Structural features and mechanical properties of Grade 4 titanium from VSMPO-AVISMA (Russia) and Grade 4 titanium from Carpenter Technology Corporation (USA), subjected to ECAP-Conform

I S Kodirov, R Z Valiev, G I Raab, G N Aleshin and A G Raab
Institute of Physics of Advanced Materials, Ufa State Aviation Technical University, 12 K. Marx str., Ufa 450008 Russia

E-mail: galioshin@mail.ru

Abstract. In this paper, we analyze the microstructural features and mechanical properties of the Grade 4 titanium produced in Russia (VSMPO-AVISMA) and Grade 4 titanium from Carpenter Technology Corporation (USA). It is shown that during the ECAP-Conform processing and subsequent drawing, a homogeneous UFG structure is formed in both Ti materials, providing an enhanced level of mechanical properties with an ultimate tensile strength σв > 1200 MPa and an elongation to failure δ ~ 12%.

1. Introduction
Commercially pure (CP) Ti and its alloys are widely applied in the chemical, aircraft-building and medical industries. CP Ti for medical applications is used in the production of implants for traumatology, orthopedics and maxillofacial surgery [1]. The development of modern processing methods, such as severe plastic deformation (SPD), makes it possible to enhance considerably the mechanical properties of Ti through nanostructuring and provide a level of properties superior to that of the Grade 5 Ti alloy (analogue of the Russian VT6 alloy) widely used in medicine [1-6]. Of special interest is the SPD technique of ECAP-Conform (ECAP-C) which enables the fabrication of products that are in most demand, i.e. long-length rods [5, 7-8]. Considering the fact that the Grade 5 alloy is toxic due to the presence of Al and V additions, replacing this alloy with the high-strength nanostructured Grade 4 Ti in applied practice is highly relevant [9]. Therefore, in this work we studied the structure and mechanical properties of nanostructured CP Grade 4 Ti produced in Russia (VSMPO-AVISMA, ASTM F 67-13, ASTM B 348-13) it terms of its applicability for medical products.

2. Material and experimental procedure
In this work, we studied the CP Grade 4 Ti produced by VSMPO-AVISMA Corporation (Verkhnyaya Salda, Russia). The material’s chemical composition is given in table 1. The chemical composition of the foreign-made Grade 4 Ti (Carpenter Technology Corporation, USA) is also listed for comparison.
Table 1. Chemical composition of the alloys under study.

| Material, manufacturer | Ti    | Mo | W   | Fe  | Sn   | C    | Al  | Co |
|------------------------|-------|----|-----|-----|------|------|-----|----|
| Grade 4, VSMPO-AVISMA  | 98.96 | <0.5 | 0.073 | 0.315 | 0.0076 | <0.0015 | 0.049 | 0.014 |
| Grade 4, Carpenter     | 99.08 | <0.5 | 0.186 | 0.122 | 0.0190 | 0.0180 | 0.012 | 0.011 |

With a view to relieve the stresses and stabilize the structure of the alloy, we annealed the as-received alloy billets in the shape of rods with a diameter of 10 mm and a length of 1000 mm in a Nabertherm furnace at a temperature of 680 °C for 1 hour [4].

Microstructural studies were performed on a Jeol JEM 2100 transmission electron microscope, and X-ray diffraction analysis was performed on a RIGAKU ALTIMA-4 X-ray diffractometer.

The resulting structural state was further regarded as the initial one. To produce a UFG structure with a view to increase the strength characteristics of Grade 4 Ti, we processed the rods by ECAP-Conform (ECAP-C) at a temperature of 250 °C for the purpose of structure refinement. 6 ECAP-C passes were implemented, and subsequently the deformed rods were subjected to drawing to a diameter of 8 mm at a temperature of 250 °C. The produced billets were subjected to tensile mechanical tests.

3. Results and discussion

The structural studies of the initial state of the alloys, both by light microscopy and by transmission electron microscopy, showed that both materials consist of the α-phase grains with sizes of ~18±3 μm having arbitrary, mainly high-angle, boundaries (figure 1). The X-ray studies confirmed the presence of the α-phase in the whole bulk of the alloys in the initial state and the absence of precipitates of any other phase. The results of the interpretation of the X-ray diffraction patterns for both materials are presented in table 2. According to these data, the lattice parameters of the alloys, their dislocation densities, the sizes of coherent scattering regions do not differ much.

