  | 176 |
| ECAP              | $\beta$  | 745     | 700           | 15  | 214 |
| ST+ aging [4]     | $\beta+\alpha$ | 686     | 630           | 17  | -   |
| 427°C/8hours      |          |         |               |     |     |

In this case one could expect that one-phase $\beta$-structure in the alloy hardened by ECAP will enable retaining the low elastic modulus unlike two-phase $\beta+\alpha$ structure produced by standard ageing [4]. As it is known the elastic modulus value in conventional coarse-grained materials depends first of all on the phase composition [13]. Severe plastic deformation of the material ensures not only an ultrafine grain size, long extension of grain boundaries, but also introduces high elastic stresses, possible
precipitation of \( \omega \)-phase particles induced by severe deformation [14]. Therefore, application of the known phase rule [13] to estimate the elastic modulus will be not correct for nanostructured and ultrafine-grained materials. Thus, the interrelation between the UFG structure formed in the studied alloy and strength and elastic modulus require more careful studies, our further efforts will be aimed in that direction.

4 Conclusions
The results of the performed studies of the Ti-34Nb-7Zr-4.6Ta ELI alloy with the initial \( \beta \)-structure subjected to processing by different SPD techniques enable stating that:

1. HPT processing at room temperature led to the formation of a UFG structure with an average grain size about 110 nm. The microhardness of the UFG alloy was 257 HV, as compared to the initial coarse-grained state where the microhardness was 176 HV.
2. ECAP processing at a temperature of 200 °C resulted in the formation of a predominantly subgrain structure with an average grain/subgrain size of 500 nm. The UFG alloy had a tensile strength of about 745 MPa, which exceeds that of the counterpart (686 MPa) after standard aging.
3. During the analysis of diffraction patterns taken from the TEM images of the alloy microstructure after HPT and ECAP, no additional spots from \( \omega \)-phase were observed. It gives grounds to expect the retention of a low elastic modulus in the UFG state of the alloy. However, this is the subject of future studies.

Acknowledgments
This work was supported by RFBR grant № 18-32-00585.

References
[1] Brunette D M, Tengvall P, Textor M, Thomsen P eds 2001 Titanium in Medicine (Berlin Heidelberg: Springer-Verlag) pp 1-1019
[2] Rho J Y, Ashman R B, and Turner C H J. Biomech. 26(2) 111 https://doi:10.1016/0021-9290(93)90042-d
[3] Niinomi M 1998 Mater. Sci. Eng. A 243(1-2) 231 https://doi:10.1016/s0921-5093(97)00806-x
[4] Qazi J I, Rack H J and Marquardt B 2004 JOM 56 49 https://doi:10.1007/s11837-004-0253-9
[5] Tang X, Ahmed T and Rack H J 2000 J. Mater. Sci. 35(7) 1805 https://doi:10.1023/a:1004792922155
[6] Abdel-Hady M, Fuwa H, Hinoshita K, Kimura Y and Morinaga M 2007 Scr. Mater. 57(11) 1000 https://doi:10.1016/j.scriptamat.2007.08.003
[7] Estrin Y, Vinogradov A 2013 Acta Mater. 61 782 https://doi.org/10.1016/j.actamat.2012.10.038
[8] Xie K Y, Wang Y, Zhao Y, Chang L, Wang G, Chen Z, Cao Y, Liao X, Lavernia E J, Valiev R Z, Sarrafpour B, Zoellner H and Ringer S P 2013 Mater. Sci. Eng. C 33(6) 3530 https://doi:10.1016/j.msec.2013.04.044
[9] Nakai M, Niinomi M and Oneda T 2011 Metall. Mater. Tran. A 43(1) 294 https://doi:10.1007/s11661-011-0860-3
[10] Valiev R Z, Estrin Y, Horita Z, Langdon T G, Zehetbauer M J and Zhu Y T 2015 Mater. Res. Let. 4(1) 1 https://doi.org/10.1080/21663831.2015.1060543
[11] Wang Y B, Zhao Y H, Lian Q, Liao X Z, Valiev R Z, Ringer S P, Zhu Y T, Lavernia E J 2010 Scr. Mater. 63(6) 613 https://doi:10.1016/j.scriptamat.2010.05.045
[12] Janeček M, Čížek J, Strášký J, Václavová K, Hruška P, Polyaková V, Gatina S and Senemova I 2014 Mater. Charact. 98 233 https://doi:10.1016/j.matchar.2014.10.024
[13] Kim H S, Hong S I and Kim S J 2001 J. Mater. Process. Technol. 112(1) 109 https://doi:10.1016/s0924-0136(01)00565-9
[14] Gatina S, Senemova I, Leuthold J and Valiev R 2015 Adv. Eng. Mater. 17(12) 1742 https://doi:10.1002/adem.201500104