Table 2. XRD analysis results of Grade 4 Ti in different conditions.

|                  | CSR size, nm | Dislocation density, m² | Lattice parameter, Å (a/c) | δ % | σ₀.² MPa | σ₀ MPa |
|------------------|--------------|-------------------------|-----------------------------|-----|------------|--------|
| (VSMPO-AVISMA)   | 114.1±2.0    | 4.78E+13                | 2.9521/4.6895              | 18  | 640        | 769    |
| annealing 1 h 680 °C |              |                        |                             |     |            |        |
| (Carpenter)      | 112.7±2.5    | 9.22E+13                | 2.9524/4.6906              | 17.6| 643        | 758    |
| annealing 1 h 680 °C |              |                        |                             |     |            |        |
| (VSMPO-AVISMA)   | 73.6±0.3     | 3.34E+14                | 2.9542/4.6885              | 12  | 1190       | 1200   |
| UFG Ti*          | 72.3±0.7     | 3.28E+14                | 2.9542/4.6890              | 12  | 1170       | 1180   |

*UFG Ti: ECAP-C + drawing

The tensile mechanical tests (table 2) demonstrated very close results for the initial states, i.e. the states after annealing at 680 °C for 1 hour. The ultimate tensile strength (UTS) of the Grade 4 Ti (VSMPO-AVISMA) is σₜ = 769±6 MPa, the elongation to failure is δ=18.0±0.5%; for Grade 4 Ti (Carpenter), the UTS is σₜ = 758±10 MPa, the elongation to failure is δ = 17.6±0.5%.
Figure 1. $\sigma$–$\delta$ curves obtained during the tension of Grade 4 Ti in different conditions: 1 – initial condition (VSMPO-AVISMA); 2 – initial condition (Carpenter); 3 – after 6 ECAP-C passes at 250°C (VSMPO-AVISMA); 4 – after 6 ECAP-C passes at 250°C (Carpenter); 5 – after ECAP-C + drawing at 250 °C to ø 8 mm (VSMPO-AVISMA).

As it can be seen from the $\sigma$–$\delta$ curves based on the results of the tensile mechanical tests of the Ti rods processed by ECAP-C, the tensile strength of the rods increases to 1100 MPa. The uniform elongation during tension for both materials reaches $\delta_u \sim 2.2\%$, and the elongation to failure reaches $\sim 12\%$.

Figure 2 shows the microstructure of Grade 4 Ti from both manufacturers after ECAP-Conform. As revealed by the microstructure images and electron-diffraction patterns, an ultrafine-grained structure is observed in both materials, having structural elements (grains, fragments) with sizes about 0.1-0.25 μm. In the electron-diffraction patterns, the presence of azimuthal blurring of spots located on concentric circles indicates a high density of crystalline defects (figure 2a). The observed grain/subgrain microstructure has boundaries of deformation origin with a predominantly high-angle misorientation. On the whole, no differences are observed in the fine structure of the two materials. Thus, the results of the structural studies by transmission electron microscopy of Ti after ECAP-C processing indicate that the USA Grade 4 Ti (Carpenter) and the Russian-made Grade 4 Ti (VSMPO-AVISMA) are practically identical in terms of structure.

Figure 2. Microstructure of Grade 4 Ti after ECAP-C at 250 °C: a – VSMPO-AVISMA, b – Carpenter. TEM.

With a view to further increase the strength of the Ti rods processed by ECAP-C for 6 passes at 250 °C, they were subjected to drawing at a temperature of 250°C to a diameter of 8 mm. The
conducted tensile mechanical tests of the Ti rods after drawing to ø 8 mm (figure 1) show that the ultimate tensile strength $\sigma_b$ increased to ~ 1200 MPa.

Therefore, the performed studies into the microstructure and mechanical properties of nanostructured CP Grade 4 Ti of Russian manufacture (VSMPO-AVISMA + IPAM, Ufa) and of U.S. manufacture (Carpenter) have demonstrated that both materials are practically identical in terms of their deformation behavior, structural state and level of achieved properties that is superior to that of the analogues used in current practice. The latter is an important condition for their use in the fabrication of nanostructured rods intended for the manufacture of medical products.

Acknowledgements
This research was supported by the Russian Foundation for Basic Research under project No. 17-08-00720/17 and by the Russian Science Foundation under project No. 19-49-02003.

References
[1] 2018 Titanium in Medical and Dental Applications ed Froes F H and Ma Q (Duxford: Woodhead Publishing)
[2] Valiev R 2004 Nature Mater. 3 511
[3] Stolyarov V V, Zhu Y T, Alexandrov I V, Lowe T C and Valiev R Z 2003 Mater. Sci. Eng. A 343 43
[4] Zherebtsov S V, Salishchev G A and Galeyev R M 2002 Defect and Diffusion Forum 208–209 237
[5] Semenova I P, Polyakov A V, Raab G I, Lowe T C and Valiev R Z 2012 J. Mater. Sci. 47 7777
[6] Langdon T G 2013 Acta Mater. 61 7035
[7] Valiev R Z, Zhilyaev A P and Langdon T G 2014 Bulk Nanostructured Materials: Fundamentals and Applications (Hoboken: John Wiley & Sons, Inc.)
[8] Utyashev F Z and Raab G I 2013 Deformation Methods for the Fabrication and Processing of Ultrafine-Grained and Nanostructured Materials (Ufa: Gilem) [in Russian]
[9] Polyakov A V, Semenova I P, Bobruk E V, Baek S M, Kim H S and Valiev R Z 2018 Adv. Eng. Mater. 20 1700863